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International Centre for Science and High Technology

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FINAL REPORT

for the

Seminar

on

"Best Available Technologies and Innovations in Ceramics Production"

30 September - 5 October 2002, Faenza (Italy)

Background

Ceramic tiles are a relevant portion of the building materials industry. The development of this latter sector is definitely a cause for improvements in the standard of living that depends on the driving force of technological innovation. In Europe, which is the main holder of innovations in building materials technologies and of ceramic tiles in particular, extensive research and development has been introduced over the last few decades to face the decrease of raw materials availability and the cost of energy for the firing process. The results is the realisation of bodies, very similar to natural stones, fired in a very short time thanks to the manufacturing of powders both in the chemical, physical and microstructural point of view. Further development of the know-how is due to the increasing appraisal and role of the "powders rheology" theory and practice in the ceramic production plant.

It is well recognised that many developing countries have greatly improved their own production capacity and experience, but they still need extensive technological transfer. At the same time, the growth in the domestic market has led to the creation of numerous small companies whose activities are not yet of sufficient quality to make them competitive on a regional, with not to say on the international market. The building industry sets the basis for economical development both in terms of investment and employment. The close links between investments in the building industry and in employment, account for a high proportion of the total work force. This figure is much higher in countries with emerging economies. Hence, if the decline of this sector is particularly serious in any given country, it is often far more dramatic in those where a transition from a rural to an industrial economy is taking place. Within this context, the ICS New Materials Area in collaboration with ISTEC organised this seminar on 'Best available technologies and innovations in ceramics production' that was held in Faenza, Italy from 30 September to 5 October 2002. See Annex 1, Aide Memoire.

Seminar Description

The seminar was organised under a subcontract by care of ISTEC (Istituto per la Scienza e Tecnologia Ceramica) of the National Research Council (CNR) located in Faenza (Italy) in the newly inaugurated classrooms and facilities of the University of Bologna for Materials Chemistry and Ceramic Technology.

The scope of the seminar was the following:

- To provide participants with the basic principles for the recognition of the technological parameters in the ceramic productions process, with special attention to the cold-forming operations carried out with dry-powders.
- To review, focus and discuss the role of forming operations in the ceramic tiles production cycle with special attention to the in-press decoration technology.
- To present the current trends in the free-form-manufacturing, theory and applications for the rapid prototyping of ceramic parts.

The seminar was organised over four days of lectures and presentations and one day dedicated to the visit to the international technical fair Tecnargilla, in the city of Rimini. The daily calendar was followed according to the programme without exceptions.

The main topics were:

- Presentation of the ICS New Materials and ISTEC-CNR.

- Presentation of powders processing theory and applications.
- The presentation of advanced techniques for free-form-manufacturing.

The seminar was scheduled as follows:

09.00 - 10.30, lectures and presentations
10.30 - 11.00, break
11.00 - 12.30, lectures and presentations
12.30 - 14.00, lunch
14.00 - 15.30, lectures and presentations
15.30 - 16.00, break
16.00 - 17.30, lectures and presentations

Lecturers were given time for answering questions and to contribute to group-discussions.

The programme is enclosed. Please refer to Annex 2.

Participants

The seminar announcement, invitations and calls for applications were circulated through ICS and ISTEC contact persons. The selection of participants was made through evaluation of the curricula returned by candidates. The educational level of participants was rated very high and many of them have several years' experience as directors or managers in national scientific agencies and industrial research and development institutions.

Participants were from Russia, Slovakia, Macedonia, Slovenia, Yugoslavia, Hungary, Latvia, Ukraine, Romania, Poland, Georgia and Turkey. The speakers were from Portugal, Germany, Yugoslavia and Italy. Please refer to Annex 3.

As for financial contributions, 12 of the participants were fully supported by ICS and 3 by a contribution of the Central European Initiative. The speakers from outside of Faenza were also supported by ICS.

Material Distributed

Together with the general information and promotional material of both ICS-UNIDO, international participants were given introductory notes to the lectures and presentations. Please see Annex 4.

Detailed information on the participants' institution/company was communicated through the self-presentations at the opening of the fourth day.

Field Visits

A visit was included in the programme on Wednesday, 2 October 2002 at the Tecnargilla international fair on machinery for ceramic manufacturing. It allowed participants to appreciate what has been accomplished up to the present day and the perspective steps envisaged for the ceramics industry and tiles productivity in the future.

Social Events

No special social event was organised as the participants were all hosted in the same hotel and shared dinner together at the same time. This enabled everyone to benefit further as the classroom discussions continued which was beneficial for all.

Seminar Evaluation

Seminar evaluation feedback was sought by distributing questionnaires during the last day. This evaluation had to be completed and returned before leaving the seminar. The results of the questionnaire are summarised and attached to this report. Please refer to Annex 5.

As a general remark, it can be said that the seminar was greatly appreciated. Indications are that the participants will disseminate the seminar content to their own and other institutes. To do so, the participants have been invited to promote and organize in-house seminars at their respective work places.

Comments and Conclusions

A comprehensive review of the technologies adopted in powders processing technologies was presented with particular emphasis on the recent technological innovations adopted by leading Italian companies. The lecturers and myself were present after the presentations for answering questions and stimulating discussions among participants.

Annex 1 - Aide Memoire
Annex 2 - Programme
Annex 3 - List of Participants
Annex 4 - Workbook:

- Presentations on forming of advanced ceramics by Mr. D. Bigoni
- Speech by Ms. E. Carignani
- Paper on modern technologies and techniques for manufacturing of tableware porcelain by Ms. R. Dumitrache
- Presentation on ceramic industry and research in the Slovak Republic: An overview by Mr. D. Galusek
- Paper on ceramic industry and research in the Slovak Republic: An overview by Mr. D. Galusek
- Paper on composition-microstructure-properties relationship for a ceramic material by Ms. A. Goleanu
- Paper on new technologies at S.C. Apulum S.A. by Ms. A. Goleanu
- Presentation on Anadolu University, the Ceramic Research Center at Anadolu University and aqueous processing of new SiAION ceramics by Mr. A. Kara
- Paper on the Georgian Technical University, Department of the Technology of Composite Materials and Items by Mr. H. Kovziridze
- Presentation on some aspects of modeling of liquid phase sintering: basic concepts by Mr. Z. Nikolic
- Presentation on some aspects of modeling of liquid phase sintering: finite difference approach by Mr. Z. Nikolic

- Abstract on science and technology of ceramics in Yugoslavia by Ms. N. Nikolic
- Paper on introduction to rapid prototyping and solid freeform manufacturing by Mr. S. Meriani
- Presentation on introduction to rapid prototyping and solid freeform manufacturing by Mr. S. Meriani
- Paper on new typologies of 'Granito' tiles and the related 'aesthetic' engineering by Mr. M. Manfredini
- Personal report by Mr. A. Matev
- Abstract on latest developments in porcelain body manufacturing: pressing of very large sheet with no die and the study of the sintering kinetics by Mr. M. Paganelli
- Abstract by Mr. M. Romagnoli
- Paper on production of refractory materials in Russia: prospects of development by Mr. V. Shevchenko
- Paper by Ms. A. Wajler
- Paper on double pressing technology by Mr. B. Spinelli

Annex 5 - Questionnaire Results
Annex 6 - Achievements
Annex 7 - Recommendations
Annex 8 - Follow-up
Annex 9 - Detailed Financial Statement

Annex 1

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"Best Available Technologies and Innovations in Ceramics Production"

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AIDE-MEMOIRE

BACKGROUND

The technology for processing ceramic materials to produce objects with defined shape and properties, has been improved in these last three decades more than in the whole previous history of ceramics. The reason of this accomplishment is based on the application of the scientific method to the various production steps, to begin with the chemistry of raw materials. However not only chemistry has contributed to this development but also the study of the physical behaviour of raw materials, both at room and high temperature. In fact, before being shaped and fired, materials are conveyed and processed mostly as finely divided powders. The methods of producing and mixing powders with a defined overall size distribution has represented the most important break-through for the attainment of reliable, reproducible and safe ceramic products.

Most of this accomplishment was due to the research of what is usually named as "high-tech" materials. However, very soon these scientific and technological achievements deeply influenced the classical ceramics field, with great results in the building materials sector and of the ceramic tiles in particular.

If in the past the differences between traditional and advanced ceramics may have been justified, presently those differences do not have any more meaning. The whole ceramic world, traditional and advanced, is now ruled by the same science and technology which at the end build-up the foundation of the ceramic materials science and engineering.

JUSTIFICATION

The aim of the New Materials sub-programme is to stream materials science and engineering into applied research in order to aid the development of less industrialised countries. Within this programme, ceramic materials rank highest in the priority list because they provide products and applications in both civil and mechanical engineering. These strategic sectors set the basis for economic development due to the fact that the market can provide an increment to the employment quality. Indeed, the sector's development links the improvements in the standard of living that depends on technological innovation.

The availability of new products at increasingly competitive prices, made possible by technological development, comes on top of the growing market demand linked to the increase in standards of living. Technological innovation creates added value. It improves the products and cuts costs, thus allowing for a greater distribution of the product on the market and an extension of the distribution range.

In Europe, which is the main producer of ceramic materials (tiles and related items) extensive technological innovation was introduced over the last four decades to face the increase of internal demand and to push production towards new and emerging markets. On the other hand, many other countries have greatly improved their own production in particular sectors, but they still need extensive technological innovation.

The workshop which ICS is organising in co-operation with ISTEC – CNR, Faenza, aims at conveying accessible information on how to increase the productivity and product quality with the introduction of technological innovations. By doing this, special efforts will focus on the needs of small- and medium-sized enterprises. Issues related to energy saving and materials design, improved environmental protection and total quality control, will be taken into consideration.

The aim of the present workshop will be to highlight recent and advanced technologies adopted in the contemporary ceramics industries, giving special emphasis to the forming and shaping processes.

Shaping operations, among the ceramic processing steps, are closest to the engineering design demands, because the final ceramic object will perform basically through its size and shape, besides through its intrinsic materials properties. Therefore, shaping operations deserve further and deeper insight as far as theory and modelling are concerned, by applying research efforts similar to what has been done and accomplished in the field of chemistry, firing and sintering of ceramic bodies.

OBJECTIVES

- To provide participants with the basic principles for the recognition of the technological parameters in the ceramic productions process.
- To review, focus and discuss the role of forming operations in the ceramic tiles production cycle.
- To present the current trends in the free form theory and applications in the rapid prototyping of ceramic parts.

EXPECTED OUTPUTS

- Enhancement of skills and awareness of technologists and experts from a number East European countries.
- Establishment of contacts among enterprises operating in the sector through international co-operations programmes.
- Spreading of a network of possible counterparts in the East European countries for a common development project.
- Project proposal that can be financially supported by identifiable national and international donors.

BENEFICIARIES

Research and development institutions and industries in East European countries.

VENUE AND DATES

The workshop will be held from 30 September to 5 October 2002 at the ISTEC-CNR premises, Via Granarolo, 64, 48018 Faenza.

PARTICIPANTS

About 10-12 technologists and technicians from the ceramics sector in target countries will be invited by ICS to participate in the workshop. Preference will be given to participants from East Europe.

All participants should have a degree in a technical field or several years experience as a technologists operating in the sector. A good command of English is essential.

All participants will be required to present a detailed paper of the state-of-the art of the ceramic production industry in their country of origin and/or company where they are employed.

The workshop is also open to cost-free participants. No registration fee will be charged.

DOCUMENTATION

The documentation for the workshop will consist of the following:

- Programme and list of participants;
- A copy of the lecture notes. All lecturers are requested to provide a hard and a soft copy of slides and transparencies used.
- ICS publication on "Ceramics building Materials"

TENTATIVE PROGRAMME

Monday, 30 September 2002
Registration and presentation of the ICS-UNIDO programme and policy. Introduction and background of ISTEC-CNR.
Principles of ceramic manufacturing: powders processing in theory and practice. Modelling of confined cold compaction and pressing methods.

Tuesday, 1 October 2002
Forming operations for the production of tiles.
New technologies in the press machinery and decoration processes, case histories, results and their evaluation.

Wednesday, 2 October 2002
Visit to the Tecnargilla exhibition.
Presentation and discussion of specific equipment and technologies by selected experts at hosting Company stands.

Thursday, 3 October 2002
Introduction to Solid Freeform Fabrication (SFF)
Available technologies and principle operation.
Extending SFF to ceramic materials, opportunities and difficulties. SFF within materials science perspectives.

Friday, 4 October 2002
Rapid prototyping in the ceramic sector. Laser sintering and UV curing, trends and applications. Case histories.
Extrusion and printing methods from 2D pattering to 3D objects.
Opportunities and constraints for miniaturisation.

Saturday, 5 October 2002
Panel discussion and recommendations

FINANCIAL/ADMINISTRATIVE ARRANGEMENTS FOR ICS-FINANCED PARTICIPANTS

For participants who are supported by ICS to participate in the workshop, round-trip air-economy prepaid tickets from the airport of departure will be issued for the most direct and economical route. Accommodation and meals will be covered for the period of attendance at the workshop.

Participants will be required to bear the costs of all expenses in their home country incidental to travel abroad, including expenditure for passport, visa, and any other miscellaneous items as well as internal travel to and from the international airport of departure in their home country.

The organization will not be responsible for any of the following costs, which may be incurred by the participant while attending the workshop:

- compensation for salary or related allowances during the period of the workshop;
- any cost incurred with respect to insurance, medical bills and hospitalization fees;
- compensation in the event of death, disability or illness;
- loss or damage to personal property of participants while attending the workshop.

VISA ARRANGEMENTS

Participants are requested to arrange for their visa as early as possible at the Italian Embassy or Consulate in their home country by presenting the official invitation letter. In case of difficulties, please advise the contact persons mentioned below.

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Annex 2

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30 September - 5 October 2002, Faenza (Italy)

PROGRAMME

MONDAY, 30 SEPTEMBER

09.00 - 09.30	Registration
09.30 - 10.00	Presentation of the ICS-UNIDO programme and policy By Mr. S. Meriani, (ICS-UNIDO, Italy)
10.00 - 10.30	Introduction and background of ISTEC-CNR By Mr. G. Babini, (ISTEC, Italy)
10.30 - 10.45	Women entrepreneurs/managers in small and medium sized enterprises in North Eastern Italy By Ms. E. Carignani, (A.I.D.D.A., Italy)
10.45 - 11.15	Coffee break
11.15 - 12.30	Principles of ceramic manufacturing: powders processing in theory and practice. Modelling of confined cold compaction and pressing methods (I)

	By Mr. D. Bigoni, (University of Trento, Italy)
12.30 - 13.30	Lunch
13.30 - 15.30	Principles of ceramic manufacturing: powders processing in theory and practice. Modelling of confined cold compaction and pressing methods (II) By Mr. D. Bigoni, (University of Trento, Italy)
15.30 - 15.45	Coffee break
15.45 - 17.30	Principles of ceramic manufacturing: powders processing in theory and practice. Modelling of confined cold compaction and pressing methods (III) By Mr. D. Bigoni, (University of Trento, Italy)
17.45	Bus for the hotel

TUESDAY, 1 OCTOBER

09.00 - 10.30	Powders rheology and treatments (I) By Mr. M. Romagnoli, (University of Modena-Reggio, Italy)
10.30 - 11.00	Coffee break
11.00 - 12.30	Powders rheology and treatments (II) By Mr. M. Romagnoli, (University of Modena-Reggio, Italy)
12.30 - 13.30	Lunch
13.30 - 15.30	Latest development in porcelain body manufacturing: the pressing of very large and thin sheet with no die-set with the LAMINA technology by System (I) By Mr. M. Paganelli, (Freelance Consultant, Italy)
15.30 - 15.45	Coffee break
15.45 - 17.30	Latest development in porcelain body manufacturing: the study of the sintering kinetics using the double beam optical dilatometer MISURA by Expert System Solutions (II) By Mr. M. Paganelli, (Freelance Consultant, Italy)
17.45	Bus for the hotel

WEDNESDAY, 2 OCTOBER

09.00 - 10.30	Tecnargilla visit
10.30 - 11.00	Coffee break
11.00 - 12.30	Advances in pressing technologies By Mr. B. Spinelli, (SACMI, Italy)
12.30 - 13.30	Lunch
13.30 - 15.30	New typologies of granito tiles and the related aesthetic engineering By Mr. M. Manfredini, (LB, Italy)
15.30 - 15.45	Coffee break
15.45 - 17.30	Tecnargilla - visit
17.45	Bus for the hotel

THURSDAY, 3 OCTOBER

09.00 - 10.30	Some aspects of modelling of liquid phase sintering By Z. Nikolic, (University of Nis, Yugoslavia)
10.30 - 11.00	Coffee break
11.00 - 12.30	Participant presentations
12.30 - 13.30	Lunch
13.30 - 15.30	ISTEC Highlights
15.30 - 15.45	Coffee break
15.45 - 17.30	Visit to the laboratories
17.45	Bus for the hotel

FRIDAY, 4 OCTOBER

09.00 - 10.30	Rapid prototyping By Mr. N. Reis, (Instituto Superior Tecnico, Portugal) and Mr. R. Sindelar, (University of Erlangen-Nurnberg, Germany)
10.30 - 11.00	Coffee break
11.00 - 12.30	Rapid prototyping By Mr. N. Reis, (Instituto Superior Tecnico, Portugal) and Mr. R. Sindelar, (University of Erlangen-Nurnberg, Germany)
12.30 - 13.30	Lunch
13.30 - 15.30	Rapid prototyping By Mr. R. Sindelar, (University of Erlangen-Nurnberg, Germany)
15.30 - 15.45	Coffee break
15.45 - 17.30	Rapid prototyping By Mr. N. Reis, (Instituto Superior Tecnico, Portugal)
17.45	Bus for the hotel

SATURDAY, 5 OCTOBER

09.00 - 12.00	Panel discussion and recommendations
12.00 -	Departures

Annex 3

International Centre for Science and High Technology

Seminar on

'Best available technologies and innovations in ceramics production'

Faenza, Italy
30 September - 5 October 2002

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Annex 4

International Centre for Science and High Technology

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WORKBOOK

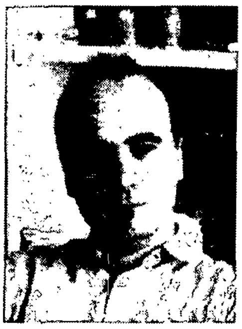
for the

Seminar

on

"Best Available Technologies and Innovations in Ceramics Production"

30 September - 5 October 2002, Faenza (Italy)



Davide Bigoni (Italy)

Davide is a Professor of "Solid and Structural Mechanics" and the Chairman of the Department of Mechanical and Structural Engineering at the University of Trento. He is also part of the Editorial Board of the "International Journal of Solids and Structures", which is a top journal in the field of mechanics of materials.

Davide attained his Civil Engineering Degree from the University of Bologna in 1985 and then undertook his Ph.D. on 'Dissertation: Localization of deformation and bifurcation in incremental nonassociative elastoplasticity: applications to brittle cohesive materials' in 1991.

His research activities are based on the mechanics of materials and structures, and some main topics of his research are structural mechanics, structural ceramics and powder compaction, interface modelling in biomechanics and finite deformations in elastic and elastic-plastic solids.

Mr. Bigoni will present a paper titled 'Principles of ceramic manufacturing: powders processing in theory and practice. Modelling of confined cold compaction and pressing methods'.

Mariano Paganelli (Italy)

Mariano Paganelli took a PhD in Theoretical Chemistry in 1977 at the University of Modena (Italy) and after the graduation started a career as researcher in the corprate laboratory of the Marazzi Group. He was then appointed Research and Development Director and left the Group in 1988.

From 1989 to 2000 he teached Ceramic Science and Technology and Glass Science and Technology as contract professor at the Engeneering Faculty of the Modena University. In the same time he started a consulting activity for all the major tile manufacturing companies around the world, in Italy, Turkey, Brazil, United States.

He developed several new products and technologies which are patented worldwide.

He is currently involved in several innovative projects, among which the Lamina project, by System, the double beam optical dilatometer, by Expert System Solutions, the third generation glass ceramic frits for porcelain bodies by Smalticeram.

Mr. Paganelli will present a paper on:

Latest development in porcelain body manufacturing: pressing of very large sheet with no die and the study of the sintering kinetics

Nuno Reis (Portugal)

Nuno holds an Engineering Degree in Materials and Metallurgy from Instituto Superior Técnico (University of Lisbon, Portugal) and specialised in Electronic ceramics - having worked towards is Diploma dissertation at the Electroceramics Division of the Corporation for Technology, Siemens A.G., Munich, Germany.

He then took a Ph.D. on Solid Freeform Fabrication of ceramics at the University of Oxford and UMIST (University of Manchester Institute for Science and Technology) in the United Kingdom.

He's currently a Research Associate at Instituto Superior Técnico, working on Biomaterials Development for various applications, ranging from dental materials to tissue engineering scaffolds. Since 2001 he's also entrepreneur of a micro-company at Lisbon's Science and Technology Park, aiming the automated production of biomedical devices and custom-made implants and prosthesis.

Mr. Reis will have two papers entitled:

- Extending solid freeform fabrication to ceramic materials.
- Extrusion and printing methods for ceramic devices – state-of-the-art.

Ralf Sindelar (Germany)

Ralf Sindelar was born in 1963 in Gelsenkirchen, Germany.

He attained his Diploma on Materials Science at the Rheinisch-Westfälische Technische Hochschule Aachen (RWTH-Aachen), Department of Mining, Metallurgy and Earth Sciences, Institute of Ferrous Metallurgy (IEHK, Institut für Eisenhüttenkunde) and his Doctors degree on "Fundamental research on materials for hip total endo-prostheses with a new remelting technique and testing of the prostheses", at RWTH, Institute for Ferrous Metallurgy.

His first employment position was as a project engineer at Werkstoff Union, Lippendorf, which is a steel works company. He later held positions with CHEMPRO GmbH, Bonn, as the Head of Department "New Materials" and then with the University of Erlangen-Nuremberg, Department of Materials Science, as Head of Group "Net Shape Manufacturing".

From 01 November 2002, he will become the Head of "Freiburger Center for crash-relevant Materials Science - crashMAT" at the Fraunhofer Institute for Mechanics of Materials.

Mr. Sindelar will have two papers entitled:

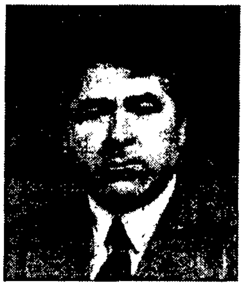
- Introduction to solid freeform fabrication.
- Laser sintering and curing processes.

Marcello Romagnoli (Italy)

Marcello Romagnoli is an Associate Professor at the University of Modena and Reggio Emilia where he teaches Applied Chemistry for the Enviroment. His current areas of research include powder handling with particular attention to the traditional ceramic field. He is technical coordinator of the "Powder Center" at Democenter. Further information can be found on:
http://www.democenter.it/laboratori/polveri/index.asp and
http://www.reolab.unimo.it).

Prof. Romagnoli has organized workshops and courses on powder characterisation and has collaborated with industries and universities about powder handling.

Zoran Nikolic (Yugoslavia)



Zoran is Professor of Materials Science and Quality Control at Faculty of Electronic Engineering, Department of Microelectronics, at University of Nish, Yugoslavia. He holds B.Sc. (1974, Computer Science) and M.Sc. (1977, Materials Science) at Faculty of Electronic Engineering, and Ph.D. (1980, Materials Science) at University of Nish.

From 1998 through to 2000 he was Vice Dean of Faculty of Electronic Engineering. He is currently President of the Board of University of Nish (2002–2004).

He is Full Member of International Institute for the Science of Sintering, Member of the American Ceramic Society, Member of Yugoslav Simulation Society, Member of ETCAN (Yugoslav Committee for Electrical Engineering, Telecommunications, Computer Science, Automatic Control and Nuclear Engineering), Member of Serbian Chemical Society.

He is Associate Editor of International Journal of Quality Technology and Quantitative Management, Member of Managing Board of International Institute for the Science of Sintering, Member of Editorial Advisory Board of Journal "Science of Sintering".

His research has largely focused on Mathematical Modeling and Computer Process Simulation (Microstructural evolution during sintering, grain growth, Ostwald ripening), Numerical Process Prognosis, Databases and Information Systems, Statistical Quality Control and Reliability, and Software Development, too.

He has more than 100 authored or co-authored publications, about 70 authored or co-authored presentations at various technical conferences and seminars at various institutions, and about 15 monographs.

CURRICULUM VITAE
Gian Nicola Babini

Date of birth:	**24th April 1944**
Place of birth:	**FAENZA (RA) Italy**
Office address:	**IRTEC CNR** **Via Granarolo 64 – 48018 Faenza RA Italy** **Tel 0039 0546 699711 – Fax 0039 0546 699719 or 0039 0546 699741** **E-mail: babini@irtec1.irtec.bo.cnr.it**

1974	Graduated in Industrial Chemistry at University of Bologna (110 first class honours)
1975	Joined the National Research Council and employed as Researcher at IRTEC-CNR (The Institute of Research Ceramic Technology – Faenza)
1985	Appointed as Director of IRTEC-CNR Faenza*
1991	Appointed as Senior Executive of the National Research Council
1993	Member of the European Ceramic Society, served as President for aterm of two years (1994 and 1995)
1994	Appointed President of the Italian Ceramic Society
1997	Director of the Subproject PF MSTA 2-CNR*

**he is currently in this position*

Scientific and Technological Activity of Dr. Gian Nicola Babini

The scientific and technological activity carried out by Gian Nicola Babini is principally focused on the sector of ceramic materials, studying their specific productive processes and those for the manufactured products, he has also undertaken the study of characterization, microstructural and functional qualification, taking into account the correlation between the characteristics of raw materials and their standards of process-property. In this regard, the main materials that have been studied from the scientific and technological point of view are those for the preparation of advanced ceramics (oxides, nitrides and carbides) and for structural, electrical and biomedical applications.

Another important aspect of his reaserch takes into account the use of traditional ceramics (chiefly composed of clay) in the buildiding industry past and present; along with this study, materials have been analyzed in respect of their re-construction, conservation and restoration as part of his work within the frame of Research on Cultural Heritage.

In addition, it is important to note that over the years his activity has also been characterized by his increased involvement in the field of (i) Innovative, Technological Transfer to Small and Medium Enterprises, (ii) start up of new companies and (iii) spin-off programmes. This activity, reported through articles of national and international magazines and by technical records, has also made a contribution at national and international conferences as well as to the scientific texts.

Over the years Gian Nicola Babini has held the following positions and carried out the activities listed below:

- Head of Structural Laboratory
- Head of Special Technology Laboratory

- Head of Advanced Ceramic Laboratory
- Head of Research Projects on advanced ceramic material
- Head of Contracts between IRTEC and Industries
- Head of Research Programmes in the frame of international collaborations of Irtec (Ist. Silicati Budapest, Ist. per la ceramica Shanghai etc...)
- Representative of the Irtec Scientific Committee
- Head of Operative Units for the governative projects P.F. – CNR (Technological Transfer)
- Promoter and Coordinator of the setting up of the *Consorzio Agenzia Polo Ceramico* Agency for Ceramics - Faenza (1986)
- Promoter and Coordinator of the setting up of the *Consorzio PRO.MO Mosaico* – Ravenna (1987)
- CNR Consultant for *CNRSM*-Brindisi in order to create a section on Ceramic Materials (1989)
- Member of the Scientific Commitee of *ISRIM* (Terni)
- Representative Member of CNR in the Board of Directors of *Consorzio Agenzia Polo Ceramico* - Faenza
- Representative Member of CNR in the Board of Directors of *PRO.MO Mosaico* Ravenna
- Member of the Feasibility Commission of PF MSTA 1 CNR (1986)
- Member of the P.N. Committee of Chemistry within the Ministry MURST (1988)
- Member of P.N. Committee on Innovative and Advanced Materials for the Ministry MURST (1988)
- Member of the Project Committee for PF MSTA 1 CNR
- Member of the Managing Committee in the frame of the Agreement signed by CNR-APC-CNRSM-Banca Dati Alkimya
- Member of the Technical Commitee for the Fair *Tecnoargilla* organized by *Ente Fiera di Rimini*
- President of the Managing Committee in the frame of the Agreement signed by CNR-ENEA-APC
- President of the Organizing Committee for the *"Prima Conferenza Nazionale Ceramici Avanzati"* "First National Conference on Adanced Ceramic Materials"
- Member of the Feasibility Commission of PF MSTA 2 CNR
- Director of the subproject "Innovation of Traditional Materials" for PF MSTA 2 CNR
- President of the Promoting Committee (CNR-ENEA-Eniricerche) for the setting up of a Science Park Technology on Ceramic Materials
- Appointed as MURST Expert in the frame of "L. 46, L. 488 programmes" for the support to the industry
- Coordinator of the Post-University degree Course in Innovative Technologies for the preparation of Inorganic Materials
- Coordinator of initiatives of Technology Transfer for the setting up of Small Medium Enterprises, Technological Innovation anf Spin Off programmes
- Member of the European Commission for the Brite programme (1987)
- Member of the European Commission for the EURAM programme (Raw Materials and Materials-Group ceramics) (1987)
- Invited Lecturer at NATO A.R.I. "Progress in Nitrogen Ceramics" – Falmer U.K. (1981)
- Invited Lecturer NATO A.R.W. "Ceramics Science and Technology" Ankara – Turkey
- UNIDO project "Feasability study for the establishment of a Centre of Multidsciplinary Research" – Member of the Mission of Damascus
- President of the Organizing Committee "CERMAT 92" – Conference and Exibition" Rimini 1992

Agreement of Cooperation between Nagoya Fair-Ente Fiera di Rimini
WorkShop on Scientific Cooperation between Italy and Japan on Advanced Ceramics

Italy 1992; WorkShop on Scientific Cooperation between Italy and USA on Advanced Ceramic – Italy 1992; WorkShop on Scientific Cooperation between Italy-Europe on Advanced Ceramic – Italy 1992

- Director for the Organization of the WorkShop Italy-Korea in cooperation with KOSEF
- Coordinator of the Italian Delegation (CNR-ENEA-UNI-IND) in Seoul 1994
- Director for the Organization of the WorkShop on Biomaterials Italy-Egypt – Italian Embassy in Cairo
- Member of the CNR Delegation for Ceramics Official Visit in Australia
- Director of NATO-ARW "Engineering Ceramics" Bratislava (1997)
- Director for the Organization of the WorkShop on the Scientific Cooperation between Japan – Italy on Advanced Ceramic Materials – Inuyama – Japan 1996
- President of the Organizing Committee of the IV European Ceramic Society Conference and Exhibition - Rimini 1995 (1500 participants)
  Scientific Cooperation in Ceramic Material in Europe (20 European Countries)
- Head of the UE Contract in the frame of the Innovation Programme
  PK 438 "Feasibility Study for PST on Ceramic Materials"

International Centre for Science and High Technology

Davide Bigoni

Forming of advanced ceramics

Workshop
on
"Best Available Technologies and Innovation
in Ceramics Production"

30 SEPTEMBER - 5 OCTOBER 2002, FAENZA (ITALY)

Preface

Part of my research activity in the last few years has potentially applications in the field of ceramic materials. In the notes which follow, I have not attempted to provide a comprehensive guide to the mechanical behaviour of ceramics. Instead, I have collected together a number of unpublished contributions, in which I was involved at different levels. These regard particular and often unrelated aspects of mechanical behaviour of ceramics. Moreover, results have been obtained following an approach peculiar to Solid Mechanics and they are not based on extensive experimental results. However, I hope that some of the presented material might stimulate the scientific curiosity of researchers in the field.

All the results presented have been obtained in co-operation with different researchers, to which I would express my sincere gratitude. In particular, I owe much to Giancarlo Celotti, Goffredo De Portu, Leonardo Esposito, Alessandro Gajo, Massimiliano Gei, Stefano Guicciardi, Alexander B. Movchan, Andrea Piccolroaz, Enrico Radi, Sergei K. Serkov, Anna Tampieri, Antonella Tucci, Monica Valentini.

Povo di Trento, January 2002. *Davide Bigoni*

Contents

Chapter 1

An introduction to the mechanical behaviour of ceramics

D. Bigoni [1]

Mechanical behaviour of ceramics is summarized with emphasis on some issues that will be addressed in the subsequent chapters. Elastic, plastic and viscous behaviour, fracture and large strain effects are considered.

1.1. Preliminaries

Since neolithic times ceramics have played a fundamental role in man's development and survival (Scott, 1954). But during the last thirty years the technology of ceramic design and production has undergone a spectacular growth.

The peculiar optical, electrical, and magnetic characteristics, connected to the excellent thermo-chemical stability at high temperatures drives the industrial exploitation of ceramics. Following a modern definition of ceramics, these are materials manufactured from non-metallic, inorganic substances exhibiting high thermal stability. A broad class of materials falls within the above definition, including – for instance – superconductors, tiles, diamonds, zirconia, alumina, and glasses (Pampuch, 1991).

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[1] Dipartimento di Ingegneria Meccanica e Strutturale, Università di Trento, Via Mesiano 77, 38050 Trento, Italy.

Structural ceramics are the main focus of the present notes. These differ from traditional ceramics essentially because of their high purity and the presence of substances different from silicates, such as oxides, carbides, nitrides, etc. Moreover, *mechanical properties* are a crucial design target within this class of materials.

Our main interest here is the mechanical behaviour of structural ceramics related to fracture initiation and growth under service conditions. In particular, the present monograph is articulated as follows.

A brief review of the mechanical behaviour of ceramics is included in Chapter 1. The treatment is far from exhaustive and the interested reader is referred to De Portu (1992), Evans (1984), Green (1998), Lawn (1993), Munz and Fett (1999) for a comprehensive view of field of ceramics and to Ashby and Jones (1980), Bridgman (1952), Cottrel (1964), McClintock and Argon (1966) and Nadai (1950) for more general notions of material science.

Chapter 2 is devoted to the analysis of cold forming of powders. Problems related to forming technology involve the major part of ceramic materials and are connected to the analysis of density and residual stress distributions in greens.

1.2. Elastic behaviour

Deformation in the elastic range of crystalline materials is related to (reversible) movements of atoms, which – for instance – may be experimentally demonstrated using x-ray diffraction during deformation of a material element. At room temperature, linear elasticity is a common behaviour of many ceramics, such as alumina (Al_2O_3) or silicon nitride (Si_3N_4).

Within the realm of linear elasticity, stress σ and strain ϵ are related through a linear relationship

$$\sigma = \mathcal{E}[\epsilon], \tag{1.1}$$

where the fourth-order tensor $\mathcal{E}$ may describe a broad class of *anisotropic* behaviours ($\mathcal{E}$ is characterized, in the most general case, by 21 material constants, when a stress potential is assumed). The behaviour of *single-crystals* is always anisotropic and the particular class of crystal symmetry defines the number of elastic constants (Love, 1927). For instance, three or five elastic constants describe cubic or hexagonal single crystals (Fig. 1.1).

At a macroscopic scale, *polycrystalline ceramics* often consist of a random array of single-crystals, so that an isotropic elastic behaviour follows. In this case, the elastic constants reduce to two, the Young modulus E and the Poisson's ratio ν. The elastic

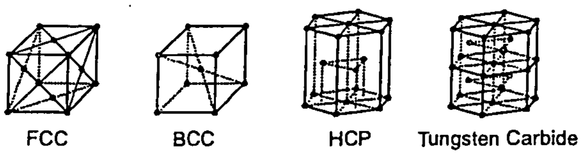

FIGURE 1.1. Crystal lattice structures: Face Centered Cubic, Body Centered Cubic, Hexagonal Close Packed, Tungsten carbide.

fourth-order tensor thus becomes:

$$\mathcal{E} = \lambda \boldsymbol{I} \otimes \boldsymbol{I} + 2\mu \boldsymbol{I} \boxdot \boldsymbol{I}, \tag{1.2}$$

where

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}, \qquad \mu = \frac{E}{2(1+\nu)}, \tag{1.3}$$

are the Lamé constants (μ is the shear modulus, often denoted by G) and $\boldsymbol{I} \otimes \boldsymbol{I}$ and $\boldsymbol{I} \boxdot \boldsymbol{I}$ are fourth-order tensors defined, for every second-order tensor $\boldsymbol{A}$, in the following way:

$$\boldsymbol{I} \otimes \boldsymbol{I}[\boldsymbol{A}] = (\mathrm{tr}\boldsymbol{A})\boldsymbol{I}, \qquad \boldsymbol{I} \boxdot \boldsymbol{I}[\boldsymbol{A}] = \frac{1}{2}(\boldsymbol{A} + \boldsymbol{A}^T). \tag{1.4}$$

Indicative values of the elastic constants for some materials at room temperature are reported in Table 1.1 (data taken from Green, 1998; Kingery et al. 1960; Meyers and Chawla, 1999; Munz and Fett, 1999; Shackelford, 1985).

1.3. Fracture

At room temperature, ceramics are typically brittle materials, which usually fail as a consequence of rapid and catastrophic fracture propagation[2]. Perhaps the major research goal of the last thirty years (in the field of ceramics!) has been indeed directed to emend this characteristic, which is unacceptable in many technological applications.

There are essentially two approaches to linear elastic fracture mechanics: the energy approach and the stress intensity approach. The former was initiated by Griffith (1920) and is equivalent to the latter, that is followed below (for a detailed presentation of fracture mechanics see Anderson, 1995; Broberg, 1999; Lawn, 1993). With reference to the coordinate system introduced in Fig. 1.2, the asymptotic stress fields

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[2] Brittle crack propagation occurs essentially by bond rupture, for cracks of atomic sharpness.

TABLE 1.1. Elastic constants E, ν at 20°C.

Material	Young modulus E (GPa)	Poisson's ratio ν
1040 carbon steel	200	0.3
304 stainless steel	193	0.29
3003-H14 aluminum	70	0.33
Copper	129.8	0.343
Polyamides (nylon 66)	2.8	0.41
Acetals	3.1	0.35
Borosilicate glass	69	0.2
Silicon nitride (HPSN)	320	0.28
Sintered alumina (95% dense)	320	0.20-0.26
Sintered stabilized zirconia	150-240	0.22-0.30
Ceramic fibre SiC	430	–
Glass fibre (S-glass)	85.5	–
Polymer fibre (Kevlar)	131	–
Ceramic whisker Al_2O_3	430	–
Al_2O_3 whiskers (14 vol%) in epoxy	41	–

near a crack tip in an isotropic, linearly elastic material, subject to symmetric boundary conditions – the so-called Mode I problem – can be expressed as (Westergaard, 1939)

$$\left.\begin{array}{l}\sigma_{11}(r,\theta)\\ \sigma_{22}(r,\theta)\\ \sigma_{12}(r,\theta)\end{array}\right\} = \frac{K_I}{\sqrt{2\pi r}}\cos\frac{\theta}{2}\left\{\begin{array}{l}(1-\sin\frac{\theta}{2}\sin\frac{3\theta}{2})\\ (1+\sin\frac{\theta}{2}\sin\frac{3\theta}{2})\\ \sin\frac{\theta}{2}\cos\frac{3\theta}{2}\end{array}\right. . \tag{1.5}$$

It should be noted that fields (1.5) satisfy equilibrium with null body forces

$$\mathrm{div}\sigma = \mathbf{0}, \tag{1.6}$$

the traction-free boundary conditions on crack faces

$$\sigma_{22}(r,\pi) = \sigma_{12}(r,\pi) = 0, \tag{1.7}$$

and the symmetry condition ahead of the crack

$$\sigma_{12}(r,0) = 0, \tag{1.8}$$

for *every value* of K_I.

Two key points emerge from an analysis of (1.5), namely:

- the stress field is proportional to the unknown amplitude K_I, the so-called *stress intensity factor*;

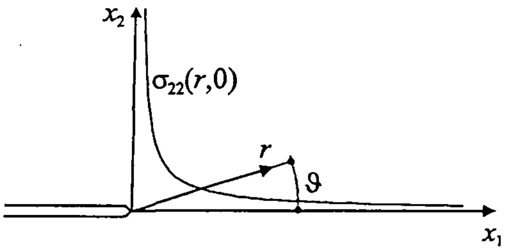

FIGURE 1.2. Polar and Cartesian coordinates used to describe crack fields. The stress component $\sigma_{22}(r,0)$ is also reported.

- the stress field is singular, in the sense that the stress approaches infinity when the distance to the crack tip r tends to zero.

The stress intensity factor completely characterizes the near-tip stress state and therefore depends on the particular geometry of the loaded structure. For instance, in the case of an infinite plate subject to a remote tensile stress σ,

$$K_I = \sigma\sqrt{\pi a},$$

for a through-thickness crack of length $2a$ and

$$K_I = 1.12\,\sigma\sqrt{\pi a},$$

for an edge crack of length a.

Being the stress infinite at the crack tip, it cannot be sustained by any real material. However, the fracture concept introduced above follows from a mathematical model, so that on one hand a perfectly sharp crack is impossible in a real problem and, on the other hand, an elastic material is also an ideal notion. Consequently, *for brittle materials* it is assumed that the stress is high, though not infinite, at a real crack tip and that it is reasonably described by representation (1.5), at least outside a *process zone*, which is very small when compared to the problem size. Therefore, let us analyze loading of a structure containing a crack. Under the hypothesis that a given stress combination leads to failure, the achievement of this must correspond to the attainment of a critical value of the stress intensity factor K_{Ic}. A fundamental assumption of fracture mechanics is that the critical stress intensity factor depends only on the nature of the material and is therefore independent of the geometry and size of the fractured body. As a consequence, once K_{Ic} is known for a given material, a failure analysis can be performed for a structure made up of that material.

In addition to the symmetric mode illustrated above, there are other two types of loading that a crack may experience, so that Mode I, Mode II and Mode III are distinguished (Fig. 1.3). However, brittle materials are more prone to fracture by normal tensile stresses than by shear stresses, so that Mode I loading has the most practical importance.

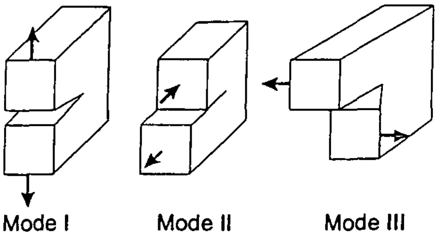

FIGURE 1.3. The three modes of crack loading.

The fracture toughness K_{Ic} can be experimentally determined by introducing an artificial crack in a testing structure, subsequently loaded to failure. Different test settings are used for ceramic materials (Anderson, 1995; Green, 1998). Some indicative values of toughness in different materials are reported in Table 1.2 (data taken from Ashby and Jones (1980); Cook and Pharr, 1994; Evans, 1989; Green, 1998; Meyers and Chawla, 1999; Shackelford, 1985).

The above presented scenario for fracture is very simple. In reality, cracks interact with material microstructure, during propagation. This interaction strongly influences toughness. In view of the fact that brittleness still perhaps remains the most important limiting factor in the design of ceramics components, it follows that the understanding of the micromechanics of fracture propagation becomes crucially important. Following Green (1998), toughening mechanisms can be classified in three groups (Figs. 1.4–1.6):

1. Crack tip interactions:
    (a) crack bowing,
    (b) crack deflection.
2. Crack tip shielding:
    (a) transformation toughening,
    (b) microcrack toughening.
3. Crack bridging.

During crack bowing process, the crack front interacts with obstacles – such as

TABLE 1.2. Toughness K_{Ic} of materials at room temperature.

Material	K_{Ic} (MPa $\sqrt{m}$)
Mild steel	140
Medium-carbon steel	51
High strength steel (HSS)	50-154
Aluminum alloys	23-45
Cast iron	6-20
Rigid PVC	3-7
Polyamides (nylon 66)	3
Cement/Concrete	0.2
Soda-lime glass	0.7-0.9
Al_2O_3	3-5
SiC	3-4
Si_3N_4	4-7
Zirconia ceramics	5-35
E-glass (73.3 vol %) in epoxy	42-60
Fibre reinforced Glass/C	20
SiC fibres in SiC	25
SiC whiskers in Al_2O_3	8.7
Wisker reinforced Si_3N_4	14

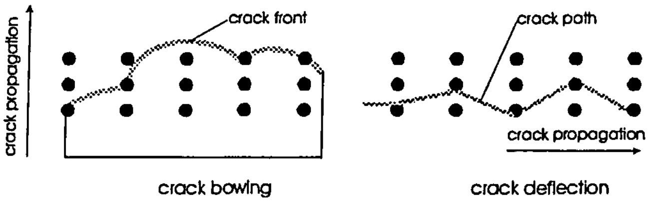

FIGURE 1.4. Crack tip interaction with a periodic composite.

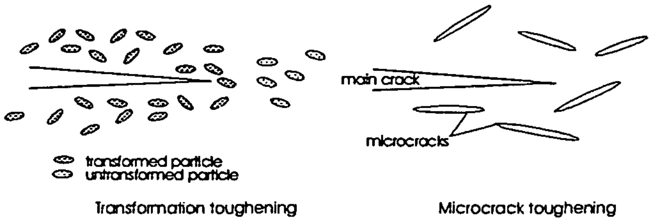

FIGURE 1.5. Crack tip shielding.

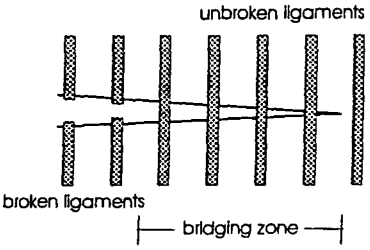

FIGURE 1.6. Crack bridging.

tough second phase particles – impeding propagation and does not remain straight. This mechanism is related to an increase in toughness, as evidenced by Bower and Ortiz (1991).

Crack deflection occurs when fractures deviates from rectilinearity, so that mixed mode loading is involved. Note that crack deflection produces non-planar fracture, whereas crack bowing corresponds to nonlinear crack front. Both toughening mechanisms are often concurrent and strongly influenced by the morphology and contact conditions of the second-phase particles. Crack deflection, which is experimentally revealed by the roughness of the final fracture surface, was analyzed by Cotterel and Rice (1980) and Faber and Evans (1983).

Transformation toughening is related to dilatant, stress-induced phase transformation of particles in a ceramic matrix.

Microcracks can be present in ceramics as induced by the fabrication process or may nucleate as a consequence of a state of prestress or, finally, can be induced by stress.

Under certain circumstances, a microcracked zone around a larger crack may yield a crack tip shielding effect[3]. This effect, analyzed in (Evans and Faber, 1981; Evans and Fu, 1985; Fu and Evans, 1985; Clarke, 1984; Rose, 1986; Rubinstein, 1986 and Hutchinson, 1987; Duan et al., 1995), is however controversial in the sense that it may be almost entirely counterbalanced by the resistance reduction caused by the presence microcracks in the material (Ortiz, 1988; Ortiz and Giannakopoulos, 1989).

Finally, crack bridging occurs when there are fibres or particles in the wake of the crack pinning its faces and therefore reducing the crack tip stress intensity factor (Rose, 1982, 1987; Cox and Marshall, 1988, 1994; Budiansky and Amazigo, 1989; Movchan and Willis, 1993; Movchan and Willis, 1996, 1997a, b, 1998). With the ex-

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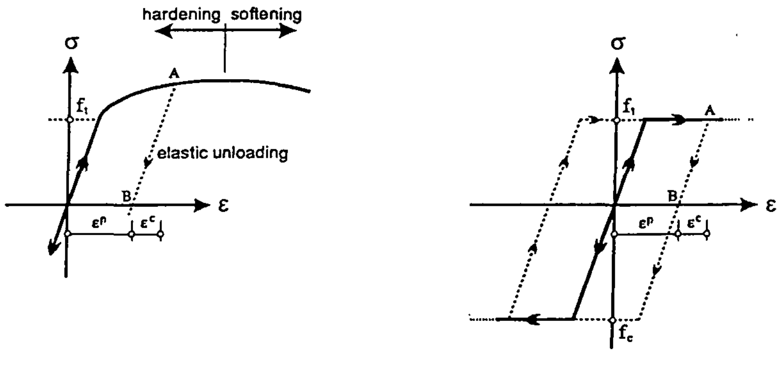
[3] Porosity decreases toughening as evidenced by Rice, 1984; Zimmermann et al. (1998) and Zimmermann and Rödel (1998).

ception of transformation toughening, crack bridging is the most important toughening mechanisms among all discussed above (Pezzotti, 1993; Pezzotti et al., 1996).

1.4. Plastic behaviour

Inelastic deformation is usually related to dislocation activity. In monolithic ceramic materials such as alumina, temperatures superior to 1300°C are needed to make dislocation motion appreciable. Therefore, although ceramics are crystalline materials like metals, plastic deformation is not exhibited in ordinary conditions. However, micromechanisms different from dislocation activity may also induce irreversible deformation. For instance, inelastic deformation of silicon nitride at high temperature is related to the viscous flow of a a glassy phase often present in the grain boundaries of this material. Completely different micromechanisms of plastic deformations take place during forming of ceramic powders. These are presented in Chapter 2 and, in summary, consist in rearrangements, deformation and collapse of particles. Finally, inelastic deformation is connected to phase transformation occurring – for instance – in zirconia-containing ceramics.

Let us consider behaviour of an elastic-plastic material deformed in uniaxial tension, as illustrated in Fig. 1.7.

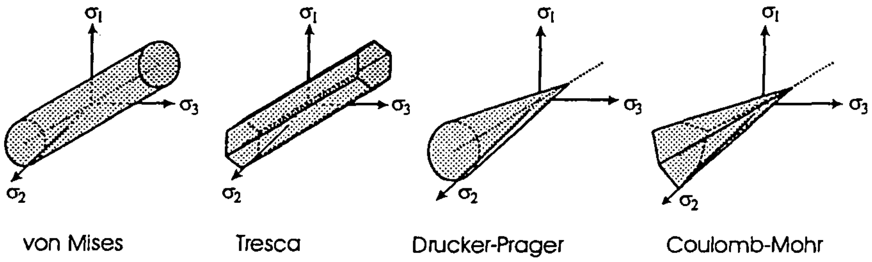


hardening/softening plasticity

ideal plasticity

FIGURE 1.7. Elastoplastic models.

When unloading occurs after a plastic state has been reached, e.g. point A, the inelastic deformation ϵ^p is not recovered. A key ingredient in any phenomenological theory of plasticity is the fact that plastic deformation is possible only when the stress state satisfies a yield criterion. For isotropic materials, a yield criterion may be visualized as a locus in the principal stress space representing elastic states of the material (Fig. 1.8). Plastic deformation is possible only when the stress state lies on the boundary of the yield locus, namely, the yield surface.



von Mises Tresca Drucker-Prager Coulomb-Mohr

FIGURE 1.8. Yield surfaces in the principal stress space.

Plastic or elastic deformation actually takes place if a loading/unloading criterion is met. This criterion is necessarily *incremental*. In fact, starting from point A in Fig. 1.7, incremental plastic or incremental elastic deformations may occur. As a consequence, time independent, inelastic deformation is described by a rate theory, as briefly explained below (the interested reader is referred to Hill, 1950; Besseling and van der Giessen, 1994; Lubliner, 1998).

The skeleton of a generic phenomenological theory of plasticity usually consists in the following hypotheses:

$\mathcal{A}1$. Additive decomposition of total strain ϵ into an elastic part and a plastic part:

$$\epsilon = \epsilon^e + \epsilon^p. \tag{1.9}$$

$\mathcal{A}2$. Elastic law (1.1) defined by the constant fourth-order elastic tensor $\mathcal{E}$ and relating the stress to the elastic deformation:

$$\sigma = \mathcal{E}[\epsilon^e]. \tag{1.10}$$

$\mathcal{A}3$. Yield function defined in terms of stress σ and $\mathcal{K}$, a generic set of internal variables of arbitrary tensorial nature, so that:

$$\begin{array}{ll} f(\sigma, \mathcal{K}) < 0 & \text{elastic behaviour is only possible,} \\ f(\sigma, \mathcal{K}) = 0 & \text{plastic deformation rate may occur,} \\ f(\sigma, \mathcal{K}) > 0 & \text{is not defined.} \end{array} \tag{1.11}$$

$\mathcal{A}4$. Plastic flow rule in terms of a symmetric, second-order tensor **P**, the flow mode tensor:

$$\dot{\epsilon}^p = \dot{\Lambda}\,\mathbf{P}, \tag{1.12}$$

where $\dot{\Lambda} \geq 0$ is the non-negative plastic multiplier and a dot over a symbol denotes the derivative with respect to a time-like, non-decreasing scalar parameter governing the rate problem.

$\mathcal{A}5$. Hardening law:

$$\dot{\mathcal{K}} = \dot{\Lambda}\,\bar{\mathcal{K}}, \tag{1.13}$$

where $\bar{\mathcal{K}}$ is a continuous function of the state variables.

The above equations yield the ***rate constitutive equations*** in the general form (Bigoni, 2000)

$$\dot{\sigma} = \begin{cases} \mathcal{E}[\dot{\epsilon}] - \frac{1}{H} < \mathbf{Q}\cdot\mathcal{E}[\dot{\epsilon}] > \mathcal{E}[\mathbf{P}] & \text{if } f(\sigma,\mathcal{K}) = 0\,, \\ \mathcal{E}[\dot{\epsilon}] & \text{if } f(\sigma,\mathcal{K}) < 0\,, \end{cases} \tag{1.14}$$

where the operator $< \cdot >$ denotes the Macaulay brackets which associates to any scalar α the value $<\alpha>= \max\{\alpha, 0\}$, tensor **Q** is the yield function gradient

$$\mathbf{Q} = \frac{\partial f}{\partial \sigma},$$

and the plastic modulus H is related to the hardening modulus h through

$$H = h + Q\cdot\mathcal{E}[P]. \tag{1.15}$$

The hardening modulus h, defined as

$$h = -\frac{\partial f}{\partial \mathcal{K}}\cdot\bar{\mathcal{K}}, \tag{1.16}$$

describes the type of hardening of the material. In particular, h is positive for strain hardening, negative for softening and null in the case of ideal plasticity. When h is constant, linear hardening occurs, but h may be function of the state, thus describing a nonlinear hardening law (Fig. 1.7). When the hardening is strictly positive, $h > 0$, the constitutive law (1.14) can be inverted

$$\dot{\epsilon} = \begin{cases} \mathcal{E}^{-1}[\dot{\sigma}] + \dfrac{1}{h} < \mathbf{Q}\cdot\dot{\sigma} > \mathbf{P} & \text{if } f(\sigma,\mathcal{K}) = 0\,, \\ \mathcal{E}^{-1}[\dot{\sigma}] & \text{if } f(\sigma,\mathcal{K}) < 0\,. \end{cases} \tag{1.17}$$

In the particular but relevant case in which the flow mode tensor is equal to the yield function gradient, $\mathbf{P} = \mathbf{Q}$, the yield function is called "associative".

Comparing to linear elasticity (1.1), two key points emerge from the analysis of the constitutive equations (1.14) or (1.17), namely:

- the constitutive equations (1.14) are written in rate form. This does not imply dependence on physical time, rather time is identified with any scalar parameter governing the loading process.
- the constitutive equations (1.14) are *incrementally nonlinear*, due to the presence of the Macauley brackets.

It follows from the above points that in any problem of plastic flow, the constitutive equations have to be integrated with respect to the time-like parameter governing the flow.

1.5. Viscous behaviour

When deformation depends on physical time, the behaviour is viscous. Viscous flow, typical of fluids, may also occur in solids and its occurrence is related to the period of time over which the stress is applied[4]. The simplest viscous constitutive equations are those for an incompressible *Newtonian fluid*

$$\boldsymbol{\sigma} = -p\boldsymbol{I} + 2\eta\dot{\boldsymbol{\epsilon}}, \qquad \mathsf{tr}\dot{\boldsymbol{\epsilon}} = \mathsf{div}\boldsymbol{v} = 0, \tag{1.18}$$

where η is the viscosity of the fluid, $\boldsymbol{v}$ its velocity and $\dot{\boldsymbol{\epsilon}}$ the Eulerian strain rate (the symmetric part of the velocity gradient), finally, $p = -\frac{\mathrm{tr}\boldsymbol{\sigma}}{3}$ is the pressure at a point of the fluid.

As a crucial point, we note that Eq. (1.18) relates the Eulerian strain rate to the current stress.

In a number of circumstances, fluids are involved in the industrial applications of ceramics, for instance during injection molding or slip casting. During the latter process, emulsions and slurries are usually employed, consisting of suspended solid particles in a fluid. Flow of these material is usually sensible to the volume fraction of particle and violate Newtonian behaviour in several ways. First, the viscous flow becomes nonlinear, so that the shear stress is a nonlinear function of strain rate. Second, the shear stress depends not only on the local strain rate, but also on its

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[4] For instance, the hot rocks of the Earth's mantle may be considered as solid when deform under the action of seismic waves. On a completely different time scale – on the order of a million years – the same rocks are unable to support shearing stresses and flow as a fluid.

history (so-called "memory effect"). The latter is described by ***viscoelasticity***, which – according to the Kelvin-Voigt scheme – can be viewed as an "parallel" combination of (1.1) and (1.18)

$$\sigma = -pI + 2\eta\dot{\epsilon} + 2\mu\epsilon, \qquad \mathsf{tr}\dot{\epsilon} = \mathsf{div}v = 0, \tag{1.19}$$

or – according to the Maxwell scheme – can be viewed as a "series" combination of (1.18) and (the rate of) (1.1)

$$\dot{\sigma} = -\dot{p}I + 2\mu\,\dot{\epsilon} - \frac{1}{\tau}\left(pI + \sigma\right), \qquad \mathsf{tr}\dot{\epsilon} = \mathsf{div}v = 0, \tag{1.20}$$

where $\tau = \eta/\mu$ is the relaxation time. Constitutive equations (1.19) and (1.20) describe two specific incompressible, viscoelastic behaviours (further details can be found in Malvern, 1969).

Finally, in applications at high temperature, ceramics often exhibit a time-dependent plastic deformation, the so-called *creep*. An elastic-visco-plastic behaviour can be defined as a generalization of (1.20), where a threshold for viscous behaviour is introduced (Duvaut and Lions, 1976; Loret and Prevost, 1990)

$$\dot{\sigma} = \mathcal{E}\dot{\epsilon} - \frac{1}{\tau}(\sigma - \sigma_0)H(f(\sigma(t))), \tag{1.21}$$

where H is the Heaviside function ($H(x) = 1$ for $x > 0$, otherwise $H(x) = 0$), f is the yield function, dependent on current stress $\sigma(t)$, and σ_0 is the projection of σ on the yield surface at time t. Differently from the usual definition employed in rate-independent elastoplasticity, positive values of $f(\sigma(t))$ are fully allowed in (1.21). Constitutive equation (1.21) describes an elastic rate-indepedent behaviour within the yield function. When the stress intensity corresponds to positive values of the yield function, the material flows with a viscous deformation rate proportional to $|\sigma - \sigma_0|$.

1.6. Large strains

Large deformations may occur in the elastic or inelastic range. For instance, ceramic whiskers – such as SiC – or silica-glass fibres may often be so strong that deformation can proceed beyond the limit of linearity to a range of nonlinear elastic deformation (Green, 1998). Moreover, during compaction of ceramic powders large plastic strains occur, while elastic deformation usually remains small. An example of this large strain elastic-plastic behaviour is presented in Chapter 2.

In other cases, deformations are actually small, but effects such as *instabilities* (for instance buckling of fibres which may occur in a composite) may be properly captured only within a theory taking into account large strain effects.

In a large strain theory, the constitutive equations involve *objective measures* of stress and strain. For instance, in an Eulerian description, an elastic constitutive law may be generically written in the form:

$$\sigma = \beta_0 I + \beta_1 B + \beta_2 B^{-1}, \tag{1.22}$$

where B is the *left Cauchy-Green strain tensor* and the scalars β_i, $i = 0, 1, 2$ are functions of the invariants of B (Gurtin, 1981).

In any rate theory of plasticity at finite strain *objective rates* of stress and strain replace the rates $\dot{\sigma}$ and $\dot{\epsilon}$. A presentation of finite strain theory is far beyond the scope of the persent introduction and the interested reader is referred to (Bigoni, 2000; Gurtin, 1981; Ogden, 1984; Holzapfel, 2000).

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Chapter 2

Forming of advanced ceramics

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and Davide Bigoni [1]

Cold compaction of powders is a basic process in ceramics forming. After a review of existing phenomenological models for mechanical behaviour of powders, experiments are presented, which were performed on a commercial alumina powder. These are used to calibrate a plasticity model for soils, namely, the Cam-clay. F.E. simulations are finally presented of a simple forming process and results are shown to be in qualitative agreement with experiments.

2.1. Introduction

Powder compaction is a process in which granular materials are made cohesive through mechanical densification. These may or may not involve temperature and permit an efficient production of parts ranging widely in size and shape to close tolerances with low drying shrinkage (Reed, 1995).

Metallurgical (German, 1984) and pharmaceutical (Lordi and Cuitiño, 1997) applications are common; moreover, forming of traditional (for instance: ceramic tiles,

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porcelain products) and structural ceramics (for instance: chip carriers, spark plugs, cutting tools) involves essentially powder compaction. The focus of this chapter is the analysis of cold compaction of ceramic powders to obtain a constitutive model capable of describing green body formation.

In the case of advanced ceramics, a ceramic powder is usually obtained through spray-drying and is made up of particles (granules) of dimensions ranging between 50 and 200 μm (Fig. 2.1), coated with the binder system. The granules are aggregates of crystals having dimensions on the order 1 μm.

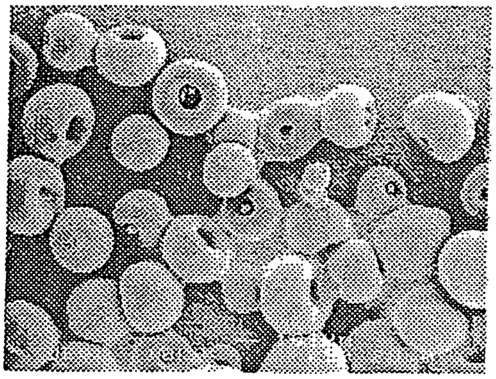

FIGURE 2.1. SEM micrograph of the analyzed alumina powder (bar = 100 μm).

Figure 2.1 refers to the specific material analyzed in the present article. This is a commercial ready-to-press alumina powder (96% purity), manufactured by Martinswerk GmbH (Bergheim, Germany) and identified as 392 Martoxid KMS-96. The data presented by the manufacturer are given in Table 2.1. It can be noted from Fig. 2.1 that the granules have a mean diameter of 250 μm.

TABLE 2.1. Granulometric and density properties of the tested alumina powder.

MWM 28 Vibration sieving	
sieve residue > 300 μm	3.9%
sieve residue > 150 μm	56.3%
sieve residue < 63 μm	2.5%
Bulk density (g/cm^3)	1.219
Green density (p = 50 MPa) (g/cm^3)	2.39
Fired density (T=1600°C, 2h) (g/cm^3)	3.77

Densification of ceramic powders induced by cold pressing can be divided in three main stages (Matsumoto, 1986; Reed, 1995; Bortzmeyer, 1996):

- **Phase I** granule sliding and rearrangement,
- **Phase II** granule deformation,
- **Phase III** granule densification.

The three phases of densification can be distinguished by the changes in the inclination of the semi-logarithmic plot of density versus applied pressure. These determine the "breakpoint pressure" and "joining pressure" points. The Phase I always occurs in early volumetric deformation of granular materials (at low stress), so that it has been thoroughly investigated for geomaterials. However, densification process in ceramic powders is often highly non homogeneous, so that usually at least two phases coexist. With reference to continuum mechanics modelling, phases II and III of deformation are related to the gain in cohesion of the material and have been scarcely investigated.

2.1.1. The need of research

Many technical, unresolved difficulties arise in the forming process of ceramic materials (Brown and Weber, 1988; Bortzmeyer, 1996). In fact, if on one hand the compact should result intact after ejection, should be handleable without failure and essentially free of macro defects, on the other hand, defects of various nature are always present in the greens (Deis and Lannutti, 1998; Ewsuk, 1997; Hausner and Kumar-Mal, 1982; Glass and Ewsuk, 1997; Thompson, 1981b), badly influencing local shrinkage during sintering (Deis and Lannutti, 1998; Hausner and Kumar-Mal, 1982). Defects can be caused by densification process, that may involve highly inhomogeneous strain fields, or by mold ejection, often producing end and ring capping, laminations, shape distortions, surface defects, vertical cracks, and large pores (Glass and Ewsuk, 1997).

In view of a reduction in the defects – crucial in setting the reliability of the final piece – simulations of the forming process become an important tool to optimize ceramics design (in terms of shape of final piece and type and composition of the powder).

2.1.2. A state-of-the-art

Though compaction of granular materials has been the focus of intense research, ceramic powders have been scarcely considered. We review various contributions and methodologies developed for mechanical modelling of granular materials of different nature.

Metallic powders. Several phenomenological or micromechanical models have been developed to describe Phases I and II densification for various metallic powders. Some of them are reviewed below.

Compaction of metallic powders under isostatic pressure was considered by Arzt (1982) and Helle et al. (1985). Other models describe the powder compaction into cylindrical dies with axial loading and concern generic powders (Thompson, 1981a; Kenkre et al., 1996).

Brown and Weber (1988) develop an elastic-plastic model at large strains based on an *ad hoc* yield function. Both experiments and numerical simulations are presented.

Micromechanical approaches have been developed by Fleck et al. (1992), Akisanya et al. (1994) and Fleck (1995). Akisanya et al. (1994) derive a relationship between pressure and density defined within the context of Phase II. Fleck et al. (1992) and Fleck (1995) obtain analytical expressions for yield surfaces at the level of a phenomenological theory of plasticity. The analyses are based on a ductile behaviour, typical of metallic powders. Other works, based on the micromechanical approach are hardly extendible to the simulation of industrial processes with complex geometries (Cuitiño and Gioia, 1999; Kuhn et al. 1991; Pavanachand and Krishnakumar, 1997; Subramanian and Sofronis, 2001; Ng, 1999; Parhami et al. 1999).

Gurson and McCabe (1992) show experimental results concerning high pressure triaxial tests on tungsten-nickel-iron powders and discuss possibility of simulating the cohesion increase by using a particular hardening mechanism.

Tran et al. (1993) use an elastic-plastic model analogous to those developed for sands, in a large strain formulation. Even if the model is limited to Phase I, the approach allows the numerical simulation of the forming process of simple components.

Lewis et al. (1993) propose a computer-aided simulation procedure for metal powder die compaction. They develop the model within the large deformation theory, using a modified von Mises criterion for porous material as proposed by Oyane et al. (1973). The friction between the powder compact and the rigid die wall is taken into account. Simulations of the die compaction of powder compact having variable cross-sections are presented. The main limits in this approach are the assumptions of a rigid-plastic behaviour and a yield surface independent of the third stress invariant.

Jernot et al. (1994) propose a microstructural approach to simulate metallic powder compression, based on tools of mathematical morphology (erosion and dilation).

Brown and Abou-Chedid (1994) illustrate pressing experiments and present an elastic-plastic model. They claim that in the field of metallic powders there are no experimental tests enabling to clarify the issue of flow-rule associativeness or lack of it.

Lippmann and Iankov (1997) describe the process of compaction and sintering by means of a rigid-plastic model, which cannot describe the so-called "springback" effect.

The large strain elastic-plastic model proposed by Oliver et al. (1996) is employed in f.e. simulations accounting for friction between powder and cast. In the constitutive modelling a yield surface independent of the third stress invariant is assumed.

Ariffin et al. (1998), Lewis and Khoei (1998) and Khoei and Lewis (1999) use a large strain formulation of a constitutive model which combines Mohr-Coulomb criterion with an elliptical cap model. Friction between powder and cast is accounted for and remeshing is used to follow complex geometries. This model does not describe the increase in cohesion when the material is subjected to hydrostatic stress states.

Using several elastic-plastic models, Sun and Kim (1997) analyze the compaction of iron and copper powders and conclude that a modified Cam-Clay model is the more suited.

Geindreau et al. (1999a;b) present experiments on lead powder for investigating the constitutive behaviour during hot pressing.

Numerical simulations of the powder compaction of a cup have been performed by Redanz (1999; 2001), using two different porous material models: that by Fleck et al. (1992a) and a material model including interparticle cohesive strength (Fleck, 1995).

Gu et al. (2001) have developed a constitutive model where the plastic flow is assumed to be representable as a combination of a distortion mechanism and a consolidation mechanism. For the distortion mechanism a Mohr-Coulomb type yield criterion with a non-associative flow rule is used, whereas for the consolidation mechanism an elliptical shape yield function with an associative flow rule is employed.

A simple isotropic and two anisotropic micromechanical models of compaction are compared in Henderson et al. (2001).

Subramanian and Sofronis (2001) present a micromechanical model for interaction between densification mechanisms in powder compaction. Elastic deformation, power-law creep deformation, diffusional mass transport on the interparticle contact areas and pore surfaces are taken into account.

Sands and granular materials. The constitutive models developed in this field are concerned with the behaviour of geotechnical materials and refer essentially to low pressures, corresponding to Phase I compaction. Despite microstructural differences, sands and clays have similar macroscopic properties, so that constitutive models have been developed for both materials, assuming that the behaviour of sands and clays is governed by different zones of the same yield surface. For instance, it is common to assume that a dense sand behaves as a strongly overconsolidated clay. Other models have been specifically developed for sands. A fundamental feature of granular materials is the presence of plastic strains at low load levels, and the occurrence of a notable anisotropy induced by the loading process. The main elastic-plastic models which can describe these aspects are very briefly summarized in the following.

Mróz et al. (1978) and Prevost (1977) propose the use of vector-valued yield functions coupled with kinematic hardening to describe the mechanical behaviour of granular materials, in such a way extending to soils an approach originally proposed for metals by Mróz (1967) and by Iwan (1967).

Dafalias and Popov (1975) and Krieg (1975) simplify the Mróz approach, by suggesting the use of two surfaces only: an inner one, describing the elastic behaviour, is subjected to kinematic hardening and an outer one, modelling the extent of the plastic strains, is fixed and named "bounding surface". A similar approach has been proposed also by Hashiguchi and Ueno (1977) with the so-called "subloading surface" model.

More specifically oriented towards sands at low loading levels are the models proposed by Ghaboussi and Momen (1982) and by Poorooshasb and Pietruszczak (1985), based on two surfaces only, shaped as two open cones with non circular cross-section and with vertices coinciding with the origin of the stress space.

Zienkiewicz and Mróz (1984) and Pastor and Zienkiewicz (1986) propose a generalized plasticity model, in which the directions of plastic loading and unloading, as well as the amplitude of the plastic strains, are defined at each point of the stress space without making reference to a yield surface or to a consistency criterion.

De Boer (1988) has developed constitutive equations for granular materials based on a "single-surface" criterion and a non-associative flow rule. A review of the state of the art of the macroscopic porous media theory can be find in de Boer (2000).

Morland et al. (1993) describe a model for the uniaxial compaction of granular materials valid at small strains.

Borja and Wren (1995), Wren and Borja (1997) present a methodology for deriving the overall constitutive relations for granular materials based on micromechanical concepts. The overall response is obtained using particulate mechanics and considers the particle-to-particle interaction at contact points. Finally, a methodology for calculating the overall tangential moduli for periodic assemblies of circular disks has been proposed.

Anand and Gu (2000) have been formulated a large deformation three-dimensional elasto-plastic constitutive model for dry granular materials at low pressure, based on the classical Mohr-Coulomb criterion. The model is used to predict the formation of shear bands in plane strain compression and expansion and to predict the stress state in a static sand pile.

The main drawback of the described models is that the same sand behaves as different materials at different densification levels. Such problem becomes important in the description of ceramic powders, where the density is a variable of the primary importance, subjected to evolution during the forming process. Recently, Manzari and Dafalias (1997) and Gajo and Muir Wood (1999a,b) have independently developed an approach originally proposed by Muir Wood et al. (1994) to account for the dependence of the mechanical properties from the densification level by means of a state parameter (Been and Jefferies, 1985). Both models are based on two open conical surfaces, with vertex coinciding with the origin of the reference system; in particular, some restrictions existing in the model of Manzari and Dafalias (1997) are overcome in the approach of Gajo and Muir Wood (1999a,b) by means of the use of a normalized stress space. Recently Gajo et al. (2001) have extended this model to include the elastic anisotropy induced during the deformation process. In this way it has been possible to show how this model can describe the onset of strain localization and the post-localization behaviour, both under axisymmetric and biaxial conditions.

Ceramic powders. A general review of the powder pressing technology is given in Volume 22 of the *MRS Bulletin* (1997). It is explicitly stated in the introduction (Ewsuk, 1997) that the numerical modelling of densification phenomena is still an open problem, that there is a need of employing a large strain formulation and that several techniques (slip-casting, pressure filtration, centrifugal casting, injection molding, tape casting, gelcasting) are much less known than the widely used dry-powder pressing. Similar conclusions are reached by Schilling et al. (1998). It may be therefore appreciated that the state-of-the-art of mechanical modelling of ceramic densification process is still rather poor. Some contributions to this specific field are reviewed below.

Shima and Mimura (1986) illustrate experimental results and formulate a yield criterion for ceramic powders. They claim that the experimental evidence points towards an associative flow-law.

The model by Kuhn et al. (1991) reduces the problem of Phase I densification to the search for the critical load of an arch. This model may be useful both for practical applications and in the description of experimental results. However, the model may be too limited to allow an adequate extension for modelling an entire compaction process.

Höhl and Schwedes (1992) discuss the possibility of extending to powders the models used in geomechanics. However, they do not formulate a new model able to improve on the limits of those currently used in geomechanics.

The relationship between density and tensile strength of ceramic powders are discussed by Bortzmeyer (1992a). A micromechanical model to determine the microscopic behaviour of packing during tensile tests is also proposed. Bortzmeyer (1992b) presents experimental results carried out on a zirconia powder with a standard triaxial apparatus and numerical simulations performed using a Cap-model with non-associative flow rule.

Experimental results are given in Shima and Saleh (1993), where it is proved that a strong anisotropy is induced during pressing. This effect is then modelled in terms of kinematic hardening.

Ahzi et al. (1993) employ crystal plasticity models for the analysis of the forming of BSCCO superconductive powders. Owing to the peculiar lamellar microstructure of their powders, their analysis is hardly extensible to powders with a different microstructural morphology.

A relationship is proposed by Santos et al. (1996) to describe the variation of the density as function of the applied pressure, valid for alumina powders under pressures above 150 MPa.

Brandt and Nilsson (1998; 1999) present an elastic-plastic model for powder compaction and sintering, with a kind of anisotropic hardening taken from models used in geomechanics (DiMaggio and Sandler, 1971; Sandler and Rubin, 1979).

A comparison between the model of Shima and Oyane (1976) and the model of Fleck et al. (1992a) is presented by Kim and Kim (1998), whereas Sun and Kim (1997) and Sun et al. (1998) compare the same models to the Cam-clay. A similar work is that of Park and Kim (2001), where a yield function is proposed, with associative flow-law and independent of the third stress invariant.

Phase I densification is interpreted by Cuitiño and Gioia (1999) as a phase transformation. Their model is based on a micromechanical approach and is applicable to a wide class of granular materials. However, it may be difficult to extend it to Phases II and III.

The "CRADA group" (Aydin et al. 1997a,b; Ewsuk et al. 2001; Keller et al. 1998; Zipse, 1997) reports about a model for powder compaction based on a proposal by Sandler and Rubin (1979) for describing mechanical behaviour of concrete. Such model appears to be not fully adequate to the description of the ceramic powder behaviour in several respects (a small strain theory is used; the cohesion gain due to densification is not accounted for; the yield surface is independent of the third stress invariant; the elastic parameters do not depend on both the current stress and the past history; hardening is present only in the cap region).

On the basis of the above reported state-of-the-art, we feel it is possible to conclude as follows:

- the description of industrial processes, in the presence of complex geometries, still requires the use of phenomenological models and could hardly be based upon micromechanical approaches;
- a realistic elastic-plastic model, able to describe the powder compaction process, should include:
  - a large strain formulation (during forming the material undergoes strains exceeding 50%);
  - description of elastic phenomena (a rigid-plastic model would miss to capture several aspects which strongly affect the strength of the green bodies);
  - pressure-sensitivity of yielding;
  - dependence of the yield function on the third stress invariant;
  - non-associative flow-law;
  - closure of the yield function in compression, in order to simulate compaction during isostatic pressing;
  - hardening and softening. In particular, the hardening must describe the increase in cohesion of the material during the pressing (Bortzmeyer, 1992a);

TABLE 2.2. Measured density as function of the forming pressure.

Forming pressure (MPa)	Mean density (g/cm^3)	Standard deviation
5	1.76	0.007
10	1.89	0.007
20	2.03	0.006
30	2.13	0.002
40	2.15	0.003
50	2.19	0.007
60	2.26	0.005
80	2.31	0.007
100	2.36	0.002
120	2.38	0.003

  - explicit introduction of density as a state variable;
  - variation of the elastic moduli with density (Brown and Weber, 1988), an effect which could be accounted for by using the theory of elastic-plastic coupling (Hueckel, 1976);
  - progressive anisotropy, both elastic and plastic, due to plastic straining (Shima and Saleh, 1993; Uematsu et al. 1995).
- Moreover, the simulation of the forming process should include:
  - effects of the deformability of the die (Matsumoto, 1986);
  - effects of friction between powder and die (Song and Chandler, 1990);
  - simulation of the complete mold extrusion process, which may cause fracture upon unloading (Bortzmayer, 1996);
  - analysis of strain localization and relevant numerical treatment.

2.2. Experimental

Experimental investigation has been performed on the alumina powder described in Section 5.1. Experiments include uniaxial strain tests in a cylindrical mold, direct shear tests and biaxial flexure tests on the tablets obtained through uniaxial strain.

2.2.1. Uniaxial strain tests

Uniaxial deformation tests have been performed in a single-sided, cylindrical mold having inner diameter of 30 mm. A universal MTS 810 machine (by MTS Systems Gmbh, Berlin, Germany) has been employed. Tests were performed without lubricant at a 2 mm/min velocity of moving punch, for pressure levels ranging between 5 and 120 MPa. Five tests have been performed at given values of pressure, selected as 5, 10, 20, 30, 40, 50, 60, 80, 100, 120 MPa. After uniaxial strain, tablets have been weighted and measured, so that the mean density has been evaluated. A quantity of 8 g of powder has been used for each test, discharged in the mold from an height of 10 cm and shaken. Experiments were performed at a relative humidity of 28%. Results are reported in Fig. 2.2 (in a natural and semi-logarithmic representation) and Table 2.2. As can be noted from Fig. 2.2, points in the semi-logarthmic plot lies on a straight line, accordingly to DiMilia and Reed (1983a,b) and Lukasiewicz and Reed (1978). A representative load F versus vertical displacement s curve is reported

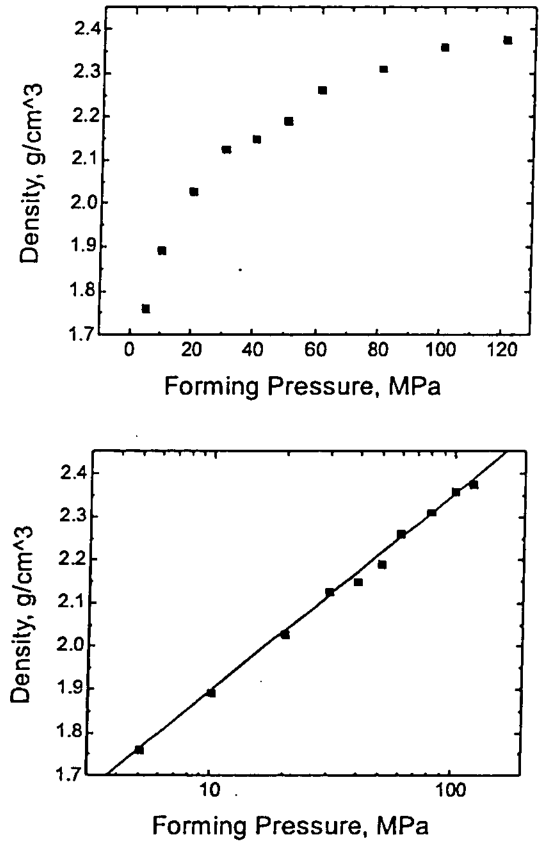

FIGURE 2.2. Compaction behaviour of the tested alumina powder (in a natural and semilog representation).

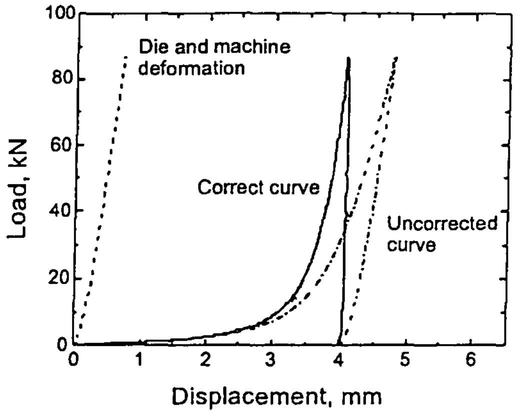

FIGURE 2.3. Load vs. displacement curve in uniaxial strain.

in Fig. 2.3, from which the density ρ versus pressure p curve can be obtained through the simple relationships

$$\rho = \frac{M}{A(h_0 - s)}, \quad p = \frac{F}{A}, \tag{2.1}$$

(where A is the sample cross-section area, M its mass and h_0 its initial height), as shown in Fig. 2.4. The strong influence of the die and machine deformations can be appreciated in Fig. 2.3. The changes in the slope of the curve in Fig. 2.4 identify the three compaction phases. In particular, the breakpoint and joining pressures are approximately 1 MPa and 20 MPa, respectively. However, the latter point is much less evident from the graph than the former. Note that results reported in Fig. 2.2 agree well with those reported in Fig. 2.4, except that Phase I behaviour is not visible in the former figure.

2.2.2. Biaxial flexure strength tests

Biaxial flexure strength tests have been performed on the tablets obtained through uniaxial strain, following the indications of ASTM F 394. For this test the velocity of the cylindrical ram was 0.4 mm/min. The increase in biaxial flexural strength as a function of the forming pressure is shown in Fig. 2.5. Results are in good agreement with existing data (Reed, 1995) and clearly show the mechanism of cohesion increase, as related to densification.

A SEM micrograph of the fracture surface after a biaxial flexural test of a tablet formed at a pressure of 50 MPa is shown in Fig. 2.6. Note that 50 MPa is the optimal

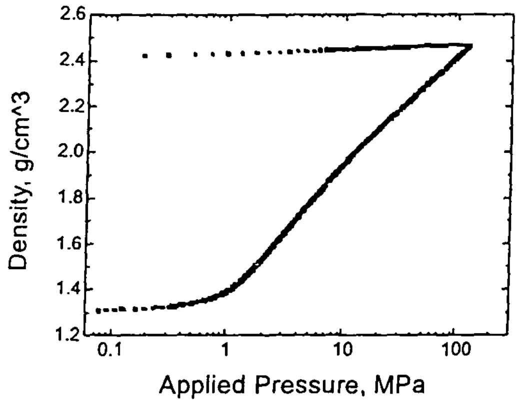

FIGURE 2.4. Compaction diagram in uniaxial strain (semilog representation).

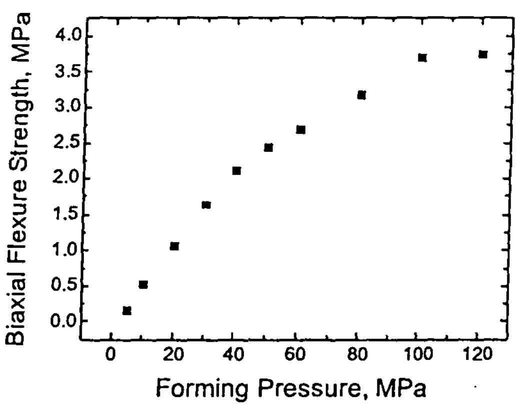

FIGURE 2.5. Biaxial flexure strength as related to forming pressure.

forming pressure indicated by the powder manufacturer.

Fracture results to be partially transgranular and partially intergranular. It may be noted that there are clusters of deformed granules with low intergranular porosity. Figure 2.7 is a detail of a fractured granule, where the aggregate crystals are visible.

2.2.3. Direct shear tests

A few direct shear tests have been performed using a standard geotechnical apparatus. The apparatus consists of a shear box which contains the sample and which is

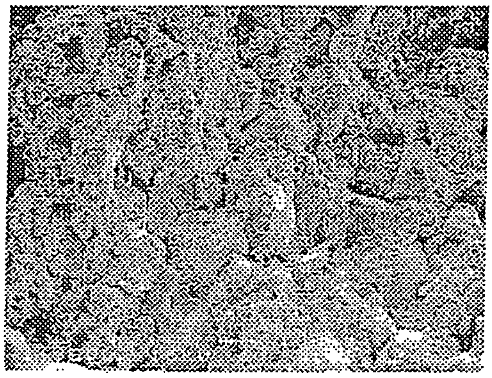

FIGURE 2.6. Fracture surface of a tablet formed at 50 MPa pressure (bar = 100 μm).

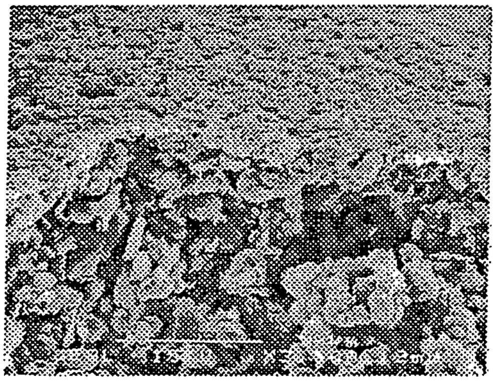

FIGURE 2.7. Particular of Fig. 2.6 (bar = 10 μm).

split in the mid-height. When a normal force is applied, the horizontal force required to induce a movement of the upper half of the sample with respect to the lower half is measured. This test is useful for the evaluation of the friction angle of a granular material, like the alumina powder in Phase I of densification. In order to investigate the shear strength of the cohesionless material, a low vertical pressure was applied: three values were considered, namely, 200, 500, and 1000 kPa. The samples were formed by carefully pouring the ceramic powder within the shear box. Shearing was performed at a velocity of 0.2 mm/min. The variation of the vertical displacement of the sample upper surface and of the applied shear force during shearing is shown in

Figs. 2.8 and 2.9.

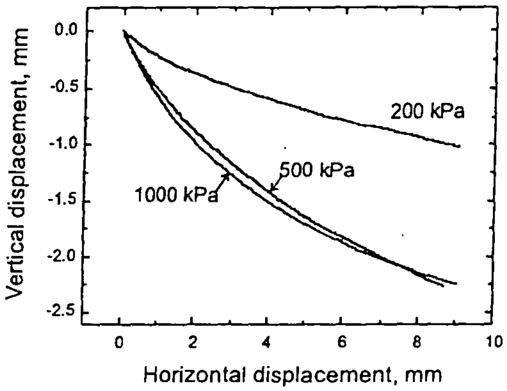

FIGURE 2.8. Vertical vs. horizontal displacements of three samples, for different vertical pressures (200, 500 and 1000 kPa).

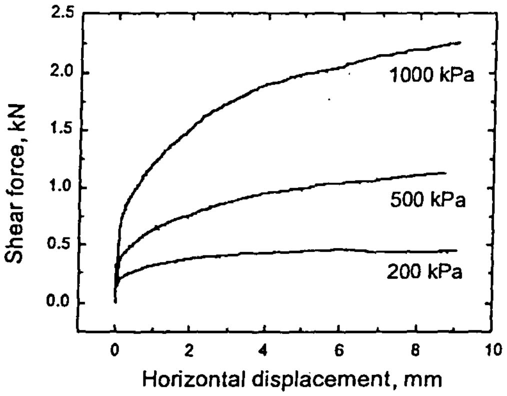

FIGURE 2.9. Shear force vs. horizontal displacement of three samples, for different vertical pressures (200, 500 and 1000 kPa).

The samples have the typical behaviour of a loose sand, with compressive volumetric strains during shearing, without a peak strength followed by a softening phase. The fact that the samples sheared at 500 kPa and 1000 kPa of vertical pressure have the same volumetric strains is probably related to a slightly looser initial condition of the former sample. It can be observed that, except for the test performed under a vertical stress of 200 kPa, the steady state condition typical of the critical state

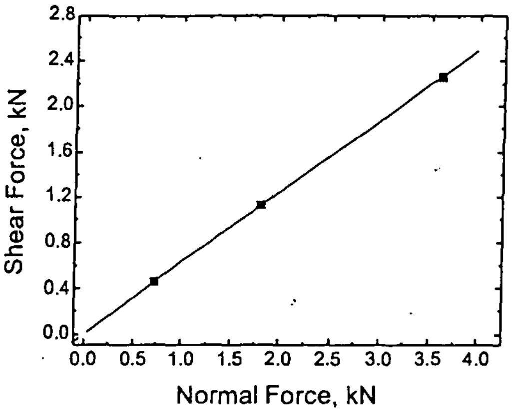

FIGURE 2.10. Maximum shear force at different vertical loads.

is not reached and at the end of the test the strength and the volumetric strains of the samples are still slightly increasing. This effect is more pronounced at larger applied vertical pressures and is probably connected to the progressive deformation and rupture of the grains constituting the alumina powder occurring during shearing even at low confining pressures. This is consistent with the experimental evidences that very large shear strains are necessary to reach the steady state in sands when grain crushing occurs.

The maximum shear force reached at the end of the test is plotted in Fig. 2.10 as a function of the applied vertical load. The results clearly lie on a straight line and may be interpreted following the Coulomb-Mohr failure criterion, to yield a friction angle approximately equal to 32°. Accepting a slight approximation, this angle was considered the critical state friction angle in the following simulations. Moreover, since experimental information on the shear strength of the cohesive material after compaction are missing, the measured friction angle was assumed to characterise also the behaviour of the material after compaction.

2.3. Modelling and calibration

It can be concluded from the above reported experiments that a plasticity model is the best candidate for a phenomenological description of powder compaction. First, in fact, an elastoplastic model is needed to simulate the irreversible deformation representing the forming process itself, second, it allows determination of *residual stresses* after forming, a fundamental parameter for design purposes.

In general, an elastoplastic model is formulated as a nonlinear relationship between objective rates of stress $\overset{\nabla}{T}$ and strain D

$$\overset{\nabla}{T}=\begin{cases} \mathcal{E}[D]-\dfrac{1}{H}<\mathrm{Q}\cdot\mathcal{E}[D]>\mathcal{E}[\mathrm{P}] & \text{if } f(T,\mathcal{K})=0\,, \\ \mathcal{E}[D] & \text{if } f(T,\mathcal{K})<0\,, \end{cases} \tag{2.2}$$

where $\mathcal{E}$ is the elastic fourth order tensor, the operator $<\cdot>$ denotes the Macaulay brackets which associate to any scalar α the value $<\alpha>=\max\{\alpha,0\}$, f is the yield criterion, function of the stress measure T and of a generic collection of *state variables* $\mathcal{K}$ (which may for instance describe the density of the material). Q and P are the yield function and plastic potential gradients, respectively ($Q=P$ for associative elastoplasticity). Finally, the plastic modulus H is related to the hardening modulus h through

$$H=h+Q\cdot\mathcal{E}[P]. \tag{2.3}$$

Elastoplasticity as described by the rate equations (2.2) is a broad context in which many constitutive assumptions are to be introduced. The similarity of the Phase I compaction with the deformation of granular materials suggests the possibility of using a model already developed for geomaterials. In particular, on the basis of our experimental results, we have decided to employ a finite strain version of the Cam-clay model (Roscoe et al. 1958, 1963; Roscoe and Poorooshasb, 1963; Roscoe and Burland, 1968; Schofield and Wroth, 1968). The model is based on the following assumptions:

$\mathcal{A}1$. Yield function:

$$f(T,p_c)=M^2p^2-M^2p_cp+q^2, \tag{2.4}$$

where $p=-\mathrm{tr}\,T/3$ is the hydrostatic stress component, $q=\sqrt{3J_2}$ (with $J_2=T\cdot T-3p^2$) is the Mises stress, M is a material constant and p_c is a hardening parameter.

$\mathcal{A}2$. Associative plastic flow rule:

$$Q=\frac{M^2}{3}(p_c-2p)I+3S, \tag{2.5}$$

where $S=T-(\mathrm{tr}T)/3I$ is the stress deviator.

$\mathcal{A}3$. Isotropic hardening rule:

$$p_c=p_{c0}\exp{(1+e_0)}\frac{1-J^p}{\Lambda-\kappa J^p}, \tag{2.6}$$

where $J^p = \det \boldsymbol{F}^p$, being $\boldsymbol{F}^p$ the plastic part of the deformation gradient $\boldsymbol{F}$, p_{c0} and e_0 are the initial values of hardening parameter and void ratio, respectively, (the void ratio is defined as the ratio between the volume of voids and volume of solid phase). Λ is the logarithmic hardening modulus and κ the logarithmic elastic bulk modulus and are represented by the slopes of plastic and elastic branches of the e vs. $\log p$ curve obtained under isotropic compression.

It may be anticipated, however, that the Cam-clay model has definitive limitations when applied to the modelling of ceramic powders. In particular, a more refined model should include the following features, not considered in the Cam-clay:

- the yield function should depend also on the third stress invariant;
- a non-associative flow-law should be introduced;
- the hardening should describe the increase in cohesion of the material during the pressing;
- the elastic moduli should depend on the increase in cohesion during densification (an effect that could be accounted for by using the theory of elastic-plastic coupling, Hueckel, 1976).

Among the above points, the dependence of the cohesion on the relative density is the more important. In the Cam-clay model, in fact, the material remains cohesionless during all the process of inelastic deformation. On the contrary, the proper description of cohesion gain during forming is a fundamental aspect for design purposes.

Calibration of the model has been performed on the basis of our experiments (with the exception of the Poisson's ratio, which was estimated from values available in the literature). In particular, the values of the parameters Λ and κ were deduced from the slopes of curves obtained by loading and unloading the samples in the uniaxial strain test. For this evaluation, we have assumed a constant ratio between

TABLE 2.3. Values of material parameters estimated from experiments.

Elastic logarithmic bulk modulus κ	0.040
Logarithmic hardening modulus Λ	0.290
Material constant M	1.287
Initial value of hardening parameter p_{c0} (MPa)	0.648
Initial values of void ratio e_0	2.054
Initial confining pressure p_0 (MPa)	0.063
Poisson's ratio ν (taken from literature)	0.26

the horizontal σ_h and vertical σ_v stresses equal to 0.47, as deduced from the formulae

$$\frac{\sigma_h}{\sigma_v} = 1 - \sin\phi,$$

which is currently used for granular media (ϕ is the angle of internal friction). The values of parameters used in the subsequent numerical simulations are summarized in Table 2.3.

2.4. Numerical simulations

Numerical simulations with finite elements have been performed – within the environment allowed by the commercial code ABAQUS (Hibbitt, Karlsson & Sorensen, 2001) – to simulate forming of the (axisymmetric) piece shown in Figs. 2.11 and 2.12. Four pieces where formed at a final mean pressure of 100 MPa starting from 5 g of powder. The axisymmetric mesh used in the simulations is shown in Fig. 2.13. Axisymmetric 4-node elements (CAX4) have been used.

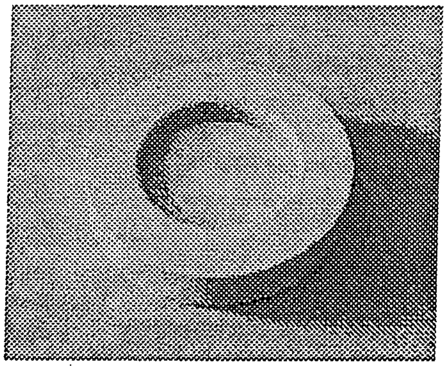

FIGURE 2.11. Photograph of the formed piece.

The following assumptions have been introduced:

- the die is undeformable;
- the contact between powder and die walls is smooth;
- the initial configuration is that shown in Fig. 2.13.

It may be worth noting that the above assumptions are not particularly strong in our specific analysis. In particular, we remark that, due to the large strains that will be reached during pressing, the assumption that the initial configuration shown in Fig. 2.13 is homogeneous does not affect much final results.

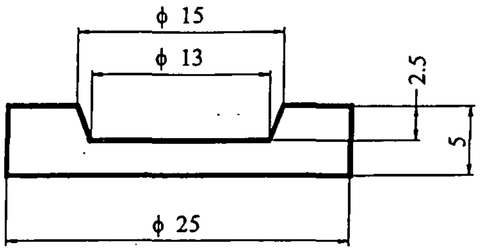

FIGURE 2.12. Geometry of the formed piece (dimensions in mm).

After the initial state – defined by initial values of void ratio and confining pressure – has been defined, the loading history is assigned, which is divided in the following three steps:

1. forming is prescribed by imposing the motion of the upper part of the boundary (3.78 mm, corresponding to the value measured during forming at the final load of 50 kN);
2. unloading is simulated by prescribing null forces on the upper part of the boundary;
3. ejection is simulated by prescribing null forces on all the boundary.

Due to the fact that the Cam-clay model is not defined for tensile stresses and is singular for null mean stress, the last of the above steps cannot be concluded and the analysis ends up when the applied external forces are reduced to a minimal percent of the values at the beginning of the step. Obviously, a more fundamental constitutive approach would require the definition of a gain of cohesion and related variation of elastic properties, as mentioned in Section 5.3.

The deformed mesh at the end of step 1 is shown in Fig. 2.14, whereas the same mesh superimposed on the initial mesh is shown in Fig. 2.15. It can be noted that the elements near the corner of the punch are unphysically distorted so that results in this zone should not be considered realistic.

It is immediate to conclude from Figs. 2.14, 2.15 that the deformation suffered by the piece is quite high. The hydrostatic stress component p (taken positive when compressive), the Mises stress q and the void ratio are reported in Figs. 2.16–2.18, respectively, at the end of step 1.

Excluding the small, unrepresentative zone near the corner of the punch, the hydrostatic stress p ranges from 25.3 MPa to 108 MPa and the Mises stress q from 15.4 MPa to 70.1 MPa. These values show that the stress is highly inhomogeneous.

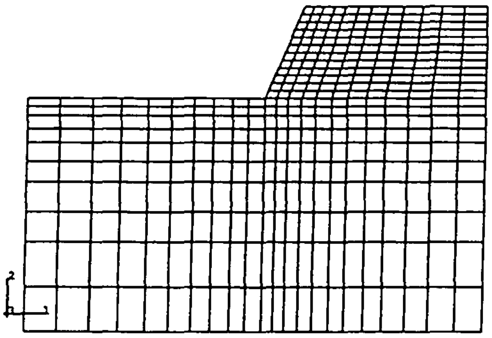

FIGURE 2.13. Initial mesh.

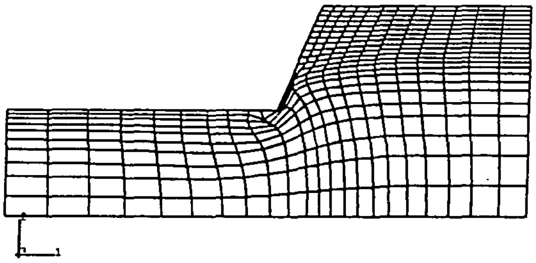

FIGURE 2.14. Deformed mesh at the end of step 1.

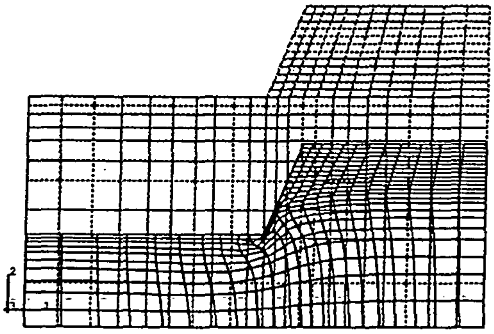

FIGURE 2.15. Initial and deformed (end of step 1) meshes.

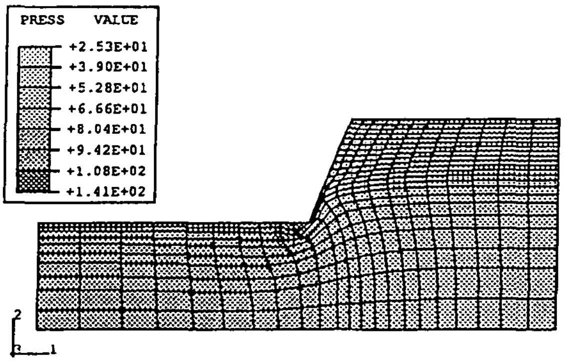

FIGURE 2.16. Distribution of hydrostatic stress component (MPa) at the end of step 1.

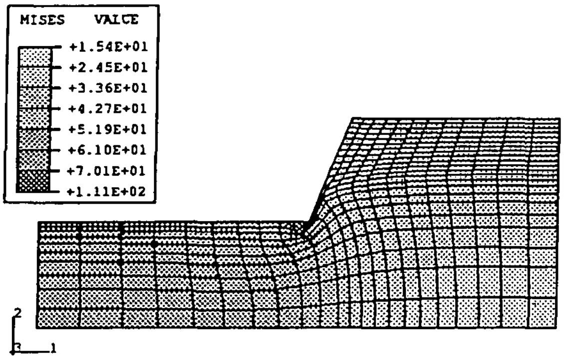

FIGURE 2.17. Distribution of Mises stress (MPa) at the end of step 1.

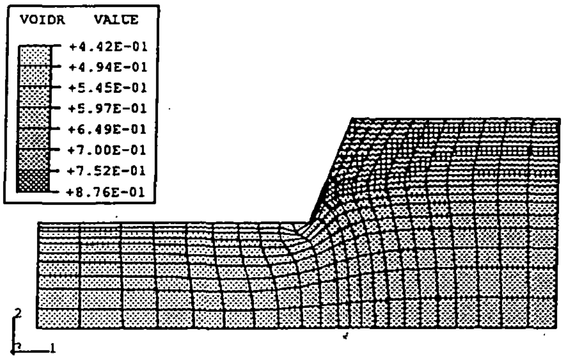

FIGURE 2.18. Void ratio distribution at the end of step 1.

The q/p ratio ranges from 0.31 to 1.14, so that it is always inferior than the value of M.

Values of the hydrostatic and Mises stress components at the end of step 2 are reported in Figs. 2.19 and 2.20, whereas the map of void ratio is shown in Fig. 2.21. It may be important to note that residual stress is quite high, due to the lateral constraint still present at the end of step 2. The knowledge of the lateral stress is important for practical purposes since the force needed for the ejection of the final piece can be estimated through Coulomb friction law, when the lateral stress at the end of step 2 is known. A rough, but simple evaluation can be immediately obtained from numerical output at the end of step 2 employing the formula

$$\textit{ejection force} = \alpha \tan\phi \ (\textit{mean lateral stress} \times \textit{lateral surface of the piece}),$$

where ϕ is the powder friction angle (equal to 32° in our case) and α is a coefficient dependent on the roughness of the die wall and ranging between 0 and 1, typically $\alpha = 0.6$.

The deformed mesh at the end of step 3 is shown in Figs. 2.22 and 2.23. In the latter figure, the deformed mesh is superimposed on the initial. The springback effect and the shape distortion are evident.

The residual stress distribution at the end of forming is reported in Figs. 2.24 and 2.25, where the hydrostatic stress and the Mises stress components are also shown. The void ratio distribution is finally shown in Fig. 2.26. Excluding the small, unrepresentative zone near the corner of the punch, the hydrostatic stress p ranges now between 0.038 MPa and 2.64 MPa and the Mises stress q between 0.32 MPa and 5.22 MPa. Moreover, the void ratio varies between 0.54 and 0.95. It can be noted that the minimum void ratio is usually associated with the maximun residual mean stress. The results suggest that two annular, concentric zones of material are formed, the inner of which is subject to high compressive mean stresses, whereas the outer tends to be subject to tensile stresses. This can represent a potentially dangerous situation, in which the tensile stresses tend to open possible microcracks induced by ejection on the external surface of the piece, leading to serious defects formation in the green. However, even when the green is approximately free of macro defects, its mechanical behaviour and shrinkage during future sintering are deeply affected by the inhomogeneities in the residual stress and density distributions.

Finally, we note from Figs. 2.24–2.26 that an annular zone of very dense material forms near the bottom of the sample. This prediction is indeed confirmed by the visual inspection of the formed sample, clearly showing an annular dark zone, Fig. 2.27.

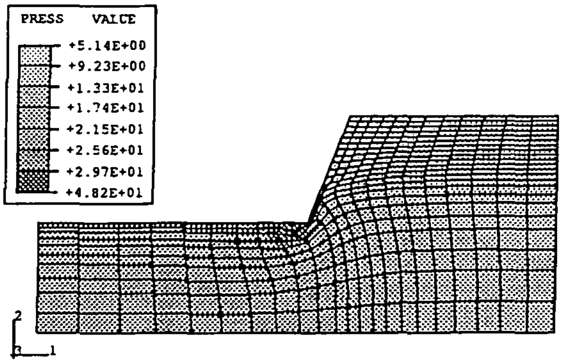

FIGURE 2.19. Distribution of hydrostatic stress component (MPa) at the end of step 2.

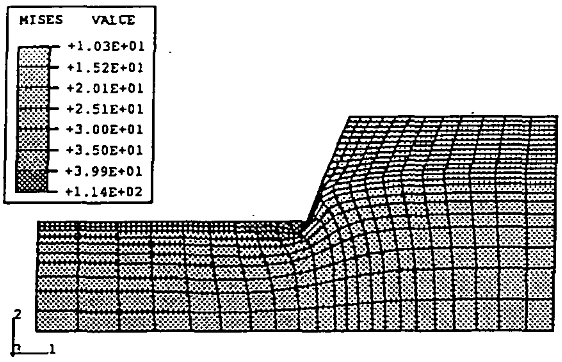

FIGURE 2.20. Distribution of Mises stress component (MPa) at the end of step 2.

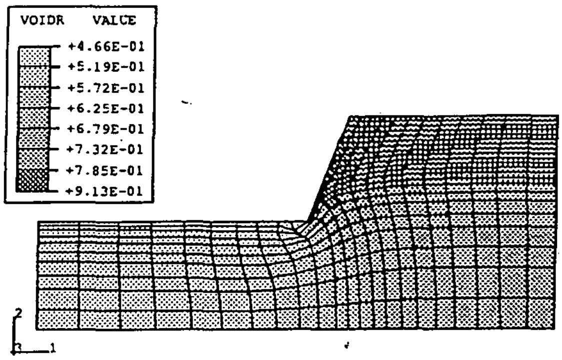

FIGURE 2.21. Void ratio distribution at the end of step 2.

Experimental and simulated load displacement curves during forming of the piece shown in Fig. 2.11 are compared in Fig. 2.28 (natural and semilogarithmic representations are reported), where a satisfying agreement can be noted.

2.5. Conclusions

Results discussed in the present chapter represent a first step toward the development of a model capable of realistically describing forming processes of ceramic materials. Even if the experimental results are still incomplete and the employed elastoplastic model, the Cam-clay, does not describe properly some important feature of material behaviour – as for instance the strong relation between density and cohesion – our results demonstrate that it is possible to realistically predict:

- the springback effect and related shape distortion,
- the force needed for mold ejection,

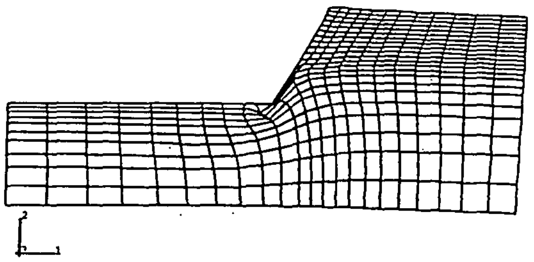

FIGURE 2.22. Deformed mesh at the end of step 3.

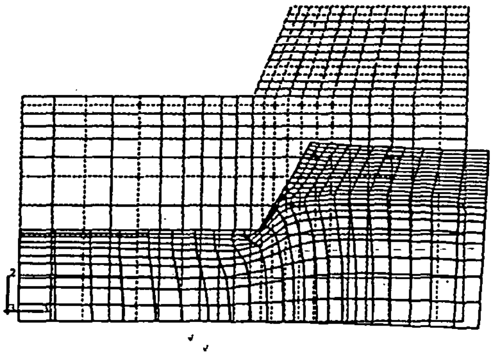

FIGURE 2.23. Initial and deformed (step 3) meshes.

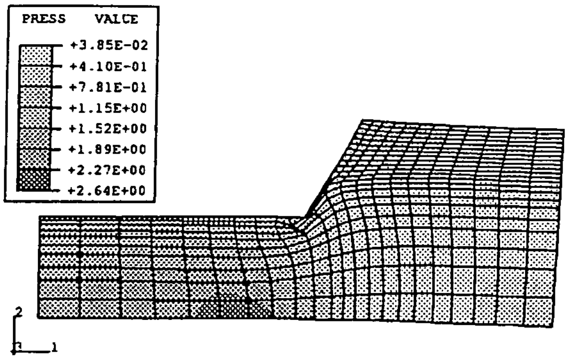

FIGURE 2.24. Distribution of hydrostatic stress component (MPa) at the end of step 3.

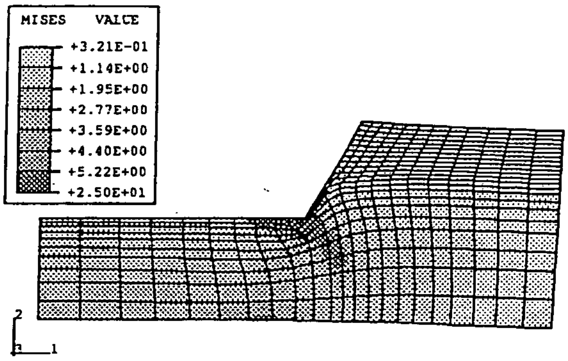

FIGURE 2.25. Distribution of Mises stress component (MPa) at the end of step 3.

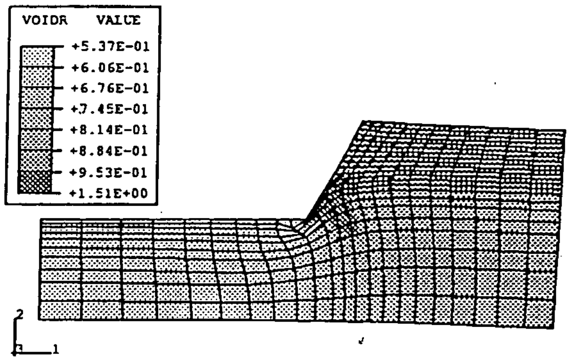

FIGURE 2.26. Void ratio distribution at the end of step 3.

- the residual stress distribution,
- the density distribution and the related presence of defects in the green body.

The final remark is related to the prediction of defects in the sintered piece and therefore its investigation has an important practical meaning.

In closure, we mention that the modelling presented in this Chapter can be extended in different directions. Referring to thermoplasticity, the sintering phase might be covered by modelling, so that simulation could be extended to the entire production process. Moreover, both sintering aids and powder characteristics might enter the elastic-plastic constitutive laws, so that the optimal powder composition and morphology could be predicted for different forming problems.

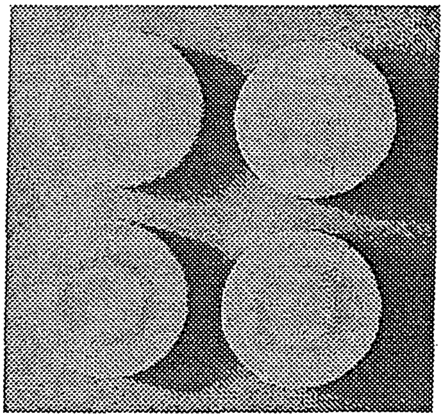

FIGURE 2.27. Photograph of the bottom side of the formed samples.

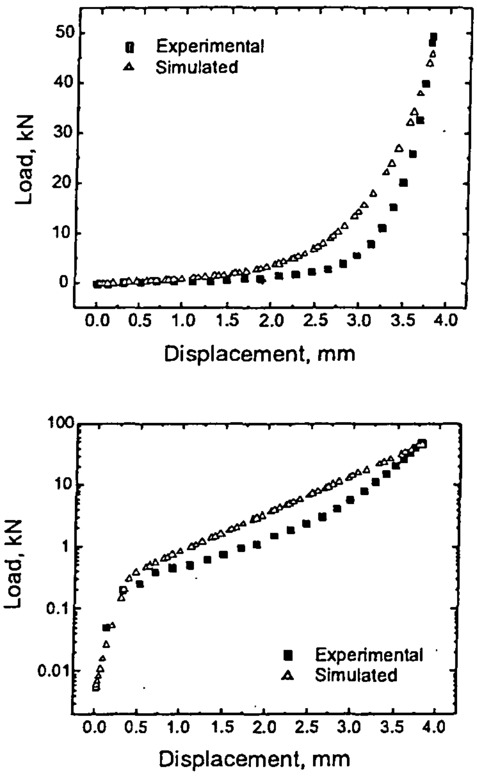

Figure 2.28. Experimental and simulated load vs. displacement curves, in a natural and semilog representation.

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ICS-UNIDO

Best Available Technologies and Innovations in Ceramics Production

Faenza, 30th September 2002

Speech by M.sa Etta Carignani

First of all I should like to thank ICS-UNIDO for inviting me to take part in this opening day of the “Best Available Technologies and Innovations in Ceramics Production” seminar, which provides me once again with the opportunity of appreciating the key role of ICS-UNIDO in promoting and spreading technology and the culture of innovation.

I should like to concentrate in my brief speech on this last aspect, with some thoughts regarding the link between innovation, competitiveness and an area’s development.

The first observation concerns the relationship between innovation and competitiveness. We all take for granted that innovation has a positive effect on competitiveness and from the theoretical point of view we know that the question can be settled by making it part of the definition, in other words by defining innovation as something which in some way increases some factor of productivity and overall productivity.

This was put forward a long time ago by Joseph Schumpeter, the economist who was responsible for the introduction of the concept of innovation in the mid-20th century. Studying the subject of competition, Schumpeter claimed that innovation is the main weapon a firm can use to build a profit margin and to defend it. Thus innovation is not independent from economic parameters; on the contrary it is the object of specific business strategies.

Quite apart from this generally accepted point, the problem is actually very complicated, since it is hard to understand just what innovation really is. In any case a glance through the literature shows there is certainly a positive correlation between innovation and competitiveness, but on one very precise condition: that the term innovation is not understood to mean always the same thing and that the concept of innovation is modified according to the field of business or situation in which it is to be applied.

This statement leads to the consideration of innovation as as an extremely complex process, which includes aspects to do with quality as well as quantity. For instance, it is clear that expenditure on research and development cannot be used to measure innovation in fields where innovation is heavily non-formalized. So the first thing is to understand better the different aspects of innovation.

Identifying innovation with technology *tout court* is a simplification which can be misleading. Innovation is technology, but its effect and its positive impact on firms and their business activities requires an equally decisive commitment to modernize processes and organization. The key to these interlinked processes is the development of human resources. So now two other measures accompanying innovation become essential: training and local area partnerships. So there is no real innovation without originality in management.

However, these efforts risk coming to nothing without an effective training policy. Everyone who has had managerial responsibility knows well how innovation and competitiveness require new individual and collective skills to manage targets and methods, which in turn leads to widespread and increased needs and to the requirements of specific areas. Here there lurks a paradox within a paradox: Italy is known throughout the world for its industrial districts, but when the ability to innovate is observed more closely, we find there is no specialized area, that these industrial districts lack the close cooperation with the advanced centres and research institutes which might turn them into local innovative systems.

There is still plenty to do in this field, particularly as regards local government intervention, which still relies on traditional measures and in any case is often hamstrung by the shortage of funds. Changes in the organization of public administrations currently taking place should bring with them a real transfer of responsibility in this field and obviously concern universities, schools and research institutes, although in fact the signs are rather contradictory.

This is a situation that really has to be sorted out for the very reason I mentioned earlier, that innovation requires a transformation in systems of management and relations within the local area. It is often said that new forms of governance are needed, but the governance of local manufacturing systems cannot take place unless local government administrators have real operational, financial and decision-making power: in other words, training and research at district level can be an important part of regional policy and be properly appreciated by local businesses only if they have real autonomy.

In conclusion I should like to make a final observation: in shifting authority from the centre and delegating to the local level it is crucial that there be a clear understanding at that level of the new powers available, particulalrly in terms of innovation policy. One of the aims of innovation policy at the local level is to support companies and this cannot come down to just developing infrastructure or renovating a disused industrial building. Decisions taken at the local level need to have breadth of vision and have a bearing on business development in the broadest sense. They should aim to boost the process of responsibility for all those involved. So, company practice and individual skills cannot remain unaltered.

What this involves is an out-and-out cultural change in company relations, both internal and external, and an assessment of their impact on the area.

It is in this respect that the question of the availability of technology and thus the problem of the spread of know-how and the transfer of technology become important.

The starting point is the awareness that know-how is the most strategic resource for a country's economy and learning its most important process. Know-how has to be aimed at the management of change, that is the management of complex phenomena created by the growing interdependence between technological, economic and social change.

These complex phenomena are emerging from the non-linear interaction between research, Innovation Technology, the market and social changes, giving rise to a highly dynamic process.

All this requires the development of an ability to understand and a deep and wide-ranging knowledge, which has to be backed up by keeping up to date with innovative technologies, assessing their possible impact on the market and consequent social effects.

These phenomena are also involved in the two fields of "space" and "time", where what is new in one place and at a certain time could already be well-known or even obsolete somewhere else.

It is therefore essental to understand the stategies brought into play, not only for the development of innovation, but also for its spread and accessibility, always bearing in mind the peculiarities of a company, a field of business or an entire area.

On the whole the transfer of Innovation Technology is associated with the following factors:

– it is a complex problem based on cultural behaviour, which assumes "knowledge" and the ability to transfer it, both in teaching and learning;
– it is a problem regarding the structure of small and medium-sized companies, which are often unable to innovate, or prevented from doing so;
– it has to link reasearch and innovation with the real problems companies face;
– it has to be built on a broad and solid structure of local area networks and clusters.

At this point it is clear that the matter cannot be confined to the relationship between company practice and innovation, but has to be opened out to include everything that defines innovation policies.

Nowadays the term innovation policy is a catch-all phrase which is virtually synonymous with development policy, because the concept of innovation policy has broadened from its original field of scientific and research policy to include industrial policy and even training, schools and development infrastructure. I have to say that in view of this evolution and the increasing debate about technological innovation and government action in this field, the results so far have been very disappointing. I need only draw your attention to the fact that research funds are still a virtually insignificant proportion of the national budget.

But we must not lose sight of the problem regarding the figure of the businessman, as it is he who is the innovator, particularly in small and medium-sized companies. Obviously the entrepreneur has to be supported by various other factors, but he shoulders a great responsibility, even cultural, in the learning, spread and use of innovation. So I must underline the central role of the entrepreneur in the process of innovation, because in many cases it is he who has the necessary technical expertise to take an active part and in any case his is the final say when it comes to taking a decision to innovate.

As I mentioned earlier, there is another critical point concerning external relations between the company and the local area. From the point of view of technological innovation, what seems critical is the fact that for the small and medium-sized company innovation is essentially something based on the skills of the workforce, and thus on traditional and well-established knowledge built up on the job. This is why nowadays many international analyses point to staff trained to carry out innovative research and development in a broad sense or units trained for this purpose as the deciding factor in assessing a firm's technological capabilities. At the end of the day these aptitudes enable a company to interact with the outside world, especially with the universities.

This is one of the most crucial aspects of the relationship between technology, innovation and business. Companies that have developed a relationship, even sporadic, with universities and research centres are still far too few. This probably also reflects a lack of understanding of what research actually does, and this touches another key point, which is the question of communication. Communication has never been taken very seriously by our organizations: the business world basically does not know what takes place inside universities and research centres, especially the public ones.

The missing feature in the lack of collaboration between research and business is generally seen to be the cultural framework in which small companies operate. In the first instance these tend to look inwards for solutions to their problems and following this they turn to suppliers or clients. The world of the university or research institutes are not considered an option, and this is a serious problem to which a solution has not yet been found in our country.

Clearly several things need to be done, and at various levels: improving the profile of universities and research centres, cutting red tape in gaining access to research programmes, adapting education and research to specialist innovation throughout the area, while still being in a position to identify and support the features that distinguish local businesses.

Only in this way can innovation constitute a process of development in a broad sense, combining growth, competitiveness and social development, factors that are so important for areas such as Faenza, which hosts this seminar today and which I should like to thank for its warm welcome.

Best available technologies and innovations in ceramics production
FAENZA, ITALY, 30 September – 5 October 2002

MODERN TECHNOLOGIES AND TECHNIQUES FOR MANUFACTURE OF TABLEWARE PORCELAIN

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1. Introduction

The technological changes and the innovation are contributing at the success of one development strategy and at the environment of the economic activity.

The rhythm and the flexibility of the technological changes are the clue of the economical performances.

The product innovation and the process innovation are based on scientific, technological, organizational, financial and commercial activities.

The innovative strategies are connected with the decisive factors in the applied – economy. The innovative projects are influenced by internal factors, external factors, economical factors and factors of the creative potential. The innovative activity inside the industry is based on the relationship between these factors. The success of one innovation require some extra competencies to be involved

Particularly, the purpose of this paper is to briefly examine the transformation occurred in the technology and fabrication techniques of the tableware porcelain in Romania. I'll present you also some information concerning technological innovation in **ARPO** factory.

2. New technologies and fabrication techniques in Romanian traditional tableware porcelain

In the obtaining of the traditional ceramics there are three major steps: body preparation, compaction and densifing. In each of these steps occurred modifications, but I'll trait next only those that imposed themselves in Romanian tableware porcelain industry, having a large use today. So, I'll present atomization as an efficient way to prepare granulates for isostatic pressing. Shaping of the ceramic bodies will be trait from two points of view: first one regarding isostatic pressing and secondly, of pressure casting. Microwave drying of products is imposing itself in ceramic industry because of its high drying speed and because of its concomitant effect of decompression of the green articles. Glazes preparation using fine grinding in annular interstitial mills is conferring a high quality of the glaze, being in connection with fast firing process of the ceramic products.

From latest 10 years experience it is obviously high connection between automatic shaping, glaze quality and firing process.

It is indisputable that a narrow grain size range with grinding fineness ensures an optimal viscosity of the glaze; a better covering capacity is achieved due to the higher specific surface of the glaze.

Basing on the characteristics of the ceramic body and of the glaze, the fast firing curve will be established and the fast firing kiln will be designed.

The modification occurred in the process engineering has implication in the product engineering in two aspects: those of the chemical effects and those of the new involved physical elements. Obtaining a proper product in condition of those modifications depends on the best using of the physical and chemical aspects [1,2].

In this context I'll briefly present the most important modifications happened in the product engineering in the Romanian tableware porcelain industry.

The manufacturing technology of these products was continuously developed in the last 10 years. For ceramic materials there is a tight link between the process engineering and the properties of the resulting product. I'll stand out this connection out trough my presentation.

Atomization is used in Romanian ceramic industry for about 30 years. In spite of energy crisis in the 70 years, and of the saving energy pressure and in spite of the alternative techniques for granulate, *atomization* technique remains desirable [2]. But for porcelain industry atomization started 5 years ago, when isostatic presses were both in Romanian porcelain factories. In some particular applications, the alternative techniques proved their efficiency, but *atomization* still is the best way to produce dry granulate which has the necessary qualities for modern ceramics.

Almost all-ceramic branches are requiring granulate sorts with specific properties to produce high quality articles using high efficient technology. But, condition for one successful production process it is of course, the connection between pressing technology and granulate production.

Today, there are modern installations for producing granulated ceramic powders by spray drying process using computers to register and control the working parameters [3].

Isostatic pressing and medium pressure casting. In the last 5 years new shaping technologies imposed themselves in Romanian ceramic industry; isostatic pressing and medium pressure casting which are at the basis of the automatic production.

The granulated body is especially prepared with specific density below 1000g/l, humidity ~3%, granulometry of 100-600 micrometers. The press is always combined with a fettling machine that removes the pressing excess sponges the product and when is necessary smoothes out the foot. There are a number of options for these machines, including automatic tool change, optical article recognition or monitoring system and data collection etc.

Pressure casting becomes possible starting with the development of a polymer with an appropriate pore structure. Today, the process is used to manufacture tableware ceramics in special installation whereby the cycle time compared to the previously used hand casting method was reduced to ca. 10%. The cycle time for a 7-mm thick piece is about 3 min.

The process occurs in 4 steps: slip admission, vacuuming, pneumatic action and water admission. All these stages are monitored and registered. In general is used conventional slip. Filtration behavior can be improved by heating the slip and by using a proper deflocculant. Special ads could increase the productivity of the pressure casting installation [3].

The clue of the process is to obtain optimal rheological parameters and to keep them constantly.

The pressure casting installations are easy to place in the automatic production lines with taking-over robots. The installation must also to be connected with dryers. Pressure casting advantages (beside increasing productivity) are: a considerable higher quality; replacing plaster moulds with synthetic moulds, so that are no more necessary stocks of plaster moulds; reduced fettling; no more remaining plaster particles on the casted articles; reduced water contain of the ware after removal from the mould (ca. 1.5% less), resulting a better handling properties.

Glazes preparation and the glazing lines have required, as I already showed, process modifications, depending on the new product engineering.

The new production methods and the fast firing technology leaded to better performance and shorter operating time on different technological stages so; the demands for the glaze and body are changed.

The classical drum ball mill is no longer able to fulfill the new requirements.

The option was to introduce the fine grinding technique, using an agitation bead mill, which operates with a continuos one way system, so the glaze, can have a precise granulometric spectrum, in the range 1-100 micrometers. Today's researches showed that the milling fineness can be obtain by one single passing trough and also by recycling [4,5].

The main advantages of the fine milling are: obtaining of a high quality glaze, small work spaces, high productivity, continuos process, small milling balls, (1-2.5 mm, from ZrO2 partly stabilized, possible with Yttrium), high energetic density, better covering properties of the glaze. Organic additives are decreasing the glaze tendency of sedimentation. The future of the good quality products is given by a proper covering effect and of a thicker glaze layer [6,7].

Shaping by isostatic pressing is changing the surface of the product, which will present a rugosity that must be balanced using a much fusible glaze, applied in thicker layer (for a better covering). Also, the isostatic pressed or pressure casting products after the first firing has a lower porosity, result decreased glaze absorption [8].

The glazing machine requires high-density glaze, in order to achieve high productivity.

In case of single firing the usually technique is the glaze spraying. So, they are glazed dry products, without biscuit firing.

The glazing machines by spraying are equipped with pre-heating, drying and cooling points. These installations could be used for glazing of vitreous china, bone china after biscuit firing.

Glazing installations by immersion are used for the production of ceramics with two firing systems (porcelain). Biscuit pieces, fired at 900°C are glazed in installations for plates, casted articles and cups. The process is full automated and includes de-dusting, stamping, immersion glazing, foot cleaning. For short lots they are used half-automatic installations.

Fast firing. Ceramics fast firing is suitable for all those three firing stages: biscuit, glost and decoration firing. Biscuit firing, particularly for porcelain (900°C) is done in continuous roller or table conveyance kilns, or in discontinuous chamber kilns for small productions. The firing time is about 2 hours, from cold to cold.

The single firing of ceramics, stoneware and sometimes vitreous are made in roller kilns and shuttle kilns. The firing time is between 2 and 6 hours, depending on the material type.

Glost firing is done in modern factories using fast firing kilns. There are two alternatives for continuous firing: roller kilns and table conveyance kilns.

Roller kilns have the lowest energetic consumption for the porcelain firing (1800-2500 kcal/kg of fired product). The refractory equipment and the rolls are made from recrystalized SiC. The kiln could include one glaze-dryer, one installation for loading and unloading and one purifying system for exhausted burned gases (to avoid Fluor evacuation in atmosphere). The entire kiln is automatically working.

Porcelain is fast-fired also using table conveyance kilns, in which case it is possible, the stopping during weekend. This kind of kilns aloud a strict control of the cooling zone: the products are cooled at an adjustable, constant temperature, depending on the production capacity, productivity, and maximum temperature, loading degree. In this mode, it is possible to strictly separate the firing zone atmosphere from those of the cooling zone and not to aloud to the burned gases to enter into the cooling zone. That has positively influence at the porcelain quality [9,10].

3. ARPO – a modern porcelain factory

ARPO Company is producing feldspar porcelain tableware starting 1974. Based on the product innovation, now the company is producing about 15 different shapes for table, coffee or tea sets, which totals over 2000 pieces with different decorations. There are also 450 models of figurines and decorative articles, decorated by hand painting. Developing the new models is the contribution of the design department to the product innovation.

Beginning 1989 ARPO managerial team started an efficient modernization plan materialized in process innovation. Until now there are more than 15 mil. Euro invested in new equipments for all the production areas: fast firing kilns for decorations, glost fast firing kilns, isostatic presses, automatic glazing machines, pressure casting machine, bead mill for glaze fine milling, decorating machine for lines and bands, polishing machine, sand blast machine, shrinking machine and also a computers network for production supervision and raw- materials administration.

The results of the intensive innovation program have been found in the increasing of the production and improving of the economical performances. This means that the crucial production departments become more efficient and the porcelain products more valuable. The profit increased to 10 billions lei yearly and new markets are opened all over the world.

The main direction of the new technologies introduced in **ARPO** Company was to increase the productive capacity and to obtain higher quality products. The existing personnel was selected and trained to use the new machines and installations.

The technological changes occurred step by step, according to a rigorous program, allowing the employers to adjust at the new working environment.

4. Conclusions

In conclusion the future in tableware ceramics is a continuously production process: the already prepared body using isostatic pressing and pressure casting, dried in micro wave and fast single fired, excepting porcelain, which probably will need double firing, in order to achieve a high quality.

The glaze preparation will be dominated by the fine milling technology, glazing by deeping for porcelain and by spraying technique, for the other ceramics.

The internal transport, feeding equipament, the stocking, loading and unloading system will make the connection between the machines during production [11].

The most important conclusion regarding until now evolution of the ceramic industry is that the process engineering and the product engineering can not be separated. This is the crucial point, which can lead to a successful, high quality product.

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Ceramic Industry and Research in the Slovak Republic: An overview

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Academy of Sciences, Bratislava, Slovak
Republic

Historical background

- ➢ **Unified Czechoslovakia:**
  - ✓Research – Slovakia
  - ✓Industry – Czechia (Elektroporcelán Louny, Jiskra Tábor, DIAS Turnov)
- ➢ **Independent Slovakia**
  - ✓No advanced ceramics industry
  - ✓Traditional production
  - ✓Strong research facilities

Industry – Overview

- Pottery – traditional earthenware
- Building materials
- Refractories
- Electroceramics

Pottery

- ➢ Traditional glaszed earthenware with hand-painted flower and figural motifs
- ➢ Technology of slip casting and turning of plastic dough

- ➢ Producers:
  - ✓ Slovak Majolic Modra
  - ✓ Traditional Ceramics Sekule
  - ✓ Number of small and family owned enterprises

Building Materials

- ➢Building bricks: (Borský Jur, Spišská Nová Ves, Lučenec, Jašim, Gbely, Wienerberger Boleráz)
  - ✓Technology of continuous vacuum extrusion, gas forming additives in plastic dough

- ➢Roof Tiles (BRAMAC, TONDACH
- ➢Sanitary wear (KERSAN, SANKER)
- ➢Wall and Floor Tiles (Novoker Lučenec, Kerko Košice)
  - ✓Non-glazed polished tiles „gres porcelanato"
  - ✓Glazed tiles

Refractories

- ➢ Respond the needs of cement industry and metallurgy
- ➢ Large deposits of raw materials
- ➢ Magnesite and chrome-magnesite refractories

- ➢ Producers:
- Slovmag Lubeník
- Slovak Magnesite Industry Lovinobaňa

Electroceramics

- ➢Production of high alumina-based electrical insulators
- ➢Technology:
  - ➢continuous vacuum extrusion of plastic dough, or isopressing of powders in plastic bags
  - ➢Machining of desired shape
- ➢Ceram Čáb, a.s.

Research

- Dept. of Ceramics, FChFT, STU, Bratislava
- Dept. of Materials, Faculty of Metallurgy, TU Košice
- Inst. of Materials Research, SAS Košice
- Inst. of Inorganic Chemistry, SAS, Bratislava

Dept. of Ceramics, FChFT, STU, Bratislava

- Corrosion of refractories by glass melts (prof. Jamnický)
- Hydroxyapatite-based bioceramics (prof. Majling)
- Synthesis of mullite and alumina-based ceramics by sol-gel, ceramic membranes with controlled nanoporosity (dr. Pach)

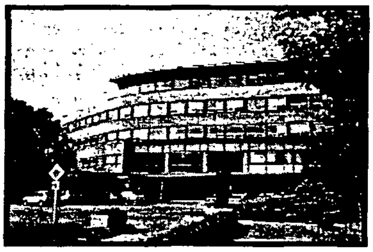
Dept. of Materials, Faculty of Metallurgy, TU Košice

- Refractories for metallurgy

Inst. of Materials Research, SAS Košice

- Relations between microstructure and properties of non-oxide structural ceramics
- Creep of ceramics

Inst. of Inorganic Chemistry, SAS, Bratislava



[redacted]

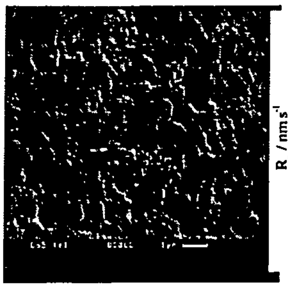
Departments of the Institute

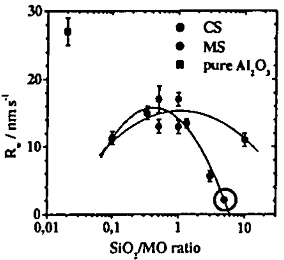
[redacted]

Oxide materials

- Relations between the composition, microstructure and properties of LPS alumina
- The role of residual stresses in alumina-based materials
- Special glasses for LPS of alumina
- Wear resistant aluminas
- Alumina-based cutting tools for high speed metal cutting
- Alumina-based nanocomposites

Wear resistant LPS aluminas

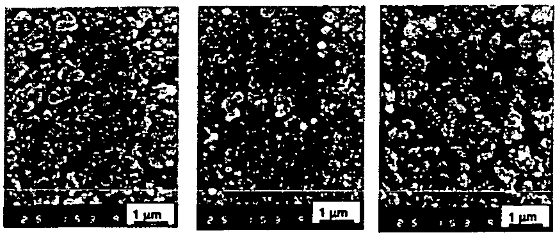




Non-oxide materials

➢Preparation of SiCN nanopowders by CVD
➢Si_3N_4/SiC based micro/nanocomposites
➢Mixed α/β-Sialons
➢Layered composites (Si_3N_4/Si_3N_4, Si_3N_4/SiC, Sialon/TiN, SiC/(TiNb)C, etc.)
➢ Cermets (Al_2O_3-NiAl(Ni_3Al), TiC-Ni_3Al, SiC-$MoSi_2$, etc.)
➢Special sintering additives, sintering and microstructure development of SiC

Preparation of SiCN nanopowders by CVD



Si_3N_4
Particle size: 50 - 100 nm

SiC
Particle size: 10 - 100 nm

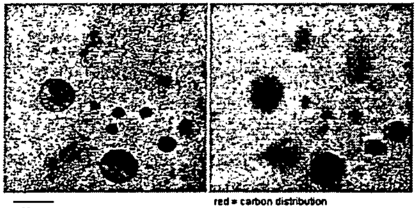
SiCN
Particle size: 50 - 100 nm

recrystallised 1580 °C/2h in Ar

Si_3N_4/SiC based micro/nanocomposites

FELMI TU Graz

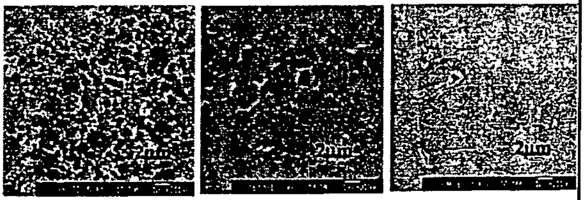
EFTEM-investigation of SiC-precipitates in a Si3N4-crystal


TEM-bright field image
RGB-image

red = carbon distribution
green = nitrogen distribution
blue = oxygen distribution

Sintering and microstructure development of SiC

Yb_2O_3-Sm_2O_3 sintering additives



α-SiC seeds **β-SiC seeds** **β-SiC seeds, annealed 5 h**

Ceramic Industry and Research in the Slovak Republic: An overview

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Abstract

The paper gives a brief overview on the state-of-the-art of the ceramic industry and research in the Slovak Republic. Due to lack of advanced ceramic processing in the country, the report on the industry is focused mainly on the traditional productions, especially pottery, building materials (bricks, rooftiles) and some more advanced applications as the ceramic electrical insulators and refractories. On the contrary, the research in the field of ceramics (and especially in the field of advanced structural materials) is well established, with good ties to leading ceramic laboratories in the world. The research covers wide range of topics from laboratory-scale preparation of ceramic powders through processing of bulk materials to investigation of relations between the microstructure and properties and final applications of the materials.

Introduction

Interestingly, there is a sort of discrepancy between the needs of industry in the Slovak republic and the main topics of the advanced ceramics research. This state is in fact a heritage of the former Czechoslovak Republic, where majority of the special ceramic industry has been concentrated west of the Slovak border, with the producers like Jiskra Tábor producing the spark plugs for automotive industry, or DIAS (now Saint Gobain Advanced Ceramics) Turnov focusing on the range of advanced ceramic products including ceramic cutting tools (both alumina and silicon nitride-based), bioceramics (artificial zirconia-based hip and knee joints) and alumina water tap seals. In the conditions of the unified Czechoslovak Republic there was no obstacle for locating most of the ceramic research facilities to Slovakia, with the research in Czech Republic concentrating more on the science and technology of glass, which was traditionally very strong in Czech. After splitting the Republic in 1993 therefore a curious situation occurred. The Czech Republic with relatively strong ceramic industry preserved just very few research facilities (the most important ones are in Brno and in Praha at the Institute of Chemical Technology), while the Slovak Republic with virtually no special ceramic industry maintained at least four groups of ceramic research, well established and equipped and with good personal and scientific links to leading research laboratories worldwide. The situation has not change since, as the producers of traditional ceramics especially due to the poor economical situation (and lack of need) did not require any massive investments into the research in their area of interest.

In the following text I attempt to give a thorough overview of the individual areas of the ceramic research and manufacturing in the Slovak Republic, including the brief overview of the used technologies and manufactured products.

Industry

Pottery

Pottery industry in the Slovak Republic has deep roots in the manufacturing of the traditional folk ceramics in the past, the Slovak Folk Majolic Modra and the Traditional Ceramics Sekule being the most renowned for their production of traditionally shaped ceramic with hand-painted flower and figural motifs. The typical products from Modra and Sekule are shown on Figures 1a,b. The typical technologies of shaping the green bodies are those of slip casting of ceramic slurries and turning plastic dough with the aid of the pottery lathe. Pre-fired bodies are then glazed and hand-painted by mineral dyes. A number of smaller ceramic companies or family-owned enterprises deals with manufacturing of traditional earthenware throughout Slovakia.

a) b)

Figure 1. Typical earthenware products from Modra (a) and Sekule (b).

Building materials

The ceramic building materials include building bricks, roof tiles and wall and floor tiles. There is a range of producers of ceramic building materials in the Slovak Republic, the brick producing plants being in Borský Jur, Spišská Nová Ves, Lučenec, Jašim, Gbely etc. The leader concerning the quality and production programme is the plant Wienerberger Boleráz, operating since 1819. The company uses the technology of continuous vacuum pressing of plastic dough through complex shaped nozzles, achieving highly complicated profile with insulating holes and low thermal conductivity of the product. The addition of gas forming additives into the plastic dough creates a porous structure of the ceramic body after firing, further improving the insulating properties of the material. Some examples of the manufacturing programme are shown on Figure 2.

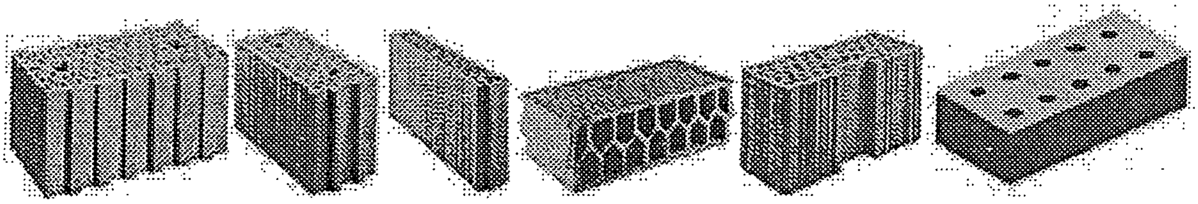

Figure 2 Some examples of the manufacturing programme of the company Wienerberger Boleráz.

The leading position on the roof tiles market in the Slovak Republic is occupied by companies Bramac and Tondach, both producing a complex range of products related to building and insulation of the roofs. The company Bramac concentrates more on concrete-based products, while Tondach produces a wide range of earthenware roof tiles, which are manufactured by pressing the plastic dough followed by drying and firing process.

The major companies in Slovakia dealing with the production of wall and floor tiles are Kerko Košice and Novoker Lučenec, producing both the non-glazes polished tiles “gres porcellanato” for interier and exterier use, and glazed tiles for interier applications.

Refractories

The production of refractories is defined by the needs of cement, glass and metallurgical industry and by large deposits of magnesite in the south-eastern regions of Slovakia. The major producers of basic, magnesite and chromium-magnesite refractories are the plants Slovmag Lubeník, Slovak magnesite industry in Lovinobaňa, which both produce a range of refractory linings for cement and lime kilns.

Electroceramics

The only producer of electroceramic in Slovakia is CERAM in Čáb, a 100 % foreign-owned company with its manufacturing programme focusing on electrical insulators. The technology involves either the vacuum extrusion of high-alumina plastic dough or the isostatic pressing of alumina-based powders in plastic bags. The raw green preform is then machined in order to achieve desired shape. The pre-fired bodies are then glazed and fired. Nearly 100 % of the production is exported to European countries, as well as overseas. Some examples of the production programme are shown on Figure 3.

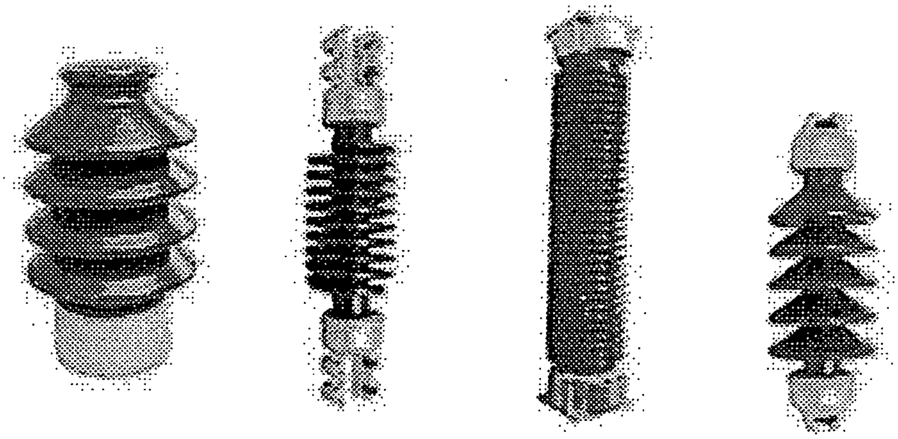

Figure 3. Some examples of the production items of CERAM Čáb, a.s.

Research

In the following text the four major ceramic research laboratories in the Slovak Republic are listed, with their main areas of interest and with the special focus on the Institute of Inorganic Chemistry, Slovak Academy of Sciences, the author's mother institution.

Department of Ceramics, Faculty of Chemical and Food Technology, Slovak Technical University, Bratislava

The department focuses its research to the area of refractories (especially the refractories for glass melting furnaces and the corrosion of refractory materials in the glass melting process – prof. Jamnický), and bioceramics (especially biocompatible materials like hydroxyapatite – prof. Majling). The sol-gel formation of alumina-based materials and mullite and the deposition of thin ceramic membranes with nanosized porosity on porous alumina substrates is also studied at the department (dr. Pach).

Department of Materials, Faculty of Metallurgy, Technical University Košice

From the point of view of the advanced ceramic materials, the laboratory is of marginal importance, as the research at the department answers mainly the needs of producers of refractories, especially for metallurgy of iron.

Institute of Materials Research, Slovak Academy of Sciences, Košice

The research activities at the Institute focus on the relations between the microstructure and mechanical properties of structural non-oxide ceramic materials, especially silicon nitride. Extensive studies have been conducted on determination of mechanisms of high temperature creep in silicon nitride-based materials and the influence of the grain boundary phase composition on creep properties.

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava

The Institute of Inorganic Chemistry is one of the 59 research institutes covered by the Slovak Academy of Sciences (SAS). With its 70 employees, the institute belongs to medium sized among the latter and in 2003 it will come to 50th year of its history. The research work at the Institute is now mainly oriented towards new inorganic materials. Nevertheless, the basic research is dominant, going as far as to the level of the electronic structure of the matter. The Institute consists of five departments, which deal with various aspects of research in the field of inorganic chemistry. These are:

- Department of Ceramics,
- Department of Hydrosilicates,
- Department of Molten Systems,
- Department of Theoretical Chemistry,
- Joint Laboratory of Glass of the Institute of Inorganic Chemistry SAS and the Trenčín University.

From the departments listed, the Department of Ceramics (prof. Šajgalík) and the Joint Laboratory of Glass (dr. Galusek) are mainly dealing with the research in the area of ceramic materials.

IIC SAS has been carrying out systematic research of engineering ceramics for two decades. The primary interest was devoted to understanding of the relations between microstructure and mechanical properties of non-oxide ceramics/composites. A limited amount of research was done also in the field of alumina-based materials, e.g. preparation of ZTA by inflitration of metalo-organic presursors of zirconia into a porous alumina matrix,[1 - 3] and alumina ceramics reinforced by β-Si_3N_4 whiskers.[4]

In prior designing in house ceramic materials great attention was focused on the understanding of sintering parameters with respect to the final state of sintered body.[5 - 10] This work deals with diffusion as the most important phenomena taking part in sintering; it attempts to understand the difference between densifying and non-densifying mechanisms of sintering, and estimate their area of dominance.

Mechanical properties of silicon nitride-based materials strongly depend on microstructure, particularly on the presence of the needle-like grains of β-silicon nitride the final microstructure usually contains. The shape, distribution and frequency of occurrence of β-Si_3N_4 whiskers depend on the composition of starting mixture and on sintering conditions. Extensive experimental work was performed, which proves that the α-β transformation of Si_3N_4 usually proceeding in the course of sintering plays a significant role in formation of a microstructure of these materials. The transformation can proceed in two principal ways: by vapour transport,[11, 12] and by liquid-phase diffusion.[13] Tailored microstructures with submicrometre or with several tens/hundreds of micrometre large grains can be prepared by promoting homogeneous or heterogeneous nucleation of β-Si_3N_4.[14, 15]

Several composite materials were prepared, applying the knowledge acquired in previous research. SiC/Si_3N_4 nano-composites were prepared, by forced homogeneous nucleation, using the SiCN amorphous nano-powder as an agent promoting homogeneous nucleation.[16 - 18] The β-Si_3N_4-whisker reinforced Si_3N_4 ceramics were prepared by seeding the starting mixtures with β-Si_3N_4 whiskers with aspect ratio of approximately 4. The whiskers preserve their original needle-like shape and serve as the heterogeneous nuclei during the α/β-Si_3N_4 phase transformation.[19 - 21] The fact that the whiskers grew in the course of sintering resulted in the idea to prepare the needle-like β-Si_3N_4 grains *in situ*, by forced heterogeneous nucleation, the starting mixture being seeded by equiaxed β-Si_3N_4 nuclei. This approach generated a large variety of microstructures with various volume fractions of elongated particles.[22, 23]

The relations between the microstructure characteristics and the mechanical response to loading at both room and high temperatures were studied simultaneously with the material design.[14 27] More detailed study revealed that except for the microstructure characteristics (shape and size distribution of phases in a sintered body), the stress state of the ceramic body plays an important role and contributes positively/negatively to its mechanical performance,[28,

[29] especially at room temperature. The role of chemistry of the grain boundaries was also studied with respect to the high temperature mechanical properties.[17, 30]

Based on previously acquired knowledge, layered silicon nitride composites were designed. Their properties are strongly anisotropic depending on the sequence of layers and the orientation of mechanical load. In order to understand their behaviour a model of the mechanical response of layered composites to applied load was developed and tested.[31 - 37] Clear proof was given that the residual stresses play an important role. Substantial improvement in strength can be achieved by introduction of surface compressive stress. The toughness can be enhanced and the sensitivity to surface flaws can be considerably reduced by the residual surface compressive stress. Based on the knowledge acquired, a new material with exceptional mechanical properties was designed.[38] For cutting tool applications layered materials with strong interfaces have high potential. Moreover, functionally graded materials can be prepared, e.g. for cutting tool application with different Si_3N_4:TiN ratio in the particular layers. Layered structures offer also a possibility of designing the multifunctional materials. Such materials have not only excellent mechanical properties, but the electrical, thermal or magnetic properties are also improved. The Si_3N_4-based layered composite was designed, with excellent mechanical properties and high electrical and thermal conductivity in the direction parallel with the layer area.

The previous text summarises in short the achievements of the Institute in the field of ceramic research in the past 10 years. At present, new projects at the Institute require an extensive research of relations between the processing conditions, chemical composition, microstructure and mechanical properties (room and high temperature) of alumina and SiAlON-based materials, which are intended as materials for cutting tools for machining of ultra hard alloys in automotive industry at high cutting speeds.

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COMPOSITION-MICROSTRUCTURE-PROPERTIES RELATIONSHIP FOR A CERAMIC MATERIAL

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This paper presents an experimental study pointing out some causal relationships between various technological aspects and the final properties of a ceramic material. The properties of the ceramic materials, which define their utilization function, depend first of all on their microstructure. The nature of the ceramic material and the firing process are the main factors which differentiate the ceramic material from each other. It is very important to know in detail the multiple interdependences between the raw materials, the technological parameters and the properties of a ceramic material in order to optimize the manufacturing process of a ceramic material with well defined properties.

1. INTRODUCTION

The ceramic materials represent a category of inorganic non-metallic (although, more rarely, they can also have metallic constituents) solids, obtained at high temperatures. At these temperature sintering, vitrification or melting, followed by their cooling and stiffening, takes place.[1,2]

The properties of the ceramic materials, which define their practical application function, depend on their microstructure – direct consequence of the composition and the thermal treatment conditions. The nature of the ceramic material (its chemical – mineralogical composition) and the firing (the complex process of chemical and physical transformations within heterogeneous systems) are the main factors which differentiate the ceramic materials one from another.[1,3,4]

It's well known that a very good thermal stability can be achieved[1,4]:

- either by a high thermal conductivity (e.g. in the category of ceramic materials-silicon carbide, carbonaceous and graphitic refractories);
- or by low thermal expansion coefficients (e.g. in the category of siliceous materials-quartz glass, cordierite ceramics, ceramic materials based on lithium silicates).

The thermal stability of the ceramic materials is also categorically influenced by their porosity and by the size of their structural constituents.

Referring to the porcelains, as part of ceramic materials, these are constituted of a glass matrix where crystalline phases and some pores are presented; the chemical nature of these phases and their proportion depend on the composition of the primary mixture of raw materials and on the particular conditions of the applied thermal treatment. Between the glass phase amount which, essentially, determines the vitrification degree of ceramic materials and their microstructural properties (such as, apparent density and porosity) there is a tight correlation. At their turn, these properties determine others, such as: water and other liquids absorption, permeability to gases, shrinkage. The proportion of glass phase also determines the phases ratio and, consequently, the mechanical, thermal, electrical and optical properties (and, as a result of the last ones, the aesthetical properties: whiteness, translucency). Considering the practical use of the porcelain products, these properties are the most important ones.[1,3]

In the case of the ceramic ware used in contact with food, such as household porcelain, faience or fine stoneware (glazed or not), the release of lead and cadmium has to be considered as a very important problem. The people's protection against possible dangers caused by using some glazes and/or decorations which release these toxic elements has to be ensured.[5]

2 . EXPERIMENTAL WORKS

The first part of this experimental study refers to the formation of *cordierite* – $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ in ceramic bodies made of different raw materials, which bring one oxide (elementary compounds) or many oxides (two oxides- in the case of the double compounds) among the three components- MgO, Al_2O_3 and SiO_2.

The stoichiometric cordierite composition (MgO- 13.8 weight %, Al_2O_3- 34.8 weight %, SiO_2- 51.4 weight %) was used to calculate the composition of the raw materials mixtures for the experimental bodies. The used raw materials, as well as the manner of their combination in the elaborated experimental bodies are presented in TABLE 1.

For each of the experimental bodies, the raw materials mixture was prepared by wet grinding. The materials were then dried and pressed into test specimens. These were pre-calcined at 1100^{O}C and were then subjected to thermal treatment in an electric laboratory kiln at 1350^{O}C, with a holding time at peak temperature of one hour.

Subsequently, the experimental researches point out the influences of the thermal treatment conditions on some important properties of the hard feldspatic porcelain products, namely: the *whiteness* and the *release of the toxic elements* (*lead* and *cadmium*).

For the whiteness study some plates have been used; a number of them have been made by shaping (using plastic body) and the others have been made by isostatic pressing (using granulate body). After drying, the samples were biscuit fired under different conditions specified in TABLE 2. They were then glazed, by dipping, with a transparent colourless glaze having an adequate volume weight for both of the two types of products (plastic shaped and isostatically pressed) and all of them were finally glost fired under the same conditions (TABLE 2).

TABLE 1. Raw materials and experimental bodies

No. of: Raw materials	Type	Double compounds		Elementary compounds						
	Prevailing oxide	Al_2O_3; SiO_2	MgO; SiO_2	Al_2O_3			SiO_2		MgO	
	Denomination	Zettlitz Kaolin	Steatite	αα-alumina	γ - alumina	Aluminium hydroxide	β - quartz	Amorphous silica	Magnesium oxide	Magnesium bicarbonate
	sample									
1	*1.1*	*	*	*	-	-	-	-	-	-
	1.2	*	*	-	*	-	-	-	-	-
	1.3	*	*	-	-	*	-	-	-	-
2	*2.1*	-	*	*	-	-	*	-	-	-
	2.2	-	*	-	*	-	*	-	-	-
	2.3	-	*	-	-	*	*	-	-	-
	2.4	-	*	-	*	-	-	*	-	-
3	*3.1*	-	-	*	-	-	*	-	*	-
	3.2	-	-	-	*	-	*	-	*	-
	3.3	-	-	-	*	-	*	-	-	*
	3.4	-	-	-	*	-	-	*	-	*
	3.5	-	-	-	-	*	-	*	-	*
	3.6	-	-	-	-	*	*	-	-	*
4	*4.1*	*	-	-	-	-	*	-	*	-
	4.2	*	-	-	-	-	*	-	-	*
	4.3	*	-	-	-	-	-	*	*	-
	4.4	*	-	-	-	-	-	*	-	*

In order to study the release of the toxic elements, some glost fired shaped plates, decorated with on glaze transfers (no.5985 and no.6032) have been used . The samples were then fired under different conditions, as illustrated in TABLE 3.

TABLE 2. Whiteness of the glost fired samples

Firing conditions for:					Whiteness of: [%]		Observation	
biscuit firing				glost firing			Loss on ignition, after biscuit firing, for : [%]	
type of kiln	maximum temperature [°C]	firing cycle [hours]	O_2 content in the combustion gases [vol.%]		shaped samples	pressed samples	shaped samples	pressed samples
traditional gas tunnel kiln	940	22.50	10.6	traditional gas tunnel kiln; maximum temperature-1380 C; firing cycle-34 hours; composition of the combustion gas in the reducing zone: CO_2-8.2 vol. %, O_2 -2.4 vol. %, CO-1.8 vol. %	70.3	70.4	0.18	0.13
traditional gas tunnel kiln	910	22.50	9.6		69.2	69.7	0.20	0.14
fast firing gas tunnel kiln	810	1.75	9.2		68.0	66.7	0.23	0.20

3. TESTING METHODS

The fired specimens for each experimental body (chapter 2) were analyzed to determine their mineralogical composition, as well their degree of vitrification and thermal expansion.

The mineralogical composition was determined by X-ray diffraction(XRD) using a

TABLE 3. Release of lead and cadmium for the decorated samples

Firing conditions:			Release of the toxic elements: [mg/dm^3]							
type of kiln	maximum temperature [°C]	holding time at peak temperature [min]	Pb				Cd			
			Samples with ceramic transfer picture:							
			no. 5985		no. 6032		no. 5985		no. 6032	
			distinct samples	average value	distinct samples	average value	distinct samples	average value	distinct samples	average value
industrial electric tunnel kiln; firing cycle-1hour 45min.	800	15	9.3158	11.1969	8.7895	7.4181	0.0611	0.0579	0.0528	0.0479
			11.6585		9.6316		0.0583		0.0556	
			8.3158		7.5745		0.0473		0.0420	
			13.0526		5.1818		0.0639		0.0393	
			13.4737		8.2632		0.0611		0.0556	
			11.3652		5.0682		0.0556		0.0420	
industrial gas tunnel kiln; firing cycle-2hours 15min.	830	25	7.8298	15.0097	13.7684	9.1757	0.0367	0.0590	0.0694	0.0553
			26.3579		4.5417		0.0889		0.0393	
			19.2289		15.1579		0.0694		0.0694	
			6.8298		3.8409		0.0420		0.0420	
			6.7872		12.6316		0.0393		0.0667	
			23.0244		5.1136		0.0778		0.0447	
industrial gas tunnel kiln; firing cycle-1hour 45min.	800	15	7.8936	8.9493	6.0213	5.3049	0.0393	0.0425	0.0447	0.0411
			9.5789		5.4091		0.0420		0.0367	
			7.8723		3.5000		0.0393		0.0393	
			8.2105		3.4545		0.0420		0.0340	
			14.2316		5.7727		0.0528		0.0393	
			5.9091		7.6809		0.0393		0.0528	
laboratory electric kiln	780	15	13.6842	13.6842	4.4167	4.0038	0.0500	0.0500	0.0367	0.0300
					3.5909				0.0233	
	810	15	7.1915	3.8617	3.2955	2.9985	0.0340	0.0240	0.0313	0.0220
			2.6383		3.2273		0.0233		0.0180	
			3.0000		3.5227		0.0207		0.0233	
			2.6170		1.9483		0.0180		0.0153	
	840	15	1.9828	2.1142	2.3617	1.3806	0.0153	0.0153	0.0180	0.0109
			2.0000		1.2414		0.0127		0.0127	
			1.7931		1.3793		0.0153		0.0127	
			2.6809		0.5400		0.0180		0.0000	
	810	45	1.6897	2.5422	2.0000	2.0030	0.0367	0.0367	0.0393	0.0373
			3.8409		2.0000		0.0287		0.0340	
			2.0638		2.0638		0.0393		0.0420	
			2.5745		1.9483		0.0420		0.0340	
	840	45	1.2586	1.6293	1.8621	1.4372	0.0233	0.0333	0.0367	0.0333
			1.6724		1.0345		0.0367		0.0313	
			2.0000		1.4310		0.0340		0.0313	
			1.5862		1.4211		0.0393		0.0340	

Siemens Diffrac 500 X-ray diffractometer with Ni filter $CuK_{\alpha\alpha}$ radiation. For the quantitative phase analysis, a method using external standards, in a version involving measurements of attenuation coefficients, was used.[1,6,7]

To estimate the degree of vitrification of the fired samples, their water absorption capacities and apparent porosities were determined. The water absorption was accomplished under vacuum and the necessary weightings were performed using a hydrostatic balance.[1]

The thermal expansion of the fired samples was determined by measuring the lineal thermal expansion coefficients using a "differential" dilatometer with thermal expansion transmission accessories of alumina.[1]

The whiteness was determined by measuring the total reflection[8] of the samples (glost fired plates- chapter 2).

The release of the toxic elements was determined by acid extraction of lead and cadmium from the surface of the samples (decorated fired plates- chapter 2) using an acetic acid solution (4 vol.%); the quantities of the released lead and cadmium were then measured by atomic absorption spectrometry.[5]

4. RESULTS AND DISCUSSION

The XRD patterns[1] of the fired samples, along with the data provided in the material literature, enabled the researcher to identify and to quantitatively determine the available *crystalline phases*.[1,6] Considering only the prevailing determined phase, TABLE 4 presents the content of cordierite in the experimental fired samples.

The values obtained for the *water absorption capacity* and *apparent porosity*- microstructural characteristics that define the compactness of the ceramic material- are presented in TABLE 4.

Some of the experimental fired bodies were selected to study their *thermal expansion*. TABLE 4 shows the values of the lineal thermal expansion coefficients determined in the temperature interval of 20-1000°C. The small values of these coefficients can be first explained by the presence of cordierite, which has a very low thermal expansion ($\alpha\alpha_{20-1000^{o}C} = 2 \cdot 10^{-6}\ {}^{O}C^{-1}$), as a prevailing phase and, to a certain extent, by the porosity of the respective samples.

The determined values of *whiteness* of the samples, correlated with the biscuit firing conditions: maximum temperature, firing cycle (cold to cold) and holding time at peak temperature, as well as the composition of the combustion gases, are presented in TABLE 2 (average values).

The results of the determination of *the toxic elements released* by the tested samples, correlated with the decoration firing conditions, are presented in TABLE 3.

TABLE 4.Partial mineralogical composition, compactness characteristics and thermal expansion of the experimental fired bodies

Number of:		Phase content (prevailing phase)	Degree of vitrification		Lineal thermal expansion coefficients $\alpha\ \alpha_{20-1000^{\circ}C} \cdot 10^6$ [$^{\circ}C^{-1}$]
series	sample	Cordierite [weight %]	Water absorption capacity [%]	Apparent porosity [%]	
1	1.1	*91*	12.80	24.37	2.40
	1.2	*85*	18.09	31.58	-
	1.3	*88*	16.99	29.84	2.80
2	2.1	*77*	20.44	35.24	-
	2.2	*70*	32.25	45.70	-
	2.3	*60*	33.61	46.84	-
	2.4	*66*	40.44	51.80	-
3	3.1	*68*	25.59	39.78	-
	3.2	*66*	32.28	46.11	-
	3.3	*60*	33.79	46.87	-
	3.4	*58*	34.03	47.18	-
	3.5	*67*	46.77	54.39	-
	3.6	*66*	38.66	50.85	-
4	4.1	*92*	0.63	1.33	3.00
	4.2	*89*	3.31	6.87	3.00
	4.3	*94*	2.90	6.18	3.50
	4.4	*91*	2.47	5.19	-

5. CONCLUSIONS

Several conclusions can be drawn from these experiments and their results :

☐ the formation of cordierite in all experimental bodies, this being the prevailing phase constituent in the respective fired samples ;

☐ the ceramic bodies containing double hydrated compounds, such as kaolin and steatite, achieved a much higher reactivity than the bodies containing elementary compounds – especially oxides, namely: aluminium oxide (αα-alumina,γ -alumina), silicon dioxide (β-quartz, amorphous silica), magnesium oxide, as well as hydroxide (aluminium hydroxide) and carbonates (magnesium bicarbonate); this fact confirms the theoretical assumption that the nature and initial structural state of the reactants influence the reactivity of the respective systems ;

☐ the variation in reactivity of the bodies regarding the interactions that lead to the formation of liquid phases (illustrated by the determined values of the compactness of the fired bodies) was similar to that indicated by the results of the XRD analyses ; the degree of vitrification of the fired bodies was further proof of their reactivity ;

☐ the decreased thermal expansion of the fired bodies, due to the presence of cordierite and due to the porosity of the materials, proves that there is a correlation between the structure and properties of a ceramic material ;

☐ the whiteness of the porcelain products, which is, first of all, ensured by the purity of the raw materials and the glost firing conditions, is strongly influenced by the biscuit firing conditions ; the increase of the maximum firing temperature and firing duration , as well as a high oxidizing atmosphere have positive influences; in the case of the isostatically pressed products, these influences are more intense, because of the organic additives of the granulated body ;

☐ the release of the toxic elements (lead and cadmium) by the decorated porcelain products, which essentially depends on the type of ceramic pigment and frit contained in the respective ceramic colour, is influenced by the decoration firing conditions; in the case of the tested ceramic transfers, the increase of the maximum firing temperature and of the holding time at peak temperature have favorable influence upon the release of lead (lowering the release of lead), while the release of cadmium is positively influenced by the increase of the maximum temperature only; firing in a gas kiln appears to produce better results than firing in an electric kiln, perhaps due to the circulation and composition of the combustion gases .

Finally, it can be asserted that *a detailed knowledge of the multiple interdependences between raw materials, technological parameters and properties is essential in optimizing the manufacturing process of a ceramic material with well defined properties* .

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3) I. TEOREANU , N. CIOCEA , A. BARBULESCU , N. CIONTEA , Tehnologia produselor ceramice si refractare , vol. I , Editura Tehnica , Bucuresti , 1985 .

4) P.P. BUDNICOV , A.S. BEREJNOI , I.A. BULAVIN , B.M. GRISSIK , G.V. KUKOLEV , D.N. POLUBOIARINOV , Tehnologia produselor ceramice si refractare, Editura Tehnica , Bucuresti , 1960 .

5) International Standard ISO 6486-1:1981 ,Ceramic ware in contact with food – Release of lead and cadmium . Part. 1 : Method of test .

6) A. GOLEANU , Ceramic Industry , vol. 151 , 7 (2001) 14 .

7) G.W. BRINDLEY , G. BROWN , Mineralogical Society Monograph No. 5. Crystals Structures of Clay Minerals and Their X-Ray Identification , Mineralogical Society , London , 1980 .

8) Romanian Standard STAS 708/1 – 91 , Household and ornamental fine ceramics . Physical tests .

New Technologies at S.C Apulum S.A , Alba iulia , Romania

Dr.Dipl.Eng. Aurica **GOLEANU**

S.C Apulum S.A is a Romanian factory that designs, manufactures and trades porcelain and stoneware products.

Founded in 1970, the company has ground rapidly to become one of the leading producers of porcelain from the South – East of Europe.

The porcelain factory APULUM is carrying out on the old ceramic traditions of the cultural and spiritual space of Transilvania. Centuries of history and ancient Daco – Roman civilization, documentary and archeologically attested by a great number of ceramic objects, found on the very place where the factory was built, have put their mark on the name of the 2500 years old town-APULUM (its name during the Roman Empire is the same name that was given to the porcelain factory) .

Geographically, Alba Iulia lies in the center of Romania. The same thing might be said about APULUM, the factory that in a very short time became the center of the Romanian porcelain industry. Through a continuos, good development of the factory taking over the best elements of the Transilvania culture and civilization, having the best professional men, it gradually became the best and biggest porcelain producer in Romania. Its production capacity is about 11000 tons yearly and it is very diversified, including household and hotel porcelain, decorative items and figurines and also stoneware items.

Since 1992, APULUM is a private company. In this process of privatization, the factory was supported by the consulting company Ernst&Young . The main share holders are the association ASSALPO S.A , formed a part of the employers, the Ion Tiriac Bank, Dacia Felix Bank and others.

The technological equipment of the factory meets today's requirements and it is completed by excellent research work. About 6years ago, the isostatic pressing method in tableware production was introduced in our factory and now 5 isostatic tableware presses are in operation; it can be said that this process has successfully superseded the conventional technologies. Since isostatic pressing technology was introduced for the production of tableware, it has gained wide recognition and has succeeded in ever more demanding fields of application. At first, only simple plates were pressed from spry-dried granulates, but nowadays the various types of isostatic presses produce extremely thin as well as complicated articles from all tableware bodies. This change often leads to costly adjustment possibilities and controls being incorporated into the press, whereas the spray-dried granulate and its properties were accepted as fixed parameters.

The under pressure casting method is an other new technology introduced in our factory, applied for a series of large articles; this method has positive effects in the quality of these products, as well as in the productivity of their making.

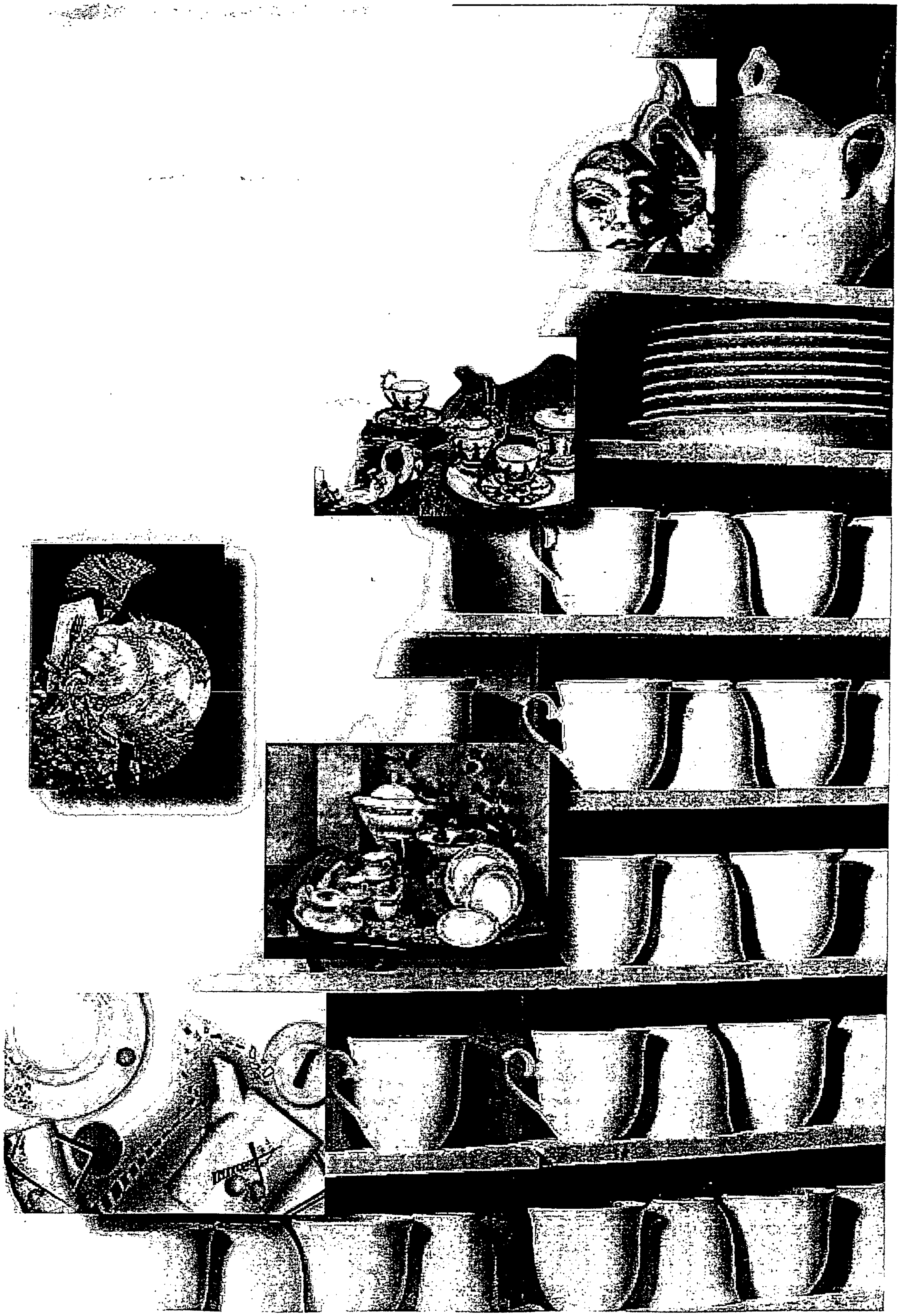
As a necessity of the improvement of the glaze quality, especially in the case of the isostatic pressed items, the advanced milling process of the glaze (in a continuously attrition mill of high capacity) has been introduced in our factory. The obtained glaze has an increased specific surface that improves its viscosity, as well as its coating behavior and, consequently, the glazed products have after the glost firing smoother and shinier surfaces. In the same time, in this process which uses ZrO_2 grinding media, the risk of contamination of the glaze with some rests of silex (from the silex balls used for the traditional glaze milling process) is decreasing and this fact avoids the negative effects, caused by the cristobalite , in the quality of the glaze surface of the products, especially after the in- glaze decoration firing.

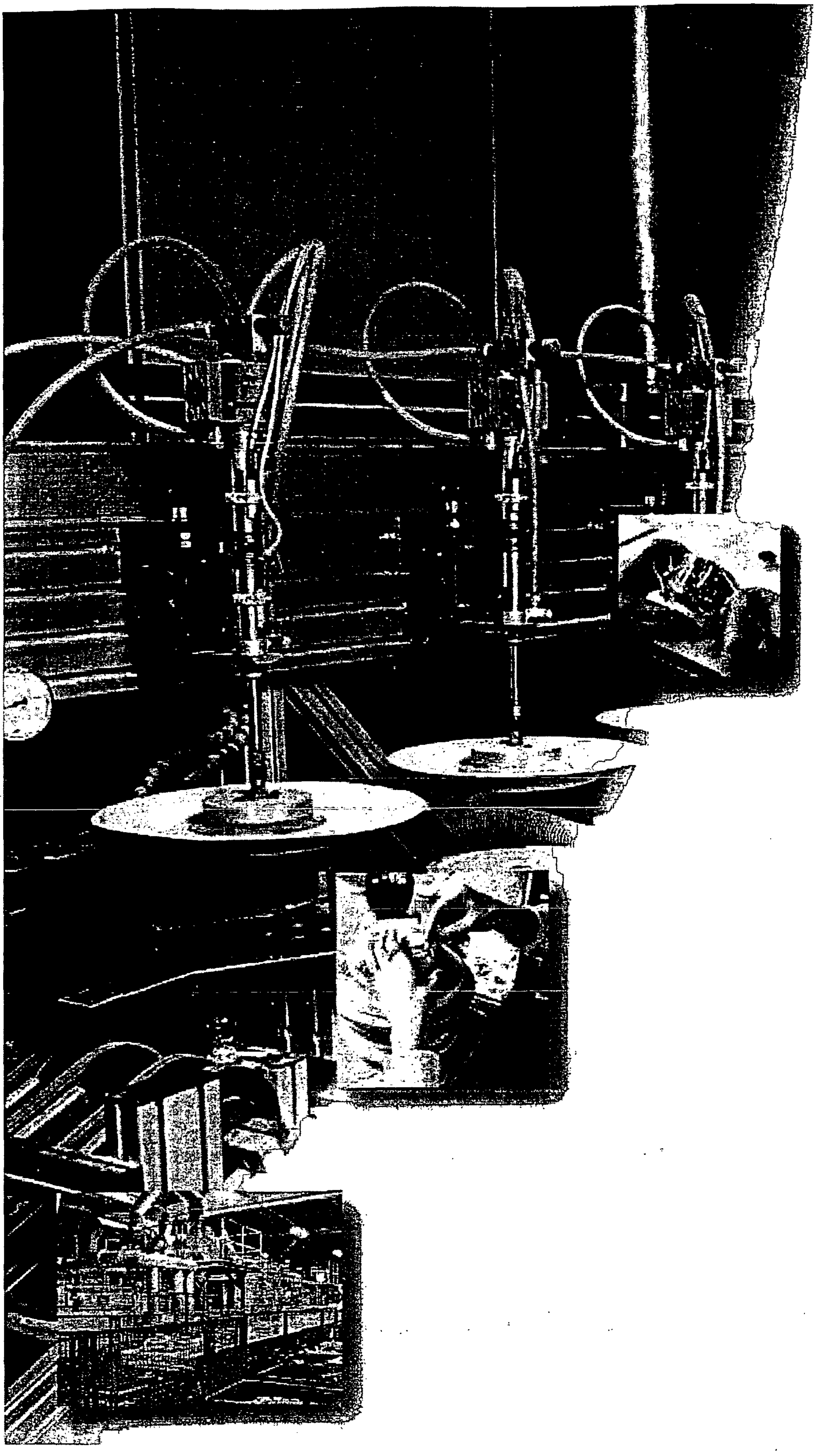
One of the most important steps of modernizing the manufacturing process in our factory was the substitution of some of the conventional firing kilns with other new fast firing kilns. Thus, 2 glost firing kilns (for porcelain and for stoneware) and 2 fast firing kilns for decoration firing (one electric kiln for on-glaze decoration and one gas kiln for in-glaze decoration) are now in operation. The firing process in these kilns assures a high and constant quality of the products, a very important increasing of the production capacity, as well as a considerable decrease of the costs, especially concerning the combustion gas.

Continual upgrading of equipment and processes incurred an ever-growing export activity and ensures the reputation of providing exceptional standards of customer service and quality of product. APULUM also offers retailers the ability to follow fashion trends, so vital today all over the world.

The trademark APULUM, contains symbols of the civilization and cultural unity of the traditions that are specific to the geographic, ethnographic and historical space of Transilvania.

Keeping up with the latest tendencies on the porcelain market, the items marked APULUM are both nice and useful. Their translucency and brightness, the diversity of shapes and decorations and their perfect match are but a few elements that assure unanimous appreciation of the trade mark APULUM and its presence on the international market.





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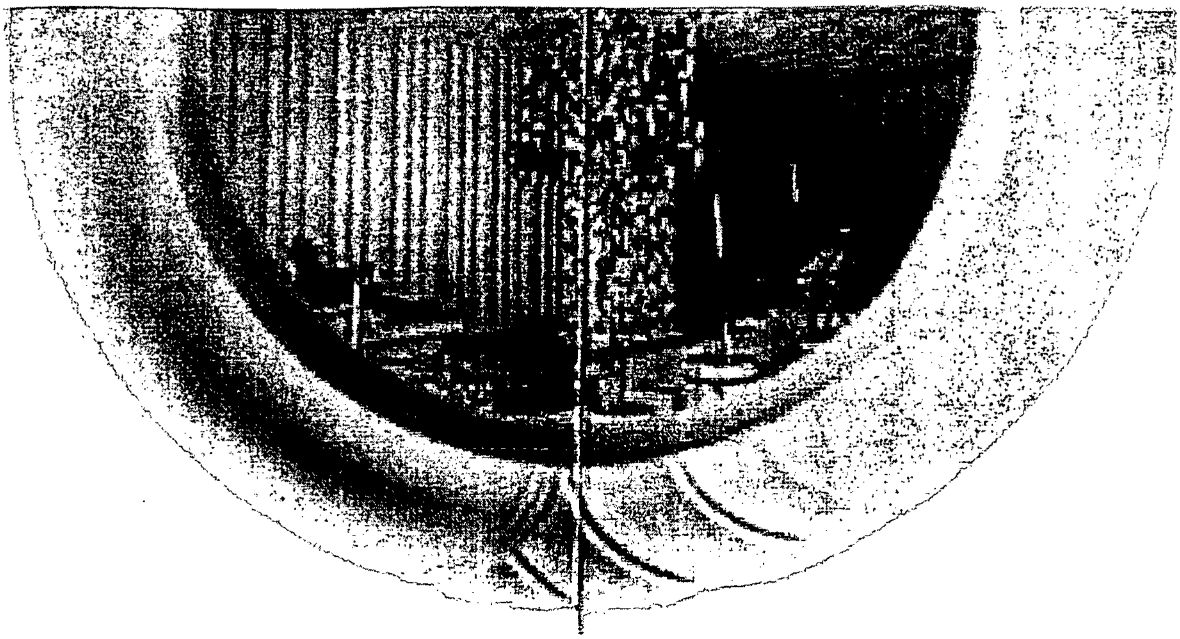
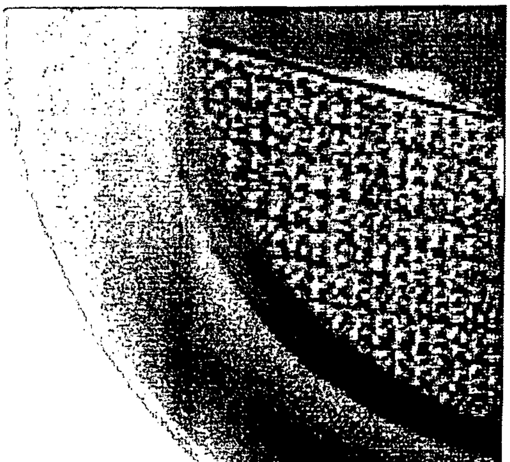
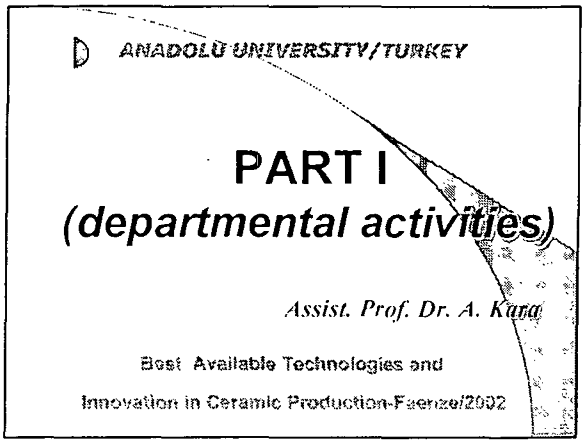
Zertifikat [illegible]

APULUM

PORCELAIN FACTORY



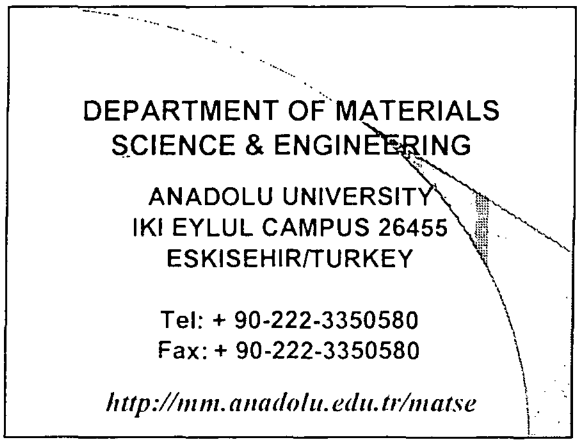



ANADOLU UNIVERSITY/TURKEY

PART I
(departmental activities)

Assist. Prof. Dr. A. Kara

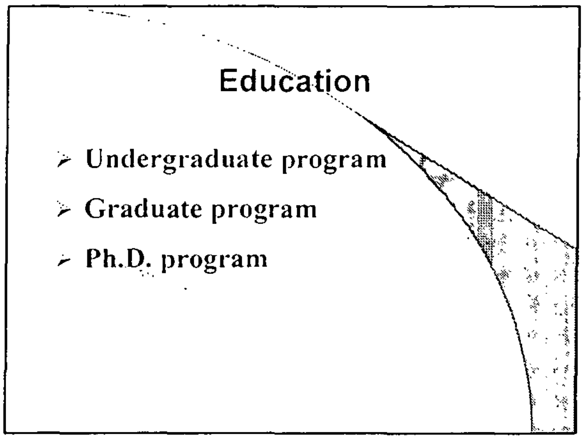
Best Available Technologies and Innovation in Ceramic Production-Faenza/2002


DEPARTMENT OF MATERIALS SCIENCE & ENGINEERING

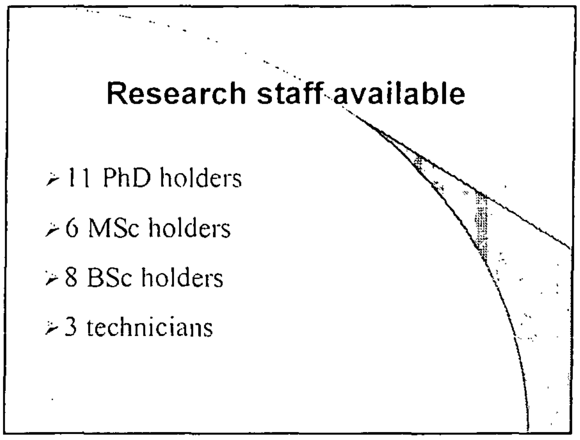
ANADOLU UNIVERSITY
IKI EYLUL CAMPUS 26455
ESKISEHIR/TURKEY

Tel: + 90-222-3350580
Fax: + 90-222-3350580

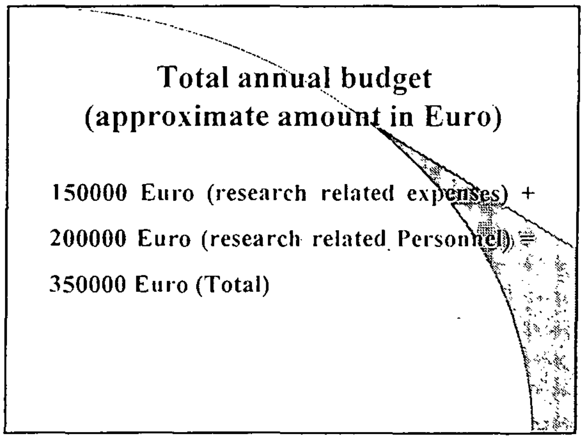
http://mm.anadolu.edu.tr/matse


Education

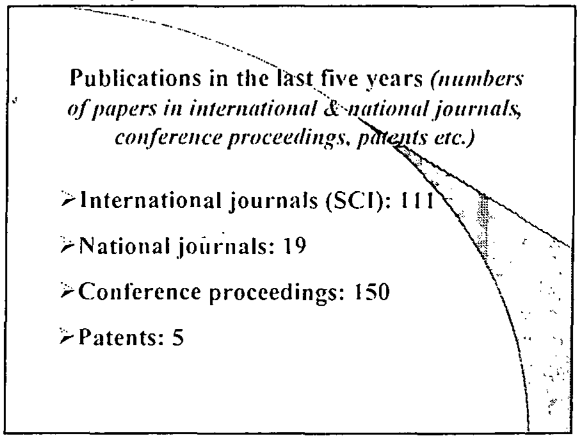
- Undergraduate program
- Graduate program
- Ph.D. program


Research staff available

- 11 PhD holders
- 6 MSc holders
- 8 BSc holders
- 3 technicians


Total annual budget (approximate amount in Euro)

150000 Euro (research related expenses) +
200000 Euro (research related Personnel) =
350000 Euro (Total)


Publications in the last five years *(numbers of papers in international & national journals, conference proceedings, patents etc.)*

- International journals (SCI): 111
- National journals: 19
- Conference proceedings: 150
- Patents: 5

Research equipment available
(major items only)

- X-ray diffractometer (XRD)
- Various high temperature furnaces
- Scanning electron microscope (SEM-EDX)
- Porosimeter
- Particle size analyser
- Hot stage microscope
- Optical microscopes
- Cold isostatic press

- Spectrophotometer
- Hardness tester
- Pilot scale processing equipments
- Standard testing equipment for traditional ceramics
- Basic electroceramic characterization units
- Rheometer
- Thermal characterization units

Collaborations

University of Cambridge (UK), University of Bath (UK), University of Newcastle (UK), Technical University of Karlsruhe (Germany), Technical University of Hamburg-Harburg (Germany), Evo Silikat Research Centre (Germany), Fraunhofer Institute (Germany), CeramTec AG (Germany), Technical University Eindhoven (Holland), University of Stockholm (Sweden), Silesian Univ. of Tech. (Poland), The Pennsylvania State University (USA), Shanghai Ceramic Institute (China), University of Monash (Australia), Synergy Materials Centre (Japan).

Ongoing major projects

- Development of novel SiAlON cutting tools for high speed machining of ferrous and non-ferrous materials
- Control of microstructure and properties via transformations in SiAlON ceramics
- Composite materials for impact applications
- Hydrothermal synthesis of nanosized electroceramic powders for sensor applications
- Pilot scale processing of advanced materials
- Alumina based cutting tools
- Manufacturing of piezoelectric composites

- Tailoring the microstructure of electroceramics via templated grain growth
- Processing of microstructure patterned ceramics
- Ceramic filters
- Vacuum heat treatment of non-oxide ceramics
- Joining of ceramics
- Nanocomposites
- Manufacturing of cymbal transducers and their applications
- Chemical synthesis of anisotropic particles
- Advanced ceramics for applications in the traditional ceramic industry
- Fluorescent glazes
- Archeometry
- Parameters affecting the spinel formation

Major projects completed in the last five years

- Improvement of novel SiAlON cutting tools for high speed machining of ferrous and non-ferrous materials
- Granulation of advanced ceramic powders
- Corrosion resistant high temperature refractories
- Factors controlling the grain growth magnesium oxide
- Boron carbide-aluminum composites
- Modeling of computer aided design of piezoelectric composite transducers
- Multi-cation doped and translucent SiAlON ceramics
- Alumina powder production by homogeneous precipitation
- Control of microstructure of mullite

- Recycling of traditional ceramic industry wastes
- Utilization of biologically derived emulsion binders in ceramic fabrication
- Characterisation of porous ceramics
- Improving the life of gypsum moulds
- Production of brown pigments using natural raw materials
- Superwhite cost-effective porcelains
- Antibactericide coatings
- Superhard glass ceramics
- Alternative raw materials for the tile industry
- The use of rice husk silica in porcelain industry
- Improvement of casting rate in slip casting of sanitaryware

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Sixth framework programme (FP6) projects

Type of application : Network of excellence

EoI title: Synthesis and property evaluation of novel vitreous and nanocrystalline oxynitrides (SPENSALON)

Number of participants: 22 participants from 20 countries

Contact point: Prof. Derek P. THOMPSON
University of Newcastle, UK)

Contact point in Turkey: Prof.Dr. Hasan MANDAL
(Dept. of Mat. Sci. & Eng)

Type of application : Network of excellence

EoI title : Nanostructured coatings, bulk materials and components (NACOBUCO)

Number of participants : 45 participants from 19 countries

Contact point : Dr. Wolfgang LACOM
(ARC Seibersdorf Research GmbH,
Austria)

Contact point in Turkey : Prof. Dr. Hasan MANDAL
(Dept. of Mat. Sci. & Eng.)

Type of application : Network of excellence

EoI title : Network for Developing New Materials for Covering (NETCOV)

Number of participants : 57 participants from 17 countries

Contact point: Prof. Museros Mª LIDON
(ALICER, Castellon, SPAIN)

Contact point in Turkey : Assoc. Prof. Dr. Ferhat KARA (Tübitak Ceramic Research Centre)

SAM

CERAMIC RESEARCH CENTER (SAM)

CERAMIC RESEARCH CENTRE

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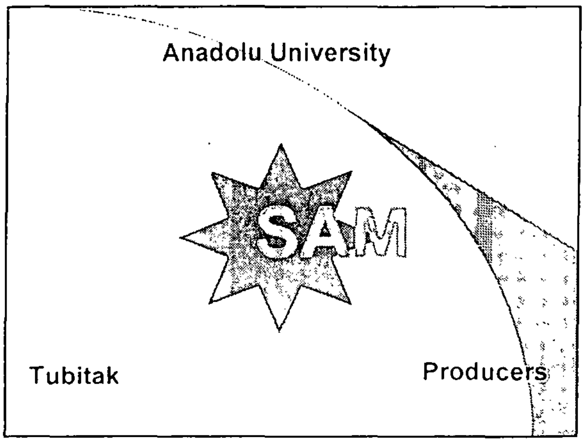
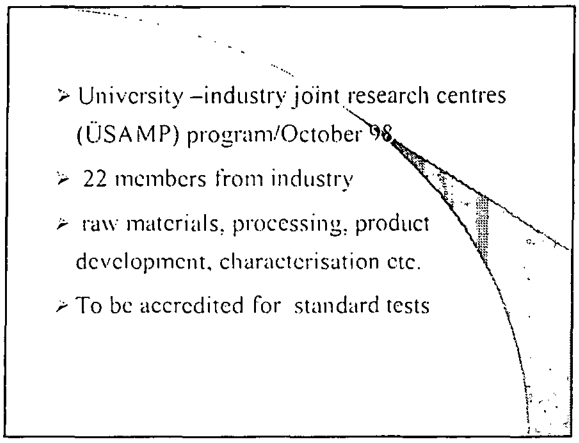
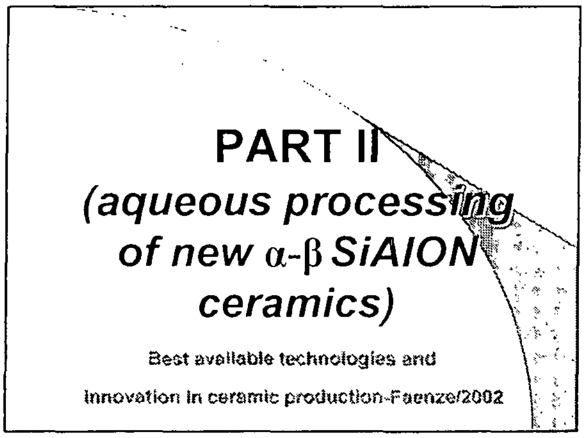

Anadolu University

SAM

Tubitak

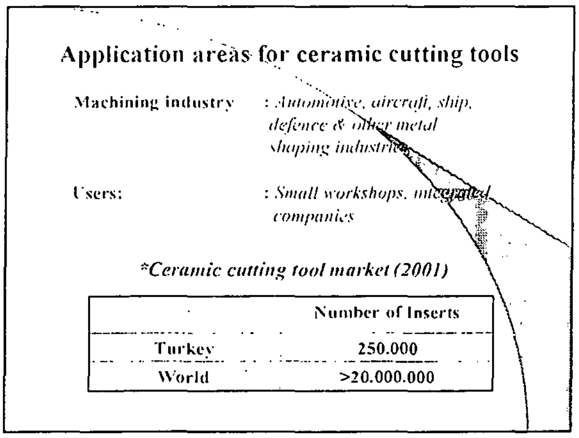
Producers


- University –industry joint research centres (ÜSAMP) program/October 98
- 22 members from industry
- raw materials, processing, product development, characterisation etc.
- To be accredited for standard tests


PART II

(aqueous processing of new α-β SiAlON ceramics)

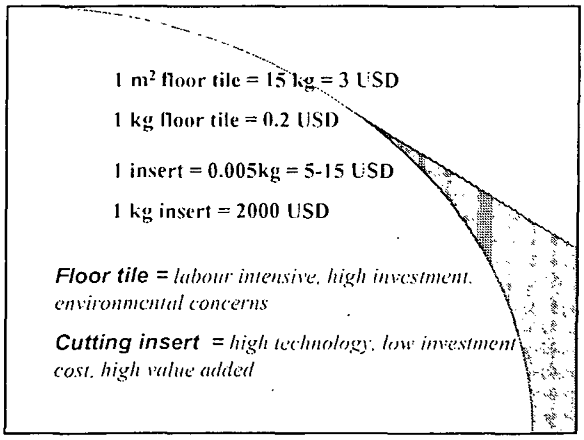
Best available technologies and Innovation in ceramic production-Faenze/2002


Application areas for ceramic cutting tools

Machining industry	: *Automotive, aircraft, ship, defence & other metal shaping industries*
Users:	: *Small workshops, integrated companies*

**Ceramic cutting tool market (2001)*

	Number of Inserts
Turkey	250.000
World	>20.000.000


1 m^2 floor tile = 15 kg = 3 USD

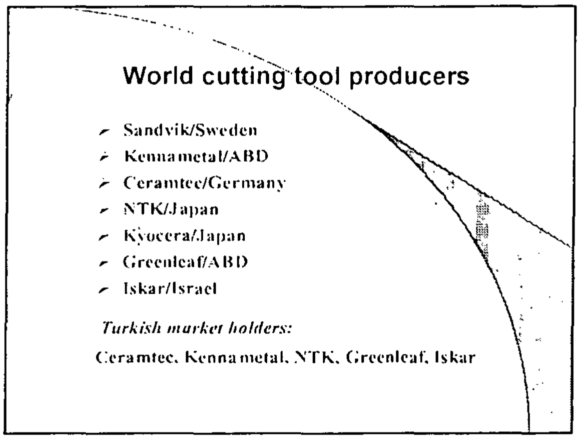
1 kg floor tile = 0.2 USD

1 insert = 0.005kg = 5-15 USD

1 kg insert = 2000 USD

Floor tile = *labour intensive, high investment, environmental concerns*

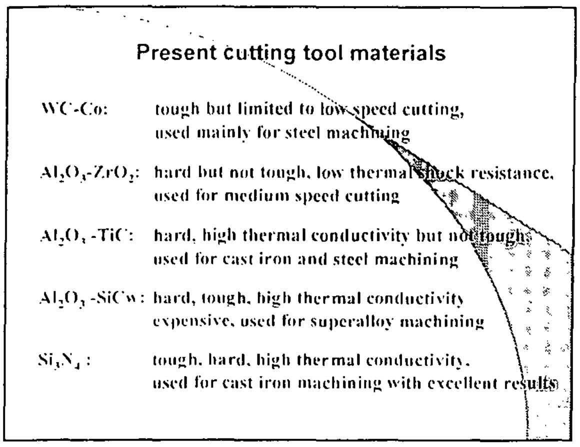
Cutting insert = *high technology, low investment cost, high value added*


World cutting tool producers

- Sandvik/Sweden
- Kennametal/ABD
- Ceramtec/Germany
- NTK/Japan
- Kyocera/Japan
- Greenleaf/ABD
- Iskar/Israel

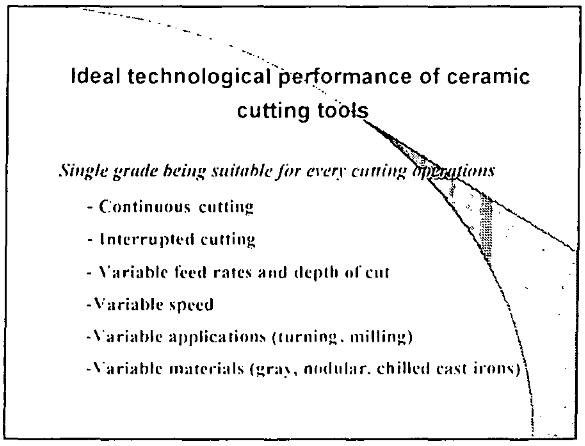
Turkish market holders:

Ceramtec, Kennametal, NTK, Greenleaf, Iskar



Present cutting tool materials

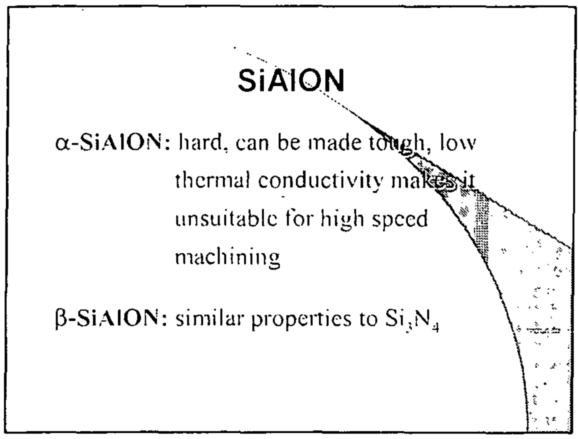
WC-Co:	tough but limited to low speed cutting, used mainly for steel machining
Al_2O_3-ZrO_2:	hard but not tough, low thermal shock resistance, used for medium speed cutting
Al_2O_3-TiC:	hard, high thermal conductivity but not tough, used for cast iron and steel machining
Al_2O_3-SiCw:	hard, tough, high thermal conductivity expensive, used for superalloy machining
Si_3N_4:	tough, hard, high thermal conductivity, used for cast iron machining with excellent results



Ideal technological performance of ceramic cutting tools

Single grade being suitable for every cutting operations

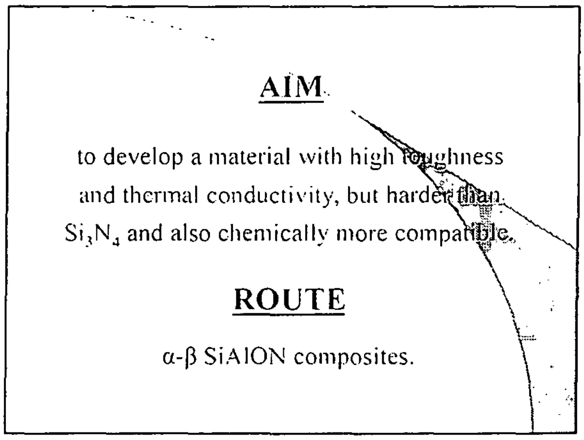
- Continuous cutting
- Interrupted cutting
- Variable feed rates and depth of cut
- Variable speed
- Variable applications (turning, milling)
- Variable materials (gray, nodular, chilled cast irons)



SiAlON

α-SiAlON: hard, can be made tough, low thermal conductivity makes it unsuitable for high speed machining

β-SiAlON: similar properties to Si_3N_4

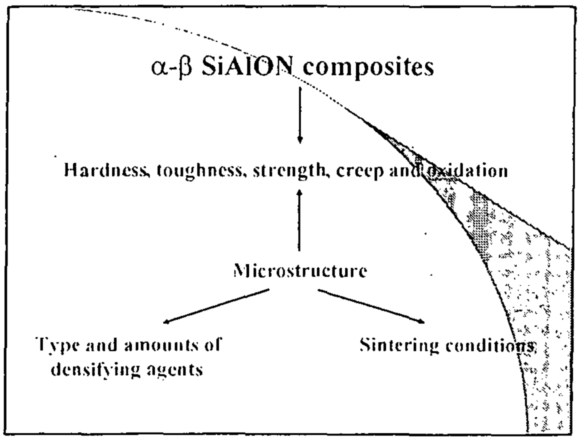


AIM

to develop a material with high toughness and thermal conductivity, but harder than Si_3N_4 and also chemically more compatible.

ROUTE

α-β SiAlON composites.



α-β SiAlON composites

↓

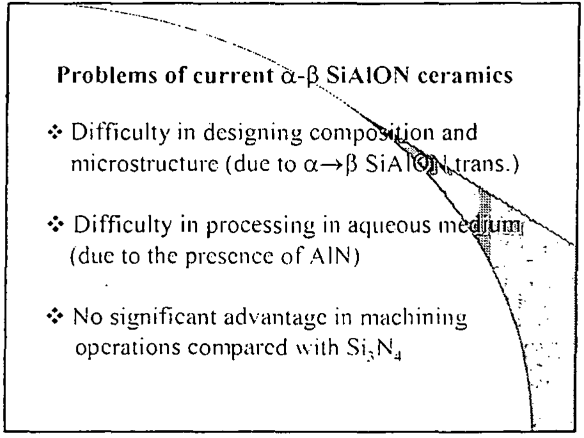
Hardness, toughness, strength, creep and oxidation

↑

Microstructure

Type and amounts of densifying agents

Sintering conditions



Problems of current α-β SiAlON ceramics

- ❖ Difficulty in designing composition and microstructure (due to α→β SiAlON trans.)
- ❖ Difficulty in processing in aqueous medium (due to the presence of AlN)
- ❖ No significant advantage in machining operations compared with Si_3N_4

Development stages in Anadolu University

CHEMICAL COMPOSITION

PROCESS PERFORMANCE

CHARACTERISATION

Sintering additives for new α-β SiAlON ceramics

$\underline{CaO}$

to avoid $\alpha \rightarrow \beta$ SiAlON transformation

$\underline{Y_2O_3 \text{ and/or } Re_2O_3 \text{ (where } Z_{Re} \geq 62)}$

to increase the stability and hardness of α-SiAlON

$\underline{Re_2O_3 \text{ (where } Z_{Re} < 62)}$

to develop elongated β-SiAlON grains and increase fracture toughness

Processing

Powder preparation (milling in aqueous medium)

↓

Spray drying

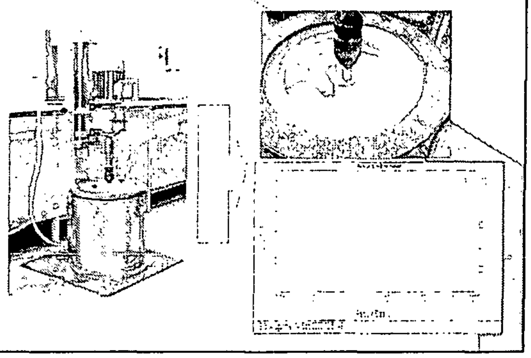
↓

Pressing

↓

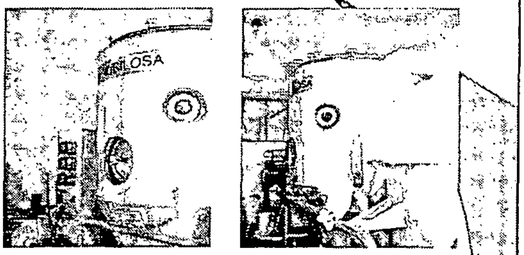
Gas pressure sintering (20 bar N_2, 1700-1800°C)

Attrition milling



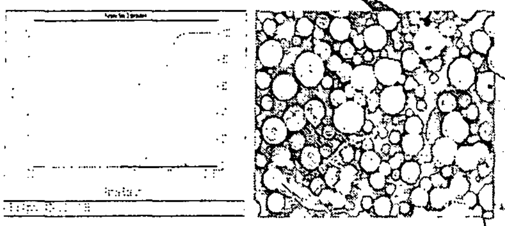
Spray drying

(Nubilosa spray drier Type LTC with a water evaporation capacity of 1 to 5 kg/hour (at an inlet temp. of max. 250°C and a max. outlet temp. of 130°C)

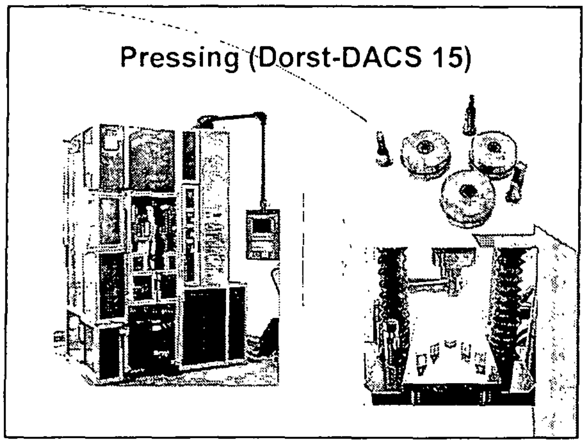


PRODUCT

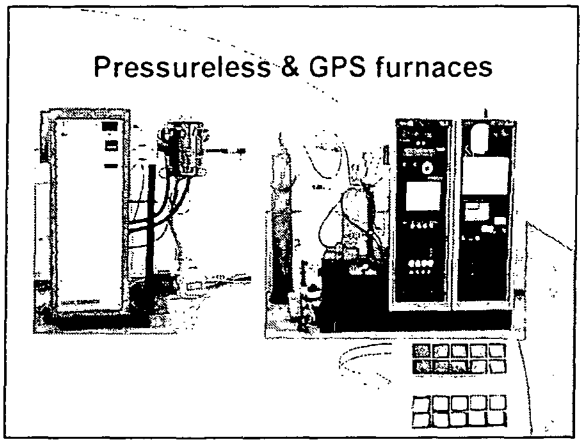
(mostly spherical within the range of 80 to 100 μm, d_{50} less than 1% R.H)

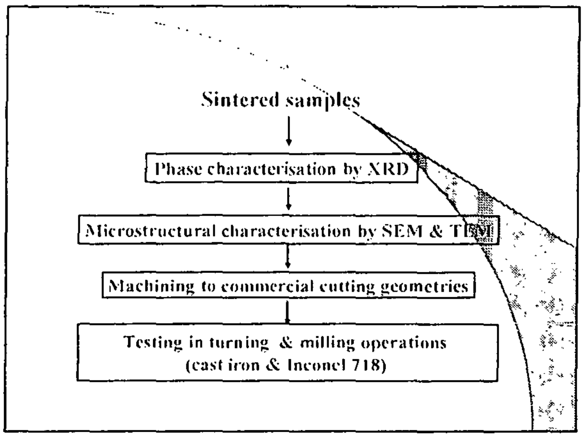


Pressing (Dorst-DACS 15)



Pressureless & GPS furnaces





Sintered samples

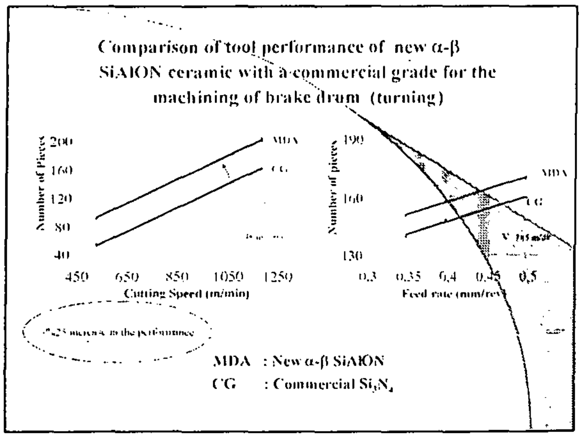
Phase characterisation by XRD

Microstructural characterisation by SEM & TEM

Machining to commercial cutting geometries

Testing in turning & milling operations
(cast iron & Inconel 718)

Comparison of tool performance of new α-β SiAlON ceramic with a commercial grade for the machining of brake drum (turning)



MDA : New α-β SiAlON
CG : Commercial Si_3N_4

Conclusion

An innovative idea

A commercial product

Prof. Dr.-habil Z.Kovziridze, Dr.-Eng. N.Nizharadze, Dr.-Eng. D.Gventsadze

Georgian Technical University, Tbilisi, Georgia.
Department of the technology of composite materials and items

The object of the paper is the design and production of condensed ceramic material stable to thermal and gas-thermal aggression.

On the basis of barite and argillaceous, ceramics is synthesised with single stage technology at 1450^0C with phase content of celsian - 93% by mass. The rest is presented with barium aluminates and silicates, as well as with a small quantity of vitreous phase. Thermal stability of ceramics with 20^0C water cyclic cooling is 480^0C. Volume electric resistance is ρ ohm/cm = 10^{16}. Dielectric losses at 1 MHz and 20^0C are $tg\delta \cdot 10^{-4} = 2$. Shift modulus is G H/mm$^2 \cdot 10^3 = 31.5$; elasticity modulus is E H/mm$^2 \cdot 10^3 = 78.5$.

A new mechanism of ceramic material formation is proposed. When celsian is formed, the yield of superstructure in the form of separated AlO_4 and SiO_4 as the double layer tetrahedrons prove the possibility of celsian synthesis with the help of metakaolin. The process should be promoted with intensive decomposition of barite at 1135-1180^0C where the products separated at decomposition act as the process mineraliser - destruction of kaolinite structure and its rearrangement into celsian position. This should be favoured with isomorphic substitution in tetrahedron, as well as octahedron layer, that makes favourable conditions of kaolinite structure rearrangement into α-celsian.

Thermodynamic analysis of reactions in the mixtures of barium sulphate with kaolin, as well as with alumina and quartz sand showed that barium aluminates and silicates formation is thermodynamically possible within the range of 800-1800^0C.

The criteria of estimation of stability to thermoshocks R', R'' and R''' are calculated. High value of $R''' 10^{-4}$ m^2/kg = 285,2 indicates that at thermoshocks ceramics may accumulate less energy that provides lower degree of its structure.

Synthesised materials are meant for service at sharp temperature changes and at its high gradients.

The researches are conducted at the department on preparation of composite ceramic materials at low temperatures on the basis of inorganic binders, particularly, on the basis of metaphosphates. This allows to receive materials having refractory, heat insulating, dielectric or current conducting and other properties. For example, on the basis of titanium oxide, corundum and single replaced phosphate, the material of 5% porosity was received, its compression strength being 500 MPa and mass 2,80 g/cm^3. The temperature of thermal treatment (burning) of such material does not exceed 700^0C, while the formation of primary samples happens within 100-200^0C in conditions of repeated hot pressure. Experiments have been carried out with the purpose to introduce discrete size carbon and basalt fibers into compositions that increases impact strength of this material.

Ferric phosphate based binder is developed in Georgia and is patented in many countries of the world. With the help of this binder the materials were tested and received on the basis of different raw materials of Georgia, such as andesite, perlite, tufa, trachyte, zeolite, etc. The final temperature of their formation does not exceed 300-500^{0}C.

We have developed the technologies and, respectively, materials for protection of thermocouples from aggressive media (slags, metals). One of them is the technology of preparing silicium carbide and synthetic corundum with silicium nitride binder. The technology of preparation of high fire-resistant housing for thermocouple protection, of pyrometric pipes and induction furnace linings are developed.

Housings and pyrometric pipes are items of different diameters from 8 ÷10 to 80 ÷ 95 mm and of 800 mm length with sealed ends.

The items are characterised with high mechanical and thermal resistance, air tightness, wear and metal resistance, endure repeated (20) measurements in melted metal at 1500-1600^{0}C, prolonged (of 1000 hr) measurements in non-ferrous metals and in air medium for 2000 hr. These materials could be used in induction furnaces for thousands of hours.

The mentioned items were successively used at many metallurgical and engineering plants in Bratsk, Volgograd, Alma-Ata, Chelyabinsk; at glass works in Surami, Ksani, Krasnoyarsk, Orjonikidze, Severodonetsk, etc.- at 250 plants all together.

The development of such fields of modern engineering that use nuclear reactors, jet engines, rockets, gas turbines, etc. increases, all the more, the requirements for heat-proof materials.

The subject of our research is the development of the technology of receiving heat-proof ceramic elements for rocket-space engineering, particularly, the development of gas turbine ceramic disks. The introduction of such disks, instead of heat-proof metals, into production will increase turbine operation quality and its efficiency by increasing working temperature up to 1200^{0}C.

[illegible] [illegible]

Our research material is notable not only for corrosion-, wear- and thermo-resistance but also for the original method of production.

It is received on the basis of alumosilicates with silicium nitride and oxynitride binder by alumosilicothermal method. On addition of aluminium powder to alumosilicates and on further burning in nitrogen medium at 1400-1420^{0}C, the material with high mechanical, thermal and wear resistance is received.

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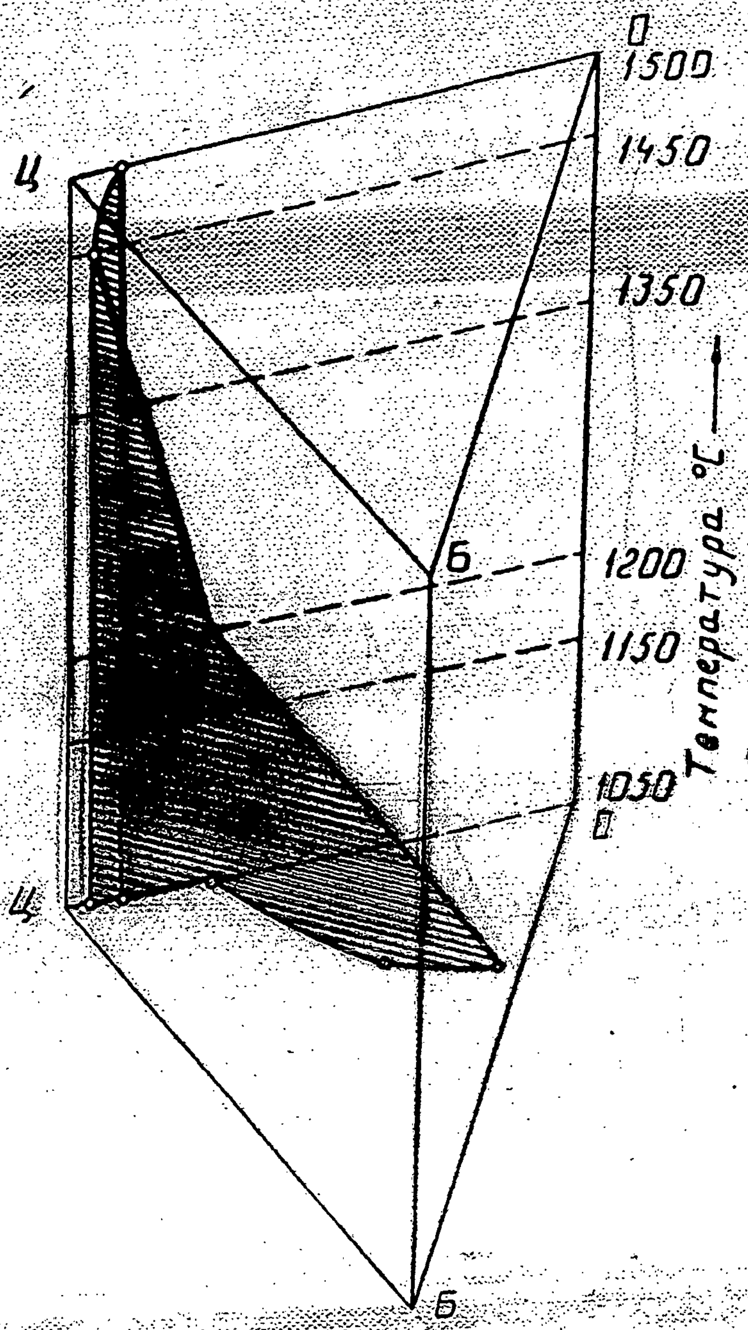
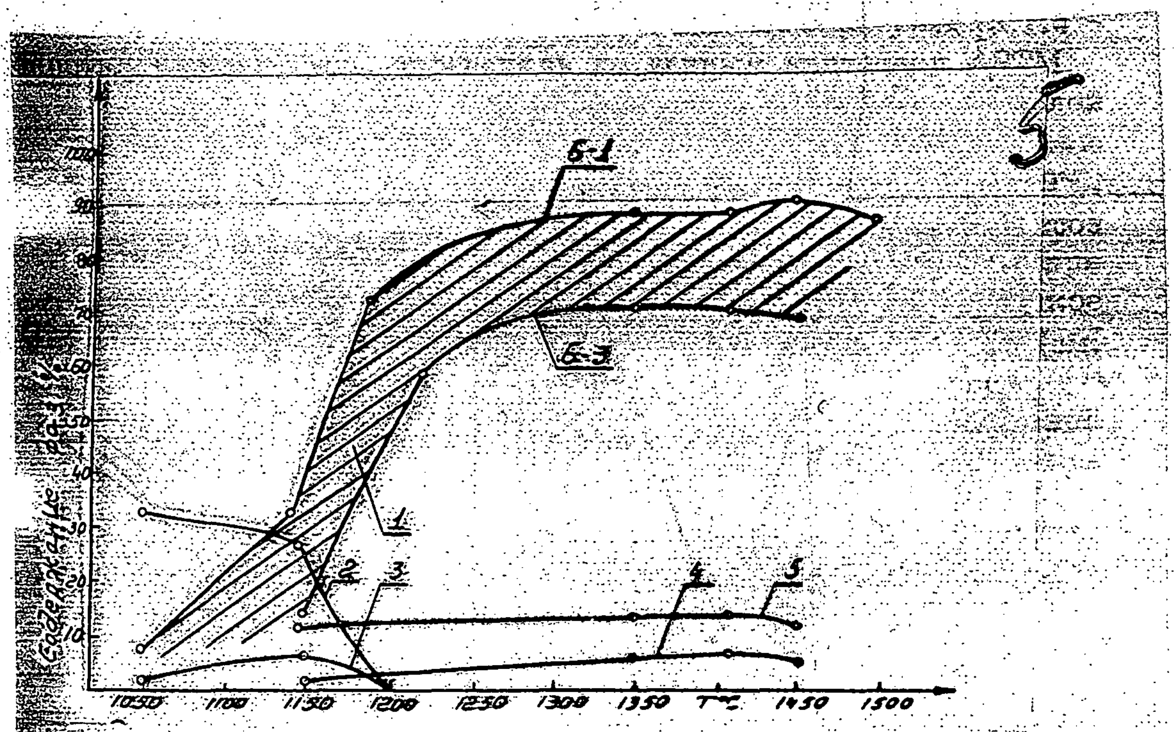
Fig. 1 represents the change of composition of crystalline phases with temperature in barium containing materials. Here, it is clearly seen that already at 1200^{0}C, barite is absent in both materials. Released BaO is coupled with Al_2O_3 and -SiO_2 creating celsian - BaO-Al_2O_3-SiO_2 and quick growth of its composition is noticed. – [illegible] [illegible]
Fig.2 shows the behaviour of triple system barite-celsian-cilicates in dependence with the fourth variable - temperature. Above 1200^{0}C, the point on the back side of the triangle represents the composition of binary system. Some turn of celsian field at 1500^{0}C proves the beginning of celsian melting.
The mechanism of material preparation in the process of its consolidation is developed.

7



Поведение тройной системы в зависимости от температуры t: Б – барит: С – силикаты и алюминаты, барит.

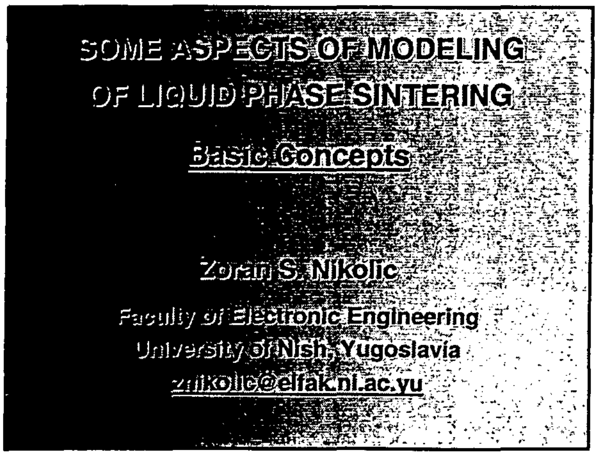


3. Изменение содержания кристаллических фаз в зависимости
пературы в барийсодержащих керамических материалах: 1.
2. Барит в Б-1; 3. Муллит в Б-1; 4. Муллит в Б-3; 5. Корунд в Б-3.

SOME ASPECTS OF MODELING OF LIQUID PHASE SINTERING. Basic Concepts

By Mr. Zoran Nikolic

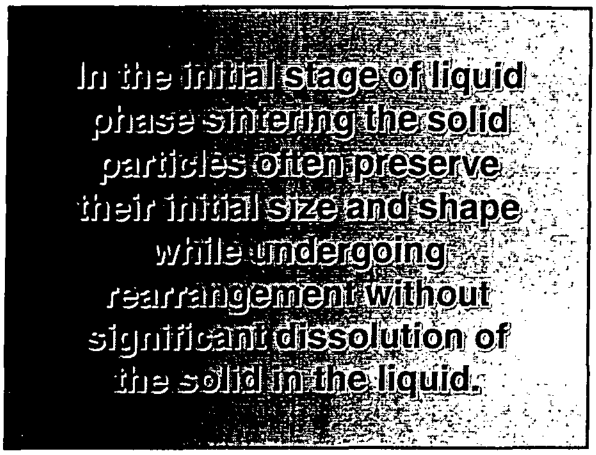
Generally speaking, the liquid phase sintering is viewed in terms of three overlapping stages: particle rearrangement, solution-precipitation, and Ostwald ripening. During the first stage rearrangement of the solid phase, in which surface tension forces act to bring about physical movement of the constituents of sintering body, takes place causing rapid densification. The rearrangement process assumes that if there is good wetting between liquid and solid phase, solid particles will rearrange themselves under the action of surface tension forces, producing more stable packing. Therefore it is very interesting to investigate how the solid particles rearrange, and also to make analysis of the resulting capillary forces as the driving forces of liquid phase sintering. This paper outlines a computer-based method for calculation of capillary force during liquid phase sintering. The simulation method developed is based on the defined model of two spherical particles The effect of two-dimensional shape accommodation and shrinkage on liquid phase distribution and redistribution, based on a physical and numerical modeling of liquid phase sintering, was considered too. The theoretical analysis assumes a numerical definition of sub-model for initial model system definition and shape accommodation process. The simulation method will be applied on two- and three-spherical particles model with the same and different radius.



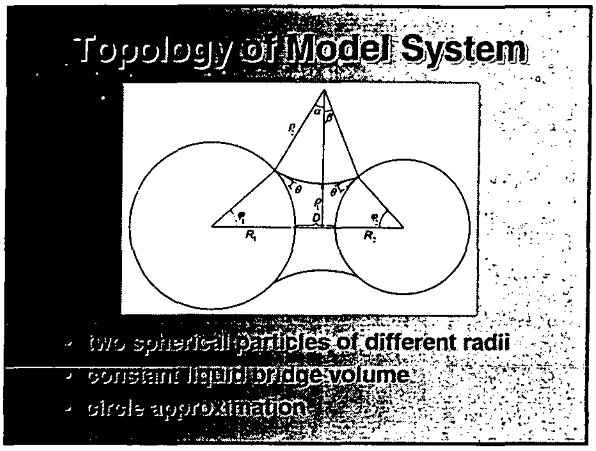
SOME ASPECTS OF MODELING OF LIQUID PHASE SINTERING

Basic Concepts

Zoran S. Nikolic
Faculty of Electronic Engineering
University of Nish, Yugoslavia
znikolic@elfak.ni.ac.yu

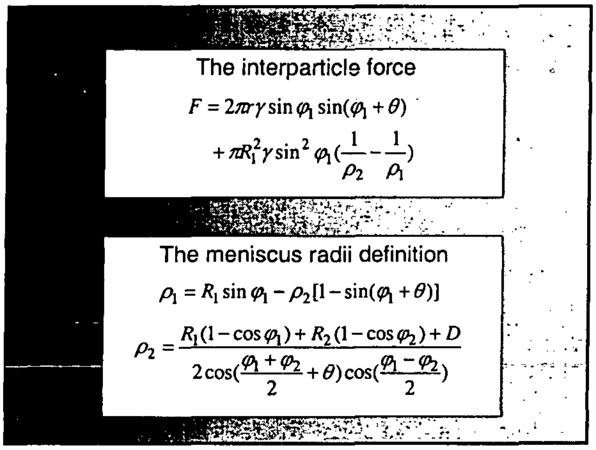


In the initial stage of liquid phase sintering the solid particles often preserve their initial size and shape while undergoing rearrangement without significant dissolution of the solid in the liquid.



Topology of Model System

- two spherical particles of different radii
- constant liquid bridge volume
- circle approximation



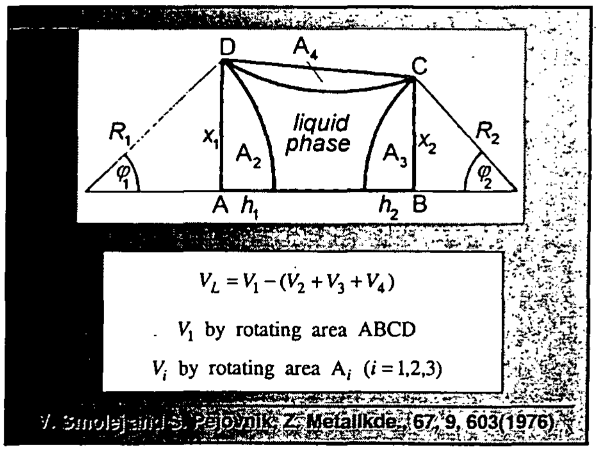
The interparticle force

$$F = 2\pi r\gamma \sin\varphi_1 \sin(\varphi_1+\theta) + \pi R_1^2 \gamma \sin^2\varphi_1 \left(\frac{1}{\rho_2}-\frac{1}{\rho_1}\right)$$

The meniscus radii definition

$$\rho_1 = R_1 \sin\varphi_1 - \rho_2[1-\sin(\varphi_1+\theta)]$$

$$\rho_2 = \frac{R_1(1-\cos\varphi_1)+R_2(1-\cos\varphi_2)+D}{2\cos(\frac{\varphi_1+\varphi_2}{2}+\theta)\cos(\frac{\varphi_1-\varphi_2}{2})}$$

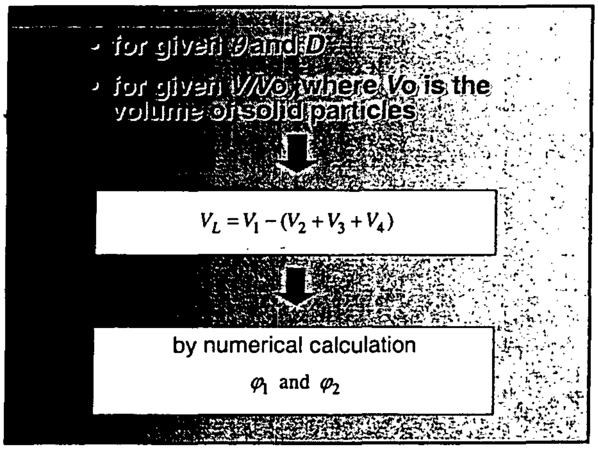


$$V_L = V_1 - (V_2+V_3+V_4)$$

V_1 by rotating area ABCD

V_i by rotating area A_i $(i=1,2,3)$

V. Smolej and S. Pejovnik, Z. Metallkde., 67, 9, 603(1976)

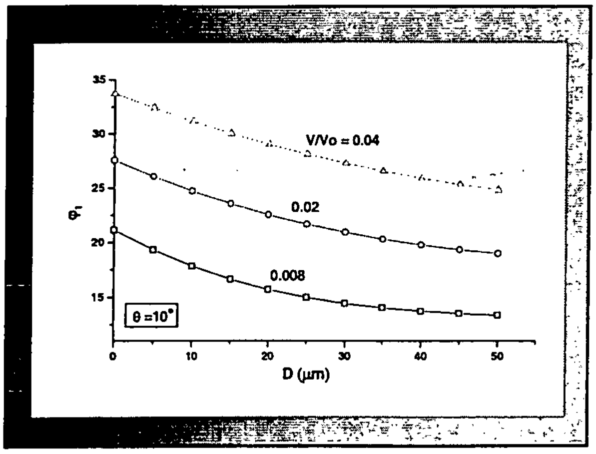


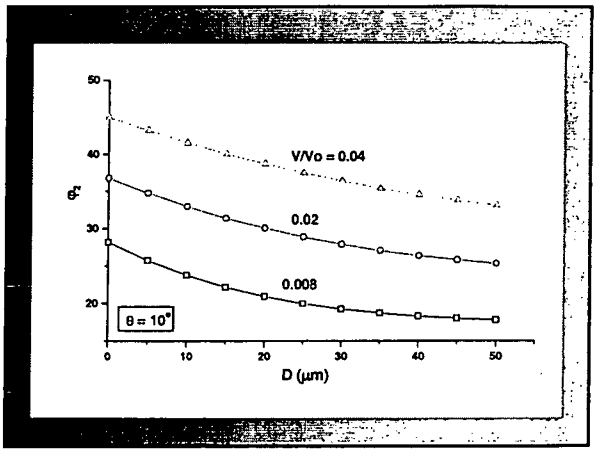
- for given θ and D
- for given V/V_o, where V_o is the volume of solid particles

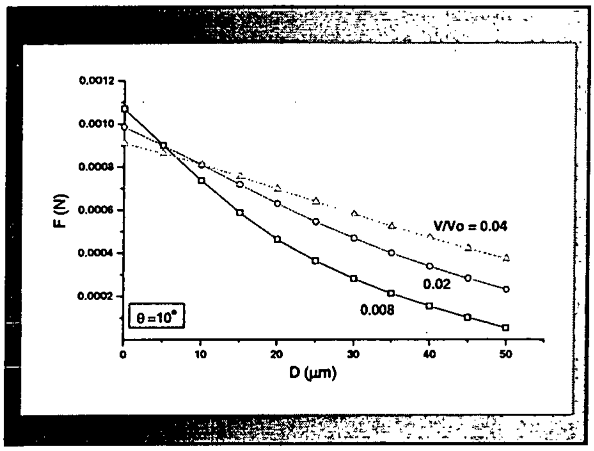
$$V_L = V_1 - (V_2+V_3+V_4)$$

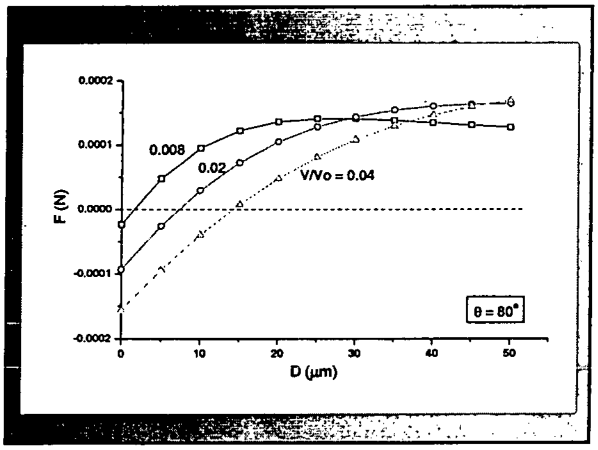
by numerical calculation

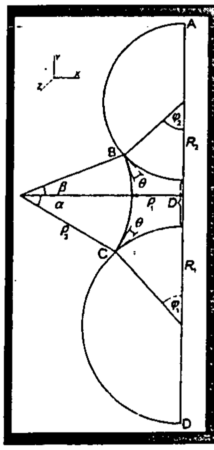
φ_1 and φ_2











A-B: for $\delta = 90°$ to $270° - \varphi_2$

$x = R_2 \cdot \cos\delta$

$y = \rho_2 \cdot \sin\beta + R_2 \cdot \cos\varphi_2 + R_2 \cdot \sin\delta$

B-C: for $\delta = \beta$ to $-\alpha$

$x = -\rho_1 - \rho_2 + \rho_2 \cdot \cos\delta$

$y = \rho_2 \cdot \sin\delta$

C-D: for $\delta = 90° + \varphi_1$ to $270°$

$x = R_1 \cdot \cos\delta$

$y = -\rho_2 \cdot \sin\alpha - R_1 \cdot \cos\varphi_1 + R_1 \cdot \sin\delta$

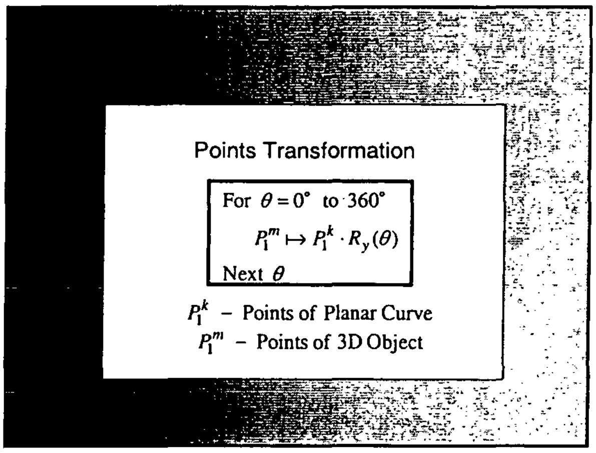
3D Object Generation by Revolution

k-th Point Definition

$$P_S^k = [S \cdot x_k, S \cdot y_k, S \cdot z_k, S]$$

Rotation Matrix

$$R_y(\theta) = \begin{bmatrix} \cos\theta & 0 & -\sin\theta & 0 \\ 0 & 1 & 0 & 0 \\ \sin\theta & 0 & \cos\theta & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$



Points Transformation

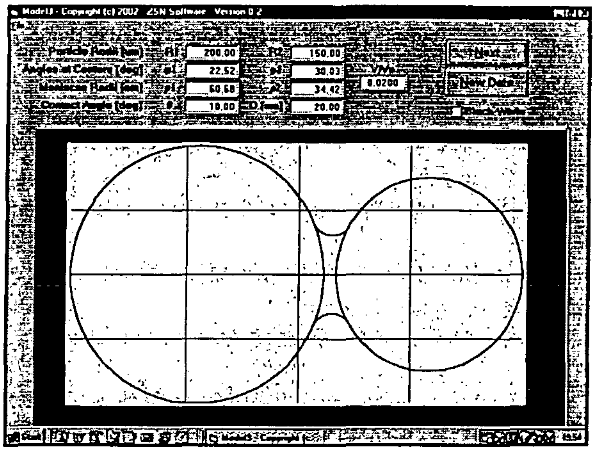
For $\theta = 0°$ to $360°$

$$P_1^m \mapsto P_1^k \cdot R_y(\theta)$$

Next θ

P_1^k – Points of Planar Curve

P_1^m – Points of 3D Object



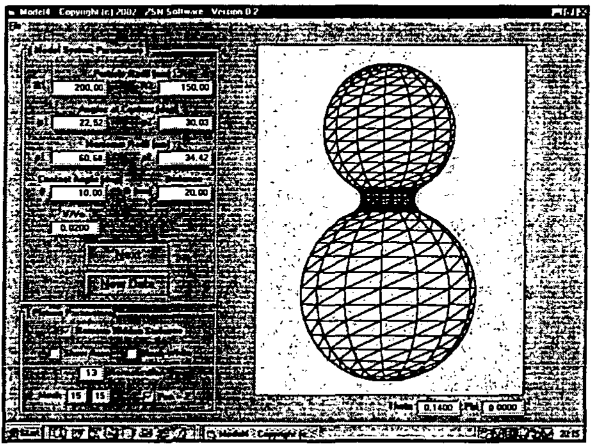
Particle Radii [nm] R1 200.00 R2 150.00

Angles at Contact [deg] φ1 22.52 φ2 30.03

Meniscus Radii [nm] ρ1 60.68 ρ2 34.42

Contact Angle [deg] θ 10.00 D [nm] 20.00

V/Vs 0.0200



200.00 150.00

22.52 30.03

60.68 34.42

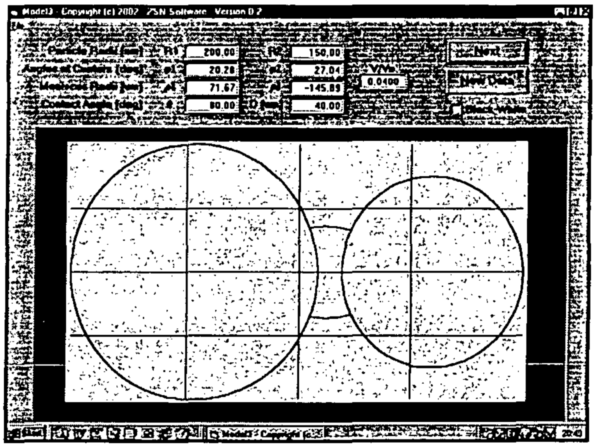
10.00 20.00

V/Vs 0.0200

13

15 15

Theta 0.1400 Phi 0.0000



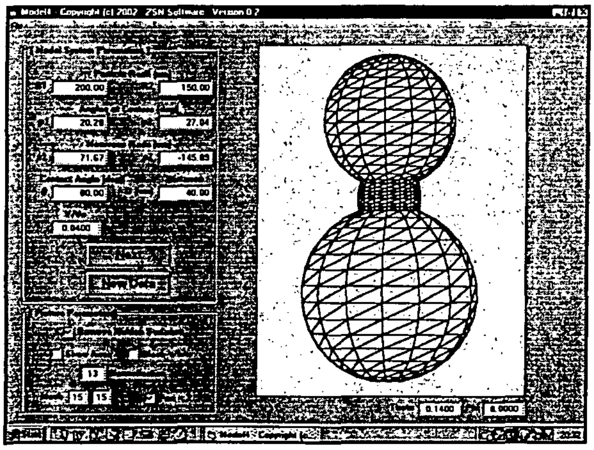
Particle Radii [nm] R1 200.00 R2 150.00

Angles at Contact [deg] φ1 20.28 φ2 27.04

Meniscus Radii [nm] ρ1 71.67 ρ2 -145.89

Contact Angle [deg] θ 80.00 D [nm] 40.00

V/Vs 0.0400



200.00 150.00

20.28 27.04

71.67 -145.89

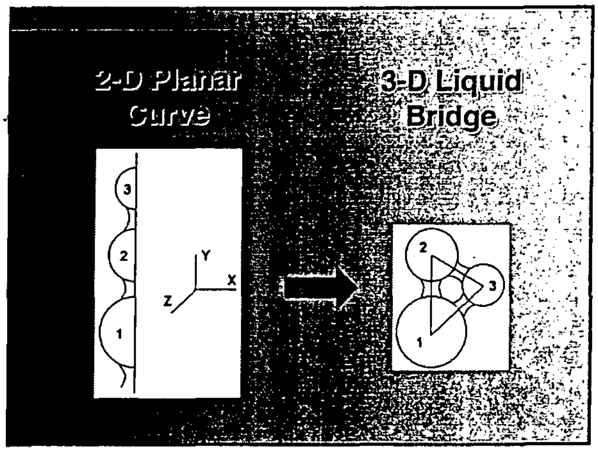
80.00 40.00

V/Vs 0.0400

13

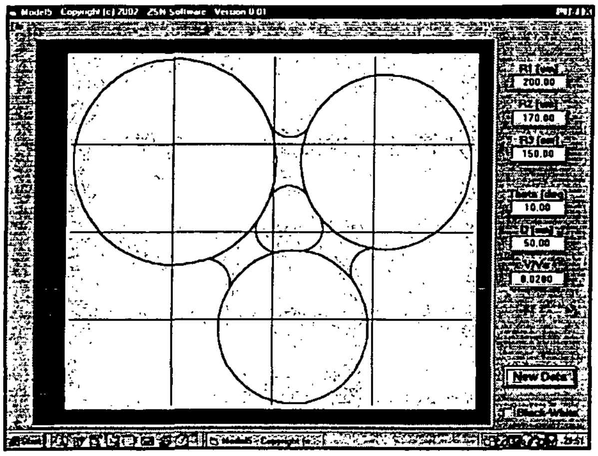
15 15

Theta 0.1400 Phi 0.0000

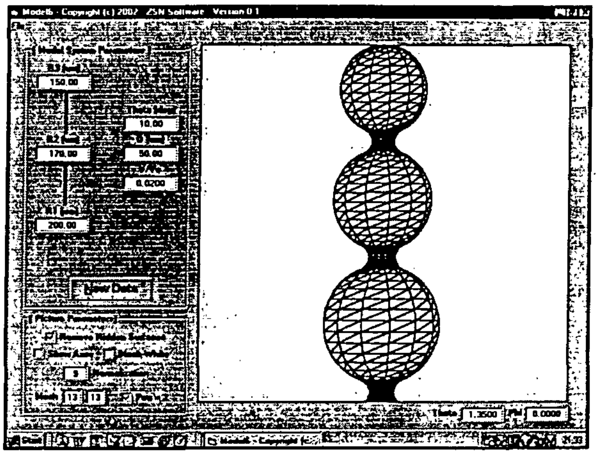


2-D Planar Curve

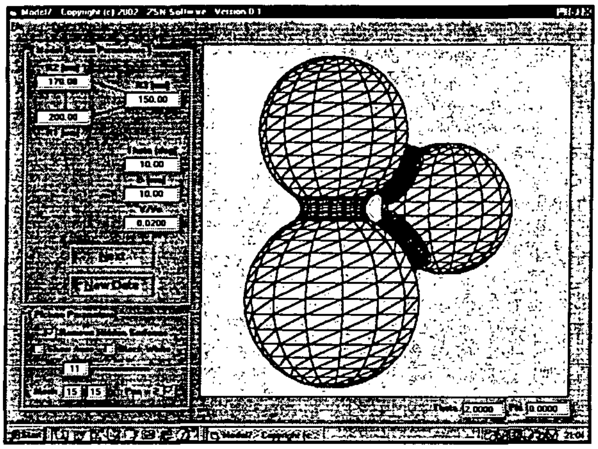
3-D Liquid Bridge


Model5 · Copyright (c) 2002 ZSN Software Version 0.01

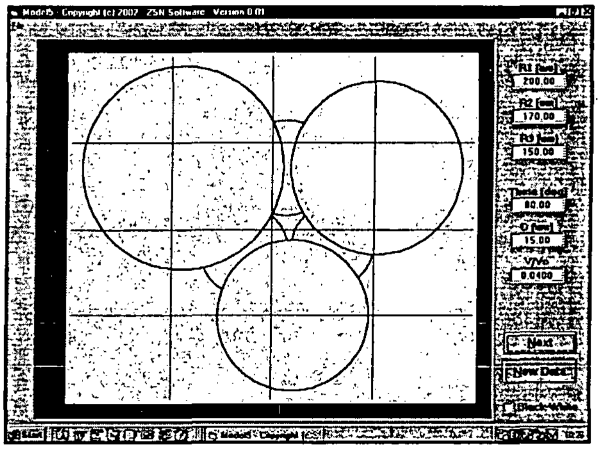
R1 [nm]: 200.00
R2 [nm]: 170.00
R3 [nm]: 150.00
Theta [deg]: 10.00
D [nm]: 50.00
V/Vo: 0.0200


Model6 · Copyright (c) 2002 ZSN Software Version 0.1

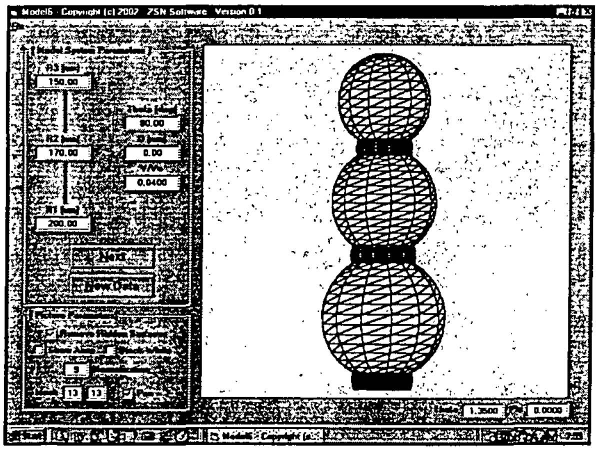
R3 [nm]: 150.00
Theta [deg]: 10.00
R2 [nm]: 170.00
D [nm]: 50.00
V/Vo: 0.0200
R1 [nm]: 200.00
☑ Remove Hidden Surfaces
☐ Show Axes ☐ Black-White
9
Mesh 13 13
Theta 1.3500 Phi 0.0000


Model7 · Copyright (c) 2002 ZSN Software Version 0.1

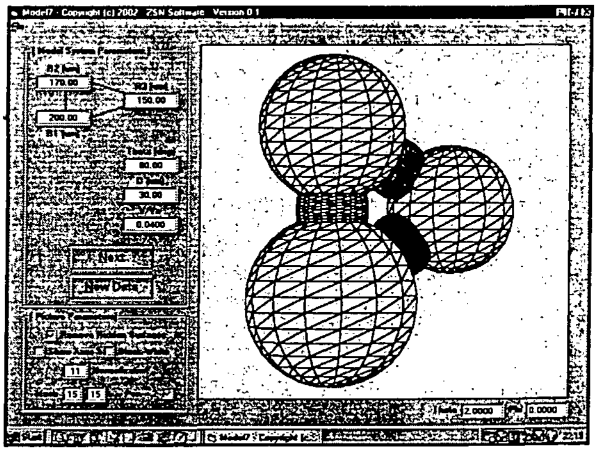
R2 [nm]: 170.00
R3 [nm]: 150.00
R1 [nm]: 200.00
Theta [deg]: 10.00
D [nm]: 10.00
V/Vo: 0.0200
11
Mesh 15 15
Theta 2.0000 Phi 0.0000


Model5 · Copyright (c) 2002 ZSN Software Version 0.01

R1 [nm]: 200.00
R2 [nm]: 170.00
R3 [nm]: 150.00
Theta [deg]: 80.00
D [nm]: 15.00
V/Vo: 0.0400

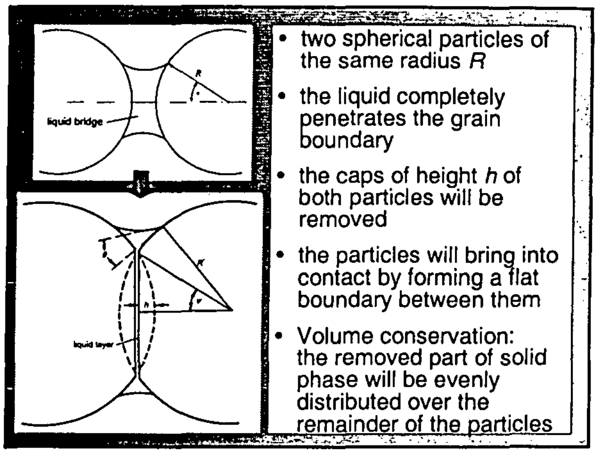

Model6 · Copyright (c) 2002 ZSN Software Version 0.1

R3 [nm]: 150.00
Theta [deg]: 80.00
R2 [nm]: 170.00
D [nm]: 0.00
V/Vo: 0.0400
R1 [nm]: 200.00
9
Mesh 13 13
Theta 1.3500 Phi 0.0000


Model7 · Copyright (c) 2002 ZSN Software Version 0.1

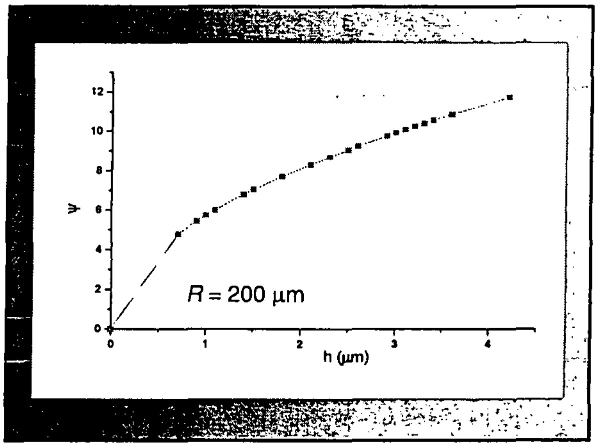
R2 [nm]: 170.00
R3 [nm]: 150.00
R1 [nm]: 200.00
Theta [deg]: 80.00
D [nm]: 30.00
V/Vo: 0.0400
11
Mesh 15 15
Theta 2.0000 Phi 0.0000

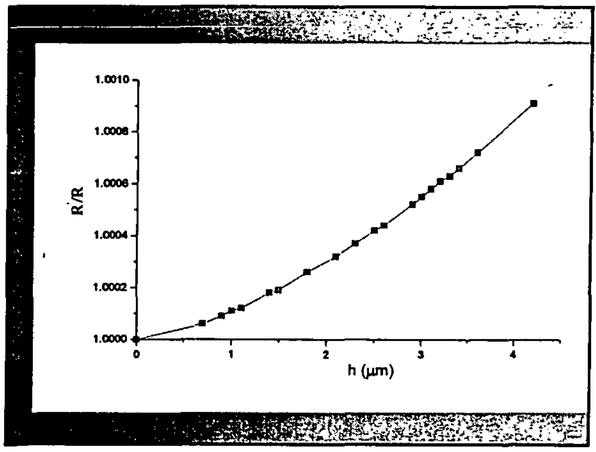
Shrinkage due to the center-to-center approach can be modeled by assuming that equal amounts of solid phase will be removed from the contact between the particles.

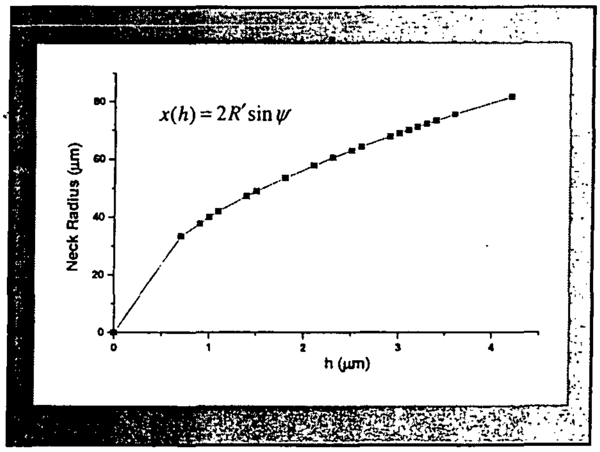


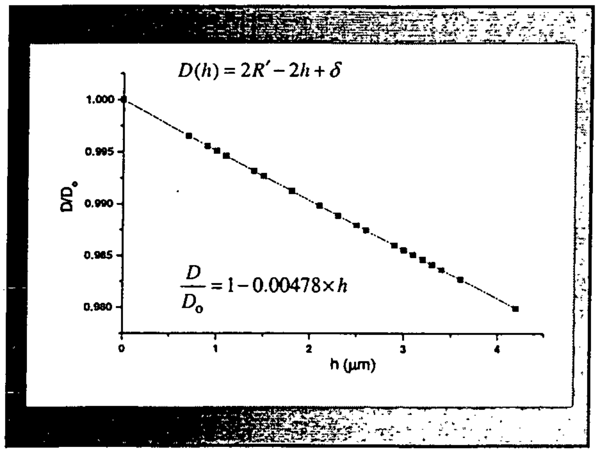
- two spherical particles of the same radius *R*
- the liquid completely penetrates the grain boundary
- the caps of height *h* of both particles will be removed
- the particles will bring into contact by forming a flat boundary between them
- Volume conservation: the removed part of solid phase will be evenly distributed over the remainder of the particles

The geometric parameters *R'* and *ψ* can be calculated numerically using the restraints that the volume of solid phase is constant.









The presented model
can be used
for investigation
how the liquid phase
will try to distribute itself
during the liquid phase
sintering

SOME ASPECTS OF MODELING OF LIQUID PHASE SINTERING. Finite Difference Approach

By Mr. Zoran Nikolic

From many experiments with mixtures of small and large particles, it can be concluded that during liquid phase sintering, smaller particles partially dissolve and a solid phase precipitates on the larger particles. Therefore, the number of smaller particles decreases due to coarsening. The growth rate can be controlled either by the solid-liquid phase boundary reaction or by diffusion through the liquid phase. This dissolution-reprecipitation process leads to further densification by rearrangement of smaller and larger particles. The microstructure may change either by larger particles growing during the Ostwald ripening process or by shape accommodation. In this study, two-dimensional simulation of grain growth by grain boundary migration based on such a physical and corresponding numerical modeling of liquid phase sintering was considered. The simulation method developed is based on the finite difference approach and applied for simulation of solution-precipitation process and grain coarsening process. Such approach can be also applied for definition of numerical models based on contour settling, translation and/or rotation for simulation of the microstructural evolution under gravity and micro-gravity conditions.

SOME ASPECTS OF MODELING OF LIQUID PHASE SINTERING

Finite Difference Approach

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Modeling and Process Simulation Important Steps...

- Definition of models and characteristic system state
- Computation of process parameters and boundary parameters
- Process simulation
- Process characterization

Model Process Assumptions

- It is assumed a pore-free structure
- The solid-liquid mixture has solid particles that initially are not in contact
- Particle contacts during LPS are not allowed ("isolated particles")
- Mass diffusion outside the particles is assumed to be the only mass transfer process
- The new geometry is a result of the evolution of the centers of mass

---

Model System Assumptions...

- Contour Size Region $[r_{\min}, r_{\max}]$
- Random Generated Size Distribution
- Randomly Distributed ("gravity free") Contour' Center Position
- No Contours Intersection

Initial Packing Process "Settling Procedure"

- Contours are subjected to a simulated gravity field: contour falls under gravity and slides down over the already settled contours
- It will be applied to each contour
- It begins with contour having lowest position in vertical direction
- Bottom wall and walls on both sides are stationary and upper wall can move

---

$$\ln\left(\frac{C}{C_0}\right) = \frac{2\gamma_{sl}\Omega}{kT}\cdot\frac{1}{r}$$

$$\Delta C = C - C_0 \text{ is small} \quad \Rightarrow \quad \Delta C = C_0 \cdot \frac{2\gamma_{sl}\Omega}{kT}\cdot\frac{1}{r}$$

$$C(\mathbf{r}_j^s) \sim \kappa(\mathbf{r}_j^s)$$

$$\mathbf{J} = -D_L \cdot \nabla C$$

- **Ostwald ripening is a typical multibody free boundary problem in which the domains alter their morphologies in response to the diffusion field**
- **After solution-precipitation, the particles grow in supersaturated liquid phase: large particles start to grow at the expense of small particles**
- **This tendency for particles to grow or to shrink depends on the size of particles relative to a critical particle size**

Contour Coarsening

Critical Particle Radius

r^* - radius for which $dr/dt = 0$

$$\begin{cases} D^s(r_s < r^*) & \text{will dissolve} \\ D^s(r_s = r^*) & \text{neither grow nor shrink} \\ D^s(r_s > r^*) & \text{will grow} \end{cases}$$

$r^* = 9\langle r\rangle/8$ - reaction controlled growth

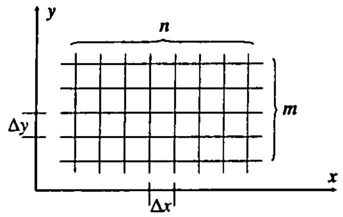
$r^* = \langle r\rangle$ - diffusion controlled growth

$$\frac{\partial C}{\partial t} = D_L \cdot \nabla^2 C$$

$$\Downarrow$$

$$\frac{\partial C}{\partial t} = D_L \cdot \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right)$$

$$(0 \le x \le a, 0 \le y \le b, t \ge 0)$$



Concentration at point (x_i, y_j) after time t_k

$$C(x_i, y_j, t_k) \equiv C_{i,j,k}$$

Classical Five Point Approximation

$$C_{i,j,k+1} = (1 - 2\lambda_1 - 2\lambda_2)C_{i,j,k} + \lambda_1(C_{i+1,j,k} + C_{i-1,j,k}) + \lambda_2(C_{i,j+1,k} + C_{i,j-1,k})$$

$$(i = 2,3,\ldots,n-1;\ j = 2,3,\ldots,m-1;\ k = 0,1,\ldots)$$

$$\lambda_1 = D_L \cdot \frac{\Delta t}{(\Delta x)^2} \quad \lambda_2 = D_L \cdot \frac{\Delta t}{(\Delta y)^2}$$

Stability Condition $\lambda_1 + \lambda_2 \le 0.5$

Initial Model System Definition

$$\{(x_c^s, y_c^s), r_s\} \quad (s = 1,2,\ldots,N)$$

Contours Definition

$$D^s = \{(x_i, y_j) | (x_i - x_c^s)^2 + (y_j - y_c^s)^2 = r_s^2\} \quad (s = 1,2,\ldots,N)$$

Solid Phase Definition

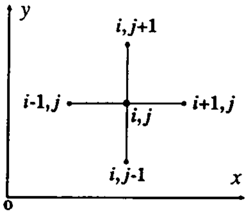
$$\bigcup_{s=1}^{N} \{(x_i, y_j) | (x_i - x_c^s)^2 + (y_j - y_c^s)^2 \le r_s^2\}$$

Flux to the point (x_i, y_j)

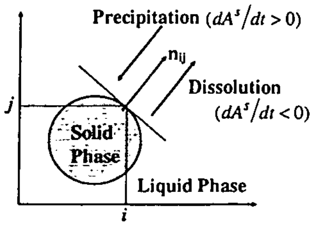
$$\boxed{J_{i,j} = J^x_{i,j} + J^y_{i,j}}$$

$$J^x_{i,j} = -D_L \cdot \left(\frac{c_{i,j} - c_{i+1,j}}{\Delta x} \cdot \delta_{i+1,j} + \frac{c_{i,j} - c_{i-1,j}}{\Delta x} \cdot \delta_{i-1,j} \right)$$

$$J^y_{i,j} = -D_L \cdot \left(\frac{c_{i,j} - c_{i,j+1}}{\Delta y} \cdot \delta_{i,j+1} + \frac{c_{i,j} - c_{i,j-1}}{\Delta y} \cdot \delta_{i,j-1} \right)$$



$$\delta_{i,j} = \begin{cases} 1 & \text{if } (i,j) \in \text{liquid phase} \\ 0 & \text{if } (i,j) \in \text{solid phase} \end{cases}$$



$$D^s(t + \Delta t) = D^s(t) + \Delta D^s(\Delta t) \quad (s = 1,2,\dots,N)$$

$$\boxed{D^s(t) = \left\{ \mathbf{R}^s(t); \mathbf{r}^s_1(t), \mathbf{r}^s_2(t), \dots, \mathbf{r}^s_{n_s}(t) \right\} \quad (s = 1,2,\dots,N)}$$

General Algorithm Structure

PREPROCESSOR

Materials Data
Analysis Conditions
Models Definition
Discretization

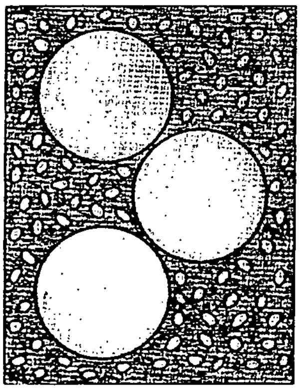
SIMULATOR

Process simulation

POSTPROCESSOR

Process Characterization
Grain Growth
Kinetics, etc.

Modeling of Shape Accommodation



Model Assumptions

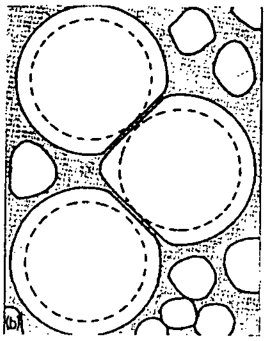
- The large particles are immersed in a "matrix" of much smaller particles of the same material
- The liquid phase serves as a fast transport medium

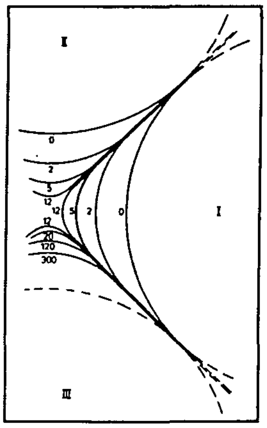
W.A. Kaysser, M. Zivkovic, G. Petzow, J. Mat. Sc. 20 (1985) 578-584

Model Assumptions...

- The average concentration of solute in the melt will above the equilibrium concentration
- The increased solute concentration will lead to a diffusion-controlled deposition of material on the large particles
- The initial spherical shape of the large particles change towards polyhedral shapes
- Any movement of the large particles is excluded

After Liquid Phase Sintering



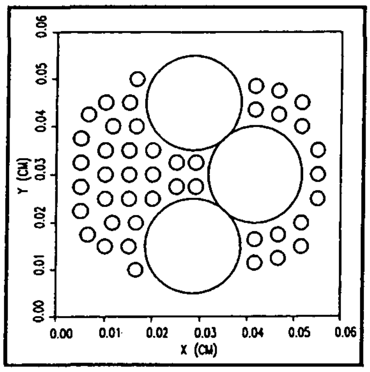


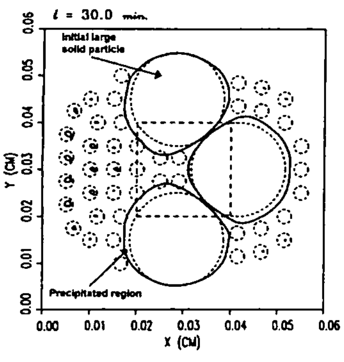
General Conclusion:

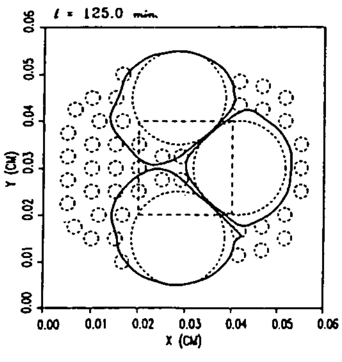
- The deposition of material in the contact area is extremely small
- The distance between the particle centres remains constant
- The large particles in direct contact show considerable shape accommodation

Application of

Finite Difference Approach







Liquid Phase Phenomena of Interest...

- Segregation (Stokes' Law Settling)
- Brownian Motion
- Densification by Solution-Precipitation
- Rotation

Model Assumptions...

- Large Amount of Liquid
- There are no pores during LPS
- Center-to-center approach within a minimal thickness of liquid layer is not allowed
- Center-to-center interaction is removed

Modeling of Contour Translation...

$$D^m \rightarrow D^{m,new}$$

$$D^{m,new} \cap D^j = \varnothing \quad (j = 1,2,\ldots,N;\ m \neq j)$$

Boundary Point of the *m*-th contour

$$BP_S^{m,k} = [S \cdot x_k^m, S \cdot y_k^m, S]$$

S - Scaling Parameter

Domain' Definition

$$D^m = \left\{ (x_k^m, y_k^m, 1) \ (k = 1,2,\ldots,n_m) \right\} \quad (m = 1,2,\ldots,N)$$

Translation matrix

$$T_{a,b} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ a & b & 1 \end{bmatrix}$$

Contour' Translation

$$BP_1^{m,k} \cdot T_{a,b} = [x_k^m + a, y_k^m + b, 1]$$

New Domain' Definition

$$D^{m,new} = \left\{ (x_k^m + a, y_k^m + b, 1) \ (k = 1,2,\ldots,n_m) \right\}$$

Stokes' Law Settling

- Under Earth-based experimental conditions, Stokes' law settling usually dominates microstructure formation
- The packing density of the settled solid depends on the density difference between the liquid and solid phases

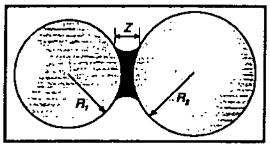
The settling velocity

$$V = \frac{2a\langle r\rangle^2(\rho_s - \rho_L)}{9\eta} \quad (\eta\text{ - liquid viscosity})$$

The average time to travel the distance between grains by gravity-induced settling

$$\tau_{settl} = \frac{9\eta\langle\lambda\rangle}{2a\langle r\rangle^2(\rho_s - \rho_L)} \quad (\langle\lambda\rangle\text{ - average separation distance})$$

The liquid bridges can produce torque, causing strong particle shearing...



The Viscous Force

$$F = 6\pi\eta\bar{R}^2\frac{1}{h}\frac{dh}{dt}\left(1-\frac{h}{Z}\right)^2$$

$$\bar{R} = \frac{R_1 \cdot R_2}{R_1 + R_2} \quad \text{Reduced radius}$$

Brownian Motion

- Brownian motion dominates under microgravity conditions
- It is induced by unbalanced random molecular forces and is active with small grains in a liquid

The Einstein expression for the mean displacement of a grain

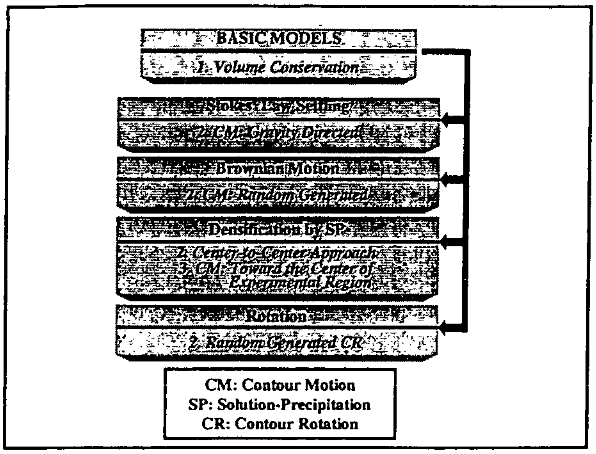
$$\chi^2 = \frac{kTt}{3\pi\langle r\rangle\eta} \quad (\eta\text{ - liquid viscosity})$$

The average time between contacts by Brownian motion

$$\tau_{Brown} = \frac{3\pi\langle r\rangle\eta\langle\lambda\rangle^2}{kT} \quad (\langle\lambda\rangle\text{ - average separation distance})$$

Densification by Solution-Precipitation

- Dissolution of small particles in-between larger particles, thus large particles grow at the expense of neighboring small particles
- Densification results from the uniform center-to-center approach of neighboring particles



BASIC MODELS

1. Volume Conservation

Stokes' Law Settling

2. CM: Gravity Directed

Brownian Motion

2. CM: Random Generated

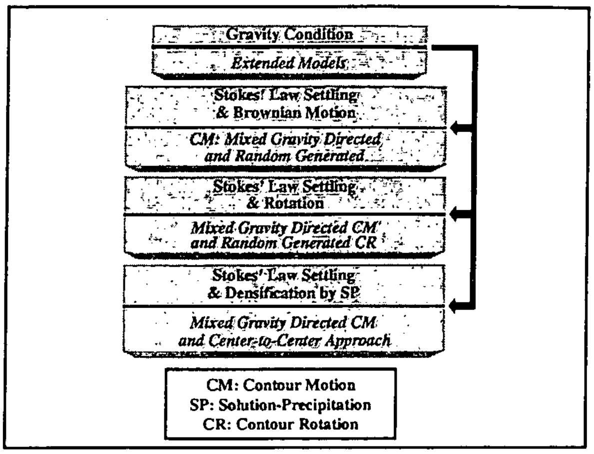
Densification by SP

2. Center-to-Center Approach
3. CM: Toward the Center of Experimental Region

Rotation

2. Random Generated CR

CM: Contour Motion
SP: Solution-Precipitation
CR: Contour Rotation



Gravity Condition

Extended Models

Stokes' Law Settling
& Brownian Motion

CM: Mixed Gravity Directed and Random Generated

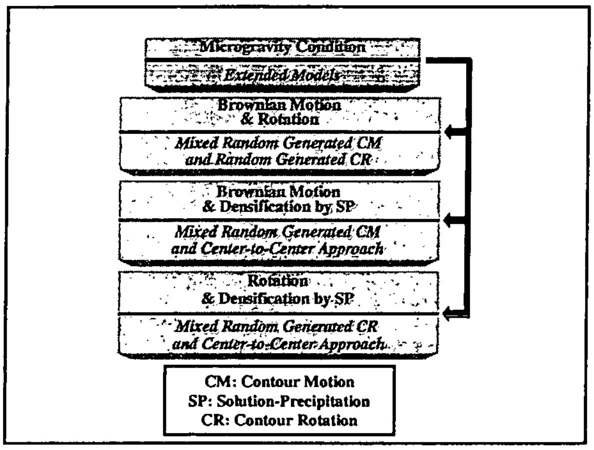
Stokes' Law Settling
& Rotation

Mixed Gravity Directed CM and Random Generated CR

Stokes' Law Settling
& Densification by SP

Mixed Gravity Directed CM and Center-to-Center Approach

CM: Contour Motion
SP: Solution-Precipitation
CR: Contour Rotation



Microgravity Condition

Extended Models

Brownian Motion
& Rotation

Mixed Random Generated CM and Random Generated CR

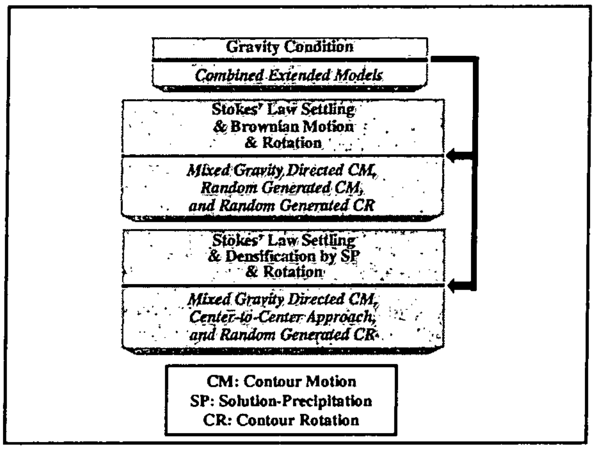
Brownian Motion
& Densification by SP

Mixed Random Generated CM and Center-to-Center Approach

Rotation
& Densification by SP

Mixed Random Generated CR and Center-to-Center Approach

CM: Contour Motion
SP: Solution-Precipitation
CR: Contour Rotation



Gravity Condition

Combined Extended Models

Stokes' Law Settling
& Brownian Motion
& Rotation

Mixed Gravity Directed CM, Random Generated CM, and Random Generated CR

Stokes' Law Settling
& Densification by SP
& Rotation

Mixed Gravity Directed CM, Center-to-Center Approach, and Random Generated CR

CM: Contour Motion
SP: Solution-Precipitation
CR: Contour Rotation

Science and Technology of Ceramics in Yugoslavia

From the ancient times and first steps in ceramics manufacturing up to the current state-of-art, engineers and scientists have always been on the search for new materials and processes. Along the way, a demand for improved or unique properties was the main driving force for developing new ceramic materials and fabrication techniques and equipment.

Classical technologies for ceramics manufacturing are still widely used in tile, brick and sanitary wear factories in Yugoslavia, such as "Polet" Novi Becej, "Potisje" Kanjiza and Keramika Mladenovac, respectivelly. In the area of electrical and technical ceramics, "Iritel" Belgrade produces semiconducting ceramic components, ceramic ultrasound sensors, piezoceramic transducers and hybrid microcircuits. Electroceramics and alumina-based products are main areas of manufacturing within the "Elektroporcelan" Arandjelovac company.

Research undertaken in the area of materials science started more than 40 years ago, first within the Materials Science Department of the Institute for Nuclear Sciences “Vinca” in Belgrade. Ever since many institutions have been involved in advanced ceramics research and development. Namely, remarkable contribution has been made by scientists from the Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade; Center for Multidisciplinary Studies, University of Belgrade, Belgrade; Faculty of Electronic Engineering, University of Nis, Nis; Institute of Nuclear and Other Mineral Raw Materials, Belgrade; Technical Faculty Cacak, etc.

Institute of Technical Science of SASA, established in 1947, started its activity in the field of materials science in 1974. Current research regarding ceramics includes biomaterials, electroceramics and functional ceramics.

It should be emphasized that a very important influence regarding ceramics technology in Yugoslavia has been performed by the International Institute for the Science of Sintering, which consist of well-known scientists worldwide, many of them renowned in the field of ceramics. After so many years of research and efforts to explain the basics, the variety of sintering processes (rapid rate sintering, selective laser sintering etc.) opens new directions and challenges for further research.

Thorough materials selection and more effective processing could lead to new advances in ceramics production and its future could be some new technical and functional ceramic materials.

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Seminar: on "Best Available Technologies and Innovation in Ceramic Production"
Faenza: 30 September - 5 october 2002

'Introduction to Rapid Prototyping and Solid Freeform Manufacturing'

1) Introduction

Solid freeform fabrication (SFF) is an evolution of rapid prototyping (RP) technology that is one of the important breakthroughs of the recent progress in the manufacturing industry. It is based on the principles of shaping science that studies how to organize materials in sequence to get three-dimensional objects with definite shape and functions.

Attached to this paper there is a list of web-sites references reported to explore what is being done and where in the world.

It is helpful to remember that RP and SFF involve mostly layered manufacturing that is one example of the shaping science alternatives.
As an example SFF may follow this operations sequence:

1) geometrical information (usually a CAD file) is preprocessed in a way that the virtual object is approximated by a set of closely spaced parallel contours,
2) some process renders a thin slab with a perimeter corresponding to each outline of the previous parallel contours,
3) the slabs are registered, stacked and fused together to make a complete object.

The chief distinction between different SFF processes is the nature of the process used to define the outlines, to register the slabs and to choose the fusion method. The chief benefit of using SFF methods is that the contours can be made without recourse to tooling.
With reference to the ceramic materials there are unique technical issues in the exploitation of SFF to better understand the fundamentals of ceramic processing. To date, the latter is much less well developed and there are reasons to believe that the production of ceramic prototypes will continue by utilizing a more conventional technology like green machining.

Given the nature of powder processing as is it needed in the ceramic manufacturing , SFF techniques are unlikely to replicate the time compression normally associated with their use in plastics. It is more likely that the impact in ceramics will be the possibility to make bodies with complicated shapes and to permit the construction of test samples, which are of use in scientific research and technical development.

2. Background

The origination of RP/SFF is considered to coincide with the introduction of stereo-lithography, in the late I 980s. But, it is helpful to remember that layered assembly has long been a standard manufacturing process, particularly for unique structures in the architecture models and planning.
Prior to the advent of SFF, prototypes were generally prepared through a combination of machining and, when necessary, joining by hand and surface finishing. The software developments that have enabled SFF also have decreases the skill level necessary for manpower to deal with these operations.

3. Application to ceramics.

The direct fabrication of ceramics through SFF include:

- stereo-lithography of ceramic suspensions (1)
- selective laser sintering of packed beds of binder/powder mixtures (2),
- selective ink jet printing of binders on to a powder bed (3),
- ink jet printing of slurries to form freestanding parts (4),
- laminated object manufacturing of ceramic green tapes (5),
- computer controlled extrusion in which either cooling, gelation or drying is used to solidify the extruded filament (6-9).

It also is true that there are antecedents to some of the SFF processes used for ceramics and other material). Laminated object manufacturing is anticipated by the processes employed in multi-layer substrate (10) and multi-layer capacitors (11). Fused-deposition modeling is anticipated by the recently developed con trolled extrusion processes used to build ceramic springs and windings in general (12). Therefore, many of the processing issues involved in SFF is the same as those that typify ceramic processing in general. And, in this context, ceramic processing refers to powder processing.

Powder processing is generally held to involve four sequential operations:

1) batching, or mixing powder(s) of well defined shape, size and chemistry with appropriate solvent(s) and additives;
2) forming to produce a powder compact that is capable of preserving its shape;
3) densification through heating to high temperature;
4) surface finishing including subtractive (e.g. machining) or additive (e.g. coating) processes.

In principle, an SFF process could replace the entire sequence of operations, but in practice this never occurs. In practice, SFF techniques are only used for shaping, i.e. to produce a green powder compact. Conventional powder processing technology is used in preparing formulations and powder compacts are subjected to standard binder burnout and firing schedules to render the part monolithic. The need for ceramic processing expertise to prepare feedstock and the fact that SFF methods only yield partially processed parts means that their introduction does not open this class of materials to new users. Thus, the field of users is practically limited to those already engaged in ceramic production or research.

To illustrate the relationship between ceramic processing issues and SFF methods used to directly fabricate ceramic parts, three separate examples, available in the open literature are reviewed.

A) Flowability of powders is considered in the context of selective laser sintering and 3D-printing.

Fine powders spontaneously agglomerate and therefore do not flow in a predictable or uniform manner. This means that SFF methods that require flowability cannot directly employ powders that are "sinterable". Both selective laser sintering and the 3D-printing process fall into this category.

The standard solution to this process in conventional ceramic processing is to intentionally agglomerate (i.e. either granulate or spray dry) the powder to form flow units containing several thousands of particles held together by an organic binder that is removed during the initial stages of firing. This approach, however, assumes the presence of tooling. Green parts formed by packing of granules have low average packing efficiency, often <30 vol.%, and packing which is inhomogeneous, i.e. inter- granular voids are often of the order of 0.1 mm, and cannot be sintered. Granules are designed to be deformed or crushed during compaction at applied pressures of several tens of MPa

Efforts to use spray-dried granules in selective laser sintering have not met with notable success. Efforts to use spray dried powders in the original 3D-printing process required post-processing of the green part to increase density.

Clearly, the success of efforts to extend 3D-printing to a slurry-based process capable of producing high green density uniform parts requires a comprehensive understanding of the manifold interrelated process control issues associated with conventional ceramic processing (13)

B) Lamination technology is considered in the context of laminated object manufacturing.

Turning attention to lamination technology, a superficial view would hold that this should be a straightforward process because of the widespread use of green-state lamination in the production of multi-layer ceramics for electronic applications. However, the standard conditions used for thermo-compressive lamination involves significant shear strain. This is tolerable when the parts are platelike and of constant cross-section. However, it is not useful when tall or arbitrarily shaped objects are to be constructed. For this reason, a solvent-based lamination approach with near-zero permanent strain was developed by workers at Case Western Reserve University (14).

C) The role of shear stress.

The role of shear stresses is considered a very important feature and a process parameter in the context of laminated object manufacturing and fused deposition modeling.

It has been clearly shown that shear stress imposed by extrusion through a small diameter orifice will favorably affect the final fired strength because it disrupts many of the local inhomogeneities in green-state particle packing which would otherwise persist into the fired state as flaws. The implication of this is that isolated elements of ceramics prepared by fused deposition modeling, which involves extrusion through very fine nozzles (0.25 to 1.25 mm) should give high strength. Further, if macro-defects associated with the packing of the extruded coil can be minimized or eliminated, then the final parts also should be of high strength and this is observed by workers at Rutgers University .

Another well known phenomenon that occurs during extrusion is that of segregation of the carrier fluid to the region of contact with the die, or, in this case, nozzle. The presence of a binder enriched film on the exterior of the extruded filament may facilitate fusion of one to another, but it will also necessarily produce anisotropic shrinkage. Such anisotropy can be readily accounted for. The point is that the two effects are related, both the high strength and the anisotropic shrinkage during firing are traceable to the same origin, the high shear field. With this view it is not desirable to alter processing to minimize anisotropy as the price may be an undesired drop in performance (15).

4. Applications of SFF to basic research in ceramic processing.

Perhaps one of the more interesting features of SFF in ceramics is the ability to assemble parts to test scientific hypotheses. There are a few examples of the use of SFF to test questions that address broadly-based ceramic processing questions. Two of the best examples that illustrate the potential of uniquely assembled specimens are both studies that employed 3D-printing. The first is the generation of a 3D grid of tracer that allows direct measurement of local strain in powder bed during compaction due to gravity (16) and the second is the use of slurry jetting to study the role of capillary stresses in cracking of powder beds (17).

Clearly, there is room for much broader application of these fabrication processes in designing and rendering test specimens for property measurement. One area that suggests itself immediately is the preparation of samples of ceramic materials that contain controlled amounts and distribution of porosity. For example, classic work on the role of porosity in heat conduction in ceramics employed samples that were prepared by a casting process (18). It is easy to envision a much broader range of pore volume fraction, shape and size distribution would have been studied had SFF methods been available. Ceramics with controlled porosity remain technically important materials (19) and SFF may be used to prepare specimens to gain fundamental data on a wide variety of properties including mechanical, thermal and optical.

5. Conclusions

As a class of industrial manufacturing techniques, SFF competes with machining. There appears to be no reason why green machining cannot become increasingly able to serve many of the current applications being promoted as suitable for rapid prototyping.

SFF has demonstrated the potential to produce unique parts. However, a thorough understanding of the processing methods associated with ceramics is necessary to exploit this potential.

SFF can be used to explore ceramic processing under conditions, which allow precise variation in properties of the powder compact.

This apparently powerful aspect of SFF has not been widely exploited.

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Introduction to Rapid Prototyping and Solid Freeform Manufacturing

Rapid prototyping is the name given to a host of related technologies that :

- Are used to fabricate physical objects directly from CAD data sources
- Add and bond materials in layers to form objects.

CAD 3D model → *"Slicing"* Files *.STL → Layer by layer manufacturing

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Rapid Prototyping applications:

Solid Freeform Manufacturing offers advantages compared to classical methods:

•Objects can be formed with any geometric complexity or intricacy

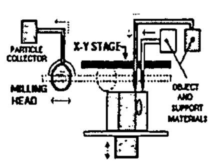
•Construction of complex objects is reduced to a manageble, straightforward and relatively fast process.

So Solid Freeform Manufacturing allows to:

- Cheaply and quickly verify design, functionality and ergonomy of new products: ***Rapid Prototyping***
- Manufacture tools for special purposes : ***Rapid Tooling***
- Produce complex objects : ***Rapid Manufacturing***

Available Technologies:

- Selective Laser Sintering
- Stereolithography
- Fused Depsition Modeling
- Laminated Object Manufacturing
- Inkjet Systems
- Three Dimensional Printing



And then Direct Shell Production Casting, Solid Ground Curing, Laser Engineered Net Shaping, etc...

More Information:

Interesting websites:

The Rapid Prototyping Home Page:
Links to industries, laboratories and universities.
http://www.cc.utah.edu/~asn8200/rapid.html

Worldwide Guide to Rapid Prototyping:
Good description of RP aims, techniques and technologies.
http://home.att.net/~castleisland/

Associazione italiana di Prototipazione Rapida:
The Rapid Prototyping Italian website.
http://www.apri-rapid.it/

Rapid Prototyping in the World:

United States:
University of Texas, laboratory for freeform fabrication:
http://utwired.engr.utexas.edu/lff//
Rutgers, the State University of New Jersey:
http://www.caip.rutgers.edu/RP_Library/
http://www.rci.rutgers.edu/~mehdi/RP.html

United Kingdom:
Manchester Materials Science Center (Prof.Brian Derby):
http://www2.umist.ac.uk/material/research_frames/researchframes.htm

Germany:
Near Net Shape Manufacturing Group, Erlangen University (Prof. Sindelar)
http://www.glass-ceramics.uni-erlangen.de/Staff/Pershtm/Sindelar.html

France:
Centre Europeen de la Ceramique, Limoges
http://www.ceramic-network.com/ang/part01/default.asp

NEW TYPOLOGIES OF "GRANITO" TILES AND THE RELATED "AESTHETIC" ENGINEERING

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AESTHETIC ENGINEERING

In modern tile industry, "design" in terms of colours, shapes, surfaces and effects has determined trends, and has created new tastes and fashions, in connection with traditions and standards of living which were unthinkable until a few years ago.

The recovery of old-time taste, the appreciation of "natural" aspect, and a more and more stone-like design have provided porcelain tiles with means and qualities to be a formidable competitor to real marbles and stones. Polishing before and after firing and many other decorative techniques have enhanced the value of masterly mixes of grains, colours, powders and sometimes also glazes.

Once relegated to strictly technical utilizations, mainly in industrial floorings, where there was no need of any aesthetics but only of high mechanical and physical properties, nowadays porcelain tiles have conquered private housings and public areas, meeting both the demands of designers and architects in terms of beauty and look, and the strictest standards of quality and techical properties, set by organizations throughout the world.

It is under these circumstances that the puzzling expression **"aesthetic engineering"** assumes a deep meaning. Generally speaking two concepts are usually considered as separated: one thing is engineering, that is dealing with something with a pretty technical approach, and one other thing is aesthetics, designs or whatever must exercize a charm on the viewer. Even the people involved in these two fields generally possess opposite qualities.

In porcelain tiles things are completely different: a new engineering approach is required, an aesthetic one. Designing, dimensioning, production, technical requirements and standards are so deeply affected by the desired aesthetic target that it is unthinkable to separate engineering and aesthetic research. "Aesthetic engineering" is what comes out, and, in LB, this has been the target of all efforts so far.

TECHNOLOGICAL TOWER

Modern porcelain tiles are the result of a combination of many different elements: powders, micro-powders, flakes, grains, glazes, oxide powders and pigments, many and many decorative elements whose only limit is the capability of equipments to keep up with imagination.

The look of the tiles is created before pressing, the endless research and improvements carried out by manufacturers and suppliers of technology makes it possible to talk about "ARTIFICIAL STONES". Many products on the market today can be easily mistaken for real marbles or granites, so perfect the resemblance is.

Having all these materials different composition, dimension and properties, they also have different needs when it comes to handling, transport, storage or press feeding. The feeder itself has become more and more complicated, and it can no longer perform the wide range of operations needed. The core of processing is transport, batching and handling of powders, and what modifications are made to them, that enable or limit the achievement of a given target.

So far LB Officine Meccaniche has been a leader in research and innovation in that part of the plant which makes the core of technical porcelain tile production. It is not by chance that LB introduced the concept of "**Technological Tower**", a plant solution enabling to exploit the characteristics of powders at their best, rather than suffer them.

By eliminating the stockpile of big amounts of powders or mixes, but, at the same time, allowing a quick and careful batching, this plant promptly matches every need of equipment or processing, following a "**just in time**" concept to manufacture mixes, micronized powders, flakes and relating batching. In combination with a computerized management of the plant the "Technological Tower" guarantees high standards of quality, limits color pollution and demixing and opens every chance to highly technical products in porcelain "granito" tiles.

The care placed in each detail connected to powders handling is fundamental, since these are the last steps before press feeding and deeply affect the final result in the tile.

Let us give a closer look to the basic working principles of this plant, which has proven to be the most flexible and reliable for technical porcelain tiles production.

EASY COLOUR

The necessity to make all these various processings brings along great complications in terms of plant, equipments and investments, just before pressing.But in this scenario, a leading light is **"Easy Color"**, one of the most important technical innovations introduced by LB Laboratory. This system goes upstream, enabling to simplify the plant lay-out and to speed up the manufacturing process.

Dry colouring process starts from a basic powder by adding metal oxides. These are made by very small particles with average dimension ranging from 1 to 8 μm, much smaller than normal spray-dried powders, ranging usually between 0.8 and 2 mm. A further difference is weight which deeply influences the higher or lower inclination in being dispersed inside the base.

Small amounts of oxides are used and range between 0.01% and 1%, the latter value for quite rare and limited applications. The colour of the oxides is responsible of its capacity to stain the basic powder and, therefore, influences the amount required.

A perfect result is obtained when each granule of powder is completely and fully coated by an even layer of oxide and, at the same time, there are no free oxide granules or uncoloured powder particles.
This ambitious target is achieved thanks to the mechanical features of the "GRC" colouring unit made for this purpose by LB.

It is made of a cylindrical body in which the two substances, still separate, enter. Thanks to the action of the intensifying bar and the rotation of the machine frame body, oxide is distributed and projected inside the basic powder. The chemical and physical properties of the two materials allow the oxide to coat the powder without addition of any kind of binding agent.

The sinusoidal part before the exit allows a homogenization of the coating process. By flowing through a pipe whose excentricity is growing up and down, the material gets a variable rotating speed. Particles with higher weight (already coated) receive a greater thrust, those with lower mass are kept longer inside the cylindrical body.

"LB laboratory" carried out long testing to compare the results obtained by different equipments in this coloration process. Different results were reached, but careful analysis proved that normal or simpler equipments all produced at the exit a high percentage of free oxides and basic uncolored powder. Only LB's "GRC" machine guarantees a 100% coloured powder completely free of oxides.

FORMAT 201

So far we have seen what it takes to prepare the combinations used in porcelain tile manufacturing. But these combinations are not enough: what is still missing is a device that can use these combinations to create a complex design in the tile body. This device is the multiple press **feeder**.

One of the greatest challenges in press feeding, is to be able to perform all the possible decorations in soft powder state. This process is one of the most advanced: powders, grains, flakes and dry glazes all have different needs.

The conventional system is to employ the feeder to fill the mould to make products in single and double charging, with the limit of the free space available between mould matrix and the cross beam of the press.

It is not by chance that the last two or three years have seen a rising production of glazed stoneware on the market. After all, decorating by glazing and printing gives the chance to create the design on the glazing line, where more space is available, and to speed up production, thus reducing manufacturing costs.

Even if to someone, glazed stoneware is a contradiction, since the material already has high technological properties, low absorption and low porosity, glazed stoneware is now a big reality, which has given life to a new family of products.

The "Technological Tower" has proven to be the most effective and flexible plant solution for batching and powder preparation, but, still, there are many limits deeply connected to the nature of the materials employed in tile manufacturing. Electronics, high level automation and developed mechanical solutions cannot overcome the laws of physics: micro-powders cannot stand high accelerations without moving or flying away, vibrations tend to separate materials according to their dimensions and weight. Flakes break when falling and the inertia due to their weight, as it is for grains, usually accumulates them at the far side of the tile or grid, where they are stopped by grid walls.

LB has made many efforts in trying to solve all these problems staying in the Technical Granito field. This means that the decoration, the design on the surface of the tile, has to be made when the powder is still soft, so that full body products can be managed. But, in order to keep every solution open, it should be possible to perform also double charging, for those technical products that need a first layer to provide mechanical strenght, like "Travertino" with micro-powders, or granite with big grains. To follow the latest trends, it may be interesting to print before pressing, and/or to apply some dry glazes in random and multiple way.

A traditional feeder cannot do all this being, at the same time, performing well in terms of productivity and cost effectiveness.

The solution could be bringing all the above mentioned operation in an **open space**, where there would be longer time to operate, more room for advanced and special decorating equipments, more chances to control and modify the design of the tile and, in the end, higher flexibility.

This is the purpose of "**FORMAT 201**".

LB has placed a lot of resources and experience in making a first prototype, presented in our booth at "Tecnoargilla 2002". It is the sum of years of studies, tests and applications that all come togheter in one machine, with **the aim to perform every kind of aesthetic effect**.

The principle is to use a certain number of **devoted devices**, that keep the powders in place and undergo all the possible decoration one after the other. In this way, starting from a first loading of the container, it is possible to add a second or third layer of powders, thus making all the kinds of tiles with high aesthetic value.

The roof free space allows to bring micro-powders, flakes, grains and whatever else even in big amounts. Now the equipments do not have to face the necessity of entering the thin space between upper and lower mould at the press.

Being the powders still contained inside a cavity, there is no risk of fall at the edges, as it happens if a pre-compacted tile is guided and free elements are added on top. Grains, flakes or powders close to the edge simply fall down, partly because of vibrations, partly by their natural gravity. A further step may be to use printing devices to increase the variability of the decoration applied. But not only glazes can be used: expensive and **special bodies** in the spray-dried form can be employed in limited amounts, thus benefiting from their qualities and avoiding the higher cost that a traditional utilization would involve.

As said before, to perform full body technical granito tiles it is necessary to work with soft powders. This allows to create decorative patterns in the whole thickness of the piece. For some applications, on the other hand, it would be better if the powders were not soft. For instance some **special bodies** in spray-dried form that guarantee a translucent effect or particularly shiny colours are very expensive and would increase production costs to extremely high levels. This is because the amount needed is quite big. If they could be applied as a thin layer, limited to some decorating areas, over a hard surface, the amount needed would be much lower and, consequently, the related manufacturing costs. Format 201 includes a **deaeration** module that allows to create this harder surface and to perform the deposition of special bodies, or glaze dry powders, in the following modules.

This deaerating is performed without any mould and, therefore the equipment stays unvaried in any condition. The tile piece stays inside the container before, during and after the deaerating process. The main advantage is that the following steps are performed with a piece still inside its container, therefore there is no risk to damage it, and it is always possible to exploit further falls of the box, thanks to its special design and properties.

The simple handling system for modules garantees a perfect positioning and a smooth movement from station to station. At the same time it allows to work with a standstill piece, performing all the operations in optimum way. Working on multiple stations at the same time expands the time available for the making and decoration of each tile. This longer time is so important in enhancing the value of some productions, that Format 201 results suitable for every kind of porcelain tile, but is perfect for the most sophisticated operations.

This shows the **true flexibility** of this concept project: the machine can be custom made. There is no fixed number of modules, neither before de-airing nor after it. Their order can be easily changed, following different production needs. Each module is an independent unit, separate from the others but, at the same time, linked to each other unit in any way. For some kinds of production it is possible to perform many decorations before de-airing, then going straight to pressing; for some other kinds of production it is possible to perform most operations after deaerating, thus imitating a more traditional manufacturing process.

In conclusion, Format 201 represents the state of the art for aesthetic engineering, designed to manufacture all the possible porcelain tile products.

DR. A. MATEV

Subject: Personal Report

Republic of Macedonia is a small pretty country in South Europe located in the center of the Balkan Peninsula. In spite of its favorable geographic location and natural beauties the country is in and extremely difficult economic and social situation. This situation is a result of the well known military actions in the Balkan region in the last several years, the inappropriately selected model of transformation of capital, very long lasting transitional period and on top of everything the war in Macedonia last year. All this contributed to the fall of the standard of living, relatively small number of companies to transform successfully, others to work of reduced capacity and others even to go to bankruptcy or be liquidated.

Ceramic industry in Macedonia is represented mostly by production of ceramic tiles, porcelain, electro porcelain, sanitary ware, bricks, roofing tiles, soft porcelain, etc. According to the availability either of machines and equipment or of kilns to be in possession of companies, they can use the suitable technology for manufacturing. In most cases they use the traditional technologies in the different working phases such as: grinding, spray drying, casting, extrusion, forming (shaping), pressing, drying, glazing, firing etc. Depending of firing cycles and type of kilns, they can produce by:

- Technology of doubly firing in tunnel kilns (porcelain- " Porcelanka " A.D, Veles)
- Technology of single-firing in tunnel kilns (bricks- " Kiro Cucuc " A.D., Veles, roofing tiles- " Pehcevo" A.D., Pehcevo, sanitary ware- " Makedonija " A.D., Strumica)
- Technology of single-firing in roller kilns (soft porcelain – "Porcelanka" A.D., Veles

and "Tipo " A.D., Skopje)

- Technology of single – fast firing in roller kilns (ceramic tiles: Monocottura and Monoporosa – " Porcelanka " A.D.,Veles).

The latest scientific knowledge, computer and software programs their days are mostly involved in state institutions within the Macedonian Academy of Science and Arts (MANU) and the University " St.Kiril and Metodij " in Skopje, supported by the government by a system of research projects and grants. An example for this is the Faculty of technology and metallurgy in Skopje where covers work on: composite ceramic materials, clean oxide ceramic, ceramic for electronic etc. In the Faculty of construction and architecture in Skopje where projects on application in building industry are being prepared by means of the Auto CAD computer program.

In the industrial sector, preparation and manufacture of prototypes on certain products are mostly based on design proposals and projects in the appropriate designing departments. The procedure for making the model and prototype is by conventional methods and technologies for particular industries. In the ceramic industry, in the porcelain and ceramic tiles factory " Porcelanka " A.D. – Veles the draft model is prepared in the designing department manually by artists. Plaster moulds are then prepared on basis of this model, which is used to manufacture a prototype by casting, which is later being tested.

In the machine industry, the factories for production of buses FAS " 11 Oktomvri " – Skopje, rail vehicles " MZT Hepos " – Skopje and " Veles " – Veles a draft drawing of a certain product is prepared using the Auto CAD computer program whereas the prototype depending on the type and shape is prepared by methods of: grinding, milling, grinding& milling, casting etc. using appropriate machines and equipment (grinding – machine, milling – machine, milling cutter etc.).

The company " Mikrosam – Makedonija " from the town of Prilep is the most successful in the field of application of the latest scientific knowledge's and computer programs. With its software and designing facilities this company designs and produces: impregnations machines, 3-Dimensional processing wood and marble processing machines as well as machines for laser processing of various materials.

According to my knowledge and information in Macedonia there are no machines and equipment for quick manufacture or prototypes (RP – Rapid Prototyping equipment), meaning also that application of methods and technologies such as:

- SLA (Stereo lithography)
- FDM (Fused Deposition Modeling)
- LOM (Laminated Object Manufacturing)
- Laser Sintering – SLS (Selective Laser Sintering)
- Powder binding – 3D printing etc.

is not functioning. But I believe that in the near future with healing of the Macedonian economy these machines and technologies will find their place in our economy also the more that there are companies (" Mikrosam – Macedonia " Prilep) which with their knowledge, experience and potential are capable to cope with this challenge in cooperation with some EURO, USA or other foreign countries partners.

Latest development in porcelain body manufacturing: pressing of very large sheet with no die and the study of the sintering kinetics

By Prof. Mariano Paganelli

In this presentation I will revue the ideas that brought System to develop the Lamina process. It is not the first time that the manufacturing of a very large sheet of porcelain body is attempted, but nobody ever tried to press it; due to the obvious difficulty to achieve the very high forces needed. System succeeded in this project with a completely new approach to the pressing: designing a machine that works in a completely different way compared to traditional presses. One outstanding feature of this way of pressing a very large sheet is the absence of the die. All the implication of this new technology will be discussed.

The second part of the presentation refers to the study of the sintering mechanism that brought to the decision for a completely radiant type of heating. The study is made possible thanks to the development of a non-contact optical dilatometre that can follow the sintering directly at high temperature. It is then possible to understand the sintering kinetics and to optimize the heating and cooling cycle.

Abstract from Marcello Romagnoli

The behaviour of a powder in an industrial process is not so well known and predictable as the behaviour of a liquid or a suspension of a solid in a liquid. This situation comes from the intrinsic complexity of powders and the ease with which their bulk properties may change.

In fact a powder is not only a collection of individual particles that make up a given mass, but it is also a mixture of solid; air and sometimes also a liquid such as water. Powders are probably the least predictable of all materials in relation to flowability because of the large number of factors that can change their rheological properties. The complexity of a powder system must be treat with specific theoretical and experimental tools, different from the models and instruments used for the characterisation of classical rheological system like liquid or suspensions.

In spite of these difficulties the knowledge about a solid in powder form increases strongly.

In the presentation, the differences between powder and liquid/suspension rheology are discussed. Examples with particular reference to the production of tile ceramic will be discussed. A brief look at some techniques for the characterisation of powders will follow the first part of presentation, with a special attention to flowability. The main technique of handling and transport, conveying belt and pneumatic transport will be considered with advantage and disadvantage.

In the final part some specific examples regarding real problems as the handling of powder in double loading, effect of chemical additives on flowabilty of spray-dried powders or granulates or dry glazing will be shown.

Production of refractory materials in Russia: prospects of development

V. Ja. Shevchenko (Academician, Director of the Institute of Silicate Chemistry of Russian Academy of Sciences);
L. M. Axelrod (General Director of JSC "Saint Petersburg Institute for Refractories")

Refractory materials are indispensable for the functioning of numerous branches of industry: metallurgy, the manufacturing of building materials, power, petroleum chemistry, etc. Before market reforms in Russia (before 1992) a big amount of refractory materials was produced (Table 1).

In the Russian Federation (part of the USSR in 1991) refractory materials were produced at 15 specialized refractory plants and 6 refractory production plants of metallurgical enterprises. With some exceptions the raw materials mined in Russia and the Ukraine, which was also part of the USSR, were used.

In the early 90-ies the production of aluminum silicate items and non-shaped materials was predominant, primarily mortars and fillers for concretes with the use of refractory clays and kaolins, refractory materials of basic composition with low magnesium oxide content and high content of impurity oxides, and also a big amount of feed powders for the open-hearth and steel-making electric furnaces.

The structure of the refractory production on the territory of the Russian Federation is determined by the demands of the domestic industry; about 65-67% of refractotories are used in ferrous metallurgy and 12-15% in non-ferrous metals production. The output decrease of refractories in the 90-ies was caused not so much by the decrease of metal production (fig. 1) and an output decrease of building materials production (cement, glass, structural clay products), as by structural change of metallurgical production, primarily, steel (Table 2), and a considerable increase of consumers' requirements to the quality of the refractories being used.

The purchase of heating plants for ferrous metallurgy, petroleum chemistry, furnaces for extermination of domestic and industrial wastes together with import lining from abroad, the change of requirements to the exported materials made in Russia, for example, to cement on 6-valency chromium content, to metal cord on non-metal inclusions, an output increase of secondary metallurgy, put forth new tasks before Russian refractory industry, being insoluble, if silica and fireclay materials are used.

Table 1. Production of refractory materials in Russia, thousand tons.

№№	Name	Years	
		1991	2001
	Items		
1	Silica	341	145
2	Aluminum silicate and alumina, including:	2829	1285
2.1	fireclay	2603	1145
2.2	high-alumina and corundum	226	140
2.3	light-weight	79,6	23
3.	Magnesium, including	790,9	511.
3.1	periclase	278,5	127
3.2	periclase-spinel (magnesia-chrome, magnesia-alumina)	389,1	295
3.3	forsterite	61,1	18
3.4	lime-periclase, pitch- and tar-bonded periclase- lime		
	Carbonaceous,	65,2	71
4	including	25,3	53,9
	periclase-carbon		
4.1	alumina-periclase-carbon	7,3	45,2
4.2	alumina-graphite	0,0	2,5
4.3	fireclay-graphite	3,8	2,7
4.4	Carbide-silicon-containing	14,2	3,5
5.	Zirconium (baddeleyte, zircon, bacor)	0,6	0,3
6.	Quartz	2,8	4,6
7	Mullite-silica fibre (heat insulation) and items made	15,5	7,0
8	from it		
	Others	18,2	6,0
9		18,7	6,2
	Total number of items	4042	2019
	Non-shaped refractory materials		
10	Fillers for concretes, dry mixes	548,4	77
	including		
10.1	low-cement hydraulic hardening concretes and items made from them	0	1,1
11	Gun mix materials	83,4	69,0
12	Mortars	84,7	54,0
13	Milled clay and fireclay powders	297,6	138
14	Runner and taphole mixes	180,7	164
15	Feed powders (periclase, dolomite)	1495	678
	Total of non-shaped refractories	2689,8	1180
	Total of refractory materials	6731,9	3199

A qualified estimate of the specific consumption of refractors per kg\ton of final product is supplied with an estimate of specific costs in dollars\ton of product. In this case not only direct costs on refractories are taken into account but also production losses from planned and non-planned unit delays, due to the use of cheap refractories with low resistance that are frequently unreliable, and from quality decrease of ready-made products, etc.

A general decrease of the production output of steel (Table 2) and a considerable change of the relationship in the methods of steel production with a ratio decrease of the open-hearth steel lead to a sharp production decrease of periclase-chromite and forsterite refractories and feed powders of the basic composition. Simultaneously, there was a decrease of consumption and, accordingly, production of fireclay and chromium-containing refractories. In cement industry, with an increase of cement manufacture in the recent years, the consumption of other refractories took place, such as periclase-spinel and refractories with high alumina content.

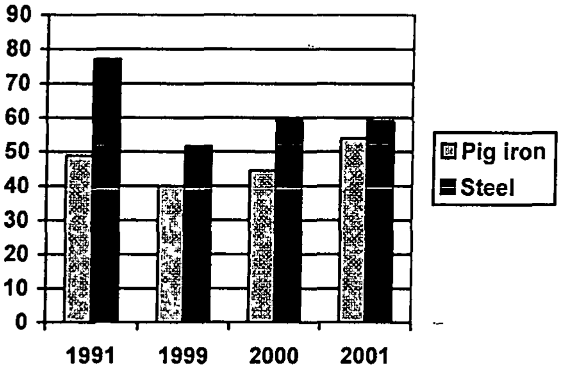

Fig.1 Production of steel and pig iron in Russia, mln tons.

Metallurgists are no more satisfied with the resistance of converters after 700-1000 meltings, also, the up-grading of electric furnaces at many Russian plants required new refractories for the lining of hearths, walls, roof and arches eccentric bottom zones.

Intensification of metallurgical processes, including the output increase of secondary metallurgy in steel ladles, lead to elimination of ramming mixes of silica and aluminum silicate composition, fireclay, mullite-silica and high-alumina refractory items from the lining of these units. At Russian refractory works production of periclase-carbon, periclase-spinel-carbon and aluminum- periclase-carbon refractories is organized, primarily ladle; the production of periclase-carbon refractories for the oxygen converter lining is expanded.

Table 2. Variations of the production outputs of steel by the main methods and in its technology of casting

	1990		2000	
	mln tons	%	mln tons	%
Total steel production	89,6	100	59,1	100
including :				
- open-hearth steel	47,8	53,4	16,2	27,4
- oxygen-blown steel	28,4	31,7	34,3	58,0
-electric furnace steel	13,4	14,9	8,6	14,6
Steel cast ratio at CCM, %		23,0		49,8

In 1996 these refractories were made at one plant and in 2001 at six plants. At all productions of oxide carbon refractories presses made by "Laes" and "Sacmi" with press power 1600, 200 and 2500 MPa, mixers made by "Eirich", computerized weighing and specialized heat treatment furnaces of Russian design are used. As raw materials domestic and foreign periclase are used, both fused (density>3,40 g/cm^3) and high-density sintered ones (density 33.3-3,43 g/cm^3), including sintered periclase made by "Dead Sea Periclase" (>99% MgO). The use of periclase made in Russia with more than 95% MgO and CaO/SiO2 >1,7 is presently restricted by the Chinese product of similar quality. In the nearest future it is assumed to partially solve this problem by using brucite and natural high-quality magnesite of Siberian deposits. We can also mention graphite, generally large-crystalline, of Russian and Chinese production, with ash content 4-6% and crystal size preferably >0,2мм; antioxidants: metal aluminum and crystalline silicon of Russian production. As a binder, phenol formaldehyde binder is used, including powder-like with free-phenol content <1%. Investigations carried out at Saint Petersburg Institute of Refractories showed the advantages of using a combination of thermo-reactive and thermoplastic binders in the production of carbonaceous refractories. After coking at 1000^{0}C such carbonaceous refractory has higher bending strength, both at low temperature and at 1400^{0}C, the pore structure is characterized by the prevalence of pores with an effective diameter less than 2,5 mkm and a percentage decrease of interconnecting pores. Figure 2 shows the microstructure of periclase carbonic refractory after coking.

Fig. 2. A microphotograph of a polished section of periclase carbonic refractory with a combined carbonic binder

1-periclase; 2-silicates; 3-graphite; 4- the product of thermodestruction of the thermoplastic binder; 5-6- pores.

In recent years investigations and production of carboniferous refractories have been developed with the use of fused corundum, alumomagnesium spinel, and high-alumina materials, including roast bauxites with mass-fraction of Al_2O_3 85- 90% in their composition. Undoubtedly, in the slag zone of steel cast ladles of the majority of metallurgical works where the basicity of slag $(CaO/SiO_2)=1,8 \div 3,2$, periclase carbonic items with high content of fused high-pure large-crystalline periclase are prevalent. For the walls and bottom lining alumopericlase-, periclase spinel- and spinel periclase- carbon bricks successfully compete with periclase carbon items. In the areas of intensive mechanical effect made by a metal jet (an impact zone of the bottom and wall near the bottom argon lance) the advantage of alumopericlase carbon refractories based on fused corundum and periclase is undeniable. These refractories have certain advantages due to their lower thermal conductivity, higher strength and thermal stability. Table 3 shows the properties of some carbon refractories made in Russia for steel ladling lining.

Table 3. Physical and chemical properties of carbon ladle refractories

Properties	Refractory grades					
	ПУКС-7	ПУКП-13	ШПУП	ПШУС	АПУ-60	АПУ-80
Mass ratio*, %						
MgO	>91	>91	>40	>50	18-20	8-10
Al_2O_3	-	-	<30	21-30	>60	>80
C	7-9	13-17	8-16	8-12	6-8	6-8
Open porosity,%	<5	<5	<8	<8	<8	>6
Compression strength, N/mm^2	>30	>30	>30	>40	>45	>60

* mass ratio of oxides per calcine is indicated

Metal aluminum and crystalline silicon are widely used as antioxidants; the use of magnesium and magnesium alloy powders is limited by strict requirements to the explosion safety of the corresponding production. The development of complex antioxidant with aluminum, zirconium and magnesium carbides and oxicarbides is underway.

Production of refractory low-cement and cement-free concretes, both thixotropic and self-casting and items made from them, is organized with certain delay. The technology based on skilful application of a "classical" scheme is being put into practice. The technology involves the use of a refractory filler - 60%: fused corundum, tabular alumina, high-aluminous materials, aluminous spinel and matrices – 40%: active and sintered alumina, microsilica, small fractions (<0,020 и <0,045 mm) of fused corundum, aluminous spinel, periclase, fused and tabular alumina, high-aluminous cement and dispersive additions catalyzing and inhibiting the process of the concrete hardening. The firms "Alcoa World Chemicals" and "Elkem" rendered a good assistance to Russian investigators and manufacturers. Burner units, nozzles and nozzle-collectors, well bricks, basal tuyeres, impact zone units of intermediate and steel ladles, partitions and dams used in the intermediate ladles of continuous casting plants for steel blanks, etc. are produced at several enterprises and the quality of these products is comparable with foreign analogs.

Concretes and repair mixes of this class are used in the lining of steel and intermediate ladles, degasser branch pipes, various thermal plants in power generation and petroleum chemical industry.

The second popular direction in the production technology of cement-free concretes and items made from them is called "ceramic concrete technology". A significant difference of this technology from classic features a high-concentrated binding water suspension based on aluminum silicates, alumina and siliceous materials, and also on spinel periclase composition used as a matrix.

In this technology the plasticization principle of dilatable high-concentrated binding systems of acid and acid-amorphous compositions is used, which made it possible to control rheological characteristics of the systems. The technology is implemented in the production of quartz (drain-cast) refractories, high-alumina concretes and refractory items of various purposes and also vibration-cast mixes for runner lining in blast furnace production.

Production of gunning mixes with basic composition used as a working layer of intermediate-ladle lining of CCM is also practiced at some Russian refractory works.

Table 4 shows the properties of a number of concretes.

Table 4. Physical and chemical properties of low-cement concretes

Properties	Grade					
	СМН-95	ССМН-95	СМУН-95	СМБ-97	СМН-83	СМН-61
Mass ratio, %						
Al_2O_3	96-98	95-98	95-98	95-98	84-86	63-65
Fe_2O_3	0,2-0,3	<0,5	<0,5	<0,5	<0,6	1,3-1,5
CaO	1,2-1,8	1,2-2,0	0,5-0,9	-	1,2-1,8	1,2-1,8
Compression strength, N/mm^2after						
100^0Cx24hrs	40-50	30-40	25-35	25-35	70-80	40-50
800^0Cx5hrs	60-70	50-60	60-70	45-60	80-90	60-70
1600^0Cx5hrs	90-100	90-100	70-80	70-80	80-95	90-100
Additional linear shrinkage, %,at T						
1500^0C	-	-	-	-	-	1,0
1600^0C	0	0	0	0	0,5	-
Type of mix	Low-cement thixotropic	Low-cement self-casting	Ultra-low-cement-thixotropic	Cement-free thixotropic	Low-cement thixotropic	Low-cement thixotropic

In Russia 95% of steel are cast (from the steel ladle) with the use of domestic slide gates. The refractories for this unit including plates of slide gates with periclase, periclase carbonic and corundum carbonic compositions are made in Russia. It should be noted that the manufacturing technology of carboniferous plates is being put into production.

Corundum graphite monoblock stopper units, immersed nozzles and pipes for protection of the metal jet made in Russia are inferior to the corresponding foreign-made products in resistance and reliability. However there are preconditions for increasing the reliability of these refractories and the corresponding works are carried out at a number of enterprises. This refers both to the materials inhibiting the process of aluminous inclusions on the channel surface of the metal duct in the system $ZrO_2 - CaO - SiO_2 - Al_2O_3 - C$, and to zirconia -based material for increasing the resistance of the slag zones of the immersed nozzles.

Long-time traditions in scientific works of Russian scientists on synthesis and application of alumina spinel have presently found a new development. Production of a wide range of compositions of fused spinel, manufacture of periclase spinel refractories, both roast and roast-free for steel ladles lining, rotary furnaces of cement industry, dry mixes for induction furnaces are rapidly developing.

The study of the crystallization process of fused spinel $MgO - Al_2O_3$ in ingot obtained by electric arc melting is continued to determine the effect of raw materials quality, liquation processes, composition of phases in various ingot zones. A technology of the material manufacture is developed taking into account calcium, alkali metals and silicon oxides located between spinel crystals as associates, involving ions of aluminum and magnesium. The amount of the mentioned impurities together with high-pure spinel and periclase phases will mainly determine both thermal stability and resistance to attack by corrosive media. Table 5 shows physical and chemical properties of items made with the use of fused spinel.

Table 5. Qualitative properties of spinel-containing refractories

Properties	Refractory grades			
	ПШО	ПШБ*	ПШАЦ	ПШПЦ-81
Mass ratio, %				
MgO	55-70	55-70	>85	>81
Al_2O_3	30-40	30-40	4-8	7-14
Fe_2O_3	<0,5	<0,5	<1,0	-
SiO_2	<0,5	<0,5	<1,0	<2,0
ZrO_2	-	-	1-3	-
CaO	-	-	<1,5	<2,5
Open porosity, %	<18	-	<17	<22
Compression strength (at low t^0), N/mm^2	>50	>80	>40	>22
Thermal stability (1300^0C-water)	>7	--	>7	>8
Additional linear shrinkage	-	-	-	0,2
at 1600^0C, %	-	-	0,7	-
at 1650^0C, %				

*roast-free items

During the last few years in Russia the manufacture of ramming and cast mixes appeared for the runner lining in blast-furnace production, including repair mixes applied with gunning machines. These refractories must replace the widely used mixes where coal-tar pitch containing high amount of carcinogenic benz-a-pyrene is used as a binder.

We assume that there are certain advantages in Russia in the technology development and use of self-casting high-temperature synthesis (SHS) in manufacturing refractory linings of various units. This technology is based on gas-free burning principles of the oxidant-fuel systems. The SHS technology is implemented to produce silicate-of-alumina linings. The technology is used for producing linings (items) from cellular (heat insulating) concretes, mortars providing the welding of items into one whole thing, oxide ceramic coatings, and solutions for carrying out repair-restoration works. The materials applicable within 1100-1700^{0}C can be used for making linings in thermal units, such as heating furnaces, reactors, roasting furnaces, gas ducts, boiler units, etc.

Russian refractory industry is obviously lagging behind in the production of fused spinel-based high-quality periclase spinel (chromium-containing spinel) refractories widely used in the lining of vacuum degassers and in nonferrous metallurgy.

We are also mastering the production of refractory materials in the system $Si_3N_4 - SiC$ for lining the side walls of aluminum cells.

Heat insulation materials made in Russia basing on refractory fibre, diatomite and calcium silicate also do not conform to the up-to-date level. This primarily refers to fibrous materials and items made from them. Russian mullite alumina fibre and the same fibre with chromium oxide addition are made by steam bulging. It is characterized by short fibre and a large amount of cold shots. In spite of a wide choice of heat insulation refractories (items) of fireclay mullite and corundum composition based on vermiculite, etc., there is a lack of heat insulation materials with heat conduction not more than 0,12 W/mK within the temperature interval up to 1200^0C and with small additional shrinkage and high strain stability in the same interval.

We should also note serious efforts undertaken in Russia to unify the existing technical documentation with standards ISO, ASTM and DIN. This work is carried out by a Stock-Holding Company "SPbIO" ("Saint Petersburg Institute of Refractories") within the framework of solving the problem of the whole country due to Russia's forthcoming joining the WTC.

During the last 5 years the production of refractory materials in Russia underwent serious structural changes, which makes it possible to hope for enterprises to be a success in their competition for marketing their products.

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Until the nineties of XX century Polish ceramic industry was the state property. At present all the enterprieces are transformed into joint-stock companies of the Treasury or privatized. Although, the Polish ceramic industry experienced many inhibitions connected with the econony transformation it finally get out of the troubles and now it is fastly developing.

In the nineties, we could observe the biggest progress in improving and moderning ceramic enterprices – especially producing tiles and sanitary ceramics. It was time when many ceramic enterprieces took steps to change the funaces for the new ones chamber-type (e.g. Grun, Riedhammer) and roller furnaces (e.g. WELKO, Riedhammer). On the other hand, however, it was also the time when some more obsolete and not prepeared for competition firms declined. Some of them, after closing and declaring bankruptcy were resold and activated once again (e.g. porcelain factory in Włocławek, Katowice and Wałbrzych).

Nowadays, the most important and modern branch of classic ceramics industry is production of tiles. Polish tiles producers have in theirs disposal: modern mass processing devices, high load presses, complex and well equiped decoration glazing lines, modern roller-type furnaces, automatic sorting, magnetic or laser controled internal transport The modernity of tiles production is also connected with a ceramic technology. It means the possibility of obtaining large format elements, developed decoration techniques and extraordinary products' quality parameters. At the same time also the other branches of ceramic industry are developing. The structure of Polish ceramic industry production is shown in the table 1.

Tab. 1 Production of ceramics in Poland in 2000 [1]

	Production	**Sale (in mln EUR)**
Porcelain [t]	42 200	100
Semi-vitreous China-ware [t]	11 500	17
Sanitary ceramics [t]	35 700 000	35
Ceramic tiles [m^2]	40 000 000	190
Building ceramics [m^3]	4 200 000	200

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[1] Kycia H., Flis Cz., Dziatko K.: Polish Ceramic Industry before European Union Enlargement; Szkło i Ceramika No.1/2002 (in Polish)

Ceramic industry in Poland has a long tradition. Some of the companies have been world-famous for many years. On the other hand, every year more and more new ceramic enterprices are being established. But both the old, well-known and completely new companies have the same problem - keeping up with the times. It would not be possible without implementing new ceramics processing technologies. The teams of a number of Polish scientific institutes and universities materials science departments are working out the technologies. One of the most important and best known in field of electronic and electrotechnical ceramics is Department of Ceramics, Seals and Composites of the Institute of Electronic Materials Technology (ITME).

The Institute of Electronic Materials Technology is a research, development and consulting institution. It was founded in 1979 by uniting research laboratories of the Electronic Materials Research and Production Center in the form of the separate organization. The Institute developes advanced technologies for the specific properties to suit the requirements of modern-day.

The activity of the Institute of Electronic Materials Technology covers research, development and small-scale production of advanced materials. ITME produces crystals of semiconductors, and optical, piezoelectric and superconductive materials. It also manufactures high-purity metals, active glass and optical fibers, new ceramic and composite materials, and other materials that have unique properties and a wide range of applications.

The Institute consists of the following divisions: Laboratory of Characterization of High Purity Materials, Department of Microstructural Analyses, Department of Ceramics, Seals and Composites, Department of Silicon Technology, Department of Semiconductor Compounds Technology, Laser Laboratory, Glass Laboratory, Silicon Epitaxy Laboratory, Department of Thick Films Technology, Department of Oxide Single Crystals Technology, Department of $A^{III}B^{V}$ Materials Applications and Department of Piezoelectronics.

Department of Ceramics, Seals and Composites is one of the Polish research group working in the area of ceramic materials and ceramics to metal seal technology. Department is a 17 workers group having among others 1 Professor, 3 Associate Professors and 3 researchers with Ph.D. The department's members have at theirs disposal a wide range of laboratory devices like furnaces (high-temperture furnaces FHD-4412 and Seco-Warwick, tunnel-tape furnace EWP-7, tube furnace Carbolite STF 16/75/818p), hot-press machine (ASTRO HP50-7010 Thermal Technology) and ZWICK 1446 testing machine combined with the system enabling direct observation of crack grown from notch or from Vickers indent.

The activity of the department covers two principal fields. The first one is research and development of new polycrystalline oxide and nonoxide ceramic materials (Al_2O_3, TZA, TZP, Y_2O_3, and Si_3N_4) with very high strength and resistance to fracture, grinding and thermal shock, and new methods of ceramics to metals bonding. Second field of the department activity is development of ceramic processing technologies and small-scale production of materials designed on customer request.

The results of research into ceramics processing technology development led in ITME Ceramics, Seals and Composites Department are:

- ceramic spraying nozzles with high precision of shape for agriculture application by means of injection molding,
- zirconia toughened alumina (TZA) for application where very high strength and excellent abrasive resistance is required i.e. cutting tools and nozzles for spraying of abrasives,
- yttria stabilized zirconia ceramics (TZP) with excellent resistance to fracture and grinding for ceramic tips of antistatic blade adjustment tools,
- ceramic-metal feed-through for vacuum and high voltage application made of pure alumina and FeNi42, FeNiCo, kovar, copper or aluminium,
- alumina-copper direct bonded substrates (CDB substrates) for use as a base for all power electronic applications like power semiconductor modules, high power circuits, transistors, rectifier bridges, thyristors, automobile electronics,
- laboratory ceramic elements made of alumina, zirconia, yttria and silicon nitride ceramics e.g. crucibles, rodes, tubes,
- bioceramic elements used for bile duct and internal ear endescopes,
- multilayered bases and packages fabricated by the thermoplastic laminating of ceramic films,
- alumina–zirconia and alumina–carbides ceramics for the applications needing thermal shock resistance,
- ceramic- metal microwave transistor packages.

Scientific interests of the department members concern ceramics–ceramics and ceramic–metal microcomposites and nanocomposites, functional gradient materials and superplastic materials. Special attention is being paid to explaining the relationships between materials microstructures and the mechanical propreties as well as the investigation of the strengthening mechanisms.

At present, there are being led in the department experiments on bonding nonoxide ceramics (AlN, SiC), nanopowders tape-casting, functional gradient materials and composite materials for electical contacts producing. At the same time we continue works on superplasticity in ceramics and numeric analises of residual stresses in ceramic-metal joints.

DOUBLE PRESSING TECHNOLOGY

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INTRODUCTION

TWINPRESS

NUOVE FRONTIERE NELLO SVILUPPO
DELL'ESTETICA DEL PRODOTTO

Sacmi has presented the market with something completely new, a new stage in the development of the ceramic industry, a new production process known as Twinpress.

Twinpress has a potentiality that makes current size and type concepts outmoded. While, at present, the value of the system especially regards aesthetic effects (giving enormous creative flexibility), it also provides a wide range of sizes.

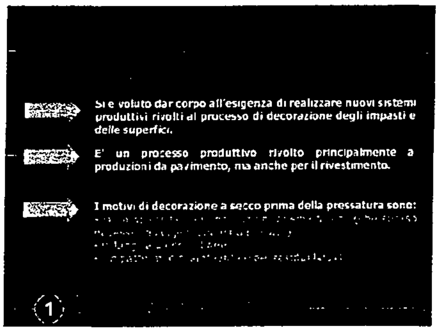
Two interdependent factors have converged to produce this result:

a) technological evolution of the product (with dry between-pressings decoration using layered coloured powders). This involves:

- purely technological aspects
- associated plant engineering aspects.

b) technological evolution of tile size and the possibility of cutting "green" slabs.

The unification of several innovative developments has produced a crucial leap forward known as double pressing technology or, more simply, Twinpress.



Si e voluto dar corpo all'esigenza di realizzare nuovi sistemi produttivi rivolti al processo di decorazione degli impasti e delle superfici.

E' un processo produttivo rivolto principalmente a produzioni da pavimento, ma anche per il rivestimento.

I motivi di decorazione a secco prima della pressatura sono:

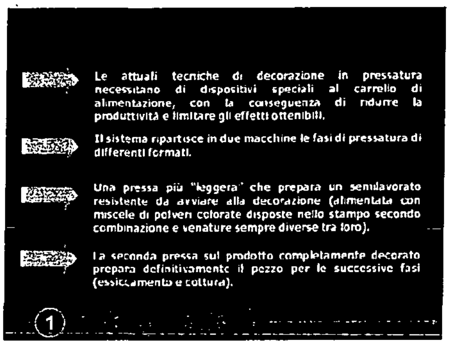
Let's now examine more carefully some of the basic reasons of the development of this type of technology:

1. There has been a lack of important esthetical developments in the porcelain tiles for some years; in particular, the single-loaded and double-loaded products did not give sufficiently real re-productions of the natural stones, but only effects obtained from the mechanical movement of devices. On the contrary, the Twin Press technology gives the possibility of decorating the tile before definitely pressing it; therefore, a completely new range of applications is now available.

2. At the very beginning, this type of process was born as application for porcelain tiles, but we believe it is possible to spread out its application field to product for internal wall tiles; therefore, using the same production line, it could be possible to quickly pass from one to another production typology, supplying the plant with a concrete flexibility.

3. Besides, the Twin Press process gives the possibility, in case of glazed porcelain tiles production, of strongly simplifying the wet glazing line, reducing it, in case, to two or three accessory applications (such as flashing, etc.), which are not however necessary for defining the finished product. Between the two presses, the decoration machines mainly work with dry applications. As to the plant, it is thus possible to foresee a

lower environmental impact; this aspect cannot be neglected in the case of ceramic industry, which is not strongly polluting.



- Le attuali tecniche di decorazione in pressatura necessitano di dispositivi speciali al carrello di alimentazione, con la conseguenza di ridurre la produttività e limitare gli effetti ottenibili.
- Il sistema ripartisce in due macchine le fasi di pressatura di differenti formati.
- Una pressa più "leggera" che prepara un semilavorato resistente da avviare alla decorazione (alimentata con miscele di polveri colorate disposte nello stampo secondo combinazione e venature sempre diverse tra loro).
- La seconda pressa sul prodotto completamente decorato prepara definitivamente il pezzo per le successive fasi (essiccamento e cottura).

①

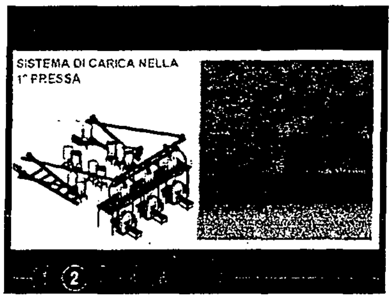
4. The present decoration techniques during pressing need special devices at the feeder and consequently reduce the productivity and limit the effects that can be obtained. With the Twin Press technology, it is possible to obtain much higher productivity values than with the double loading process, because the application of the second layer of glazes o semi-finished bodies is carried out as on the traditional glazing line, that is by means of specific application machines.
5. The system divides the pressing phases into two machines of different sizes:

   A "lighter" press, which prepares a resistant semi-finished product for the decoration (which is fed with coloured powder mixtures lied on the die according to always different combinations and veins).

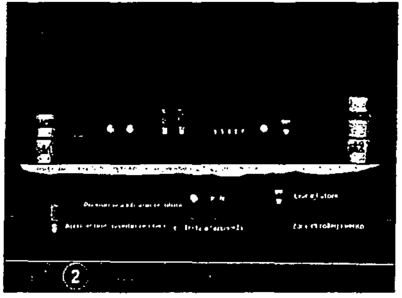
   The second press acts on the completely decorated product and prepares the piece for the following phases (drying and firing).

6. At last, but not least, important aspects such as production speed, size flexibility and great typology versatility can be **easily** reproduced in time by using the Twin Press technology.

Let's now see, in general, what the Twin Press production line consists of.


SISTEMA DI CARICA NELLA 1° PRESSA

We can appreciate how it is possible to prepare the "support" to be decorated: different working sections can be seen, equipped with mobile silos, which contain different coloured powders that, mixed at the press with the MDR device, permit to prepare a single-loaded demixed base as showed in the photo.



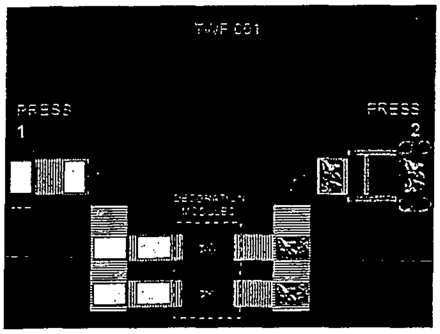
This slide shows how our basic Twin Press line is assembled: in particular, we can see, after the first press, two spaces for silk-screen printing applications by means of rotary machines, a device for the application of semi-finished products (micronized powders, spray-dried powders, flakes, etc.) on the whole tile, a roll up silk-screen printing machine with several heads, a further rotary machine and a device for the application of grains and pelletized products on the whole tile. Finally, before the second press, there is a device for the introduction and centering of the tiles in the cavity of the second press for the final pressing.

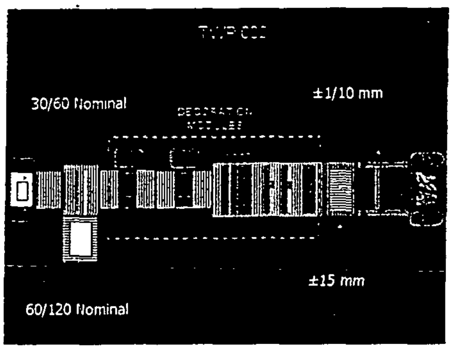
The natural evolution of a basic production line might include several different solutions that reflect the specific needs of the customer. These solutions are illustrated below.

Basic plant engineering solutions

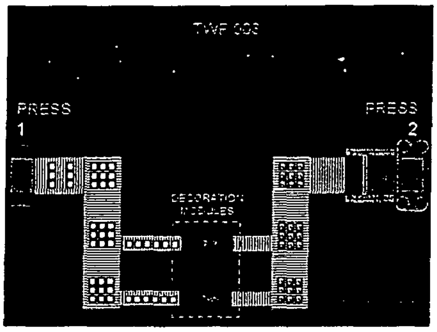
Basic principles generally involve the following lay-out:

- Tile feed side towards the decorating machine (TWP001-TWP002).

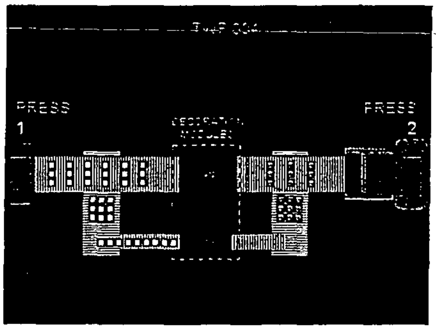




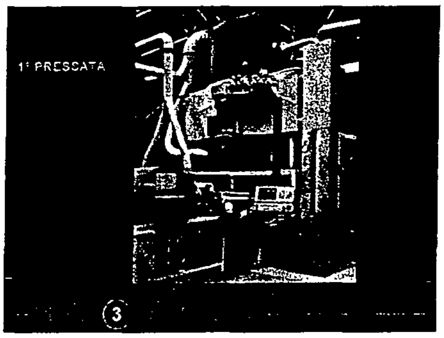
- The option of feeding tiles from multi-outlet dies using a single-file feeder solution or a system where the tiles advance in rows as per the die outfeed pattern (TWP003)



- Press positioning can be staggered to optimise use of space.
- The possibility of exchanging a system that feeds the slabs in rows (as with multi-cavity die outlets) with a single-file feed system (TWP004)



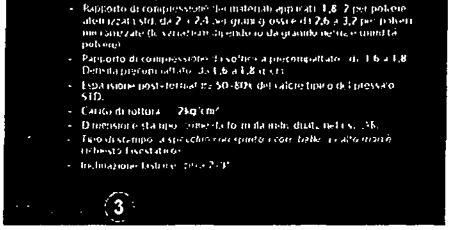
As a function of the above several different plant systems have been developed to meet different needs.



The production line features a first "lightweight" press that pre-compacts the powders to produce a tough semi-finished item that can subsequently be decorated. This press can be fed with coloured powder mixes that are arranged in the cavities to produce aesthetically effective random combinations and streaks.

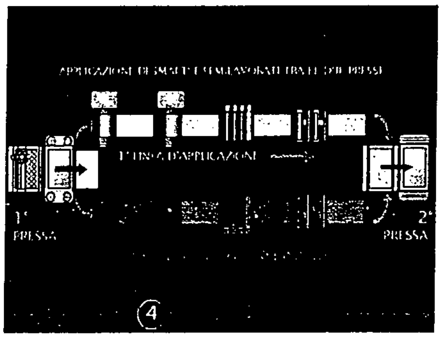
This figure shows the pre-compacting phase.

The parameters for reference are the following ones:

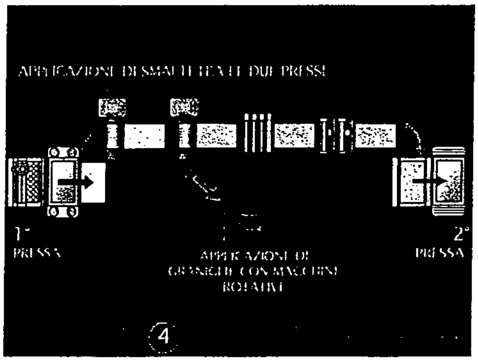


- Pressione di formatura 50-80 kg/cm²
- Umidità polveri 4-6%
- Granulometria polveri STD
- Rapporto di compressione dei materiali applicati 1,8-2 per polvere atomizzati std. da 2 a 2,4 per [illegible] e da 2,6 a 3,2 per polveri [illegible] (le variazioni dipendono da granulometria e umidità polveri)
- Rapporto di compressione da soffice a precompattato da 1,6 a 1,8 Densità precompattato da 1,6 a 1,8 [illegible]
- Espansione post-formatura 50-80% del valore tipico del pressato STD.
- Carico di rottura 2kg/cm²
- Dimensione stampo [illegible]
- Tipo di stampo a specchio [illegible]
- Inclinazione [illegible] 2-3°

-Forming pressure: **50-80** kg/cm2
-Powder moisture: **4-6%**
-Powder particle-size distribution: **STD**
-Compression ratio of the applied materials: **1.8-2** for std spray-dried powders, **2** to **2.4** for big grains and **2.6** to **3.2** for micronized powders (the variation depends on the particle-size distribution and the powder moisture)
-Compression ration of soft clay filling and pre-compacted powders: **1.6** to **1.8** Density of the pre-compacted product: from **1.6** to **1.8** g/cm3
-Expansion after pressing: **50-80%** of the STD pressed product value.
–Breaking load value: < **2kg/cm2**
–Type of mould: mirror die with pushers (face upwards) – isostatic die not needed



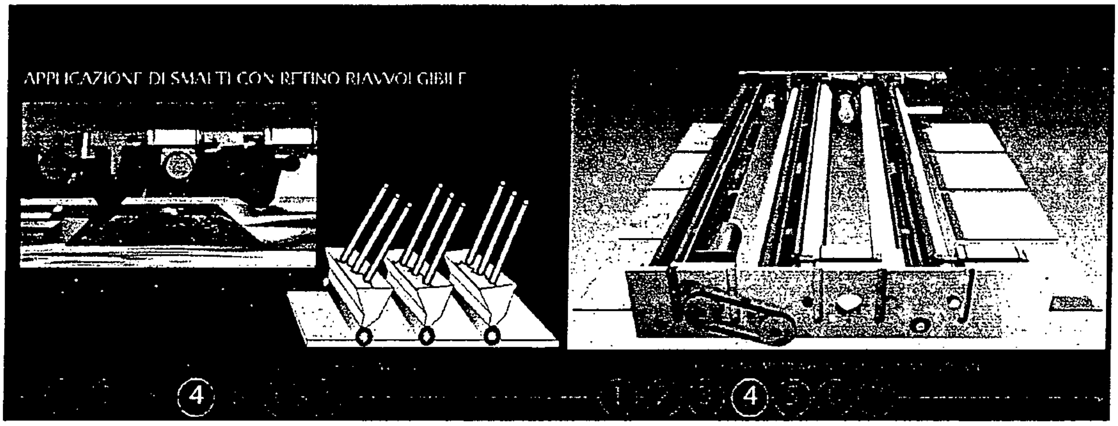
In details the machines for the glaze application and semi-finished products. **Let's remind you** all the pre-compacted tiles (i.e. those that have been compressed in the first lightweight press) are decorated by passing them under dry application units stationed between the pre-compaction press and the high-pressure press, thus providing a high degree of synergy between surface decoration and the underlying body.



The rotary silk-screen printing unit can be equipped with rollers having a different nature and diameter:

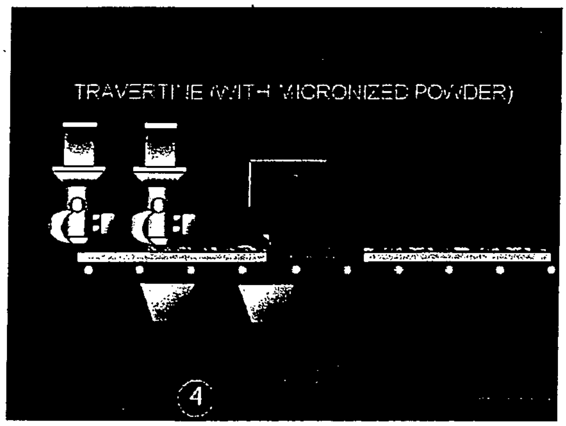
- Stainless steel circular screens 30x60 (diam. 400 mm)
- Stainless steel circular screens 60x120 (diam. 525 mm)
- Mesh apertures of 0.5 - 5 mm

Applied weight: from 100 to 1500 g/m^2 (rustic), from 200 to 2500 g/m^2 (polished), variable depending on graphics.



Another device for silk-screen printing is the tapparella unit:

- laminated screen 260x120 mm
- laminate holes with mesh sizes from 5-6 to 0.18 mm depending on graphics and applied material (glassy or spray-dried powders)
- Applied weight from 100 to 2500 g/m^2.



In the case of a "double-loaded" product, a device able to apply a big amount of material previously demixed must be used on the whole surface (see figure).

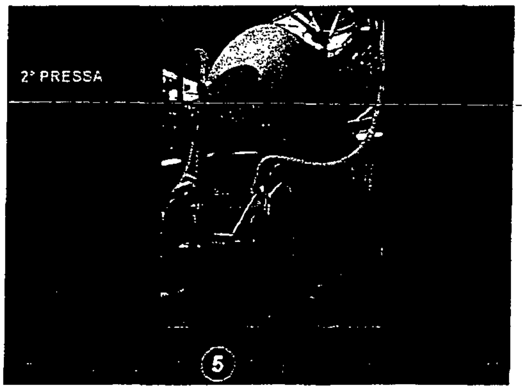
The product range in this regard is vast, as is the corresponding range of effects. Such products can also be used as composite systems and sub-divided into:

- Base compositions for porcelain tiles
- Mixed systems with compounds.

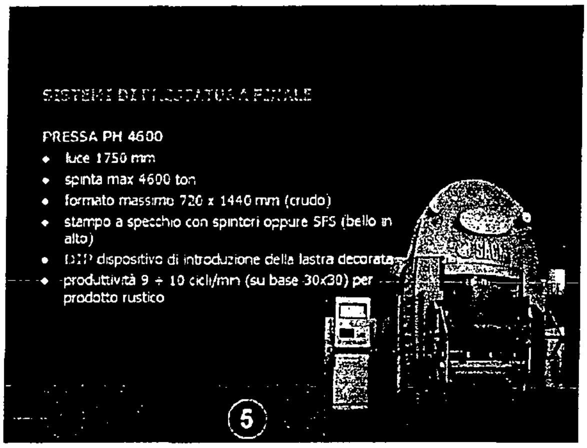
These families include the following (sub-divided into 3 different classes):

- Coloured and uncoloured spray dried body (class 1)
- Mixed body-glaze spray dried systems (class 2)
- Spray dried glaze (class 3)
- Micronized forms of the above three classes
- Flake forms of the above three classes
- Grain forms of the above three classes
- Glass forms of the above three classes
- Agglomerate forms of the above three classes
- Pellet forms of the above three classes.

These are the products currently available on the market. New ones are being studied, and this will undoubtedly encourage research into new, ever-more innovative materials, especially as regards the conferring of surface transparency and depth, particularly on polished products.



The second pressing is therefore effected on an already-decorated tile and prepares a product that is ready for subsequent stages of the production process (drying and firing).



SISTEMI DI [illegible] A FINALE

PRESSA PH 4600

- luce 1750 mm
- spinta max 4600 ton
- formato massimo 720 x 1440 mm (crudo)
- stampo a specchio con spintori oppure SFS (bello in alto)
- DIP dispositivo di introduzione della lastra decorata
- produttività 9 ÷ 10 cicli/mn (su base 30x30) per prodotto rustico

You can see which are the reference parameters of the final formula:

-Specific pressure: ~400-500 kg/cm^2 according to the product

-Type of mould: mirror die with pushers or SFS

-Productivity: in accordance with the size and the product (to 9-10 cycle/min).

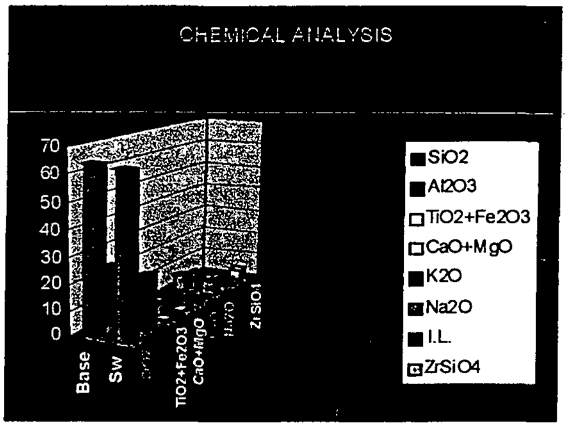
Technological factors of the pressed tile as a function of product to be prepared

Very important vis-à-vis the final product: when it comes to selecting the final product type the base composition plays an essential role and involves both aesthetic and cost factors.

The key base composition characteristics are:

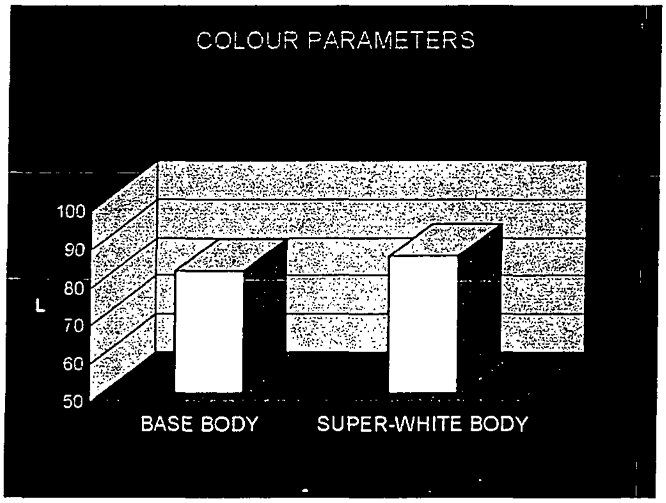
- chemical analysis

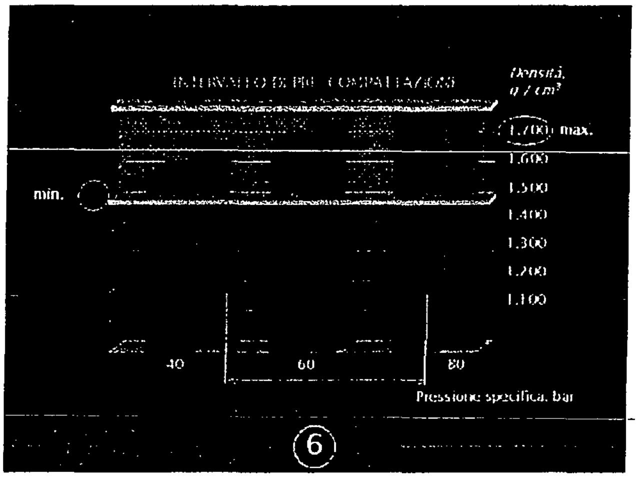
CHEMICAL ANALYSIS



- degree of whiteness (L; a; b)

On the basis of the technical characteristics previously shown the best pre-compacting range, as by the figure below:





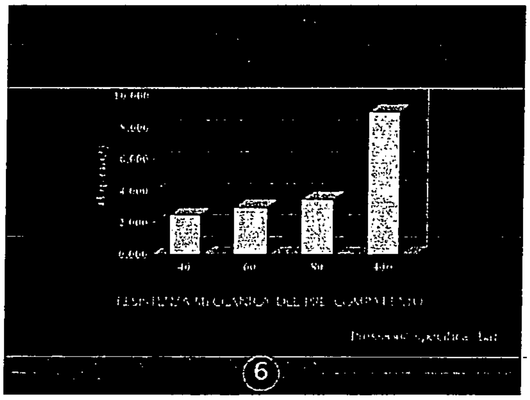
The minimum pressure is defined when the support to be decorated shows minimum 2.5-3 Kg/cm^2 breaking load value. From an experimental point of view this specific pressure is around 50-70 bar.

The bulk density of 1.65-1.7 g/cm^3 corresponds to such values.

Usually the top level of pre-compacting is about 80-90 bar.

That comes from the figure below:

Starting from the top figure you can see the outline of the spray-dried grains; of course this is no longer possible when the forming pressure is over 90-100 kg/cm^2 (see both figures below). Therefore the pre-compacted material is not similar to the pressed one: the fact that the grains can "get closer" and keep their shape allows to dry apply glaze and grains and to achieve an "intimate" matching without any lamination of the interface, which is well defined and regular.

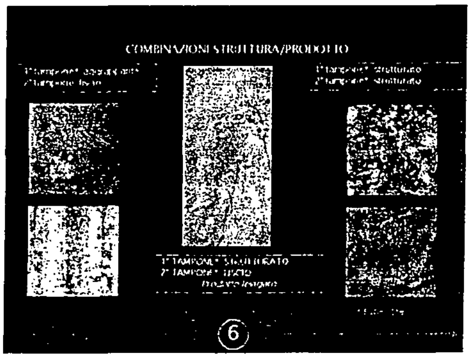


3) *Breaking load at low specific pressing pressures*

The diagram illustrates different base composition types typical of Italian output in order to evaluate:

- handling performance (bending strength)
- capacity of green tiles to sustain manipulation/transformation without their downstream "workability" (and/or dry colouring capacity) being compromised.

Let's see what we can produce by this kind of technology:



COMBINAZIONI STRUTTURA/PRODOTTO

1° tampone* strutturato
2° tampone* strutturato

1° TAMPONE* STRUTTURATO
2° TAMPONE* LISCIO
Prodotto levigato

⑥

It is opportune to divide the range of products that can be realised into two great families:

-polished products (such as marbles and travertines)

-rustic products (such as quartzite)

According to the type of product to be realised, different structure combinations can be applied between the first and the second press, and in particular:

1. Products with grip structure on the first press and smooth punch for the final pressing

it deals with those products where the powders application is carried out with weights superior to 2 kc/cm2 and it is thus necessary to avoid material waste in the sides.

Examples: Guatemala green, white Kashmir, Marmorinos, etc.

2. Products with relief structure and the second punch is smooth:

in this case, the quantity of applied powder is usually inferior to 2 kg/cm2 and the application is carried out mostly by means of roll up silk-screen printing machines; usually, after firing, the quantity to removed by polishing is about 5-6 tenths of mm.

Examples: Azul Bahia, Azul Macauba, Green Onyx, etc.

Products with structured punches for both first and second pressing:

This last case is relevant to the rustic products in general, where it is not necessary to apply large quantities of glaze and the first press structure is always a joint with the silk-screen printing applications in the line; everything is fixed by the final structure, giving a very fine mixing between the support and the applied glaze to the finished product, which cannot be obtained with the traditional decoration techniques in the glazing line. The quantity of applied glaze is very low: from 500 to 1000 g/m2.

Examples: Quartzite, slate, etc.

Annex 5

ICS-UNIDO SEMINAR
EVALUATION QUESTIONNAIRE RESULTS

Seminar Title: 'Best available technologies and innovations for ceramics production'
Faenza, Italy, 30 September – 5 October 2002

A. Organization:

1. How did you obtain information about this seminar?
    - From ICS-UNIDO = 3
    - From colleagues = 1
    - Internet page of ICS = 3
    - Through the Director of the Filicate Society = 1
    - From CEROM – The Romanian Ceramic Society = 2
    - By the head of department (SI) = 1

		Excellent	Very Good	Good	Fair
2.	The information process was	4	6	1	0
3.	The announcement and pre-course material was	2	6	3	0

- Describe the content of the seminar:
    - New information on shaping and processing techniques in the field of traditional and advanced ceramics.
    - Very interesting and useful.
    - Scientific and technological aspects regarding forming operations of ceramic powders.
    - The aim was to present the current state of the art in the field of ceramics technology, with the emphasis on free form manufacturing and rapid prototyping of ceramics.
    - Excellent

		Excellent	Very Good	Good	Fair
4.	I found the scientific programme	3	8	0	0
4.1.	Applied lectures	4	7	0	0
4.2.	Use of small working groups	3	5	0	0
4.3.	Case studies	1	7	0	0
4.4.	The time spent by lecturers in class and after class on specific questions/examples	6	5	0	0

		Balanced	Unbalanced
4.5.	Students scientific knowledge was	11	0

B. Duration of programme:

		Just right	Too long	Too short
1.	Number of days	9	1	1
2.	Length of working days	9	2	0

C. Training facilities & Hotel:

		Excellent	Very Good	Good	Fair
1.	Lecture/training rooms	7	4	0	0
2.	Breaks/refreshments	3	7	1	0
3.	Hotel accommodation	1	3	6	1
4.	Meals at the hotel	1	4	5	1

- The hotel facilities were low, including people who hardly spoke any foreign language, so the meals were always a 'small surprise'.

D.	**Organizer's response to participants needs**	8	3	0	0
E.	Overall programme organization	6	3	2	0

F. Would you recommend to others from your institution/country to attend a similar activity in the future?

Yes	Maybe	No
11	0	0

1. Which part of the seminar did you find most useful?
    - The part entitled 'Principles of ceramic manufacturing: powder processing in theory and practice'.
    - Talks on application, technology, visiting fair and discussions.
    - Talks on powder rheology, visit to TECNARGILLA, also talk on rapid prototyping.
    - Latest development in porcelain body manufacturing: the pressing of very large and thin sheet with no die-set with the LAMINA technology.
    - Rapid prototyping.
    - Expert system solutions.
    - Information on the recent achievements in research and development.
    - Powders rheology and treatments – Latest development in porcelain body manufacturing.
    - To my opinion, the most useful were endless talks after lectures, during breaks and discussions with participants of different backgrounds.
    - All of them.

2. Which part of the seminar do you think should be expanded?
    - The part regarding the theory of the behaviour of ceramic raw materials and ceramic materials.
    - Visit to the fair.
    - Visits to relevant places.
    - Computer simulation and visits to companies.
    - Advanced ceramics area.
    - Rapid prototyping.
    - Case studies.
    - Latest development in porcelain body manufacturing – Recent development in ceramic raw materials.
    - I think that the visit to Tecnargilla was a very good idea and that the future meetings should be planned in a similar way.
    - None.

3. Which part of the seminar do you think should be dropped?
    - Some parts concerning the advertising of commercial products.
    - Some aspects of modeling of liquid phase sintering.
    - None.
    - None.

4. Any other suggestions for future improvements to the programme?
    - To be introduced a part regarding (e.g.) the principles of developing new ceramic materials having certain specific final properties.
    - Alternative platforms for discussions.
    - More time for the participants presentations.
    - More speakers.
    - Industrial problems of new technologies and solutions for problems and examples.
    - A closer check of the organizers abilities and hotel facilities, if the meeting is organized outside Trieste (maybe).
    - To add some lectures of magnetic ceramics or nanotechnology, perhaps.

5. Do you think that the topics/tools you studied during the seminar could be used by industries in your country? If so, how? If not, why not?
    - Yes. In our company (a porcelain and stoneware factory) the isostatic pressing technology is applied for the production of tableware and I found the topics regarding the 'Principles of ceramic manufacturing' indeed very useful. I feel the same about 'Powder rheology and treatments' and 'The study of the sintering kinetics using a double beam optical dilatometer'.
    - Yes, both in research and industry.
    - Yes. Gaining information on such special matters will arise further interests and lead to some research on these.
    - Yes, I believe that in the near future with healing of our economies these machines and technologies will find their place in our economy also the more that there are companies which with their knowledge. Experience and potential are capable to cope with challenge in cooperation with some EU, USA or other foreign countries partners.
    - Not all (mostly because of high cost), but none of them could be used.
    - Yes.
    - Yes – by innovators.
    - By transferring new knowledge and information.
    - Yes, I'll try to find new solutions to: - improve the powder rheology for dry spried powders used in isostatic pressing in ARPO company – use vitroceramic materials in porcelain recipe.
    - Yes, especially due to the fact that most of ceramics factories need to change the production lines and equipment urgently and the new wave of foreign investments regarding industry are expected.
    - Yes, perhaps.

6. Can you suggest any programme and future activities that ICS could pursue in order to help with the technological and scientific advancement of your country?
    - By organization of training courses and specializations for our technologists and scientists in Italian institutions.
    - Solid free forming (SFF).
    - Solid free forming (SFF).

- Other seminars similar to this one whose contents could be focused on different processes of ceramics materials (e.g. firing process).
- A scientific information center in the ceramic field.
- Workshops on recent R&D results and industrial applications of advanced structural materials.
- I don't have the answer at the moment, and, if so in the future, I will inform contact persons from the ICS.

7. Do you think you have benefited from participation in this seminar? If so, how? and your institution?
    - Yes – More knowledge especially in rapid prototyping.
    - Yes, both because of learning about new technologies and getting to know about other institutions activities.
    - Yes, with new information for best available technologies and innovations in ceramics production.
    - Yes, as I've mentioned above, I've gained knowledge on matters such as rapid prototyping and solid free forming techniques.
    - Yes, by learning new technologies, meeting the people arranging further cooperation.
    - Yes. The information that I received attending this seminar completes my knowledge and could help me in my research work and in my technological applications and in this way a benefit for my company will be obtained too (I am chief of technology lab department).
    - Yes, by being more informed and establishing new contacts.
    - Yes – For my doctorat degree it was a training – For my factory like I already told in 5.
    - Yes, I did gain new knowledge regarding innovations of ceramics and visit to Tecnargilla was more than good. I have already informed my senior colleagues about this visit and we will see what happens.
    - Yes, I have. On this seminar I've got a lot of useful information which I'll try to present then to my colleagues in the institute.

8. How do you intend to disseminate the information you have acquired during the seminar once back in your own country?
    - By lectures to the institutions.
    - Seminar at the mother institute.
    - At national ceramic society meetings, internal seminars at my organization, etc.
    - By writing a report and sending information about the content of the seminar (copy of lectures) to colleagues.
    - I'm planning to give a talk about this workshop.
    - By giving a lecture to the department and other relevant staff.
    - I intend to give copies of the seminar material to the other ceramic specialists from my company as well as from other institutes.
    - By delivering lectures for industrial partners and university students.
    - I informed my teacher (Prof. I. Teoreanu – Materials Science Faculty). I spread the materials to Mrs. M. Preda (Ceramic Professor in Materials Science Faculty, Bucharest) and to other colleagues from my country.
    - Mainly by a direct contact with colleagues in the related field.
    - In the form of presentations.

G. Evaluation of Lectures and Speakers

		Excellent	Very Good	Good	Fair
1.	Course material	3	8	0	0
2.	Resident lecturers presentations	6	5	0	0
3.	International lecturers presentations	6	5	0	0
4.	Ability of lecturers to answer specific questions	6	5	0	0

Any comments:

- Beside the important information upon basic and applied science of ceramics, the seminar also offered the participants the possibility to know more about science research and production of ceramics in different countries. I would like to suggest to allocate more time for personal reports of the participants.
- A suggestion for the next meeting – Biomaterials.

ACHIEVEMENTS

The achievement of the seminar was the presentation of an overview on how concepts of the theory and practice of powdered materials processing and forming could improve industrial productivity, energy savings, enhance quality control and design aesthetic, to a number of representatives coming from East European countries.

Participants were provided with information on dry-powders, cold-forming technologies from the theoretical point of view (powders rheology) and with a practical outlook on the current plants for the realisation of ceramic tiles and their in-the-press decoration. A number of these methods were presented taking as examples case histories related to the recent past and the present production trends aimed to the realisation of natural-stone-like ceramic tiles. The preparation of ceramic powders and colours and their processing into valuable decorated tiles was discussed by reviewing the materials cycle with special care of the protection of working environment within the factory.

Ceramic powders forming technologies, at the advanced level of research and development, have been presented as a specific topic the wider Free Form Manufacturing and Rapid Prototyping processes.

RECOMMENDATIONS

The following recommendations about management of powders, both as ceramic bodies bases and colouring agents, were outlined in order to be developed into concerned actions by the attendees in the respective countries. The recommendations were as follows.

1) Producers of raw-materials as powders should consider the need for avoiding wastes, for incrementing materials re-use and recycling and for disposing, when necessary, in environmentally compatible sites, the by-products, thus cutting the cost of the raw materials.
2) Producers of colouring agents (pigments) should operate under an even more stringent rule of caution because often pigments are made of heavy metal ions of relatively high hazard.
3) Re-use and recycling should have priority over disposal.
4) Noxious waste from any production site should be treated separately.

In order to prevent problems becoming damages, the concerned factory-keeping rules should provide ordinance with the aim of:

a) reducing the endangering to air, waters and soil,
b) reducing the noxious load in potentially recyclable materials.

The means to obtain such results can be envisaged in the separation of storage and selection of powders and pigments, that is the obligation of separate disposal and the prohibition of mixing of various categories of waste. The measures should have the following contents.

a) The obligation of separate disposal; that means noxious waste have to be collected, treated and kept separately from other residues of tiles production.
b) The prohibition of mixing; that means noxious waste must not be mixed with other residue materials.
c) Prohibition of disposal for noxious waste on sites or other areas provided for disposal of harmless residues.
d) Obligation of documentation; that means producers are required to keep documentation of type and quantity of managed waste and to keep records of them and their delivery.

ANNEX 8

FOLLOW UP

The seminar has gathered a number of people coming mainly from the research and technical areas of national agencies and production companies.

The immediate follow-up has been the availability of the lecture notes and documents presented and discussed at the seminar, made available to the participants on-site. A further action as a follow-up will be the extension of the lecture notes and documents into soft copies to be made available any other interested person as a soft-copy resident in the ICS New Materials website. A limited number of hard copies (CD and printed matter) are being prepared autonomously for the ICS records and bibliography purposes.

Further follow-ups have been envisaged in the programming of inter-countries meetings, promoted by the participants' agencies and institutions, with the advisory activity of UNIDO-ICS.