Iron droplets can be entrained into the slag phase when gas bubbles pass through the molten iron/slag interface. The physical phenomena occurring during passage of single bubbles through the interface were investigated by using in-situ X-ray transmission techniques and optical microscopy of the cooled specimens afterwards. Based on the X-ray observations, two mechanisms of entrainment of iron droplets into slag were proposed: large droplets are entrained by jet formation, fine droplets by the rupture of the metal film covering the gas bubble releasing from the iron/slag interface, respectively. The results provide novel erudition of the interaction between the ascending gas bubbles and the slag/iron systems.

KEY WORDS: mechanism; entrainment; gas bubble; iron; slag; interface.

Mechanisms of Iron Entrainment into Slag due to Rising Gas Bubbles

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1. Introduction

In most metallurgical treatments, the iron or steel melt is covered by a layer of molten slag. Gases, which are introduced into the metal melt (Ar, N₂) or produced there by reactions (CO, CO₂, H₂, N₂), pass through the iron/slag interface. In this occurrence, the rising gas bubbles might entrain the heavier liquid iron from the bottom layer into the top layer of lighter liquid slag. This can be either desirable or detrimental, depending upon the special applications; for example, iron droplets entrainment in the slag can significantly increase both heat and mass transfer between the two immiscible liquid layers, and so greatly increase the desired chemical reaction such as decarburisation, desulphurisation and dephosphorisation. On the other hand, dispersed iron droplets in slag can result in a decrease of the post combustion ratio in converter or in-bath smelting reduction processes, and can also cause financial loss if the slag containing iron droplets is discarded without further treatment. This phenomenon is therefore of considerable practical interest. Several investigations in low temperature media have been conducted, however, the data are quite rare, especially with respect to high temperature systems. Poggi, Minto and Davenport investigated the entrainment mechanisms by using mercury/water-glycerin, lead/fused salt and copper/slag (1200°C) systems. They proposed that the metal was entrained into slag mainly through the rupture of the metal coating on the gas bubble. Recently, Chevrier and Cramb observed the bubble separation at iron and slag interface (1450°C) by using X-ray fluoroscopy techniques, and noticed emulsification of metal droplets in the slag. For a quantitative description of heat and mass transfer or reactions via metal droplets in slag, the mechanisms of droplet formation should be clarified in detail. Therefore, the physical phenomena occurring during the passage of single bubbles through the interface were investigated by using in-situ X-ray transmission technique and optical microscopy of the cooled specimens afterwards to reveal the entrainment mechanism at slag/iron interface due to rising gas bubbles.

2. Experimental Apparatus and Procedure

The experimental apparatus used here was modified from that used in the previous work. As shown in Fig. 1, it consisted of a vertical electrical resistant furnace, an X-ray imaging system and a gas supply and control system. The X-ray imaging system consisted of an X-ray generator and receiver; the X-ray tube could be operated both in continuous conversion mode and in pulse mode. The first option allows real-time radiological imaging, and the condition was set at a current of 60 mA and maximum voltage of 110 kV. The conditions in the second option were as follows: X-ray voltage range 85–90 kV; current range 120–200 mA; exposure time 1.0–2.0 sec. A high resolution CCD camera was used to capture the images produced by the X-ray receiver and to record them on a cassette tape. A slag-adding device to add the slag to the iron-melting crucible from above, constituted of a graphite crucible axially connected to an upper end closed alumina tube (O.D. 8 mm), while a hole with a 6 mm diameter was made through the bottom to allow the slag melt to flow out. The slag samples were pre-melted in an induction furnace under vacuum conditions. In most experiments the iron droplets entrained into the slag by gas bubbles were attempted to get gathered by a ceramic collector plate. An alumina plate was holed in the centre and semispherical pits of 2 mm in diameter or grooves 2×2 mm were drilled or ground on the whole upward flat surface to collect metal droplets (Fig. 2). Normally, the diameter of the hole was
3–4 mm larger than the equivalent diameter of a bubble (typically 10–14 mm). The sharp edge of the hole on the downward side was ground smoothly by a diamond tool.

In each typical experiment the furnace was preheated to 1 580°C, then an alumina crucible-capillary system and a graphite crucible were introduced into the furnace tube from the bottom and the top, respectively. The alumina crucible with 35 mm I.D. and 60 mm height contained 135 g iron sample. The iron sample was obtained by melting two types of electrolytic iron, (granules and flakes to pack it densely) in an alumina crucible, in an induction furnace under vacuum condition and deoxidised by aluminium. The compositions of the raw materials and a sample after an experiment are listed in Tables 1 and 2, respectively. Three different alumina capillaries were used to produce bubbles with different size, their I.D./O.D. were 2/4, 1.6/3 and 0.7/1.3 mm, respectively, all their length was 550 mm. The alumina plate was located inside the crucible above the iron charge. The graphite crucible with 35 mm I.D. and 65 mm height was filled with 55 g slag (50% Al₂O₃ and 50% CaO). This kind of slag has a low melting point and no chemical reaction with the metal. However, it dissolves some alumina from the crucible. Hence its composition was about 41% CaO and 59% Al₂O₃ after the experiment.

After the furnace tube was purged by pure argon about 2 min, 90% Ar plus 10% H₂ mixture gas was introduced as protection atmosphere. The alumina crucible was moved upwards slowly to the high temperature zone, while the graphite crucible was moved gradually downwards to the furnace centre. After the iron was partly melted and covered the mouth of the alumina capillary (the pressure curve appeared on the monitor screen), the graphite crucible was quickly moved downwards to be seated on the alumina crucible to melt the slag and allow it to flow onto the iron melt. The whole period of the crucible moving and materials melting took about one hour; during this period the gas flow rate from the capillary was very low (~0.2 m³/min). After the iron and slag samples were totally melted, the alumina plate, with a density (about 3.8 g/cm³) greater than the density of the slag (about 2.6–2.8 g/cm³) but lower than that of liquid iron (about 7.1 g/cm³), floated on the surface of the iron melt submerged in the liquid slag. When experiments with gas bubbles passing through the iron/slag interface were conducted both with and without the alumina plate, no significant differences were observed. When the gas flow rate was set to the proper value (normally, 1.7–5.0 m³/min), observation of the phenomena and counting of bubble numbers began by means of X-ray imaging. Bubble formation frequency was 20–40 bubbles/min during observation of entrainment caused by single bubbles, and 300–400 bubbles/min when multi-bubble gas flow was used. After a certain number of bubbles were injected into the iron melt, the gas supply was shut down, and the two crucibles were slowly moved to the two ends of the furnace tube and discharged. The crucible was cooled down and cut into two parts from the centre, then the cross-section was observed under microscopy, as shown in Fig. 2. Solid iron and slag were then sampled and sent for analysis. The surface tension of iron melt (1 700 mN/m) and the interfacial tension between iron and slag melt (1 270 mN/m) were calculated according to the chemical analysis results by using Cramb’s equations. The slag viscosity (0.4 Pa s) and surface tension (550 mN/m) were estimated from the literature.
3. Results and Discussion

3.1. Behavior of a Single Argon Bubble at the Iron/Slag Interface

Once the bubble approaches the interface, it lifts an iron dome into the slag phase (Figs. 3(a) and 3(b)) and the dome is thinned by the drainage as the bubble reaches the interface. When the bubble hits the interface, sometimes a rebounding phenomenon could be observed; subsequently the bubble rested under the interface for a shorter or longer time depending on its size. It could not pass the interface without any delay. During the resting time, the bubble was still covered by a thin iron film (Fig. 3(c) and Fig. 4). The bubble finally broke through the interface at the initiation of the film rupture, moved into the slag phase (Fig. 3(d)) and metal droplets were entrained into the slag by the gas bubble. The rest time of a bubble depended on the time of the drainage process and the time when the iron film began to rupture. As there is no suitable model to describe drainage and film rupture at the moment, it is difficult to predict the resting time. According to experimental observations, a bubble with a diameter of about 10 mm could stay sometimes more than 10 sec beneath the interface, but for a 13 mm bubble, the resting time was normally less than 2 sec.

3.2. Mechanisms of the Droplet Formation

In-situ observations of the iron droplet formation and entrainment into slag were performed by using the X-ray unit connected to a CCD camera. The phenomena happening inside the alumina crucible at the high temperature could be directly observed on a computer monitor and simultaneously recorded on a video tape. Some typical experiments were reviewed frame by frame from the videotape. By this method, plus the microscopy observation, the mechanisms of iron droplet formation and entrainment into the slag could be revealed.

It was found that there were two distinct groups of droplets formed when a big bubble (>11 mm) passed through the iron/slag interface, they were called the jet entrainment and film entrainment, respectively, because they were formed from the iron column dragged into the slag by bubble or formed from iron film ruptured.

3.2.1. Jet Entrainment

The series of X-ray images in Fig. 5 show how the jet droplets formed when an argon bubble passed through the interface between liquid iron and slag. The interface was flat before the release of the bubble (a). When a 13 mm bubble reached the interface it lifted the interface and formed a dome (b). With the drainage process the bubble film thinned and the bubble shifted more into the slag (c, d). In this case, a second smaller bubble reached the interface when the first bubble resting there (e), the two bubbles coalesced quickly and formed a 13.7 mm bubble (f, g). Finally, the iron film ruptured and the bubble entered the slag immediately and pulled an iron jet into the slag (h). The iron jet had a large length to diameter ratio, about 4-6; it became unstable and broke up forming one droplet (i). As indicated by the arrows, the droplet fell down and was captured by the alumina plate floating above the iron melt (j, k, l). It can be seen that the shape of the iron droplet was not spherical during its descent (k), but was dragged into an irregular shape by viscous force. When it was resting on the ceramic plate, the interfacial tension made it form a round ball (l). The whole process took about 2 sec.

The series of X-ray images in Fig. 6 represent the influence of the bubble wake. After the bubble expanded and the film ruptured (b), a thin and long jet formed by the combination of the cavity collapsing and dragging from the bubble wake (c). The wake of the bubble not only pulled the iron melt to form a jet, but also dragged out a secondary gas bubble. This made the jet even higher and unstable until the jet finally broke to form three jet droplets.

The present observations differ from the mechanism described by Suter and Yadioglu(2) shown in Fig. 7, in the low temperature medium. According to their observations, dispersion of the lower fluid into the upper one can take place by two distinct entrainment mechanisms:

1. Entrainment takes place if the bubble separates from the liquid column and rises, still surrounded by the film of the lower liquid; this film drains downwards, separates from the bubble, and forms drops.
2. If the column of the heavier liquid has a large length-to-diameter ratio, it becomes unstable and breaks up into drops.

It can be seen from Fig. 7 when the jet was drawn into the lighter liquid, the bubble was still covered with a layer of the heavier liquid film and connected with the jet. A sim-
ilar procedure was observed in water/mercury systems by Reiter and Schwerdtfeger, who observed that a contraction developed at the foot of the bubble when a $N_2$ gas bubble entered water from mercury. Then the bubble was connected to the mercury bath only by a thin mercury tail; the bubble at that moment was still covered with a mercury film. These observations can be explained by the interaction between the buoyancy force and the interfacial tension. If the buoyancy force is much greater than the interfacial tension, the bubble will pass through the interface with a negligible delay, and there is no time for the film to drain and rupture, and a jet is dragged into upper liquid by the bubble. This concerns the study of Suter and Yadigaroglu, who used water/toluene, water/benzene and water/paraffin as experimental media. These liquid pairs have very low interfacial tension compared to the metal and slag system. The repelling force is negligible when a bubble comes, and, because the density difference between the pair liquids is not very high, the contraction step was not observed in their cases. In the case of Reiter and Schwerdtfeger, the interfacial tension between water and mercury (375 mN/m) is much higher than in the experiments of Suter and Yadigaroglu. However, the buoyancy force is also very great due to the high density of mercury, so bubbles can still penetrate the interface into water with a mercury film cover. It was because the density difference between the water and mercury was so high that the contraction at the
foot of the bubble happened. In the present experiments, the interfacial tension is strong enough to retard the bubble and to make it possible for the iron film to drain and rupture.

In the current experimental observation, it was found that the iron film ruptured first, then the jet formed. This means the jet was formed by the combination of the wake of the bubble and the cavity collapse driven by the surface tension of molten iron. The schematic diagram of the mechanism of iron droplet formation in slag/iron system is shown in Fig. 8. With the drainage of the iron film (a), a hole is formed on the apex (b), the inner surface of the iron film moves rapidly downward, driven by the surface tension of iron, while the outer surface moves downward, driven by the interfacial tension of slag/iron. Meanwhile, the inner surface of the iron film is dragged by frictional force from the upward flowing gas phase, while the outer surface is dragged by the slag phase. These can cause a velocity difference between the two surfaces of the iron film and so form local stress that will break the iron film. This seems one of the mechanisms of the formation of fine droplets, film entrainment, will be discussed further in the coming section. After the film ruptured, the cavity collapsed in a manner that differed in some respects in comparison with the same process on the free surface without slag layer. Firstly, when a bubble bursts on a free surface of a liquid, the cavity collapses in such a manner that a layer of fluid flows down the cavity wall preceding the toroidal movement, as the liquid converges at the bottom of the cavity, a jet is created.13) However, when a bubble bursts at the slag/iron interface, the surface of the cavity is under the pressure of the gas bubble, which makes the formation of a jet more difficult than in the case without that pressure, because more energy will be consumed on the friction between the shear flow layers. Secondly, when a bubble bursts on the free surface, the rapid movement of the toroidal rim helps the jet formation,3) but when a bubble bursts at the slag/iron interface, the frictional energy consumed between the iron film and the slag retards the movement of the toroidal rim and thus impedes the iron jet formation. Therefore, the kinetic energy from the wake of the bubble will have the decisive influence on the formation of the jet. As shown in Fig. 8(c), a jet was formed inside the gas bubble. Is this really possible? As reported by MacIntyre, 17) once a bubble film breaks, it expands with a maximum velocity of the order \((2\sigma/\rho H)^{1/2}\), independent of the hole diameter. By and large, a hole in a 2-\(\mu\)m-thick iron film spreads at about 17 m/s when its surface tension is about 1.2 N/m, while the rising velocity of a gas bubble in liquid iron is about 1.2 m/s.14) Thus the bubble bursting process is much faster than the bubble rising on the interface, and hence, an iron jet could be formed inside the gas bubble. When the jet was high enough, it would be unstable and formed jet droplets (Fig. 8(d)). Examples of iron droplets formed in the slag are shown in Fig. 9. The iron globules were collected from the slag sample which was crushed after the experiment. It should be noticed that the big globules are formed by coalescence of several small iron droplets when resting on the collector plate during the bubbling period. The initial droplet size is typically 1–3 mm only.

3.2.2. Film Entrainment

Entrainment of fine droplets of metal or matte into the slag phase is a well-known phenomenon in pyrometallurgical processes that use gas agitation.5,16) It can be observed afterwards because fine droplets separate slowly. Consequently, a small amount of the heavier liquid phase remains dispersed in the lighter liquid phase in the form of fine droplets long after agitation has ceased. For industrial scale processes such as secondary steelmaking and smelting reduction, long settling periods decrease the productivity whereas the residual entrained metal reduces the yield. Both of these effects have sparked the current interest in the mechanism of fine droplet formation. It seems that most of the fine droplets are formed from the bubble film, as described in the earlier section. However, the mechanism of a bubble film rupture at a liquid-liquid interface is not clear; hardly any related research reports could be found, and direct observation of bubble film rupture and of the mechanism of film droplet formation were beyond the ability of the X-ray unit. Thus indirect observation and deduction were the only possible ways to examine the problem.

Minto and Davenport13) characterized bubble behaviour at liquid-liquid interfaces by using an energy balance. They defined a “film coefficient” \(\phi = \sigma_{s} - \sigma_{m} - \sigma_{s,m}\) and a “flotation coefficient” \(\Delta = \sigma_{s} - \sigma_{m} + \sigma_{s,m}\) to describe the bubble film stability and the droplet flotation. According to their analysis, in slag/iron systems, a gas bubble cannot carry an intact film of iron into the slag phase because the film coefficient \(\phi\) is always negative. This was also confirmed by the current experimental observation. Hence the fine iron droplets were produced at the moment when the film ruptured and the bubble simultaneously moved into the slag phase. The bubble was able to tear off some iron pieces from the iron film by frictional force during its rapid acceleration and expansion. In the current experiments, most of the fine droplets dispersed in the slag were less than 10 \(\mu\). Thus they originated from the film rupture. For the selected slag composition, the flotation coefficient \(\Delta\) was positive, thus the iron droplets could seize the gas bubble and float upwards in the slag.
Further mechanisms were proposed by Shahrokhi and Shaw (18) who studied the origin of fine droplets in gas-agitated liquid-liquid systems at low temperature by using a microscopic camera. According to their observations, fine droplet production (<100 μm) could also arise from other two sources: jet droplet erosion during collisions with gas bubbles, and bubble-attached jet droplet rupture at the free surface of the upper liquid caused by feedback force when the bubble bursts. In this study fine iron droplets were observed even in the cases where no jet droplet formation happened (Fig. 10). So the film rupture is anticipated to be the major mechanism to produce fine iron droplets.

3.2.3. Entrainment Caused by a Multi-bubble Gas Flow

Increasing gas flow rate brought some new phenomena to the mechanism of iron entrainment by gas bubbles. The experimental procedure was similar as previously but the gas bubble frequency was raised up to about 5–7 bubbles per second. Thus a kind of bubble column was formed in the melt. As shown in Fig. 11(a), the succeeding bubble could push the previous bubble upwards before it ruptured, and an iron ring, from which an iron droplet could form, was formed between the two bubbles. In Figs. 11(b), 11(c) and 11(d), it can be seen that several bubbles could coexist without coalescence, thus forming a “foam cluster” in which the bubbles were still covered by a thin layer of iron film. Under this situation, it is less probable that a jet could form by the wake of bubbles. Under these circumstances large iron droplets were mainly formed by the “ring” mechanism of the collapsed iron rings between the bubbles. Fine film droplets are formed also in this case by the iron film rupture covering the bubbles.

4. Conclusions

The physical phenomena occurring during passage of single bubbles through the iron/slag interface were investigated by using in-situ X-ray transmission technique and optical microscopy of the cooled specimens afterwards. The mechanisms of the entrainment at the slag/iron interface due to rising gas bubbles were proposed based on the X-ray observation. The iron droplets entrained into the slag were mainly formed from two sources, jet entrainment and film entrainment. Jet entrainment was caused by the collapsing of the cavity after the iron film ruptured and with the help of the bubble wake. Film entrainment was caused by the iron film rupture and interaction with the slag phase. By comparing these mechanisms with those in low temperature media, the differences are significant and mainly caused by the big difference in the interfacial tension.

With higher gas flow rate interaction of gas bubbles resulted in formation of bubble column or foam which caused entrainment of metal droplets into the slag by collapsing of the metal ring around the neck between the clustered bubbles. The proposed mechanisms give a better understanding of the interaction between the ascending gas bubbles and the slag/iron systems.

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