4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

OBSERVATIONS ON THE ROLE OF INTERFACIAL PHENOMENA IN MATERIALS PROCESSING

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Synopsis:

Examples of the role interfacial phenomena can play in materials processing are highlighted in the description of a number of recent research studies conducted at Imperial College. The reduction of ilmenite to iron and titanium carbide or titanium oxycarbide has been studied with the ultimate aim of achieving separation of the titanium and its subsequent conversion to pigment grade titanium dioxide. A further project has been generated involving the identification of conditions for achieving good dispersions of refractory carbides including titanium carbide in iron alloys. The importance of interfacial considerations has also been highlighted by our studies on the production of aluminium-titanium-boron grain refining master alloys from fluoride fluxes. Entrapment of the products can result from emulsification occurring during the reduction reactions. A detailed study of this phenomenon has been conducted using a modified sessile drop technique. Finally, the role of interfacial phenomena in influencing the kinetics of the reduction of slags has been studied in an investigation of the kinetics of alkali metal oxide release from silicate melts.

Key words:

Interfacial Phenomena; Materials Processing.

Introduction:

This paper seeks to highlight examples of the role interfacial phenomena can play in materials processing by describing a number of recent research studies conducted by Imperial College.

Reduction Carburisation of Ilmenite:

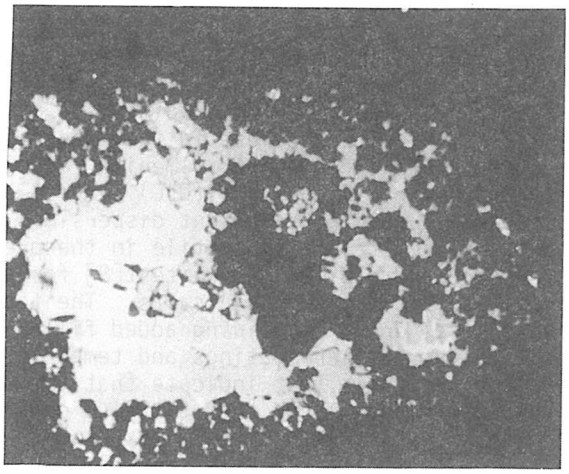
The reduction-carburisation of ilmenite (nominally $FeTiO_3$) to iron and titanium carbide or titanium oxycarbide has been studied [1,2] with the ultimate aim of achieving separation of the titanium content and its subsequent conversion to pigment grade TiO_2.

A considerable volume of research work has been devoted by many workers to the reduction of ilmenite to produce oxide and iron. In all cases physical separation of the oxide proved difficult. The need to achieve good separation of iron from other reaction products is a prime concern and with this in mind it was felt by us that production of a carbide rather than an oxide phase might prove beneficial. We have therefore conducted a detailed study [1,2] of the effect of reducing conditions on the mechanism of the carbothermic reduction of ilmenite by considering kinetic data and microstructural examination and x-ray diffraction of research products.

Reduction Products:

The experimental evidence obtained from x-ray diffraction analysis clearly shows that titanium oxycarbide can be formed from both Ti_3O_5 and Ti_2O_3 produced by the reduction of ilmenite. At 1314°C conclusive evidence has been produced to show that the oxycarbide forms from Ti_3O_5. At 1517°C on the other hand evidence has been produced to show that the oxycarbide forms from Ti_2O_3. At 1413°C our results indicate that the conditions for formation of oxycarbide from ilmenite are closely balanced for production from Ti_2O_3 and Ti_3O_5. A progressive increase in the carbon content and associated decrease in the oxygen content of the oxycarbide phase was observed with increasing reduction temperature.

For reduction at 1314°C micrographic examination showed that in the initial stages of reduction Ti(O,C) existed as a separate phase between iron and Ti_3O_5 with clear separation from the iron phase as shown in Fig. 1. However, as the reaction proceeded the oxycarbide phase became dispersed in the molten iron as shown in Fig. 2. This suggests that the initial phase separation of iron occurs from titanium oxides at which time oxycarbide forms. The oxycarbide is initially separated from the iron and then gradually becomes dispersed in the molten iron phase. A similar development of product microstructure was observed during reduction of 1413°C except that the reaction occurred more rapidly.

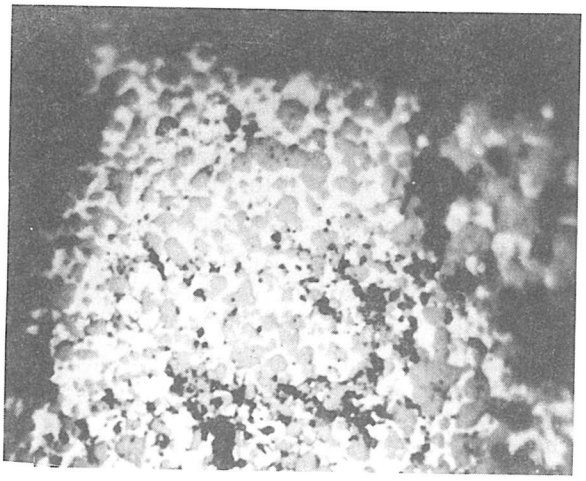


X870

1 hour reduction

Fig. 1 wms Ilmenite + coal 1314°C.

Optical microscopic examination of the reaction products of reduction at 1517°C revealed several differences in structure from the lower temperature reduction products in which Ti(O,C) formed from Ti_3O_5. After 5 mins oiron and Ti_2O_3 formed and separation of the two phases started to occur. A small quantity of oxycarbide phase was observed at the outer edge of the oxide phase. After ten mins oxycarbide formed a continuous product layer around the outside of the titanium oxide. The iron spread over this layer but did not penetrate it. The results of our studies therefore show that titanium oxides show a tendency to separate from the iron produced and that titanium oxycarbide was initially separated but as reaction proceeded became dispersed in the liquid iron.



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20 hours

Fig. 2 wms Ilmenite + coal 1314 C.

White phase: iron Dark grey: M_3O_5

light grey: titanium oxycarbide;

Conditions for Dispersion:

Kiparisov and co workers [3,4] have performed sessile drop studies to determine the interfacial tension of various tool steels on titanium carbide. It was found that in a hydrogen atmosphere less wetting occurred than in an argon atmosphere. It is known that oxygen is surface active in solution in liquid iron and hydrogen could therefore be responsible for removing oxygen thus reducing the wetting. In the case of titanium carbide, this explanation is not sufficient as it is known that titanium oxides separate from liquid iron so any reduction would enhance wetting. Hydrogen is also likely to cause decarburisation

of liquid iron. Although carbon is known to have little effect on the surface tension of liquid iron, there is evidence that in the presence of carbide forming elements such as silicon and chromium, it has a considerable effect[5]. Belton[6] presented an analysis of work carried out on the effect of chromium and carbon on the surface tension of liquid iron and proposed that a surface active "compound" CrC was formed. It seems reasonable to suggest that titanium and carbon will behave in a similar manner thus causing a reduction in the surface tension of liquid iron as the titanium and carbon content increases. Such an effect would explain the observations of a reduction in wetting of TiC in a hydrogen atmosphere as a result of decarburisation of the iron. Our observation on the reduction of ilmenite can also be largely explained by this hypothesis. As reduction of ilmenite takes place dissolution of titanium and carbon in the molten iron product will also occur eventually permitting wetting of the titanium oxycarbide formed and there producing its observed redispersion. Further support for this hypothesis was gained by our observations [2] that a decarburisation treatment of pre-reduced ilmenite permits separation of globules of metallic iron.

Production of Fe-TiC Composites:

The observed dispersion of oxycarbide in iron during the reduction of ilmenite defeated one of our major objective i.e. easy separation of iron from the titanium bearing constituent. However, the condition of dispersion of refractory materials in liquid metals is of prime interest in the production of wear resistant composite materials. We have therefore extended our ilmenite reduction work with a view to producing good dispersions of TiC and/or Ti(O,C) in iron bearing matrices [7]. We have achieved notable success in obtaining excellent dispersions of Ti(O,C) in iron matrices by the direct reduction of ilmenite and rutile in the presence of iron. As part of this study, we have developed a simple levitation test[8] for assessing the dissolution and dispersion of ceramic particles in molten salts. The technique employs levitation and quenching of liquid metal drops containing added filler materials to permit assessment of alloy compositions, filler coatings and temperature on matrix/filler interactions. Results obtained from this test indicate that titanium carbide is more readily dispersed than titanium oxycarbide and that titanium oxycarbide produced in situ in molten iron is more readily dispersed than titanium oxycarbide produced by a separate process. The results also show that dispersion is strongly favoured by high contents of dissolved titanium and carbon in the molten iron. The results also indicate the merit of producing ceramic additions in situ and thus avoiding detrimental effects of surface oxides with respect to dispersion.

Dispersion of Second Phase Particles in Liquid Superalloys:

The levitation technique we have developed for assessing the dispersions of second phase particles in molten metals is also applicable to the study of factors influencing inclusion removal. We have utilised the technique in a study of conditions required for dispersion or non-dispersion of second phase particles in liquid superalloy[8.9]. As part of the study wetting characteristics of liquid nickel, with ceramic particles have been assessed. A notable finding is that whilst binary oxides such as MgO and Al_2O_3 were found to be non-wetting on their own when present together as the aluminate $MgAl_2O_4$ they were found to be wetted by the nickel melts. This is indicative of some form of cooperative or associative effect occurring at the interface. Similar effects have been observed in systems such as NiO/Al_2O_3, CaO/Al_2O_3 and MnO/Al_2O_3. This ability to form aluminates which are wet by liquid nickel poses significant problems with the removal of inclusions from melts held in magnesia or calcia crucibles.

Production of Aluminium-Titanium-Boron Alloys:

Al-Ti-B alloys are commonly used to impart grain refining in the casting of aluminium. They are produced by the reaction between molten aluminium and potassium fluorotitanate K_2TiF_6 and potassium fluoroborate KBF_4. Significant problems associated with this production route include entrapment of $KF-AlF_3$ flux product in the metal alloy product

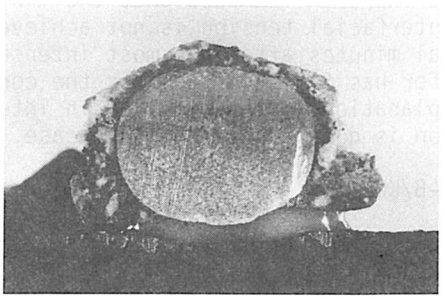
and agglomeration of TiB_2 particles in the alloy product. We have conducted a detailed study of interfacial phenomena related to these reaction and have reported our results in full elsewhere[10,11]. The experimental procedure employed essentially involved a modified sessile drop technique in which molten aluminium alloy was contacted with an appropriate salt or flux composition in a graphite crucible. The crucible and its contents were then quenched to room temperature and sectioned to determine the shape of the metal drop. Experiments were conducted using an aluminium pellet contacted with a $KF-AlF_3$ flux of eutectic compositions (45 mol% AlF_3, 55 mol% KF) to which were added additions of K_2TiF_6 and/or KBF_4.

$Al-Ti-KF-AlF_3$:

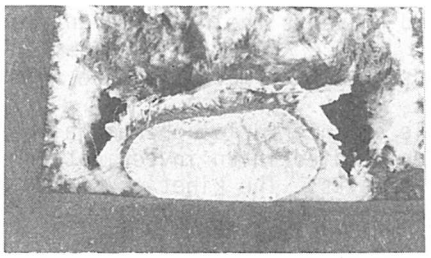
Fig. 3 shows the results obtained by reacting various flux compositions with aluminium at 720°C. These results show a reduction in interfacial tension with increasing K_2TiF_6 level in the flux and hence with increasing resultant Ti level in the aluminium alloy product. At a critical K_2TiF_6 level, initial level in the flux a metal emulsion is formed as shown in Fig. 3(iii). At K_2TiF_6 concentrations in the flux lower than this the $TiAl_3$ produced by the aluminium/flux reaction is dispersed in the metal phase. Addition of Ca or Mg to the system was found to increase the interfacial tension and prevent emulsification as shown in Figs. 3(iv) Mg and Ca are known to be surface active in aluminium. It appears that Mg and Ca are effective in preventing emulsification by occupying surface sites in the aluminium and so inhibiting the $Al-K_2TiF_6$ reaction. The rate of formation of $TiAl_3$ is decreased and and a build up of $TiAl_3$ at the surface which may cause metal-flux emulsification is prevented. Our results indicate that a certain critical level of Mg or Ca in the flux is required to prevent the $TiAl_3$ being dispersed in the flux.

$Al-B/KF-AlF_3$:

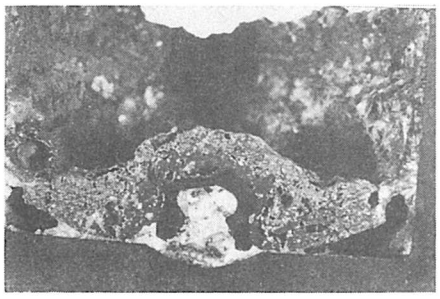
AlB_{12} forms as a metastable phase during the reaction of $KF-AlF_3$ containing KBF_4 with liquid aluminium. The AlB_{12} phase can be dispersed in either the flux or metal phase depending on the process conditions. In this case magnesium and calcium additions are not effective in increasing interfacial tension and we have attributed this to the formation of magnesium and calcium hexaborides. When KBF_4 was added to Al under $KF-AlF_3$ flux at 740°C. The interfacial tension was seen to decrease initially achieving a minimum value after four mins of reaction and then



(i) 2.7 wt% K_2TiF_6 in $(KF-AlF_3)_E$



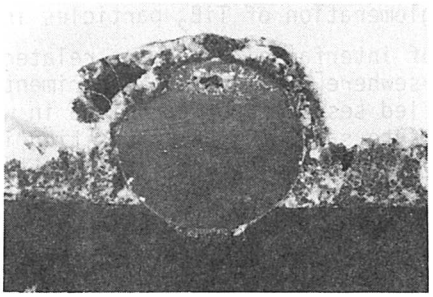
(ii) 7.5 wt% K_2TiF_6 in $(KF-AlF_3)_E$



(iii) 12 wt% K_2TiF_6 in $(KF-AlF_3)_E$

Fig. 3 The reaction of Al with fluxes at 720°C for 15 minutes.

beginning to increase again after 7½ mins. Such lowering and disappearance of interfacial process during the course of a reactio reaction has previously been explained as a result of intense mass transfer at the interface. Our observations indicate that reduction of KBF_4 by aluminium is likely to occur within the first 30 secs of reaction and this therefore should be the period of most intense mass transfer. The fact that the minimum in the interfacial tension is not achieved until several minutes after the most intense mass transfer has finished suggests the conventional explanation for the minimum in interfacial tension is questionable in this case.



(iv) 7.5 wt% K_2TiF_6 + 1 wt%CaF_2 in $(KF\text{-}AlF_3)_E$

Fig. 3. CONTD

Al-Ti-B/KF-AlF_3:

Co-reduction of K_2TiF_6 and KBF_4 salts by aluminium in the presence of KF-AlF_3 flux produces TiB_2 particles that can be wet by either the flux or metal with high salt levels in the flux favouring wetting by the flux. Our findings indicate that it is this wetting by the flux during ythe initial stages of the commercial production of grain refining alloys that leads to the production of TiB_2 agglomerates in which the TiB_2 is held together by the flux. This flux effectively shields the TiB_2 particles from the aluminium melt and prevents their subsequent redispersion.

Kinetics of Alkali Metal Release from Slags:

The role of interfacial phenomena in influencing the kinetics of reduction of slags has been studied in an investigation of the kinetics of alkali metal release from silicate melts. The kinetics of K_2O and Na_2O release during heating in graphite crucibles have been studied [12-15] from binary alkalioxide-silica melts and from a wide range of CaO-Al_2O_3-SiO_2 slags. The overall aim of the work was to establish mechanism and kinetics of alkali release from slags relevant to blast furnace iron-making and coal gasification and combustion processes.

Alkali Release from K_2O-SiO_2 and Na_2O-SiO_2 Melts:

Fig. 4 shows data obtained for the rate of K_2O release from K_2O-SiO_2 slags plotted in the form of log $\frac{K_2O(t)}{K_2O(0)}$ versus time. This figures clearly shows the establishment of two distinct regions each showing an approximately linear relationship with time. The data for the 60% Na_2O and 60% K_2O melts have been shown to be consistent with an initial stage controlled by mass transfer in the slag phase associated with slag stirring brought about by gas bubble nucleation. The second stage results when gas bubble generation ceases and diffusion becomes the only means of transporting alkali oxide to the slag/gas interface.

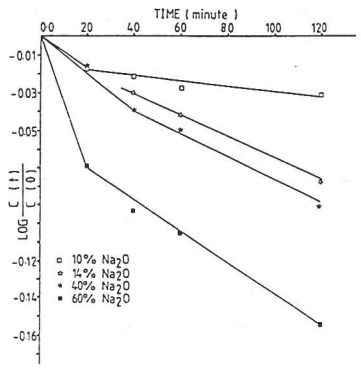


Fig. 4. Kinetics of Na_2O release from Na_2O-SiO_2 slags at 1500°C.

Conclusions:

Our recent work at Imperial College has highlighted the importance of several interfacial phenomena in controlling the dispersion of reaction products and the kinetics of reactions. Of particular note are our observations highlighting:

- the apparent role of associative adsorption phenomena in altering interfacial properties and thus permitting dispersion of phases under unexpected conditions;
- the role of the formation of interfacial products in altering interfacial properties and thus permitting dispersion of phases;
- anomalous decreases in interfacial tension during the course of reaction apparently not capable of being explained by the role of intense mass transfer during the reaction;
- the role of gas bubble generation at interfaces in promoting bulk stirring of phases and enhancement of reaction kinetics;
- the role of the formation of interfacial products in altering interfacial properties and in thus altering geometrical configurations of reactants with resultant changes in diffusion paths and reaction kinetics.

Such phenomena undoubtedly operate in many other systems and situations of industrial relevance. Their identification and control can only serve to assist the improvement and development of materials processing routes.

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