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NEW THEORETICAL DEVELOPMENTS IN THE FIELD  
OF STEELMAKING <sup>1/</sup>

by

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<sup>1/</sup> The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO.



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SUMMARY

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We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

A permanent evolution of problems and conditions in the field of steelmaking (intensification of steelmaking processes, changing in charge materials, increase in ingot weight, development of new steel grades, narrowing the ranges of constituents concentration in the old commonly used steel grades etc.) makes for developing the theoretical basis of steel production as well as continuous improvement of longstanding concepts on the mechanism and nature of individual processes and reactions as well as creating new chapters of the theory of steel melting, deoxidizing and casting.

Of great influence on the theory of steel production is the application of oxygen, the development of the oxygen-converter process, an increasingly urgent demand of a more complete metal refining from detrimental impurities and the presence of local overheatings of molten metal and slag in a number of processes.

The scientific foundations of the process theory of steel production are: physical chemistry, hydro- and aerodynamics and thermal physics of mainly liquid and gaseous mediums.

Further successes of the development of steelmaking processes theory are backed by a complex application of the improvements in all the three sciences in step-by-step consideration of all the process stages starting from the steel melting process up to the formation of steel ingots.

Of late big successes have been achieved in the field of investigating the structure and properties of molten metals, particularly, the form of impurities present there.

The availability of information about various properties of liquid alloys of iron enables us to judge with more credulity about the impurities relationship forms in molten metal, about the forms of sub-groups formed by their coherence and atoms of the solvent metal and create certain process models of their removal from the metal.

These data are the corner-stone of the kinetics of refining processes and the mechanism of metal refining.

However, reliable and practicable interpretation of modern methods of intensifying the steelmaking processes in open-hearth and electric furnaces or the steelmaking process in oxy-

gen converters can be given only by a detailed development of the problems of mass and heat transfer in a vigorously stirred bath of this or that steelmaking unit.

Of late special attention of researchers-metallurgists has been drawn to the problem of the composition of molten slags as refining media. Up-to-date clarifications of the ion theory of slag composition created as far back as 1940' enable us not only to quantitatively assess the activity of different ions but also form a concept of the nature and the process mechanism of steel refining.

There is no doubt that this fact has played a positive role in the development of such new processes as electroslag remelting, steel treatment by synthetic slags etc..

It is very characteristic of the modern theory of steelmaking processes that researchers pay a special attention to the so-called "surface phenomena", i.e. phenomena taking place on the boundary lines of adjacent phases. In this case purely chemical processes are meant, such as oxidation by gaseous oxidizers of surface of liquid-gas boundary components of molten metal (e.g. sulphur oxidation), processes of boundary transfer of liquid-gas phases without chemical transformation (e.g. process  $(H) = H_{ads}$ ), processes accompanied by inter-phase surface change (slag foaming, coagulation or coalescence of particles dispersed in liquid etc.).

The surface phenomena with regard to the steel deoxidation processes, the formation and removal of non-metallic inclusions are of a special interest in physical chemistry. It should be noted, however, that the idea of an exclusive role of inter-phase tension on a metal-inclusion boundary in the process of metal inclusions removal seems to be erroneous (of great importance is the kinetics of inclusions coarsening, availability of slagging medium, availability of convective metal flows etc.).

For the last few years substantial progress has been made in the chemical thermodynamics of steelmaking processes representing a science enabling to assess the maximum grade possible of some metal impurities removal that directly answers the question of further ways of raising the steel ingot quality, of limiting its segregation phenomena, the provision of physical homogeneity (crystal structure homogeneity and the size of inclusions etc.).

The growing availability of thermodynamic data on metal and slag as well as multicomponent phases and reactions going on among the components of these phases (inside them and on the boundaries) was greatly influenced by the development of experimental techniques of research and the growing precision of parameter measurements of high-temperature processes.

The following works should be pointed out as of special significance: the ways of direct application of the activity of some components, the process research in the field of temperatures approaching the iron rimming temperature, the specified data on heat capacity and allotropic transformations.

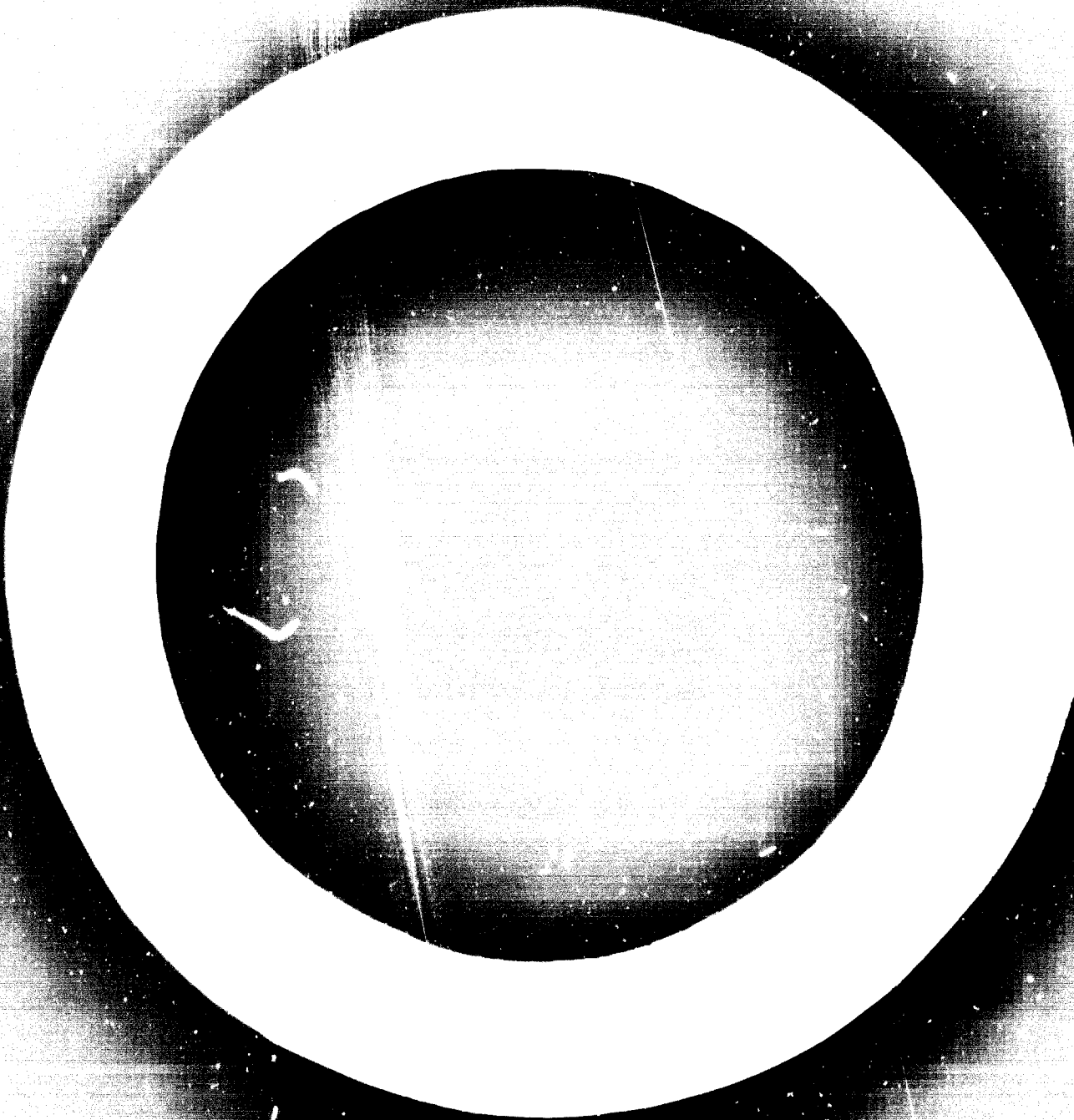
At present there is a good deal of printed matter on the activity of components in multicomponent molten metal, the value of "individual" activity ratios (taking into account only the effect of only one constituent of a complex solution on the activity of another one) and "individual" parameters of their reaction.

The greater part of these data covers molten metals. The case of molten slags leaves much to be desired and so far they are considered as "regular" solutions and the values of "heat of mixture" are mostly used when calculating the activities.

In conclusion it should be noted that up till now metallurgists have paid little attention to physicochemical processes taking place at the final stages of crystallising the steel ingot. It was considered that metallurgists have no know-how available to combat the forma -

tion of "secondary" inclusions being formed in the crystallization method revealing surface activity on the liquid metal-crystal boundaries with a development of "microsegregation" of gases etc.

However, of late the development of new powerful means of microanalysis: electronography, neutronography, x-ray engineering, various "microguns" (electronic, leizer), mass-spectrometry for gases microanalysis, gives every ground that having studied the processes making for non-homogeneity of the composition, structure and, consequently, the micro-volume properties of metal the metallurgists will find the ways to control these processes by reducing their development and further improve the quality of the cast steel ingots.





## NEW THEORETICAL DEVELOPMENTS IN THE FIELD OF STEELMAKING

A permanent evolution of problems and conditions in the field of steelmaking (the intensification of steelmaking processes, changes in charging materials, increase in ingot weight, development of new steel grades, narrowing the ranges of constituents concentration in the old commonly used steel grades, etc.) makes for developing theoretical basis of steel production as well as continuous improvement of long-standing concepts on the mechanism and nature of particular processes and reactions and creating new chapters in the theory of steel melting, deoxidating and casting.

Of great influence on the theory of steel production is the application of oxygen, the development of the oxygen converter process, an increasingly urgent demand of more complete metal refining from detrimental impurities and the presence of local overheatings of molten metal and slag in a number of processes.

The scientific foundations of the process theory of steelmaking are physical chemistry, hydro- and aerodynamics and thermal physics, mainly of liquid but partly also of gaseous mediums. Further successes in the development of steelmaking processes theory are backed by a complex application of the improvements in these three sciences in step-by-step consideration of all the process stages starting from steel melting process up to the formation of a steel ingot.

The problems solved by metallurgists in most cases come to the following three types:

1. The determination of the direction of the process under the given initial conditions.
2. The determination of the parameters of the final (equilibrium) state of the system, in which the process proceeded.
3. The determination of the rate of the process and the time necessary to complete one or another stage of this process (for instance, to reach a certain concentration of carbon or phosphorus in the molten metal).

To demonstrate the simultaneousness of the development and interaction of thermal, hydrodynamic and chemical processes in a metal bath, it is most convenient to apply to the kinetics of steel refining processes.

It has been shown by many investigations that the most of particular processes of steel production "take place in the diffusion zone", i.e. that their rate is determined not by the very act of the chemical reaction, but by the mass transfer of reacting particles,

by their entering the zone of a chemical reaction. Just this process is the most slow.

Let us consider, as an example, the oxidation of carbon on the surface of an oxygen bubble, which penetrated into the depth of molten metal as a result of blowing (in an open-hearth furnace or in an oxygen converter).

Because of a number of reasons (the oxygen being spent in reactions, floating up of the bubble of a complex composition:  $\text{CO}_2 + \text{O}_2 + \text{CO}$  etc.) the life-time of such a bubble in molten metal does not exceed several seconds (2 to 5 seconds).

Around such a bubble there is a certain zone of metal which is described in literature as an unmixable diffusion layer of liquid, i.e. such a layer in which the mass transfer of material particles takes place as in a quiescent liquid.

It should be noted that hydrodynamics admits the existence of an unmixable layer on the surface of moving liquid or a quiescent body contained in it (or, on the contrary, on the surface of a body moving in quiescent liquid).

In the theory of heat transfer to moving liquids, all calculations are based on the supposition that as though quiescent layer exists in the vicinity of the liquid contact-surface, heat transfer being only by direct conductivity in this layer, with convection not taking part in it.

It is doubtful, that under the given conditions of liquid motion) there exists quite a definite layer of unmixable particles. It is accepted, for instance, that the thicknesses of the diffusion, hydrodynamic and thermal layers are not identical. Therefore it is correct to speak about some "effective" layer, which is not equal to a certain geometrical concept.

The thickness of the hydrodynamic layer is given by the equation

$$\delta_{\text{hyd}} = \frac{\ell}{\sqrt{Re}} \quad (1)$$

where  $\ell$  = the length of the canal or wall along which the liquid moves;  
 $Re$  = the Reynolds criterion.

The thermal unmixable layer has a thickness

$$\delta_{\text{therm}} = \frac{\delta_{\text{hyd}}}{\sqrt{Pr_{\text{therm}}}} \quad (2)$$

where  $Pr_{\text{therm}}$  = the Prandtl thermotechnical criterion;

$$Pr_{\text{therm}} = \frac{\nu}{\alpha} \quad (\text{where } \nu = \text{dynamic viscosity, } \alpha = \text{thermal conductivity}).$$

Similarly, the diffusion layer has a thickness

$$\delta_{\text{diff}} = \frac{\delta_{\text{hyd}}}{\sqrt{Pr_{\text{diff}}}} \quad (3)$$

where  $Pr_{\text{diff}} = \frac{\nu}{D}$ , and  $D$  is a coefficient of molecular diffusion in liquid.

On the analogy of mass and heat transfer in metal and employing Gauss' method, based on the use of the Fourier-Fick criterion, it may be written that with the complete decarbonization of the monomolecular layer situated on the surface of the given bubble, the carbon concentration  $C/x$  at the distance  $x$  from the surface of the metal will be expressed by the equation

$$C/x = C_{\text{limit}} \cdot f\left(\frac{x}{2\sqrt{D_c t}}\right) \quad (4)$$

where  $C_{\text{limit}}$  = the initial carbon concentration (assume  $C_{\text{limit}} = 1.0\%$ );  
 $D_c$  = carbon diffusion coefficient (at  $t = 1600^\circ\text{C}$  this coefficient is equal to  $6 \times 10^{-4} \text{ cm}^2/\text{sec}$ );  
 $t$  = diffusion time (in this case the time of the existence of the oxygen bubble, assume  $t = 4 \text{ sec}$ ). It can be calculated that during the time of

the existence of the bubble, the depth of the diffusion wave penetration  $X = 4\sqrt{D_c \tau} = 0.2 \text{ cm.}$ , i.e. at this depth  $C/x = C/\text{unit}$  already, because the criterion function  $(\frac{x}{2\sqrt{D_c \tau}})$ , according to Goussier is equal to unity and that the maximum flow of the carbon diffusion, according to Fick is

$$V_c = \frac{dC/dt}{dx} = \frac{D}{dx} \frac{dC}{dx} \quad (5)$$

which will amount to  $0.28 \text{ kg C/m}^2 \text{ hour}$ . This is essentially lower than the carbon flow which is oxidized under the conditions of an oxygen converter process (e.g., for a 50-ton converter, the rate of carbon oxidation related to the conventional bath-surface,  $V_c = 1200 \frac{\text{kg C}}{\text{m}^2/\text{hour}}$ ).

This means that the average relative contact-surface of oxidizing gases and metal during a heat is at least three orders of magnitude larger than the conventional bath-surface of the converter.

At the same time, to provide for intensive decarbonizing a thin (1 to 2 mm.) layer of metal contacting a gaseous phase, it is necessary to have a continuous feed of carbon to these layers and this feed must be vigorous enough so as to support a small thickness of the diffusion layer and a large value of carbon-concentration gradient in it.

In this case a turbulent mass-transfer in the depth of metal is of paramount importance.

The effective coefficient of the turbulent diffusion can be represented in its general form by the following equation:

$$D_{\text{eff}} = \frac{0.028 V d}{\nu^{0.25}} = 0.028 V^{0.15} d^{0.15} \nu^{0.25} \quad (6)$$

where  $V$  = the velocity of liquid motion;

$d$  = hydraulic diameter of the flow;

$\nu$  = kinematic viscosity of the liquid.

It has been found experimentally that the effective diffusion coefficient with the basic open-hearth process has a value in the range of 25 to 80  $\text{cm}^2/\text{sec}$ . With an oxygen converter process it amounts to several thousands  $\text{cm}^2/\text{sec}$ , i.e. it exceeds the molecular diffusion coefficient  $10^6$  to  $10^7$  times.

In this connection it becomes clear that the rate of oxidation processes is closely connected with the hydrodynamics of a molten bath. To find new ways of intensifying the process requires a complex investigation of its chemism, hydrodynamics and heat transfer in metal.

It is premature to say that at present the quantitative solving of problems arising in this field is already available, but many points are already becoming clear, for instance, by means of simulation, naturally, with taking into account specific features of each of these three processes: hydrodynamics, mass transfer and heat transfer.

The investigation of mass transfer in liquids (in metal and slag) has been greatly assisted by use of man-made radio-active isotopes as well as by the development of new methods for laboratory investigations of diffusion in molten metals and slags, an improved measuring technique for high temperatures and other achievements of physical chemistry, therotechnology and hydrodynamics.

The combined application of the laws of heat transfer in liquids, hydrodynamics (mass transfer, in particular) and physical chemistry of metallurgical processes has rendered a great service in investigation of such processes as electroslag refining, the continuous spray process of steelmaking (BISRA), in discovery of a number of important details in the interaction between liquid metal drops and slag, in explanation of the role of gas bubbles (for instance, CO) in this process, in estimation of the role of heat convection and mechanical agitation of metal. In this way, some important features have been discovered of such "old", processes as open-hearth and converter ones though dominating because of their importance.

In the past few years significant success has been attained in the field of investigating the structure and properties of metallurgical melts both of metal and slag, and, specifically, in investigation of the forms of presence of various components in these melts.

It is safe to say that understanding the nature of metal refining processes, crystallization of metal, the appearance of some fine-structure defects in cast metal is completely based on the modern theory of liquid metal structure and the forms of impurity occurrence in melt.

It is natural that the quest for ways of perfection of refining processes and improvement of the structure of crystallized metal is in its main points based on the established principles of the theory of the structure of liquid metals and metallurgical slags.

Among numerous, though still insufficiently supported by experiments, theories of structure of liquids, in application to metal refining, it should preferably be used the model of an ideal crystal in which the long-range order of atomic arrangement has been completely disturbed, but the order of the arrangement of the neighbouring atoms, in respect to each given atom, has survived.

This partial ordering of structure, called "short-range order", is corroborated by the investigations into a number of properties of liquid metals (density, vapour tension, thermal capacity, etc.) as well as by thermodynamic and X-ray structural analysis.

It has been shown, for instance, that the static distribution curves for pure iron are similar to those for  $\alpha$ -iron (i.e. they correspond to the structure of a volumetrically centered cube), whereas X-ray patterns for iron-silicon alloys are similar to X-ray patterns for germanite (face centered cube).

When liquid metal is cooled, especially when its temperature approaches the liquidus temperature, there occur changes in the physical properties of metal (its viscosity, thermal conductivity, etc.) due to an increase in the volume of the short-range order, i.e. approaching solid state.

Investigating forms of the presence of impurities in metal is of great importance for the theory of metal refining processes. The thermodynamics and, probably in a greater degree, the kinetics of removing impurities from metal greatly depend on the binding energy of the particles dissolved in the metal as well as the solvent itself, on the forms of this binding, and the type of grouping formed by the impurities with atoms of the solvent.

Without having recourse to a description of numerous experimental investigations of this problem, only certain most likely results of such investigations will be presented herein.

Some oxygen and sulphur are dissolved in their ion form  $O^{2-}$  and  $S^{2-}$  in molten metal. They form relatively stable groups with the surrounding iron ions,  $Fe^{2+}$ , at the expense of the Coulomb forces (a heteropolar bond). The bonds between the ions within these groups are stronger than their bonds with the surrounding particles of the solvent (though, under favorable conditions an iron ion neighbouring with an  $O^{2-}$  oxygen may be replaced by another iron ion). The weak bonds between groups  $Fe^{2+} - O^{2-}$  or  $Fe^{2+} - S^{2-}$  and solvents result in the displacement of these groups to the boundaries between the melt and the phase surrounding it (lowering of the surface and phase interfacial tensions of the melt) or in their passing into other phases, for instance, into slag. Phosphorus and nitrogen are characterized by a smaller energy of interparticle interaction with atoms (ions) of iron, this accounts for the fact that they to a lesser degree affect the thermodynamic characteristics and physical properties of liquid iron. However, most likely is their forming relatively stable groups of the type  $2Fe-P$  and  $2Fe-N$ . Only at high

concentrations of phosphorus or nitrogen the bonds within such groups become completely saturated, i.e. molecules  $Fe_2N$  with heteropolar bond are formed, which manifests itself, for instance, in a substantial lowering of surface tension of the melt, in an increase of its viscosity at a given overheating above the liquidus line, etc.

Taking into account the different degrees of bond saturation within individual groups  $Fe-S$ ,  $Fe-O$ ,  $2Fe-P$ ,  $2Fe-N$ , the simultaneous presence of two or more forms of existence of each of these metallides dissolved in iron is often spoken about. It appears that this supposition is justified primarily for iron-carbon alloys. By analogy with certain alloys of Fe-S it may be expected that some of the carbon is present in its ion form  $C^{4+}$  or  $C^{2+}$ . On the other hand, according to some data, already at low concentrations of carbon (0.5 to 0.7%) there begins a process of consolidation of graphite particles and formation of graphite colonies.

Finally, there is much data indicating that groups are formed which in their composition approach  $Fe_3C$ . Despite the foremost importance of Fe-C alloys, too little reliable experimental data is accumulated, and it is difficult to estimate the portion of carbon contained in each of these three forms of existence, or to say with certainty that none is present.

As to alloying components (Mn, Cr, Ni, Mo, etc.), they all form in iron solutions which approximate ideal ones in which binding forces between identical atoms (or ions) approximate those between different atoms (or ions)  $x^i$ . That is  $A \leftrightarrow A \leftrightarrow B \leftrightarrow B \leftrightarrow A \leftrightarrow B$  i.e. such melts as Fe-Mn, Fe-Ni, etc., resemble to a certain degree, intrusion solid-solutions.

Only silicon and, to a certain extent, aluminium show an increased energy of binding with atoms of iron when dissolved in it. At any rate in Fe-Si alloy have been found groups approximating stoichiometric composition of Fe-Si, which has been completely proved, and with 33% by weight, content of silicon, the melt preserves, to a certain degree, many typical features of liquid metals.

The past few years have been characterized by considerable successes in investigation of the structure of liquid metallurgical slags.

As far back as forties, the ionic theory of the structure of metallurgical slags was created and developed as an independent science. It should be noted that by that time, in many fields of chemistry, technique, petrography, it had been recognized that the crystal lattice of such minerals as oxides, sulphides, halides consists of electrically charged ion particles, that they do not represent a conglomerate of electrically neutral molecules with the completely saturated valent (ion) bonds within each of them.

Even such almost electrically non-conducting minerals as quartz ( $SiO_2$ ) or rutile ( $TiO_2$ ) represent a continuous "tying" of cations (in the present case  $Si^{4+}$  and  $Ti^{4+}$ ) and oxygen anions.

Melting such minerals yields solutions of relatively small ions (cations such as  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$  etc. and anions,  $O^{2-}$ ,  $S^{2-}$ ,  $N^{3-}$ ) and large complexes, always negatively charged, for instance, silicon-oxygen, aluminium-oxygen, phosphorus-oxygen, etc. ( $SiO_4^{4-}$ ,  $Si_2O_7^{6-}$ ,  $Si_3O_9^{6-}$ ,  $AlO_2^-$  etc.).

The divergence of opinions of the investigators came, in the main, to the point concerning the portion and, consequently, the role of the energy of ion heteropolar bond within separate anion complexes. Assumptions have been stated that electrically undissociated molecules exist together with ions, though such a conception should be considered erroneous.

The hypothesis of microheterogeneity of slag caused by Coulomb forces has played a great role in understanding processes taking place with participation of slag.

For instance, in a melt consisting of the following ions:  $Fe^{2+}$  (0.83%),  $Ca^{2+}$  (1.06%),

x/ In fact these melts are still not ideal, but they approximate the ideal ones closer than other solutions in iron.

$O^{2-}$  (1.4Å),  $SiO_4^{4-}$  (2.7Å) (everywhere in parentheses are shown the effective radii of the ions), oxygen ions bunch primarily near the iron ion, because it is a stronger one (the force of the ion is estimated according to the value of the ratio of its charge to the effective radius), whereas as the share of the weaker calcium ions and as their neighbours, remain  $SiO_4^{4-}$  ions (which to a lesser degree are subject to polarization) or  $Si_2O_7^{6-}$  ions which result from the disintegration of  $SiO_4^{4-}$  ions according to the equation:  $2SiO_4^{4-} = O^{2-} + Si_2O_7^{6-}$ .

All the studies of this kind have enabled metallurgists to profoundly analyse the transition of impurities from metal into slag, to realize the role of the slag as a substance transferring oxygen or hydrogen to the metal from the furnace atmosphere, protecting the metal from penetrating nitrogen and sulphur into it from the furnace atmosphere and as a medium which is able to assimilate non-metallic inclusions which come to the surface from the liquid metal. As is generally known, on this case these methods for metal purification as electroslag refining, a treatment by means of synthetic slags, casting under exothermic slags, an application of exothermic ferroalloys, etc.

The investigation of the mechanism and kinetics of the processes of refining metal by means of gas and slag phases gave rise to the emergence of a new branch of the theory of metallurgical processes, the physical chemistry of surface phenomena, i.e. a branch of physical chemistry which studies processes taking place on contact surfaces such as metal-slag, metal-gas and even metal-solid (refractories). Unlike any particle situated within a volume of liquid, the resultant force of mutual attraction between this particle and its neighbours is not equal to zero. It is directed toward, and perpendicular to the surface of the liquid, and determines a specific energy state of the surface layer of the particles which is termed as "surface energy" or "surface tension".

This specific energy state of the surface layer results, for instance, in a pronounced irregularity of the distribution of the dissolved matter and, to a certain extent, in enriching the surface layer of the liquid by this matter, i.e. in so-called adsorption (symbolized as  $\Gamma$ )

$$\Gamma = - \frac{1}{R T} \cdot \frac{d\sigma}{dC} \quad (7)$$

where  $C$  = concentration of dissolved matter;

$\sigma$  = surface tension, erg/sq.cm.

Using the conception of adsorption it is possible, at least semiquantitatively, to estimate the concentration of the dissolved matter in the adsorption layer, if the influence of the concentration of the dissolved matter has been determined experimentally. For instance, it is known, that at a sulphur concentration of 0.05 to 0.06 % by volume, the ratio of the quantity of the atoms of iron and sulphur in the surface layer is equal to one, i.e. in its composition, this layer approximates the compound FeS.

The theory of adsorption processes is to be employed when are investigated such processes as the oxidation of carbon and sulphur on the surface of metal drops situated in an oxidizing gas, as the adsorption of gases from a gas phase, for instance,  $H_2 = 2H$ ,  $2H = 2H_{ads}$  and  $2H_{ads} = 2H$  and the reverse processes (gas desorption). A number of physical phenomena are also connected with and determined by surface forces and the motive power of all these processes is the excessive surface energy, which has been concentrated on the surface of some dispersed phases.

It is evident, that the more dispersed is the given phase, the larger is the specific contact surface of this phase with the phases surrounding it:

$$f_{spec} = \frac{S}{V}$$

( $F$  = total surface of the particles of the phase,  $G$  = total weight of the particles of this phase), the clearer manifests itself the action of the surface forces.

As the examples showing the manifestation of these forces can serve the formation and "settling" of slag foam, dissolving of hard particles in slag, "wedging" effect, the Merangoni effect, "structuring" of the surface slag-layer, etc.

The theory of surface phenomena has found an especially wide application in refining metal from non-metallic inclusions namely, the products of decaridation. All the stages of this complex process, i.e. the conception of the inclusions, their growth, their coalescence, or mutual adhesion, and, finally, their floating up and being absorbed by slag media, are caused by the tendency of the system to the decrease in the energy concentrated in it and to the decrease, according to the second law of thermodynamics, in the surface energy content according to the equation:

$$\Delta Z = \Delta S \times G' + \Delta Z$$

where  $\Delta Z$  = change in the interphase surface of the system,

$G'$  = interphase specific energy of the system,

$\Delta Z$  = change in the isobaric-isothermal potential.

In the literature there are statements to the effect that a high value of the specific interphase energy at the interface of the phases, namely, inclusions-molten metal, are the main cause providing for an extremely high rate of the removal from the metal of inclusions which are as if in a "physical disagreement" with the surrounding metal.

This point of view should be considered as erroneous. The interphase energy alone does not represent a vectorial value and cannot cause a directed movement and removal of inclusions, it can only either facilitate or hamper this process.

If the interphase energy at the interface of metal-inclusions, is large, this facilitates the mutual adhesion of inclusions, their consolidation; the force causing floating up increases; also increases the probability that inclusions will be carried out by the upward convection currents of metal and, in most cases, increases the rate of the absorption of inclusions by the slag layer, if there is such on the surface of the metal.

Chemical thermodynamics has achieved great successes in the mathematical description of individual processes of steelmaking. As a science describing the equilibrium of the processes, thermodynamics, with the modern level of experimental technique, has great possibilities for finding the equilibria itself and studying the dependence of the equilibrium state on external conditions.

In the recent years the tasks of the chemical thermodynamics of steelmaking processes have been as follows:

1. The verification of the formerly obtained data concerning the change of the thermodynamic functions of the system state with heating, with allotropic changes, the formation of solutions and chemical reactions.
2. Studying the equilibrium of various processes in widened temperature ranges.
3. Studying the nature of molten metal and slag, the possibility of the application in such studies of the laws which govern the ideal, real and regular solutions and finding ways for determination of the activity of components of such solutions. Under conditions of modern metallurgical processes, are involved rather high temperatures (2500-3000°K and even higher), which metallurgists had not to deal with before, and for which it would be erroneous to extrapolate the relations experimentally found for considerably lower temperatures. In this case are involved extremely high temperatures of the reaction zone involved with oxygen blowing in converters and open-hearth furnaces, strong overheating of metal in electroslag refining and vacuum arc remelting and any other processes.

As an example of the necessity of an experimental study of high temperatures, below will be given two equations for the solubility of nitrogen in pure iron:

$$\lg S_N = \lg \frac{[N]}{\sqrt{p_{N_2}}} = - \frac{262}{T} - 0.95, \text{ G. Shenk et al.}$$

$$\lg S_N = \lg \frac{[N]}{\sqrt{p_{N_2}}} = - \frac{1050}{T} - 0.815 + \frac{1}{2} \lg \left( 1 - \frac{P_{Fe}}{P_{bar}} \right), \text{ the present author et al.}$$

Where  $P_{bar}$  is the barometric pressure during the experiment,  $P_{Fe}$  is the iron-vapour tension at the temperature of the experiment. Both equations give very similar results for temperatures in the range of  $T = 1800^\circ - 1950^\circ \text{ abs.}$  whereas at temperatures in the range of  $T = 2800^\circ - 2900^\circ \text{ abs.}$  the first equation gives almost twofold greater values, for it does not take into account the evaporation of iron and, consequently, when the pressure is fixed at 1 atm in any part of the recipient, it does not allow for the fact that we cannot produce the same nitrogen pressure in a side-volume of the gas contacting the liquid iron. The evaporation of iron creates, as it were, a kind of "blowing-off" of the nitrogen from the surface of the iron.

The one-atmosphere pressure of the nitrogen contacting the overheated iron can be obtained only under a considerably higher pressure of this gas in the whole reaction volume.

An extremely complex task confronted the metallurgists in the field of estimating the activity of the components of molten metal and slag. Numerous experiments show that in the temperature ranges usual for steel production, metal and slag are very far in their properties from ideal solutions. Therefore, in all expressions of equilibrium constants, not the concentrations of the reacting substances must be present, but their activities. This involves difficulties in determining activity values ( $A$ ) or activity coefficients ( $\gamma$ ) according to the composition of the melt and its temperature

$$A_c = \gamma_c / C$$

where  $C$  is a weight concentration of the dissolved substance. Only if for the melt under investigation we assume a certain model, for instance, that the solutions of Cr, Ni, Mn, etc. in iron approximate ideal ones, or, that the solutions of S, C, O, etc. in liquid iron close by regular ones, it is possible to give some recommendations for calculating activity coefficients ( $\gamma$ ) or interaction parameters for solution components ( $\epsilon$ ) (as is generally known, the interaction parameter is determined by the expression

$$\epsilon = - \frac{2 \lg \gamma_c}{C}$$

Even these simplified cases of calculating ( $\gamma$ ) involve difficulties associated with the fact that we generally have to deal with multi-component solutions in which several components usually influence the value of the activity coefficient of a given component. In other words, the following relation is true for multicomponent melts:

$$A_c = \gamma_c / C = \gamma_1^c \cdot \gamma_2^c \cdot \gamma_3^c \dots / C$$

To determine each of the particular values of  $\gamma$  is extremely difficult. G. Shenk has done it for three component solutions in iron, assuming that the iron itself does not influence the activity coefficients of both dissolved substances and taking into account only their reciprocal influence (i.e. taking into account only the values of  $\gamma_1^c$  and  $\gamma_2^c$ ).

In view of the inevitability of rough assumptions and inaccuracy of such calculations, of particular interest is the direct experimental determination of the activity of components dissolved in metal.



As far as it is known, substantial successes in this direction have been achieved only in determining the activity of dissolved oxygen.

To determine the activity of components in slag, use has also very often to be made of different models, such as the perfect ionic solution, the regular solution, etc.

It is obvious that each of these models is more or less applicable to only a certain group of slags, to a certain extent of their compositions.

For the basic slags consisting of oxides: FeO (molar fraction  $N_1$ ), MnO (molar fraction  $N_2$ ), CaO (molar fraction  $N_3$ ), MgO ( $N_4$ ), SiO<sub>2</sub> ( $N_5$ ) and P<sub>2</sub>O<sub>5</sub> ( $N_6$ ), assuming them to be regular solutions, V.A. Kozhurek derived equations for activity coefficients and these equations have already found a wide application. They are as follows:

For ferrous oxide:

$$\lg \gamma_1 = \frac{1000}{T} \left[ 2.13N_1 + N_5 + 9(N_3 + N_4)N_5 + 10.5(N_5N_6) \right]$$

For manganese oxide:

$$\lg \gamma_2 = \lg \gamma_1 - \frac{2100}{T} N_5, \quad \lg \gamma_3 = \lg \gamma_1 - \frac{10500}{T} N_3, \text{ etc.}$$

The numbering for the coefficients  $\gamma$  is preserved the same as that for molar fractions.

The calculations of all the coefficients which stand in the right equation-members are based on the heat of mixing of the oxides. For MnO and SiO<sub>2</sub>  $\Delta H_{2,5} = -10000$  cal. For CaO and SiO<sub>2</sub> as well as for MgO and SiO<sub>2</sub>  $\Delta H_{3,5} = \Delta H_{4,5} = -22700$  cal. For CaO and P<sub>2</sub>O<sub>5</sub>  $\Delta H_{3,6} = -48000$  cal.

The heat of mixing FeO with SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> is assumed to be equal to zero.

A wide popularity have also acquired the triple and quasitriple diagrams of slag systems, permitting, for instance, to determine the activity of ferrous oxide or calcium oxide. An exceptional success in this field has been achieved by D. Chipman's school.

In conclusion, it is expedient to dwell on one more field of the theory of steelmaking processes. It may be conventionally termed as physical chemistry of micrometallurgical processes, i.e. such processes which occur in submicro- and microvolumes of metal when it solidifies.

Work in this field is challenged to discover the dependence of the properties of the produced (primarily, cast) metal on those processes which take place during the crystallization of the metal in the small volumes of metal which are still liquid and are enclosed among growing dendrite axes.

In these volumes still go on deoxidation processes due to the fact that with the drop in temperature of the metal, changes occur in equilibrium concentrations of the deoxidizing elements and dissolved oxygen, non-metallic inclusions, such as sulphides, precipitate because of the decrease in their solubility in metal when it cools, and, finally, there takes place the evolution of gases from the solution and the formation of some types of porosity.

Till quite recently, studies of these processes were greatly hampered by lack of appropriate technical means.

At present, in different countries have appeared and been successfully applied various methods for structural analysis: electronography (electron diffraction study), roentgenography, neutronography (neutron-diffraction study). Of especial value for the purposes which have been mentioned above are such instruments as scanning (i.e. successively examining the specimen from edge to edge) electron microanalyzers. They are based on the appearance of X-radiation on bombarding the surface of metal by electrons. This enables a quantitative determination of components in the exposed portion of the metal, for instance, an analysis

of non-metallic inclusions which occur in the irradiated area.

Interesting data can be obtained by combining a laser and a mass-spectrometer. By means of such a device it is possible, for instance, to study microirregularity in the distribution of hydrogen in metal. It should be noted that different structural components of steel (ferrite, perlite) or cast iron (cementite, perlite, ledeburite, graphite) have different contents of hydrogen. In specimens of cast austenitic steel, hydrogen content is almost uniform in the whole volume of a grain, but is highly increased (by 5-4 cu.ca. /100 g) in boundary zones of the grain.

It may be presumed that the development of methods for microanalysis will permit to disclose the genesis of the appearance of some defects in metal and to develop methods for their prevention.



