Surface Phenomena: A Cornerstone of Iron and Steelmaking Processes

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Mr. Masao YUKAWA was a very prominent personality of the Japanese Iron and Steel Industry. This year, on his 90th birthday, I am pleased to contribute to acknowledge the very important part he played in the spectacular development of Iron and Steel Technology in Japan, which was also taken as a lesson in many industrial countries in the world.

As a good example of his spirit of international cooperation, it is worthwhile to mention his participation in the construction of the USIMINAS steel plant in Ipatinga, Brazil, which I had the opportunity to visit and to see in successful operation some years ago.

It is, for me, a great honour to have been invited to join, in 1993, the very impressive list of distinguished YUKAWA Memorial Lecturers.

As Masao YUKAWA had a very wide perspective of Iron and Steelmaking Processes, I will try to day, in memory of him, to show the importance of Surface Phenomena, a real “cornerstone”, in pyrometallurgical processes involved in steel production.

1. Introduction

Most of the important chemical reactions involved in pyrometallurgical methods, and particularly in iron and steelmaking processes, are essentially heterogeneous. The different phases taking part in these reactions are separated by interfaces through which various substances must move.

The intention of this review is to try to give a synthetic idea of our present knowledge of the important role played by interfacial phenomena (at high temperature) in iron and steelmaking operations.

Various aspects of these interfacial phenomena have

been examined by many authors, from the first decades of the XXth century.

The first of them was very likely Darken, when pointing out the importance of the extent of interfacial areas in discussing rates and kinetics of the open hearth reaction,^{1,2)} as it was mentioned at the Darken conference³⁾ by Elliott, the 1974 Yukawa Memorial Lecturer. Pioneering work in this field was also carried out by Kozakevitch who considered, in numerous papers, the surface properties of liquid metals and oxide melts,^{4–10)} and interfacial features between liquid metals and solid or liquid oxide phases.^{11–14)} This work was continued at IRSID for many years.^{15–18)}

In 1971, Richardson, the first Yukawa Memorial Lecturer, published careful considerations on bubbles formation in extractive metallurgy.^{19,20)}

More recently, research work was performed in the USA by Cramb *et al.*^{21,22)} and, to a larger extent, in Japan, where a special ISIJ Committee of Interfacial Transport Phenomena, created in 1986 and chaired by Tokuda²³⁾ organized the activities of 5 working groups, which were summarized in the January 1992 special issue of *ISIJ International*.

Several prominent examples demonstrate the important controlling behaviour of interfacial phenomena in steelmaking reactions:

(1) Every steelmaker knows that the rate at which carbon monoxide bubbles nucleate and grow plays a dominant role in the dynamics of refining steel and this rate is largely controlled by interfacial properties: it must be remembered that in a 200 t BOF converter, the total interface area was estimated to be more than 50 000 m² due to metal–slag emulsion formation.²⁴⁾

Iron shot was found occasionally in blast furnace slags,

Fig. 1.
Iron shot extracted from a slag:

but it can be very abundant in BOF slags and Fig. 1 shows droplets extracted from such a converter slag.^{25,26,9)}

(2) Consequently, the expansion of molten slag by CO bubbles evolving from slag-metal interface, the slag-foaming,^{27,28)} can produce an overflow from the lip of the furnace, causing a metal loss and interruption of the operation. A similar foaming phenomenon is also observed in newly developed pretreatments of hot metal and bath smelting of Fe and Cr ore.^{29,30)}

(3) Adsorption precedes absorption and it is well established that the flux of nitrogen into liquid iron is strongly reduced by the presence of minute amounts of strongly adsorbed species such as oxygen and sulphur^{31,16)} as shown on Fig. 2.

(4) In secondary metallurgy, the formation of solid inclusion clusters, coalescence of liquid inclusions and

Fig. 2. Kinetics coefficient of nitrogen absorption in liquid iron as a function of oxygen content around 1 550°C.

Fig. 3. Scanning electron microscope image of alumina clusters.

Fig. 4. X-ray photograph at 1 500°C of a sulfur containing iron drop.

possible elimination of both are much affected by interfacial phenomena: for example, wetting or contact angle values between liquid metal and oxide phase are quite determining.^{32,33,21)} Figure 3 presents an example of alumina inclusions clusters.³³⁾

(5) Inclusions can be entrapped at a refractory interface and this phenomenon is responsible for nozzle blockage and also for the possibility of steel filtration using ceramic structures.²¹⁾

(6) There is much evidence that the interface between certain oxide phases and molten iron alloys may be upset by spontaneous interfacial motion. Kozakevitch,^{11,12,13,9)} was the first to observe such a phenomenon in a metallurgical operation (desulphurization of hot metal by a blast furnace slag) as illustrated by Fig. 4.⁹⁾ Another example was given by Riboud and Lucas when an oxidizing slag is in contact with a liquid steel, rich in a strong deoxidizer such as Al.¹⁷⁾

(7) In the corrosion of refractory materials, preferential attack is often observed at gas/slag and slag/metal phase boundaries as shown on Figure 5,³⁴⁻³⁶⁾ example mentioned by Richardson³⁴⁾ of the corrosion of an alumina crucible by lead and a SiO₂-PbO slag.

With regard to these erosion patterns traditionally referred to as "slag-line" or "flux-line" erosion, and, more generally, considering the spectacular increase of the mass transfer in some metallurgical reactions, the importance of Marangoni flows at the slag-metal interface, almost completely ignored for a long time, has been demonstrated these last 30 years by many authors.³⁷⁻⁴⁰⁾

The purpose of this paper is to present a condensed overall survey of the various aspects of interface phenomena involved in the iron and steelmaking processes by considering successively the following topics:

- Quantitative approach of interfacial properties at equilibrium: surface tension of liquid iron alloys and slags, interfacial properties between liquid metal and oxide phases, including contact angles.
- Study of the evolution of interfacial properties during mass transfer: liquid metal/slag interface upset by spontaneous interfacial reaction and consideration of the role of the Marangoni effect in the interfacial turbulence.
- Examination of various examples along the steel production line: BOF steelmaking, secondary metallurgy including inclusions removal, nozzle blockage, corrosion of refractories.

Fig. 5. Preferential attack of a laboratory crucible at the meniscus level slag/gas and metal/slag observed by F. D. Richardson.

2. Quantitative Approach of Interfacial Properties at Equilibrium

To understand interfacial phenomena in steelmaking, the necessary first step is to measure, as exactly as possible, surface properties at equilibrium: surface tension relative to the different liquid phases involved, contact angle and interfacial tension between liquid steel and relevant solid and liquid oxide materials.^{41,46)}

2.1. Iron

The surface tension of pure liquid iron (and also that of most common metallic alloying elements) is very high: about $1800 \text{ mN} \cdot \text{m}^{-1}$ at 1550°C (25 times larger than the surface tension of water), as was found by Kozakevitch and Urbain,^{5,8,9)} using the sessile drop method.

When examining literature, values obtained from 1950 until now are extending from around 1400 to $2300 \text{ mN} \cdot \text{m}^{-1}$.^{43,44)} Data from recent and very careful measurements carried out by Jimbo and Cramb⁴⁴⁾ induce these authors to propose:

$$1905 \pm 50 \text{ mN} \cdot \text{m}^{-1}.$$

By the way, it is interesting to take notice of a negative temperature coefficient of this surface tension [$-0.54 \text{ mN} \cdot \text{m}^{-1} \text{K}^{-1}$, after Schade *et al.*⁴⁵⁾] which leads to a γ_{Fe} value of around $2200 \text{ mN} \cdot \text{m}^{-1}$ at 1025°C , in undercooled state.

Typically non-metals, and more generally the elements of “B” columns of the periodic table, but particularly of the VIth group, are highly surface active in liquid iron, as shown in the diagram of Fig. 6.^{5,8,41,42,46)} The strong surface activity of sulphur and oxygen is of particular interest in iron and steelmaking.¹¹⁾

—Numerous investigators have studied the influence of oxygen, using different methods: sessile drop^{5,22)} pendant drop, maximum bubble pressure, or oscillating droplet,⁴⁷⁾ and argon, helium, H_2 – H_2O , vacuum or CO – CO_2 as surrounding atmosphere.⁴⁸⁾ In Fig. 7, the results of Jimbo and Cramb⁴⁴⁾ are compared to previous ones^{49,8,50)} and to calculated curve, drawn from Belton’s equation, based on a combination of Gibbs and Langmuir isotherms,^{51,44)} in good agreement itself with Kasama *et al.* studies.⁴⁷⁾

Fig. 6. Influence of additions on surface tension of liquid iron. Solid line shows the results measured at 1823 K by Kozakevitch. *et al.* Dotted line shows the results measured at 1873 K by Ogino *et al.*

Fig. 7. Comparison of surface tension measurement for liquid iron as a function of oxygen content in metal.

Their apparent scatter could be a part of explanation of the discrepancy relative to the surface tension of “pure iron”, the other reasons being relative probably to initial purity of the metal, pollution of it by the atmosphere or by contact with refractory materials, and temperature variations of the specimen (an increase of 50°C produces an increase of γ_{Fe} of 20 to $30 \text{ mN} \cdot \text{m}^{-1}$ ^{44,46)}).

—The impressive lowering of the surface tension of liquid iron due to the increasing content of sulphur is presented in Fig. 8.¹⁸⁾ The curve represents the results of Kozakevitch *et al.*⁸⁾ (for an oxygen activity around 30 ppm) as expressed by Belton formulation.⁵¹⁾ The number next to each point refers to the oxygen activity (in ppm). These results, obtained by Lucas¹⁸⁾ show that, at least at high sulphur content (above 0.1%), an increase in oxygen content up to 400 ppm does not significantly lower the surface tension, in slight disagreement with a work reported by Popel *et al.*⁵²⁾ who found a decrease in surface tension larger in the ternary than in the binary, even at relatively low sulphur contents.

—Considering the influence of Carbon, there is also some

Fig. 8. Surface tension of Fe-S-O alloys at 1600°C vs. sulphur activity in logarithmic scale. Solid line is for Fe-S alloys. The number close to each point refers to oxygen activity. (in ppm)

disagreement between previous studies,⁸⁾ which reported an absence of evolution or a slight decrease, and more recent work⁴⁴⁾ where C is shown to cause a small increase of γ_{Fe} (of 30 mN·m⁻¹/wt% C). A decrease of γ_{Fe} , apparently due to carbon, could be explained by a possible contamination with trace amounts of sulphur when adding C to the melt.

—Very little is known on the surface tension of liquid steels, but major constituents of them: Co, Cr, Ni have high characteristics between 1500 and 1800 mN·m⁻¹ at melting point, except Mn: 1030 mN·m⁻¹ at 1550°C.⁴³⁾

2.2. Oxide Systems and Slags

In comparison with metals, the surface tension of liquid slags has not yet been so largely investigated, in spite of numerous recent studies.

Surface tension data for pure liquid oxides and slags are significantly lower than for metals: between 200 and 700 mN·m⁻¹, in absolute value. In **binary systems** based on liquid FeO, Kozakevitch⁴⁾ has determined the surface tension decrease due to the addition of different oxides, using the dipping cylinder methods, see Fig. 9. SiO₂, CaO, MnO, TiO₂ lower it moderately. Al₂O₃ has a slight increasing effect and Na₂O and P₂O₅ behave as capillarily active substances.

Considering **ternary systems**, it was found⁵³⁾ see Fig. 10, that the surface tension of an equimolecular mixture is not much affected by the addition of MgO and ZrO₂ but is lowered by the addition of SiO₂, TiO₂ and also CaF₂ and NaF which have a sharper effect.⁵³⁾

For all basic slags containing silica, it seems that their surfaces have a tendency to become richer in SiO₂. It also worthwhile to mention that sulphur is very surface-active in silicate slags (as S⁻² ions) but about four times less than in metals, on a molar basis.¹⁶⁾

A comprehensive report on surface tension of simple

Fig. 9. Influence of additions in liquid FeO at 1420°C after Kozakevitch.

Fig. 10. Surface tension of CaO-Al₂O₃-Me_xO_y slags in 1610–1680°C temperature range after Evseev and Filippov.

oxides, fluorides and slags containing fluorides, was published some years ago by Keene and Mills.⁵⁴⁾

2.3. Equilibrium Interfacial Properties

As already mentioned, the properties at interfaces between liquid iron alloys and metallurgical oxide phases are known to influence kinetics of many reactions occurring in the processing of iron and steel^{28,33)} and concerning the mass transfer between the two phases.⁴¹⁾

2.3.1. Contact Angle between Solid Materials and Liquid Phases

It is commonly observed that when a liquid is placed on a solid, it forms a droplet which has a specific equilibrium shape and contact angle (Fig. 11). The equilibrium contact angle θ is a measure of the ability of a liquid to wet a solid and varies from 0° (complete

Fig. 11. Form of a droplet of metal resting on a solid oxide support. a) no wetting; b) wetting tendency

Fig. 12. Influence of added elements on contact angle of liquid iron on alumina at 1873 K.

wetting) to 180° (only one point of contact).

In the past, very careful measurements, using sessile drop method, carried out by Lucas at IRSID,^{14,32,33)} have shown that, for most of the pure oxides: Al_2O_3 , SiO_2 , CaO , ZrO_2 , MgO , La_2O_3 but also for some aluminates and nitrides (TiN , BN), the contact angle with pure liquid iron is larger than 90° : $110 \pm 1^\circ$ for polished Al_2O_3 of very high purity,³³⁾ Jimbo and Cramb⁴⁴⁾ proposed 124° , in apparent agreement with previous data (121° – 136°).

The contact angle between liquid iron and Al_2O_3 change with concentrations of some surface active elements, as shown in Fig. 12: it decreases as the Oxygen concentration increases, but it increases when there is an increase in the Selenium and particularly in the Tellurium content.⁵⁵⁾ Sulphur has little effect while at high oxygen concentrations, most refractory oxides tend to be wetted by liquid iron.

The contact angles between liquid slag and refractory materials have been recently reviewed by Nakashima and Mori,⁴⁶⁾ Cramb and Jimbo.²¹⁾ They observed that liquid slags wet most refractories, especially when there is a tendency to react with each other, but they do not wet silicon carbide or graphite. Generally speaking, slags with higher FeO content have relatively lower contact angles.

2.3.2. Interfacial Tensions between Iron-based Liquid Alloys and Slags

Interfacial tension depends upon compositions of both liquid metal and oxide slag: In addition, their compositions can change because of reactions taking

Fig. 13. Interfacial tension between liquid iron and liquid $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag.

place after their contact, which introduce another source or uncertainty, in addition to difficulties due to high temperature experimentation.

Many results which will be reported here have been obtained by making use principally of two experimental methods previously fully described:

- the X-ray observation of the profile of a sessile metal drop immersed in the slag,^{18,22,44)}
- the observation of a slag droplet resting on its liquid metal substrate.^{15,18)}

Influence on Alloying Elements in Metal Phase

Commercial steels contain many elements which have an influence on the interfacial tension. As it was mentioned by Nakashima and Mori,⁴⁶⁾ from published data, except W, the addition of all elements produces a decrease of the interfacial tension, their influence being more pronounced in this order: Ni, Mn, Cr, Mo, Si, P, C, V, Ti.

System Fe-O-Si/SiO₂-CaO-Al₂O₃-FeO_x at 1600°C

All experiments on this system were performed at IRSID using the method of the slag drop resting on a liquid metal substrate.¹⁵⁾ The results are reported on Fig. 13: the interfacial tension obtained, in good agreement with previous investigations,¹⁸⁾ show a decrease, as the SiO_2 content in the slag is increased, from $1240 \text{ mN} \cdot \text{m}^{-1}$ (0% SiO_2) to $1000 \text{ mN} \cdot \text{m}^{-1}$ (50% SiO_2) but part of these results can be attributed to an increase in metal oxygen content, as discussed later. On the same diagram, data from Jimbo and Cramb,^{22,44)} have been plotted for comparison. They are relative to “pure” iron droplets in contact with $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slags at 1550°C . These last results are around 300 to $400 \text{ mN} \cdot \text{m}^{-1}$ higher than the IRSID ones but they agree qualitatively with the influence of SiO_2 concentration.

System Fe-O-C/SiO₂-CaO-Al₂O₃

Figure 14 demonstrates the light surface active effect of silica at the interface liquid Fe-C alloy/ $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ slag with the exception of C saturated iron, whose interfacial tension remains almost constant, whatever the silicon content may be in the slag.¹⁸⁾

It can be useful to precise that the contact angle

Fig. 14. Interfacial tension γ_{ML} between Fe-C alloys and CaO-SiO₂-Al₂O₃ slags.

Fig. 15. Interfacial tension between liquid iron and liquid CaO-Al₂O₃-SiO₂ slags as a function of SiO₂.

between slag and metal decreases from around 65° for SiO₂-free slags to about 15° for slags with 50% SiO₂ whereas a variation of the CaO/Al₂O₃ ratio, at constant SiO₂ content, shows little effect.

Influence of Oxygen and Sulphur in the Metal Phase

A sensible effect of the oxygen concentration in the metal phase is shown in the Fig. 15 which presents three groups of results: from Ogino *et al.*,⁵⁰⁾ Gaye *et al.*¹⁸⁾ and Jimbo and Cramb.⁴⁴⁾

All follow the trend that an increase of oxygen content in the iron phase produces a decrease of the interfacial tension. These data, when compared to the curve [drawn from Belton's equation⁵¹⁾], relative to surface tension of liquid Fe-O alloy, show that the presence of a slag lowers the surface properties of the iron phase.

A more complete description of IRSID results¹⁸⁾ is presented in Fig. 16 in which interfacial tension values are expressed as a function of the oxygen activity in the metal phase. The solid curve represents the medium data for slags of the CaO-SiO₂-Al₂O₃-FeO system.¹⁸⁾ The dotted curve is derived from Ogino *et al.* study⁵⁰⁾ for CaO-SiO₂-FeO system, in close agreement with IRSID results.

For compositions corresponding to continuous casting slags (30 to 60% SiO₂) containing Na₂O and CaF₂ (up to 15-20%), the interfacial tensions (see Fig. 16) are higher at identical Oxygen activity (by about 200 mN·m⁻¹), for large CaF₂ contents, whereas MnO containing slags lead to lower interfacial values (a decrease of about

Fig. 16. Influence of oxygen activity on the interfacial tension between Fe-based liquid alloys and various slags at 1600°C. The solid curve corresponds to SiO₂-CaO-Al₂O₃-FeO_x slags, the dashed curve is given by Ogino *et al.* for CaO-SiO₂-FeO_x slags.

Fig. 17. Influence of sulphur activity on the interfacial tension between Fe-S-O-Si liquid alloys and slags of the system CaO-SiO₂-Al₂O₃-FeO_x at 1600°C.

200 mN·m⁻¹, for the MnO-SiO₂-Al₂O₃ system).

To express the influence of sulphur in the metal phase, the interfacial properties between 5 slag compositions (CaO/Al₂O₃ close to 1 and % SiO₂ varying from 0 to 52%) and Fe-S-O-Si alloys with various Sulphur contents up to 0.7% are presented on Fig. 17 as a function of log₁₀ a_S. An almost linear decrease is observed for the

SiO₂ free slag, and similar trends exist for the other slag compositions.¹⁸⁾

Assuming that these decreasing effects on interfacial tension are simply attributed to oxygen or sulphur adsorption on the metal side of the interface, it is possible to estimate the excess oxygen or sulphur quantities, using the GIBBS adsorption isotherm: values of 15×10^{-6} and $9 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ were found respectively for oxygen and sulphur, in satisfactory agreement with the values reported by various authors.¹⁸⁾

Influence of Slag Composition

Considering the influence of slag composition on the interfacial tension between liquid iron and slags, it was previously observed that FeO and MnO additions are producing a decrease in interface properties,¹⁸⁾ which is confirmed by the review paper published by Nakashima and Mori⁴⁶⁾ who indicated also slight changes in interfacial tension due to the addition of CaO, BaO, SiO₂ and Al₂O₃, but also a large decrease due to P₂O₅. El Gammal and Stracke have also reported strong decreasing effects of Na₂O and CaF₂ additions on the interfacial tension between liquid CK 45 steel and CaO–SiO₂–Al₂O₃ slags, from measurements made by the drop detachment technique⁵⁶⁾

3. “Dynamic” Interfacial Properties during Mass Transfer

The first clear evidence of a perceptible deformation of a metal/slag interface during intense mass transfer between the two phases was reported, as mentioned at the beginning of this review, by Kozakevitch¹¹⁾ as soon as 1955, in the case of desulphurization of a liquid carbon alloy with a blast furnace slag.

This observation was confirmed by Minaev and Grigorian⁵⁷⁾ by Deryabin *et al.*⁵⁸⁾ around 10 years later, and later on by Ooi *et al.*⁵⁹⁾ The latter have observed the same phenomenon during the reactions of Fe–Al alloys with CaO–Al₂O₃–SiO₂ slags and of Fe–Ti alloys with CaO–Al₂O₃–TiO₂ slags. In these experiments, the deformation of the interface was noticed only when initial Al or Ti contents were higher than 4 and 7 % respectively (see Fig. 18).

Kozakevitch¹¹⁾ attributed the interface deformation, and the consequent tendency towards spontaneous

emulsification to a drastic decrease in interfacial tension during mass transfer.

On the same line of thought, Defay and co-workers,^{60,61)} proposed a theoretical description of the interfacial layer by means of a model of equidistant planes which permits the calculation of the interfacial tension for any given distribution of matter.

According to this model, transitory states of zero interfacial tension can occur on account of opposite concentration gradients of two components in the interfacial layer.

A large number of experiments was conducted at IRSID^{17,18)} to determine the conditions under which interfacial tensions seem to disappear. In most cases, the reactions corresponded to a reduction of the slag with elements dissolved in the metal phase and chemically active towards oxygen as Al, Ti, but also Si, P, B, Cr.

For all systems studied, a drastic decrease of dynamic interfacial tension was observed, provided slag–metal initial disequilibrium was large enough,¹⁷⁾ using direct X-ray observation at high temperatures of the profile of a metal droplet immersed in a slag. Examples of X-ray images, characteristic of the main periods are presented in Fig. 19^{17,18)}.

Progressive Lowering of Dynamic Interfacial Tension

The droplet immersed in the slag is observed to flatten progressively. The rate of reaction is not yet very high at this stage probably because of some oxidation of the droplet surface during preheating, and the computed interfacial tension does not reach very low values (Fig. 19(a)).

Apparent Vanishing of Interfacial Forces

When the phenomenon is in its most intense form, the interface becomes roughly horizontal, see Fig. 19(b). Interfacial tension cannot be estimated at all. X-ray images suggest disturbance of the interface, which can be observed, after quenching, on a polished section (Fig. 19(d)).

Recovery of High Interfacial Values

When slag–metal reactions slow down, the interfacial tension rapidly recovers (Fig. 19(c)) a high value and the

Fig. 18. Evaluation of interfacial tension vs. time, in minutes, after alloy addition: (from Ooi *et al.*)
a) between Fe–4%Al alloy and CaO–SiO₂–Al₂O₃ slag
b) between Fe–7.4%Ti alloy and CaO–SiO₂–TiO₂ slag

Fig. 19. Successive X-ray pictures of the profile of a metal droplet immersed in a slag, after: a) 7 min; b) 18 min; c) 40 min; d) polished section, after quenching of a droplet corresponding to configuration b).

Fig. 20. Interfacial tension (upper part) and metal aluminum content (lower part) as a function of time: metal initial composition: Fe-4.45%Al; slag CaO-Al₂O₃-SiO₂.

droplet assumes again an almost spherical shape.

The reactions taking place between slag and metal are characterized by three transport steps, see Fig. 20^{17,18}:

- a flux of oxygen in the slag towards the interface
- a flux of oxidizable element (here Al) in the metal towards the same interface
- a flux of the oxide product of the reaction, diluting itself in the slag.

In order to compare the results of the various systems investigated, it was chosen to express reaction rates in terms of equivalent flux of oxygen, assuming stoichiometric reactions, as for example:

where $\dot{n}\text{Al}$ is the overall flux of the oxidizable element leaving the metallic phase.¹⁸⁾

Results of such calculations, combined with interfacial tension estimates lead to the following conclusions:

- for the (various) systems which were studied at IRSID,¹⁸⁾ interfacial forces seem to disappear when the oxygen flux $\dot{n}(\text{O})$ is larger than $0.1 \text{ g}\cdot\text{atm}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$;
- for values of this flux $\dot{n}(\text{O})$, lower than $0.01 \text{ g}\cdot\text{atm}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, the interfacial tension rapidly recovers high values, often very close to the ones measured at equilibrium;
- differences in chemical potentials between the two phases should be very large, in the initial state. For example, in the case of the system Fe Al alloy and silicate slag, the SiO₂ content of the slag and the Al content of the metal should initially be both high enough (SiO₂ > 20%, Al > 2%)¹⁸⁾;
- the reaction should not be blocked by accumulation of reaction products at the interface: this passivation can be more sensible when these products are very

viscous or solid.

Interfacial Turbulence—Marangoni Effect

As early as 1855, Thomson⁶²⁾ described the spreading of a drop of alcohol on the surface of water and suggested properly that the observed phenomenon was due to local differences in surface tension. But 16 years later, an Italian scientist, Marangoni,⁶³⁾ interpreted correctly similar phenomena and referring to earlier publications, he likely claimed the right to be considered as the first in this field. Such interfacial motion has now come to be known as the “Marangoni effect”.

Since these ancient days, spontaneous interfacial convection has been found to exist in a great number of systems, involving particularly aqueous and organic substances,^{37,64-66)} but also in systems of interest to the process metallurgist.^{38,67,68,39,69)} A mathematical analysis of hydrodynamic instability related to interfacial turbulence has been detailed by Sternling and Scriven³⁷⁾ and will not be described here.

In fact, it is difficult, when considering interfacial phenomena taking place during mass transfer, to separate three mechanisms¹⁷⁾:

- lowering of effective interfacial tension
- spontaneous emulsification by diffusion and precipitation
- hydrodynamic phenomena originating from interfacial tension gradients on the interface, which are considered as real “Marangoni effects”, but are also often contributing to the two precedent processes.

Motion of liquid induced by Marangoni effect (Marangoni flow or convection) can be described by the interface shear stress τ in the direction x ⁶⁹⁾:

$$\tau = \frac{d\gamma}{dx} = \frac{\partial\gamma}{\partial T} \cdot \frac{dT}{dx} + \frac{\partial\gamma}{\partial C} \cdot \frac{dC}{dx} + \frac{\partial\gamma}{\partial E} \cdot \frac{dE}{dx}$$

This relation indicates that the interfacial tension gradient is directly related to the gradients of temperature T , concentration C of the surface active component and electric potential E at the interface.

Without any source of mechanical energy, spontaneous interfacial movements may occur, the driving force being the difference in interfacial tension between adjacent regions.

The eddies resulting from interfacial turbulence are oriented towards zones having the highest interfacial tension.

The main result of the Marangoni effect in metallurgical process is the increase of the mass transfer coefficient of metallurgical reactions by a factor of several units.^{18,39)} But on account of the complexity of these phenomena, it seems now of particular importance to substantiate the occurrence of Marangoni effect in steelmaking processes and to quantify its contribution.

4. Applications to Iron and Steelmaking Processes

As mentioned previously, numerous steps of the steel production are dependent on interfacial phenomena, but only a few examples will be given here.

4.1. Hot Metal Refining in Oxygen Converters

The very essence of the BOF process is its speed,²⁸⁾ the Kinetics of this process depending essentially of the formation of considerable reacting interfaces, producing a tremendous quantity of CO bubbles, general attention was drawn, some 35 years ago, to emulsifying of the metal in slag and also to slag foaming. Kozakevitch produced very detailed analysis of such phenomena.^{13,27,28)}

He has shown that during the early stages of the blow, the stabilization of the metal in slag emulsion is due to adsorption phenomena and to mass transfer through the reacting interface. In later stages, slag crystallization (in silicates or silicophosphates) could be the cause of overrunning.^{27,28)}

In the original LD top blowing process, metal and slag were remaining out of equilibrium till the end of the blow and often causing slag overflow. More recently developed combined top and bottom blowing processes, as LBE, permit to approach equilibrium more closely and to avoid this drawback.

Another example of the important role of surface behaviour is deduced from the results obtained by Gaye and Grosjean⁷⁰⁾ in a LBE pilot converter: as shown in Fig. 21, observed decarburization is much lower when, after the oxygen blow, a bottom injection of oxidizing gas (air), rather than nitrogen, is made, the injected oxygen contributing to increase the interface contamination.

4.2. Slag Foaming in Other Pyrometallurgical Processes

Besides basic oxygen steelmaking, the slag foaming phenomenon is also observed in pretreatment of hot metal and bath smelting of iron and chromium ores.²⁹⁾

Slag foaming is particularly vigorous when CO gas bubbles are very fine (less than 2 mm in diameter) and that the slag contains surface active components such as SiO₂, P₂O₅ or CaF₂ (see Chap. 2) which stabilize slag films. The mechanism of the stabilization is now considered to be largely a surface tension driven flow, namely the Marangoni effect.²⁹⁾ It was confirmed that the addition of carbonaceous material (as coke), which is not wetted by slag, may limit or even suppress slag foaming.^{29,71)}

4.3. Inclusions Removal⁷³⁾

The contact angle value θ between liquid metal and solid oxide allows to discriminate between easy or improbable inclusion cluster formation,^{14,32)} and to evaluate the stable position in the partial emersion of an inclusion at a free surface.

This wetting angle θ should be larger than 90°, which is the case of most of the pure oxides except TiO₂ and Cr₂O₃ (see Sec. 2.3.1 and Ref. 72)), to build possible clusters since two inclusions in contact present to the liquid metal a smaller interface than when they are isolated. The free energy required to separate them is (per surface unit):

$$\Delta G = 2\gamma_m \cos \theta \quad (\gamma_m \text{ is the metal surface tension.})$$

Some 12 years ago, IRSID experiments have concerned

Fig. 21. Change in carbon content during metallurgical stirring with nitrogen (●) or air (*) and theoretical values for inert gas injection (○) (6t pilot converter)

Fig. 22. Lines of equal value of contact angle (90, 100 and 110 degrees on the dashed lines) between Fe-Mn-O alloys and alumina or spinel at 1600°C. Solid lines are delimiting fields of stable oxides.

the influence of oxygen activity on the contact between iron-manganese alloys and alumina or spinel Al_2O_3 -(Mn-Fe)O.⁷²⁾ Results are presented in Fig. 22.

When the oxygen content is low ($<0.013\%$), the contact angle value is always large and cluster formation is possible. For larger oxygen contents which could correspond, for example, to reoxidation of Al killed alloys, cluster formation may become impossible:

$$\begin{aligned} \underline{O} &> 0.036\% \text{ at } 0.6\% \text{ Mn} \text{ and} \\ \underline{O} &> 0.055\% \text{ at } 0.28\% \text{ Mn} \end{aligned}$$

In intermediate cases, for contact angles slightly larger than 90°, surface forces may not be strong enough to maintain the contact between elementary inclusion particles.

But to increase the relative proportion of the emerged part of the clusters, θ should also be as large as possible (see Fig. 23).

The most spectacular case demonstrating the importance of contact angle is the emersion of alumina inclusions from Tellurium containing steel: $\theta \approx 160$ – 170° .⁵⁵⁾ It was observed by Gatellier⁷⁴⁾ that alumina clusters and dendrites were floating out of the slag-free surface metal containing Tellurium.

4.4. Nozzle Clogging

The blockage of tundish nozzles during the casting of Al killed steels or any steels containing solid reaction products is still a significant problem.^{75–77)} It is driven

Fig. 23. Stable position of emersion for solid inclusions: influence of contact angle for different shapes.

by inclusion precipitation and growth, followed by separation at the liquid metal/refractory interface, according mainly to mechanisms mentioned above.

An interesting example of such phenomena was very recently described in the case of stainless steels containing Ti⁷⁷⁾: the steel flow rate from the casting ladle decreased with increasing Ti content and this was due to the build-up of TiN particles in the teeming hole (the contact angle for TiN has been found to be around 130°.¹⁴⁾

To overcome these difficulties, several approaches have been proposed⁷⁸⁾:

- a better control of the number of inclusions in liquid metal,⁷⁷⁾
- an improved geometry and surface roughness of the nozzle,⁷⁸⁾
- the use of new ceramic materials which could inhibit inclusion adhesion.⁷⁸⁾

A lot of work is still certainly necessary in this field.

4.5. Preferential Attack of Refractories

Enhanced erosion of refractory materials at metal/gas, metal/slag and slag/gas interfaces is a well known phenomenon in metallurgical systems (converters, tundish refractories, pouring tubes...).

Careful observations, made by Lucas *et al.*³⁴⁾ of the boundary line solid oxide (pure Al₂O₃)–liquid metal (pure iron)–gas (Argon + 5% H₂) during a study of contact angles by the sessile drop method, induced to propose a mechanism involving the fast surface diffusion of the metallic element (Al) constituting the main oxide phase of the refractory material. A schematic representation is proposed on Fig. 24.

Mukai and co-workers^{35,69,79,80)} have studied intensively local corrosion of various refractory materials by metals and slags. An example is given on the Fig. 25. For these authors, the local corrosion of solid oxide (SiO₂) at the slag surface is caused by a Marangoni flow of slag (PbO–SiO₂) film formed on the surface of solid oxide. Differences in SiO₂ content between upper and lower parts of the film cause a surface tension gradient resulting in this Marangoni flow.

In this field, there is a relatively large number of theoretical or laboratory studies, but it should be necessary to follow them with a scientific analysis of industrial observations.

Fig. 24. Schematic representation of possible mechanism of preferential attack by surface diffusion.

Fig. 25. Typical flow pattern of slag film on a cylindrical silica specimen 6 mm dia. immersed in PbO–SiO₂ slag.

5. Conclusions

An expansion of vigorous approach of process control of the successive steps of steel production suppose a satisfactory knowledge of kinetics of heterogeneous metallurgical reactions. The purpose of this presentation was to show that these last 30 or 40 years, a lot of work has been done to collect informations on surface and interface properties of the various phases involved, but the challenges, iron and steel makers will face in the next decades, impose to extend this investigation of surface phenomena, which are responsible of enhancing, but also of limitation of kinetics of processes⁸¹⁾:

- to improve automation and quality control of existing processes
- to succeed in developing new or future processes:
  - reduction smelting
  - near net shape casting

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