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INTERFACIAL PHENOMENA IN METALLURGICAL PROCESSES AND INTERFACIAL PROPERTIES OF SLAGS

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Synopsis: How to approach interfacial phenomena observed in metallurgical processes is discussed. It is pointed out that accurate knowledge of elemental phenomena related to interface such as adsorption, wetting, adhesion, foam, emulsion and so on, is required to analyze the interfacial phenomena exactly. Slag foaming phenomena is cited as the example.

Key Words: interfacial phenomena, Metallurgical process, elemental phenomena slag foaming, surface viscosity, bubble.

Although interfacial phenomena play an important role in various metallurgical processes, major researches for the processes have focussed on thermodynamic or kinetic studies until now. There are not so many works on the interfacial phenomena in comparison with the physico-chemical studies.

I review here my opinion regarding the studies on the interfacial phenomena in metallurgical processes.

1. Significance of observation oh the interfacial phenomena in the metallurgical process.

In order to analyze a role of the interfacial phenomena in metallurgical processes, I ,firstly, would like to point out an importance of exact recognition of features about the interfacial phenomena. The method of observation of the interfacial phenomenon the metallurgical processes is roughly divided into two parts;macro-observation and micro-observation. In the macro-observation, the interfacial phenomena in a furnace has been observed directly with naked eyes or fiber scope. However, this observation was only a top view in the furnace. Observation of the inside of the slag or the metal was impossible with naked eyes. Therefore, observation of the interfacial phenomena of the inside of the slag becomes feasible by using an X-ray radiography technique. Then, as an example, phenomena at a slag-metal interface reappearance in a small size crucible and was observed by using X-ray[1,2]. However, the macro observation of small region under 1mm was impossible by the technique.

The macro-observation of the interfacial phenomena in the metallurgical processes becomes feasible by hot filament technique[3] and high temperature microscopy[4] using small samples. A wetting phenomena of SiC fiber(100 μm in diameter) by a liquid metal was observed by using a high temperature microscopy. It seems that this technique is applicable to studies of wetting phenomena such as wetting of non-metallic inclusion by liquid steel. Electron microscopy or scanning electron microscopy enable to observe interfacial phenomena at hot stage. However, no observation has been reported in the metallurgical processes.

2. Elemental phenomena on interface

Many interfacial phenomena in typical metallurgical processes are complex. however The interfacial phenomena may involve some elemental phenomena on the interface,for example; adsorption, wetting, adhesion, foam, emulsion, surface flow, electrical surface phenomena and so on. therefore, accurate knowledge of the elemental phenomena on the interface is required in order to make the phenomena clear in the metallurgical processes. These elemental phenomena on the interface are selected referring to interface chemistry at an ordinary temperature.

It seems that metal droplets and gas bubble are also related to the elemental phenomena stated above, because they play an important role in the interfacial phenomena at high temperature.

3. Elemental phenomena related to interface and physical properties of metallurgical substances.

Elemental phenomena related to the interface was governed by physical properties of various metallurgical substances concerned with the interfacial phenomena. Following table shows the physical properties of the various metallurgical substances.

Table 1 Relation between physical properties and the elemental phenomena

Elemental phenomena	Physical properties
Adsorption	surface tension of melts interfacial tension between slag and metal
Wetting	surface tension of melts surface tension of solids
Foam	surface tension of slag surface viscosity of slag viscosity of slag
Interfacial electric phenomena	interfacial tension between slag and metal
Surface flow	surface tension of melts

The physical properties of the various metallurgical substances shown in Table 1 can be rearranged as follows,

1. Surface tension of melts(metal, alloy, slag, flux, matte, in other words, metal oxide, fluoride, sulfide and so on).
2. Surface energy of solid(metal and ceramics).
3. Interfacial energy between melt and solid(liquid metal/solid metal, liquid metal//ceramics, liquid slag/ceramics liquid slag/solid metal and so on).
4. Interfacial energy between two melts(metal/slag,metal/flux and slag/matte).
5. Density and viscosity of melts(metal, slag, flux and matte).

The physical properties of liquid slag have been measured mainly for fundamental systems, such as pure oxide, pure fluorides, binary silicates, aluminates, ternary silicate, binary or ternary oxy-fluoride and so on. However, it has been rare for the physical properties of practical slags to be measured.

4. Study on interfacial phenomena in metallurgical processes.

Slag foaming is a typical interfacial phenomena in metallurgical processes. Kitchner and Cooper[5,6,8] measured the foam life of molten slags by a gas injection technique and we also measured the foam height and the life by the same technique[7]. In those fundamental studies on slag foaming, surface tension of slag melts was a key parameter to be measured. Most of slag foaming studies were essentially a successor to the pioneer study by Kitchner and Cooper. As a result, there are some limitation to explain the phenomena.

Currently, in my laboratory, new fundamental researches on the slag foaming is developed in order to break through the limit at a different viewpoint; surface viscosity of oxide melt and characteristics of a single bubble of the melt.

4.1 Measurement of surface viscosity of oxide melts

It is known that in some aqueous solution systems, higher foaminess results from higher surface viscosity of the solution[9]. There are not so many works on high temperature foam in relation to the surface properties of melts, except for the surface tension.

We have measured viscosities on the surface of melts in the systems, Na_2O-P_2O_5, BaO-B_2O_3, Na_2O-B_2O_3 and Na_2O-SiO_2 by using a modified rotating viscometer to estimate a relation between foaming of oxide melts and its surface viscosity[10,11]. For some melts, we found that the viscosity on the surface is higher than that in the bulk phase. The highly viscous layer on the surface suggests that concentration of surface active component such as B_2O_3 in the system BaO-B_2O_3 is higher on the surface than in the bulk phase. Highly foaminess of the BaO-B_2O_3 melts was also observed.

In Fig.1, the foam height is shown as a function of the surface viscosity, ηs and the value, $\Delta\gamma$/mol%. From the facts, the following idea could be deduced that higher surface viscosity of a melt is necessary, but it's not enough to stabilize the foam and furthermore a higher $\Delta\gamma$/mol% values is required.

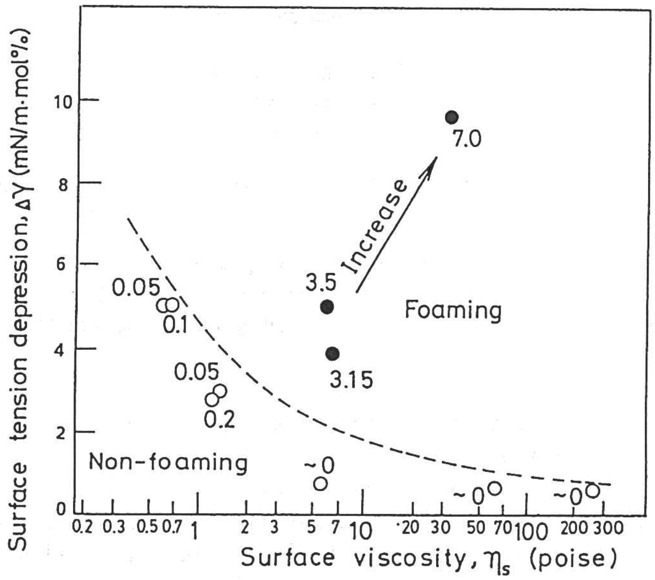

Fig. 1 Effects of surface viscosity η_s and surface tension depression by unit concentration change of melt, $\Delta\gamma$ on foaminess(numerical value: foam height(cm) at Ar gas flow rate of 5 cm^3/min)[11].

4.2 Study on characteristics of a single bubble of oxide melts

The study on characteristics of a single oxide bubble has three purpose as follows; (1)measurement of bubble life, (2)measurement of tension of thin film of the melt, and (3) observation of the bubble when it touches an iron ore or graphite.

(1)Bubble life : Bubble life is one of the measures of bubble stability. Figure 2 shows the bubble life of the BaO-B_2O_3 melts as a function of $Ca_3(PO_4)_2$ concentration to be added. The bubble life of the BaO-B_2O_3 melts was about 20~30sec, but when the melt contained above 1mol%$Ca_3(PO_4)_2$, the bubble life increased remarkable by about a hundred times of that for $Ca_3(PO_4)_2$ free melts. It suggests that the increase of bubble life depends on the concentration of surface active P_2O_5 on the surface. Bubble life of CaO-SiO_2-Al_2O_3-MgO melts is very short(about 1sec),but when $Ca_3(PO_4)_2$ was added, it slightly increased up to 2~10sec.

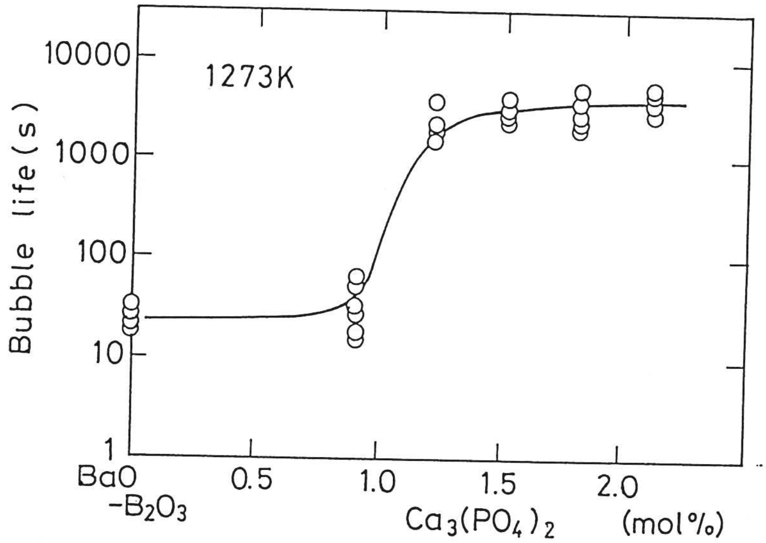

Fig. 2 Relation between bubble life and $Ca_3(PO_4)_2$ content.

(2) Tension of oxide bubble lamella: Tension of $BaO-B_2O_3$ bubble lamella was always larger than that of surface tension of the same melts, since it slightly increased with time. Addition of P_2O_5 to $CaO-SiO_2-Al_2O_3-MgO$ slag slightly stabilized the bubble, but tension of the slag lamella is smaller than surface tension of the slag, even if it contained a small amount of P_2O_5. According to observation of flows on the bubble lamella, the flows on the slag lamella was always downward, while direction of the flows on the $BaO-B_2O_3$ lamella was not fixed and changed at all times. On the other hand, mode of break down of both bubbles is different. For the slag bubble, thinning of the lamella results in the break down, while the borate bubble bursts abruptly ,just as a soap bubble does.
Those facts suggest that for the borate bubble, some stability mechanisms such as Gibbs' elasticity,or Marangoni flow works, but no stability mechanism appears on the slag bubble.
(3)Reaction between gas bubble and various materials: After a single bubble of $BaO-B_2O_3-(Fe_2O_3)$ melt is formed under air, various solid materials such as iron ore and graphite touch a part of bubble film to observe behavior of the bubble lamella.

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