OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

19255

Distr.
LIMITED

ID/WG.519/13(SPEC.)
31 October 1991

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

Expert Group Meeting on
Processing and Application of
New Materials

Vienna, Austria, 4-6 November 1991

DEVELOPMENT AND PROJECTION OF ALUMINA FIBRES FROM NATURAL RESOURCE-BASE MATERIALS (CLAY/BAUXITE): DEVELOPMENT AND PRODUCTION*

Prepared by

Anthony M. Coka**

72

* The views expressed in the document are those of the author and do not necessarily reflect the views of the Secretariat of UNIDO. Mention of the names of firms and commercial products does not imply endorsement by the United Nations Industrial Development Organization (UNIDO). This document has not been edited.

** Planning and Analysis Group Council for Scienfitic and Industrial Research, Accra, Ghana.

V.91-30193

1. ABSTRACT

This paper discusses the possibility of developing at low cost, alumina fibres based on natural resources such as clays and bauxite. The emphasis, however, has been on clays (alumino-silicates); since they serve as cheap source of material which provide an easy way of entering advanced ceramic materials by developing countries.

2. INTRODUCTION

Clays are formed from the weathering or decomposition of felspathic rocks, and are composed essentially of hydrated aluminium silicates such as $Al_2SiO_7.2H_2O$ together with others. The particle size of clay is less than 0.002 mm.

A typical analysis of clay material from Ghana is shown in the table below.

Content	Clay 1	Clay 2	Clay 3	Clay 4	Average Total
SiO_2	69.1	59.2	58.5	47.5	58.6
Al_2O_3	14.0	18.4	17.0	13.7	19.7
FeO_3	4.8	5.4	5.5	4.4	5.0
CaO	1.9	3.3	6.4	15.6	6.8
MgO	1.1	3.3	2.2	0.8	1.9
K_2O	3.6	1.6	3.0	1.6	2.9
Na_2O	-	-	2.2	2.8	2.5
Ignition Loss	4.8	9.2	3.4	12.9	7.6

Source: Kirkendale, G: A Laboratory manual for Testing Clays for use in the Production of Building Products; Technical Publication, Building and Road Research Institute (Ghana), August 1975.

2.1. Resource Base

Ghana has a large reserve of clay deposits spread throughout the country. The total clay reserve is estimated at 4 514 230 366 MT. Some of these deposites have been found from analysis to be suitable for paint manufacture as well as for the production of burnt brick and tiles and other traditional ceramic products.

2.2. Ceramic

The term "ceramic" is traditionally, generally applied to anything made by heating clay (e.g. pottery, porcelain, stone-ware, bricks, etc.). Ordinary clay is a plastic, thixotropic material, which hardens irreversibly when heated sufficiently strongly. The occluded water and water of hydration is first lost at about 400° - 700°C, and above this temperature the alumina and silica react to form a new anhydrous aluminium silicate. The reaction is complete at 1100° - 1200°C. The resulting burnt clay will not recombine with water and so does not soften and reform the initial plastic clay.

$$Al_2Si_2O_7 \cdot 2H_2O \xrightarrow{400-700^\circ C} Al_2Si_2O_7 \xrightarrow{700-1200^\circ C} \text{Ceramic}$$

Natural clays therefore can serve as an easy entry into research and development (R and D) and the high research and development (HRD) area for a developing country to develop and produce alumina fibres as furnace insulators and high temperature materials.

3. ALUMINA FIBRES - REVIEW OF STATE OF THE ART

Alumina fibres have become a new generation of fibres. High-Alumina fibres have become available in both staple and continuous forms since 1970. They offer advantageous high temperature property combinations. Their application potential is compared with those of carbon and silicon carbide fibres.

3.1. Introduction

Most common metals that are used have low melting points and low specific stiffness (see Fig. 1). Many ceramic materials possess both higher specific stiffness and high melting or decomposition points. This is because ceramics contain low atomic number elements (especially those of Groups 3 to 5) which are capable of forming only 3 or 4 strong directional covalent bonds. In principle such materials would lead to large weight savings in high temperature applications (e.g. aerospace engines) if they could be utilized in the same manner as metals.

Ceramics have two main disadvantages. They are brittle and difficult to shape. Much progress have been made in recent years to develop better strengths in monolithic ceramics, but ceramic materials often exhibit their best properties in the form of fibres.

This arises from the fact that their strength and fracture properties are controlled by microdefects which are introduced by the manufacturing process and better control is obtainable in fibrous forms than in monolithic forms. The availability of ceramic fibres have paved the way for the production of COMPOSITES possessing most of the advantages of the ceramic, but without disadvantages.

The three main families of advanced ceramics available as fibres are carbon, silicon carbide and high-alumina fibres, and there are several possible fibre morphologies available. Fibres may be classified by their diameter, namely:

(1) whiskers (less than 1 micron)

(2) staple (1-10 microns)

(3) continuous multifilament yarns (5-25 microns)

and (4) continuous monofilament (100 microns).

Fibres are sold as aggregate secondary forms such as wool or rigid preforms (whiskers, staple) and as yarns and woven (continuous fibres). Silicon carbide fibres are available in the widest diversity but none of these has attain commercial maturity. However high-strength carbon fibres have been in use commercially in advanced composites (usually in epoxy resin matrix). The world-wide capacity is estimated at 500 t/a.

Alumina fibres are available either as staple or as multifilament continuous yarns.

4. ALUMINIUM FIBRE COMPOSITIONS, TYPES AND AVAILABILITY

It is unusual to find chemically pure alumina fibres. The amount of and location of impurities has an important effect on the physical properties of the fibres. Very often, the difference between products depend mainly on the purity; (secondary elements may be added deliberately for synthesis reasons). The alumina-silica family is quite diverse and Fig. 2 shows the phase diagram for this system. Only products containing more than 50 per cent by weight of alumina are of interest. There are broadly three composition ranges which are of interest. Between 50-60 per cent alumina there are melt-spun glassy alumino-silicate fibres (often called kaolin) which were originally developed in the 1950s as high-temperature insulating materials. The best grades can only be used in insulation up to 1400°C because of the low-melting silica rich eutectic (1595°C). This phase (alumino-silicate) fibre should be of particular interest to developing countries of Africa where large deposits of kaolin (clay) exist and therefore could serve as an easy point of entry into advance insulating alumina fibre materials research, development and production.

For use at higher temperature however, alumina-silica fibres containing less silica than mullite (which includes all available continuous fibres) are most desirable since the relevant eutectic temperature is then 1840°C. It should be noted however that high temperature equilibrium phases in this region of the phase diagram are mullite and corundum (α-alumina). Polycrystalline products containing 70-80 per cent alumina are often referred to as mullite fibres. Products containing more than 70 per cent alumina can generically be referred to as high-alumina continuous fibres.

The development of all such fibres dates back to about the 1970s. What the phase diagram implies is that high-alumina continuous fibres cannot be made by conventional melt-spinning processes as the melting temperatures are too high.

5. FIBRE PRODUCTION AND ECONOMICS

Very broadly, the relationship between inorganic fibre cost (1987) and availability is summarized in Fig. 3. While the production of carbon fibres and glassy alumino-silicates can be regarded as established with many second generation products appearing, the situation for most other fibres is in the developmental stage. The processes for producing novel fibres are proprietory so that in most cases the only information available is derived from the patent literature. Many of the new products especially the stream of products from Japanese workers are expensive (up to £800/kg) as a result of small-scale manufacture on pilot plants. The cheapest fibres currently, are staple products made for the insulation markets (£1-20/kg). Continuous multifilament yarns cost from £50/kg (carbon fibres) to £400/kg ("Nicalon" silicon carbide fibre).

Whisker products have intermediate prices (£150 - 300/kg). The prices of secondary product forms (e.g. wovens) may be double that of the primary fibre.

These high prices, no doubt, has somehow inhibited the wide-spread commercialisation of the applications of many composite materials. There is therefore scope for the reduction in cost through increased volume of production and also improved fibre manufacturing technologies.

6. TECHNOLOGY OF FIBRE MANUFACTURING

Fibre manufacturing technologies can be classified into three; namely,

(1) Melt spinning - only practical for 50-60 per cent alumina-silica glassy fibres.

(2) Solid-state transformations - carbon silicon carbide, alumina-silica (see Fig. 4), fibres. Both are continuous multifilament and staple fibres. In these processes a meltable or soluble precursor is fiberised and then crosslinked before being converted by high temperature heating to the desired ceramic fibre.

(3) Growth from vapour phase e.g. whiskers (silicon carbide) and monofilament fibres (silicon carbide/boron). Monofilament fibres are made by deposition on a carrier fibre of tungsten or carbon using a CVD process. It is relatively easy to incorporate thin barrier layers onto the fibre by this technique.

Each method has its advantages and disadvantages. The melt spinning process is very cheap but only gives low quality product.

Vapour phase processes give generally very high quality products (especially the monofilament) but at high cost. Many solid-state transformation processes have been developed and usually, the products are of intermediate quality and cost. Those giving carbon fibre from a variety of starting polymers have been extensively investigated but the sol-gel type processes have also been widely exploited in various versions for making alumina fibres.

7. CHEMICAL PROPERTIES

The great merit of alumina is that it is extremely inert, stable at high temperature and (potentially) cheap (see Fig. 5). It is stable in oxygen containing atmospheres up to its melting point (whereas carbon fibre oxide above 400°C and silicon carbide at Ca 1200°C). It can even remain unchanged in reducing atmospheres to about 1200°C. It is exactly for this reason that high-alumina fibres in staple form are popular as high temperature insulation materials in both metal-working and ceramic firing furnaces.

It can be used in both metal and ceramic-matrix composites because, similarly, it resists attack by molten light metals and it is thermodynamically unable to react with carbide ceramics. Only very aggressive materials such as metallic titanuium and some basic refractory metal oxides can attack it slowly above 1000°C. The reaction of alumina with silicon nitride to form β-sialons is also very slow below 1500°C and SiC fibres are by contrast easily attacked by oxygen, metals and oxides.

8. PHYSICAL PROPERTIES

The prime physical properties exhibited by high alumina fibres are low thermal conductivity, high thermal shock resistance. They are therefore used widely as hot-face linings in industrial furnaces. Unlike monolithic linings, fibre linings can tolerate fast heat-up and cool-down and so the productivity of intermittent furnaces can be greatly increased thereby reducing fuel usage to 10-20 per cent. The US Space-shuttle thermal protection tiles also incorporate such fibres because of their excellent thermal shock resistance.

In short, the physical characteristics of fibres which are most important to their uses in composites are:

- high aspect ratio
- high stiffness and strength (maintained) at high temperatures
- low density
- low coefficient of thermal expansion
- high hardness
- good processability (flexibility) to desired secondary forms.

9. APPLICATIONS OF ALUMINA FIBRES

Historically, high-alumina fibres were first developed as high temperature furnace insulation, but more recently they have been attracting attention as a component of structural light-weight parts for use at high temparatures experienced in engines and by leading edges of rocket and space planes. They may also have future potential in electrical engineering and undersea hardware.

10. INSULATION APPLICATIONS

The current largest-scale use for high-alumina ceramic fibres is that of staple fibres as insulation above 1250°C; below this temperature, melt-spun fibres are commonly used. The application of such high-alumina staple fibres began in the early 1970s with ICI "Saffil" alumina and there are now several manufactures of similar performance fibres (e.g. Denka's "Alcen" and Carborundum's "Fibermax"). All these products have diameters in the range 1-7 microns for maximum thermal efficiency. The use of fibre hot-face insulation on existing brick-insulated furnaces leads to energy-savings of approximately 10-20 per cent; higher-values corresponding to intermittent or cyclic operations. A variety of insulation methods have been developed using both rigid boards and flexible blankets or staple fibres.

11. CONCLUSION

Staple high-alumina fibres are the cheapest form available and find wide-spread use in furnace hot-face insulation. They have also been used in thermal protection systems for Space Planes and are beginning to be used in Aluminium alloy metal-metal composites (MMCs) for improving wear resistance and and thermal fatigue.

12. NATIONAL POLICIES AND PRIORITIES FOR MATERIAL SCIENCE TECHNOLOGY RESEARCH AND DEVELOPMENT (R&D) AND HIGH RESEARCH AND DEVELOPMENT (HRD)

To set up a national policy in material science development, one may ask the question as to why we should draw up national development plans at all. But national development plans are drawn with the objective of raising the living standards of the people so that at least every member of the society can have access to those basic needs of life. For example, reasonably cheap or affordable food, clothing, housing, good drinking water, health-care, energy and so on.

The link between material science and technology development should therefore be seen in terms of providing those materials needed to be produced cheaply, efficiently and with high durability and strength to meet such basic needs of the society.

In setting national policies and priorities therefore, one must determine the basic constraints in the particular country that is preventing the achievement of those basic needs. For example, reasonably decent and cheap housing or accommodation has been one of the most important problems facing most developing countries of Africa, quite apart from providing cheap food, health-care and education for their people.

Some of the basic constraints in providing reasonably cheap houses for the people even where natural resources such as good reserve of clay and timber are available may be summed up as:

- the high cost of imported building materials such as cement, iron rods, roofing sheets and fittings(doors, window frames, etc.)
- the high energy cost of producing some of these natural resource-based materials considered "cheap" such as burnt bricks, tiles and shingles, wood products, etc. by using inefficient and badly insulated kilns (ovens, furnaces) in the production process.

A national policy objective in material science and development should be:

- to reduce immediate causes of high production cost of burnt brick and tile by introducing energy-efficient kiln with good insulating materials like High-alumina fibres in the construction of kiln. To this end, deliberate and conscious attempt should be made to encourage material scientists and technologists to explore the possbility of developing and manufacturing high-alumina fibres form national natûral clay reserves.
- Governments of the various countries be urged to form material science and technology councils/committees to oversee the coherent development of materials necessary for meeting basic national needs of the society.
  To this end, adequate financing should be provided for vigorous research and development (R and D) and prdduction in areas of material science and technology deemed as of great national priority.

- at the international level there should be inter-regional cooperation in the development of material science and technology. To this end, International Agencies are urged to assist capable R and D Institutions, Universities and Centres of Excellence for training material scientists and technologists in areas relevant to their immediate national development and in the achievement of basic societal needs.

BIBLIOGRAPHY

1. M.H. Stacey: "Production and characterisation of fibres for metal matrix composites"; J. Material Science and Technology, March 1988, Vol. 4, 227.

2. M.H. Stacey: "Developments in Continuous Alumina-Based Fibres"; Paper presented at Basic Science Meeting at Harwell, May 24, 1988.

3. Kelly, A. and Macmillan, N.H., "Strong Solids", 3rd Ed. 1986, Clarendon Press Oxford.

4. Aramaki, S and Roy, R.J. Am. Ceram Soc. 42, 644 1959 (No. 314 in "Phase Diagram for ceramists" Eds. Levin, E.M., Robbins C.R., Mc Murdie, H.F., American Ceramic Society, Columbus, 1964.

5. Garside, J.E. and Phillips, R.F.: A Textbook of Pure and Applied Chemistry, pp. 611, 1962.

6. Kesse, G.O.: The Mineral and Rock Resources of Ghana; A.A. Balkoma - Rotterdan/Boston, 1985.

ACKNOWLEDGEMENT

In preparing this paper I have used freely to some extent notes prepared by Prof. Dr. M.H. Stacey, FRS; ICI Advanced Materials Department, England for the Commonwealth Science Council Workshop on Awareness of Rapid Advances in Science and Technology (ARAST) on Materials Science and Technology held at the National Physical Laboratory, New Delhi, India; February 19 - 24, 1990.

I was a participant at this Workshop.

<u>NOTE</u>: All the figures attached to this paper come from Ref (1).

MATERIAL SCIENCE AND DEVELOPMENT IN GHANA: TECHNICAL ASSISTANT

Work in this area is scattered. There is some work being done by individual scientists in the physics, chemistry and engineering departments of the Universities of Ghana. But these are all scattered individual efforts.

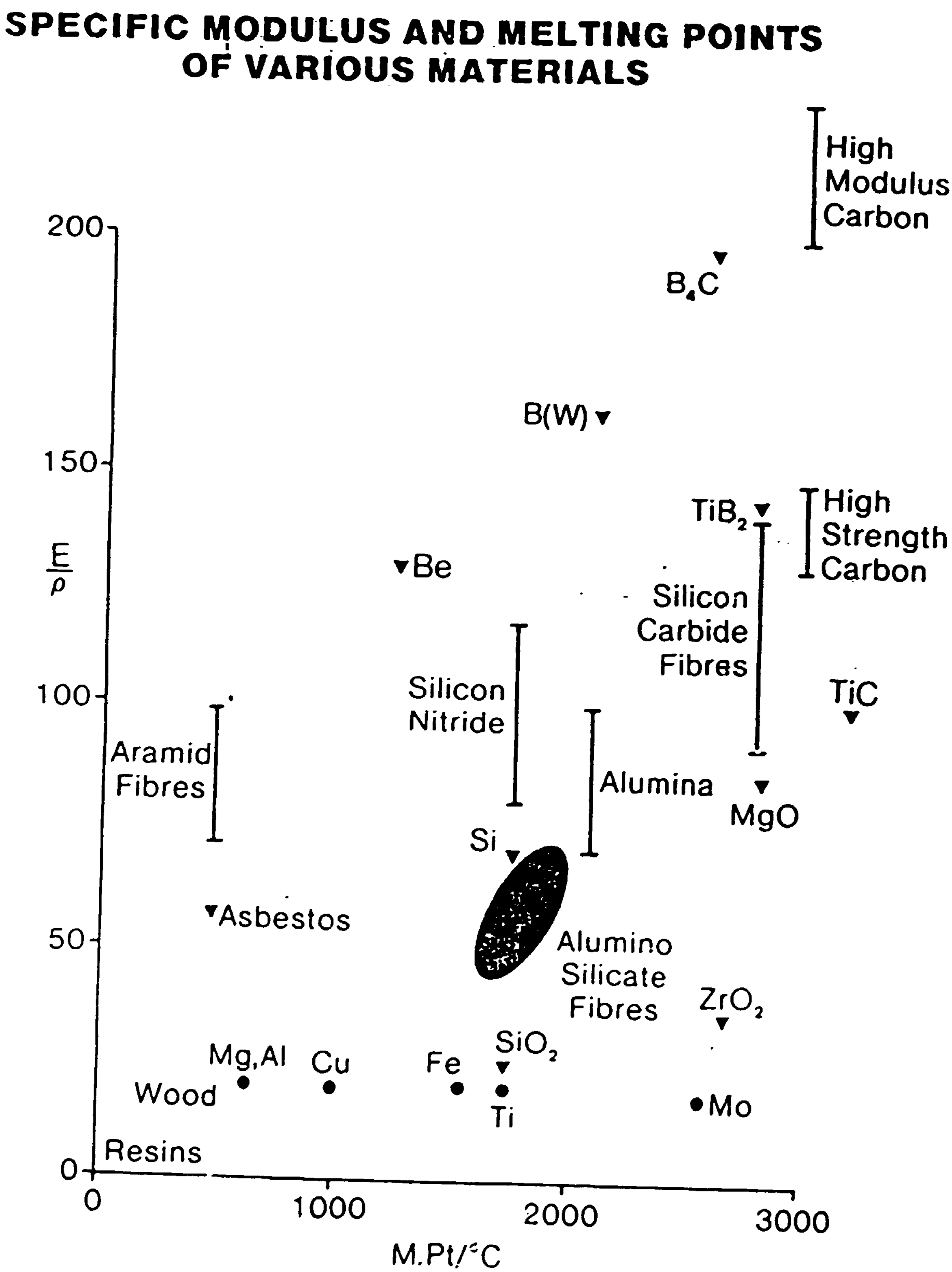
There is however a Division of materials research and testing located at Materials Division of Industrial Research Institute and the Building and Road Research Institute of the CSIR which carry out research and development work on bauxite and kaolin materials. The other groups which are located in the Government Departments undertake mostly material testing, survey and mapping of natural resources.

In the development of a strong base for material science and technology, the Materials Division of Industrial Research Institute of the CSIR should be strengthened in human, financial and infrastructural facilities. Presently, the Division is not well equipped in human, materials and financial resources. There is the need to provide these resources and reorganise the Division, train the necessary manpower and provide equipment for both the laboratory work and pilot work. Most of the researchers in this Division are young and in experienced and need well groomed up scientists and technologists to work with to acquire the much needed know-how and expertise.

Work has been going on for years in the development of insulating refractory materials for kilns and ovens but no result of any significance has emerged as at present even though some in-roads have been made on glazes for the traditional pottery industry.

UNIDO could therefore assist this Division to grow on its own feet as materials research and development institute by providing human, material, financial and the necessary know-how to convert the vast clay/bauxite resources of Ghana to a more economic use and thus solving some of the basic needs of the country as in the provision of cheap houses by use of burnt bricks at low emergy costs, cement and other such important materials in the socio-economic development of third world countries such as Ghana.

Fig. 1


SPECIFIC MODULUS AND MELTING POINTS
OF VARIOUS MATERIALS
High
Modulus
Carbon
B4C
B(W)
TiB2
High
Strength
Carbon
Be
Silicon
Carbide
Fibres
Silicon
Nitride
TiC
Aramid
Fibres
Alumina
MgO
Si
Asbestos
Alumino
Silicate
Fibres
ZrO2
SiO2
Mg,Al
Cu
Fe
Wood
Ti
Mo
Resins
E/ρ
200
150
100
50
0
1000
2000
3000
M.Pt/°C

Al_2O_3-SiO_2 PHASE DIAGRAM

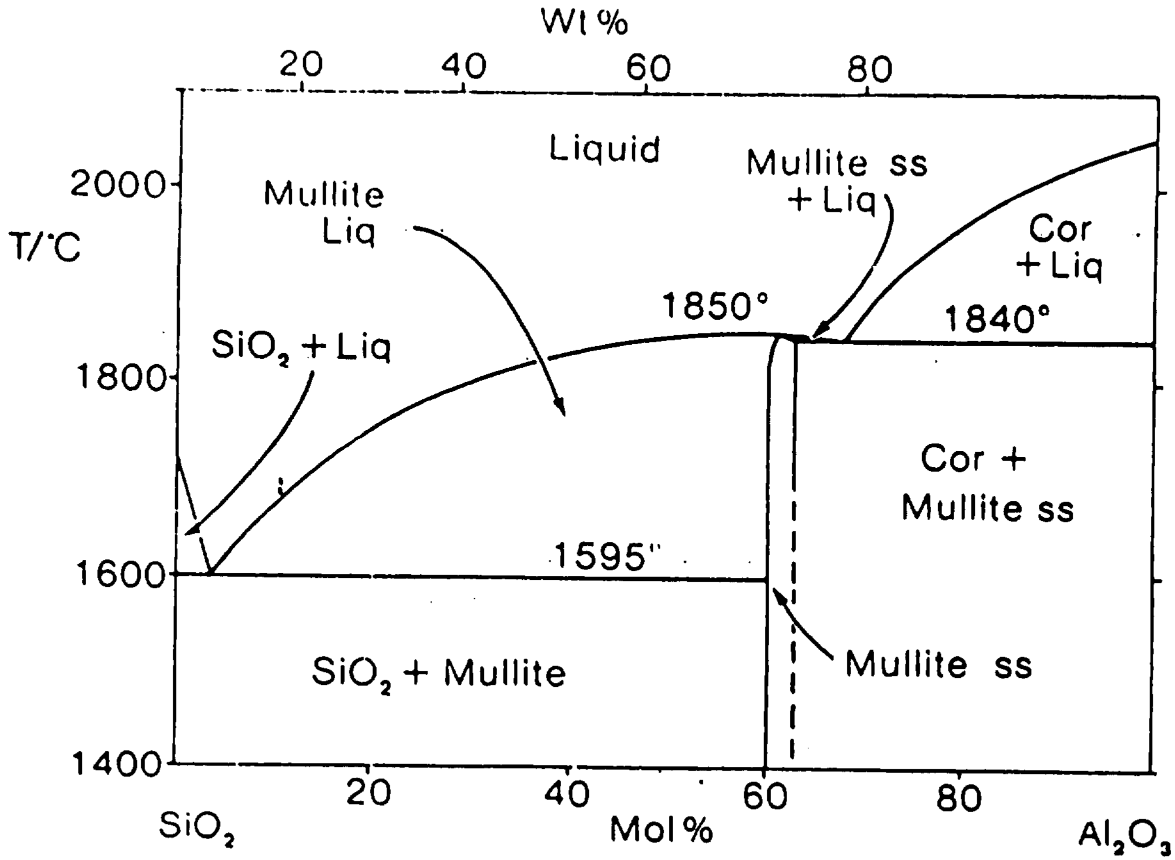


Fig. 2

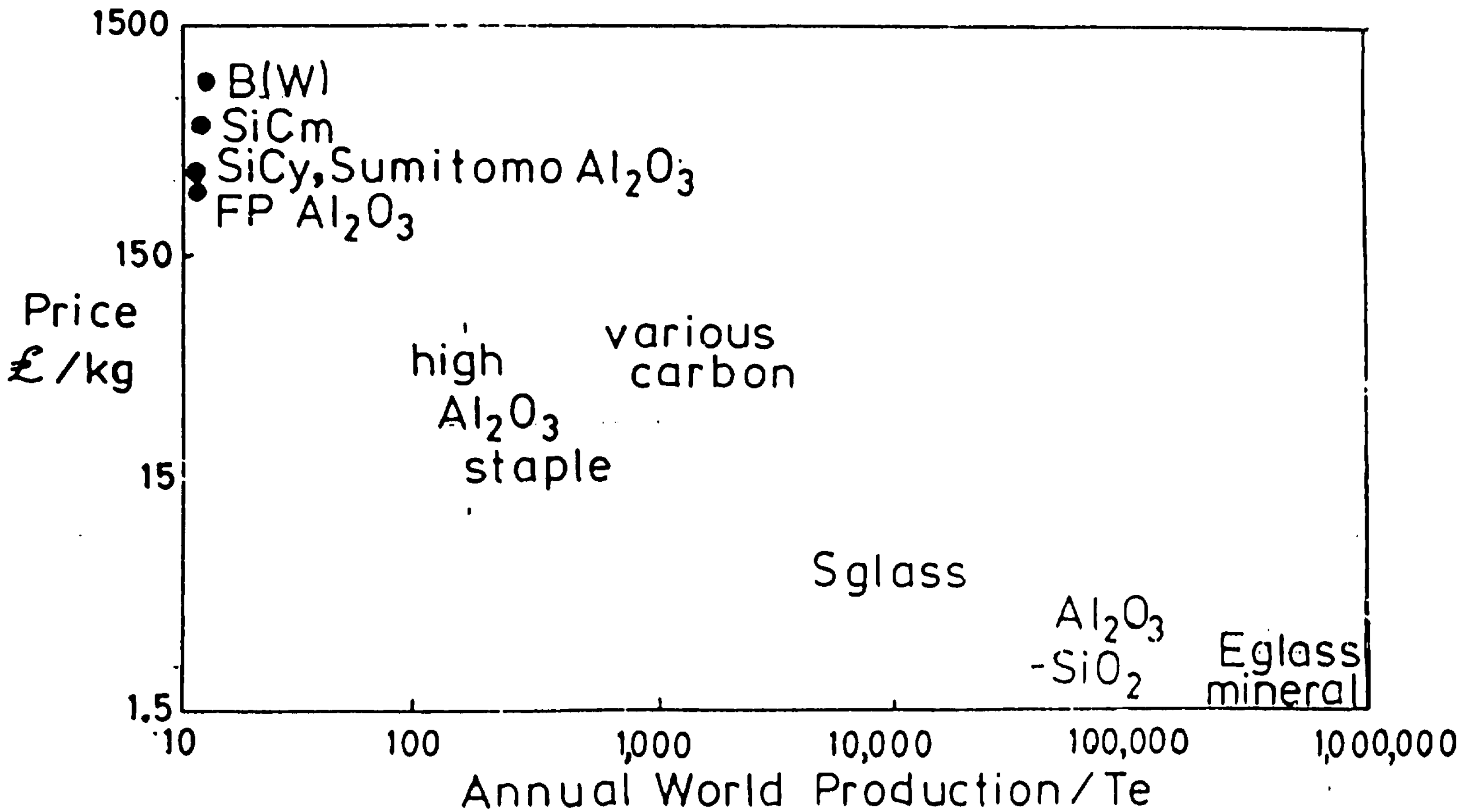
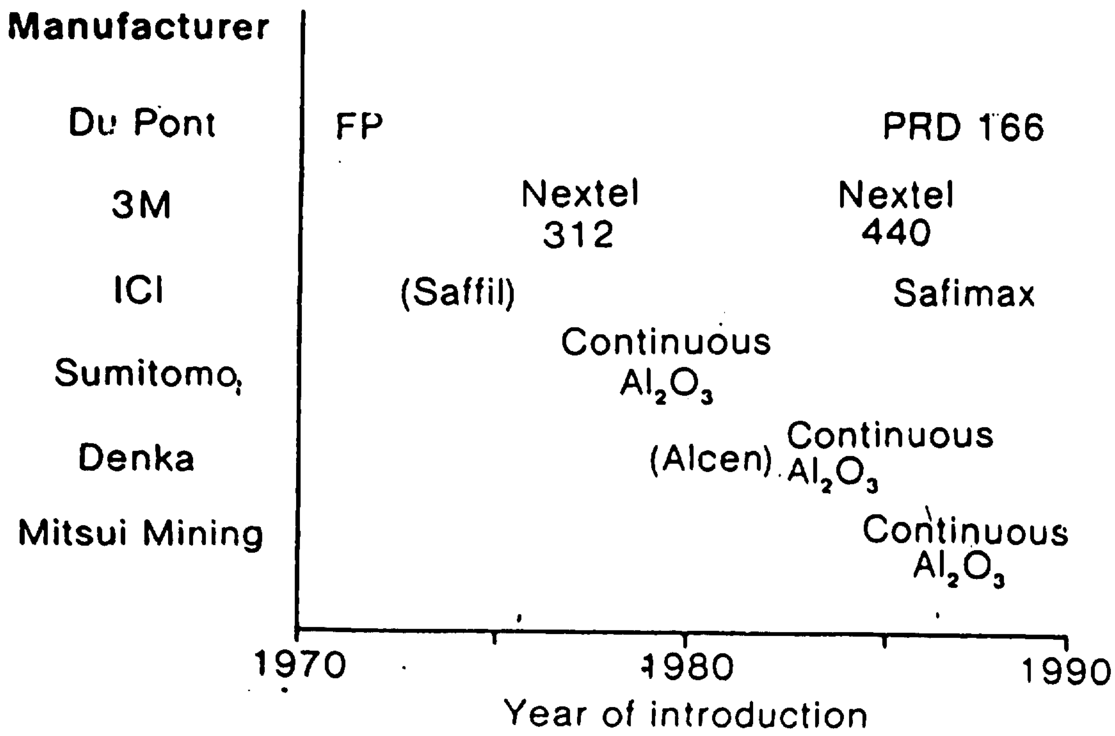

1500
B(W)
SiCm
SiCy, Sumitomo Al2O3
FP Al2O3
150
Price
£/kg
high
Al2O3
staple
various
carbon
15
Sglass
Al2O3
-SiO2
Eglass
mineral
1.5
10
100
1,000
10,000
100,000
1,000,000
Annual World Production/Te

Fig. 3

CONTINUOUS ALUMINA FIBRES UNDER DEVELOPMENT



( ) Staple fibres

ALUMINA FIBRE PROCESSES

Solution or Sol or Dispersion —(Dry Spin)→ Green fibres —(Heat)→ Ceramic fibres

Examples

1	**Solution**	Polyaluminoxane + polyethyl silicate/benzene
2	**Sols**	Basic Al salt + silica sol/water
3	**Dispersion**	Basic Al salt + 0.5μ αAl_2O_3/water

Improvements

1 Rheology modifiers

2 Grain growth inhibitors

3 Reproducible raw materials

ALUMINA FIBRE PROPERTIES

1 Potentially **cheap**

2 Chemically **inert** at high temperatures (>1000°C) in oxidising or reducing atmospheres

3 Compatible with molten **light metals** and **non-oxide ceramics**

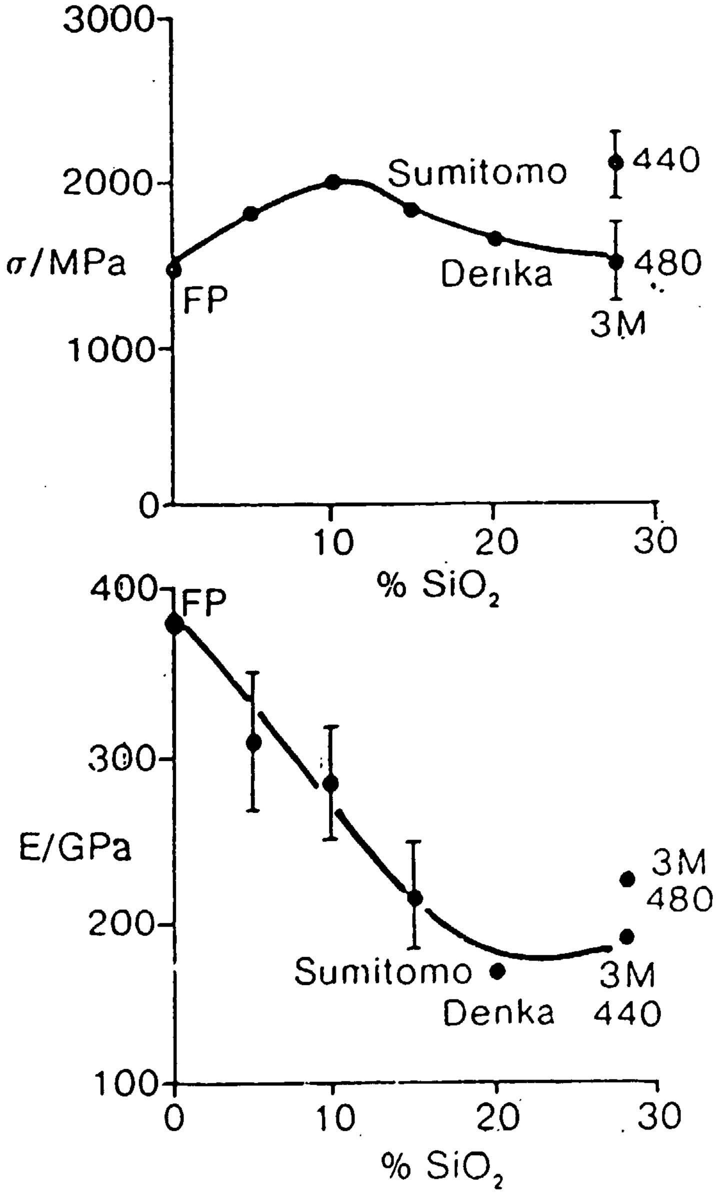
4 Electrical **insulator** with low **dielectric constant**

5 Optically **transparent/translucent**

6 **Fairly good mechanical properties** (cold) Maintained up to ca 1000°C

DEPENDENCE OF STRENGTH AND MODULUS ON SILICA CONTENT

Dinghra 1986, 3M, Sumitomo and Denka Data Sheets



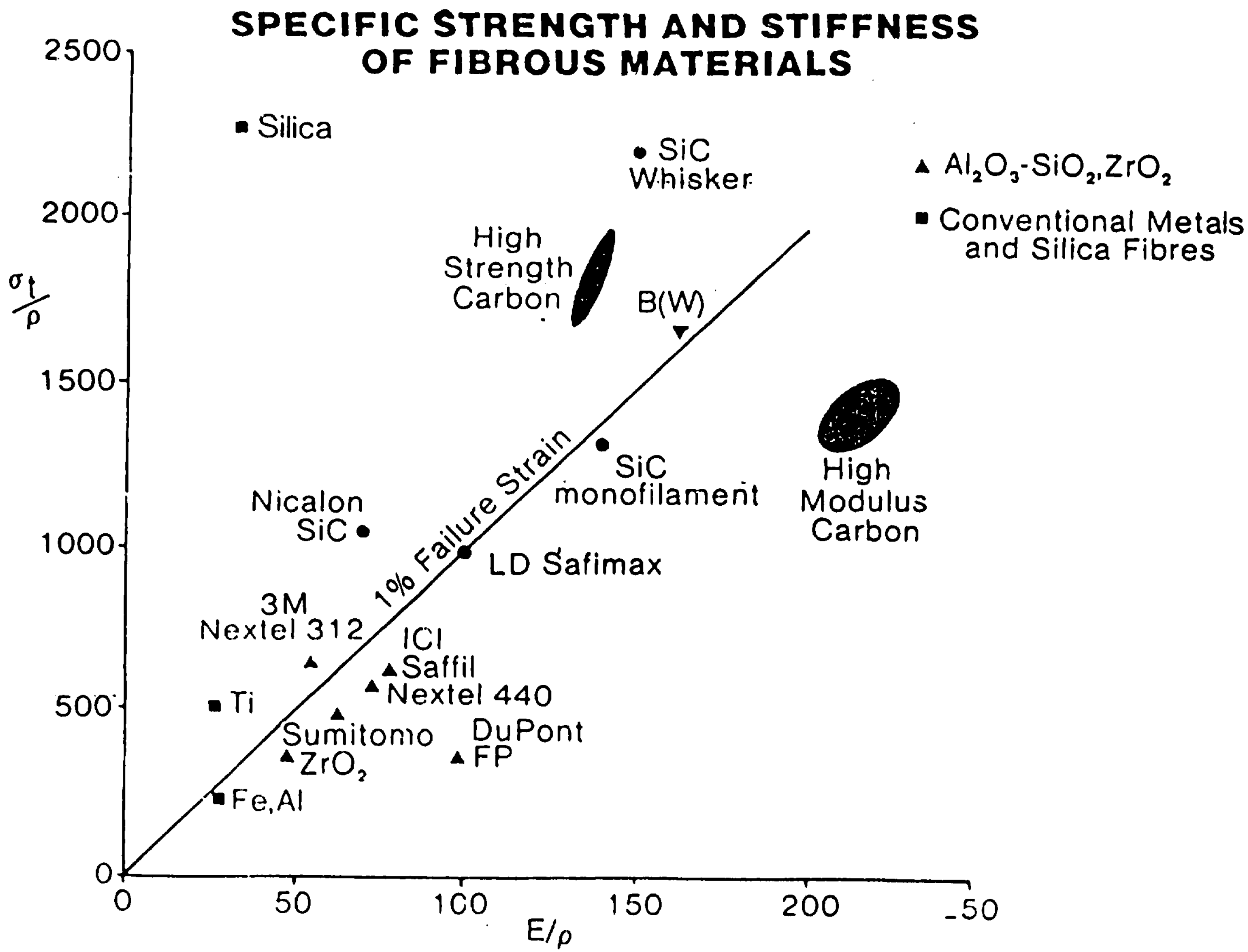

SPECIFIC STRENGTH AND STIFFNESS OF FIBROUS MATERIALS
2500
2000
1500
1000
500
0
σ_t/ρ
0
50
100
150
200
250
E/ρ
Silica
SiC Whisker
High Strength Carbon
B(W)
1% Failure Strain
SiC monofilament
High Modulus Carbon
Nicalon SiC
LD Safimax
3M Nextel 312
ICI Saffil
Nextel 440
Ti
Sumitomo
ZrO_2
DuPont FP
Fe,Al
Al_2O_3-SiO_2,ZrO_2
Conventional Metals and Silica Fibres

Fig. 5

FLEXIBILITY OF CERAMIC FIBRES