Influence of Sulfur Content and Temperature on the Carbon Boil and CO Generation in Fe–C–S Drops

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Carbon boil in liquid iron has been studied as a function of some key parameters such as sulfur content (0.005–0.4 %) and temperature (1 370–1 450°C) in a horizontal tube furnace. The metal–gas reactions and their time dependence, that is their dynamic nature, were observed *in-situ* at the temperature of interest. Experiments of Fe–C–S drops were also conducted in a vertical super-kanthal tube furnace to permit rapid quenching of metal drops and their subsequent analysis. The starting time of carbon boil phenomenon was determined using a CCD camera coupled with a time/date generator connected to a video recorder. The initiation time of carbon boil was in the range ~5 and ~20 sec under the conditions in this study. Mechanism for carbon boil has been proposed.

KEY WORDS: sulfur content; temperature; oxygen absorption; decarburisation; surface reaction; subsurface reaction; nucleation of CO; heterogeneous nucleation; CO gas generation; carbon boil; Fe–C–S droplet; metal gas reaction.

1. Introduction

In direct smelting processes, the metal droplets are generated and consequently ejected from the metal bath into the gas phase due to the intense turbulence in the bath as a result of gas and coal injection. Upon entry into the top space, the metal droplets could react with oxidising gases resulting in surface and sub-surface CO generation. The occurrence of carbon boil phenomenon in molten Fe–C–S drops can result in excessive spitting and sometimes even complete destruction of a metal drop. This could significantly promote the decarburisation of liquid metal, reduce the post combustion and increase the energy consumption in the smelting reduction processes.

Numerous studies have been conducted on topics related to the reaction of molten iron drops with oxidising gases including decarburisation, sub-surface CO formation and oxygen absorption kinetics. These studies have reported the occurrence of explosive disruption of the droplet commonly referred to as carbon boil. Decarburisation as well as carbon boil phenomenon are detrimental to direct smelting processes due to their negative effects on post-combustion. Numerous smaller droplets generated as a result of carbon boil accelerate the rate of decarburisation and re-oxidation of iron even further. Notwithstanding the significance of carbon boil, a comprehensive study of the carbon boil relevant to the bath smelting process has not been conducted.

The influence of initial carbon content, drop temperature and partial pressure of oxygen on decarburisation was studied by Roddis.¹⁾ It was found that the manner of carbon re-

moval *i.e.* via a surface or subsurface reaction was affected by the metal drop initial carbon content as well as gas composition at 1 600°C. A sub-surface reaction was not observed until carbon content reduced to 3 %, 2 % and 1 % at oxygen partial pressure of 1, 0.7 and 0.5 atmospheres, respectively. Similar studies were also carried out by El-Kaddah and Robertson.²⁾ They concluded that the supersaturation of CO or subsurface reaction was due to larger oxygen transfer rate into the bulk than the carbon transfer rate towards the surface. Models of CO nucleation were proposed.^{3,4)} The role of oxide film on the metal surface has also been discussed in different studies. Hayer and Whiteway⁵⁾ investigated the decarburisation of iron melts containing 1–3 % carbon and up to 3 % sulfur using an oxygen–argon gas mixture. It was found the decarburisation rate was proportional to the content of oxygen in the gas stream when sulfur level is less than 1 %. An increasing in sulfur content usually increases the tendency of oxide formation on the liquid surface under otherwise similar conditions. In some cases the solid oxidation product appeared to become mixed into the melt by convection currents. This led to bubbling and ejection of droplets of the melt into the gas-stream. Robertson and Jenkins⁶⁾ studied the behaviour of pure iron and its alloys with carbon and silicon in pure oxygen using a levitation technique. Carbon boil occurred but they could not observe the formation of iron oxide.

Distin *et al.*⁷⁾ studied the oxidation of drops of iron containing carbon using levitation method; O₂, CO₂, O₂–H₂O and Ar–O₂ gas mixtures were used. They found that boil commenced as soon as an oxide film appeared on the drop

surface. See and Warner⁸⁾ studied the Fe–C and Fe–C–Si drops by allowing the droplets to fall through a column containing O₂, CO₂ and air. For a Fe–C droplet, carbon boil was not observed by pure CO₂. For Fe–1%C–Si specimens, subsurface generation of CO increased in intensity until eventually there was explosive disruption of the drop. At a constant silicon level, an increase in carbon content resulted in the drop reacting in oxygen for a longer time before exploding. Metal drops containing 0.8–4.5% C were reacted with oxygen during free fall through a 3 foot column by Baker and Ward.³⁾ They reported that carbon boil occurred at all carbon concentrations between 0.8 and 4.5%. The boil intensified as the carbon concentration decreased and destruction of the droplet by explosion occurred at about 0.5% carbon.

The oxygen absorption kinetics has been studied by a number of researchers. Sano *et al.*^{9,10)} found that oxygen absorption was observed at the oxygen partial pressure as low as 10^{−4} atm. Emi *et al.*^{11,12)} measured the rate of absorption of oxygen by liquid iron under various conditions. They found that the absorption process proceeded in two stages. In the initial stage, the rate of oxygen uptake was dependent upon oxygen pressure and the gas/metal interfacial area, but independent of melt volume and stirring. In the second stage, oxygen absorption continued at a much lower rate in the presence of an oxide phase covering the melt. Distin *et al.*⁷⁾ reported that the oxygen concentration reached 0.08% at boil when O₂, CO₂, N₂–O₂ and Ar–O₂ gases were used. Vig and Lu¹³⁾ reported that the oxygen absorption rate was about 0.2%/sec for a one gram iron droplet containing 0.024% carbon and total of 0.1% other impurities in the presence of 30% O₂–He. It was reported that sulfur had no effect on oxygen absorption in the range 0.003 to 0.016% by Greenberg and McLean¹⁴⁾ and in the range 0.08 to 0.14% by Choh and Inouye.¹⁵⁾

Examination of the literature has revealed that the occurrence of carbon boil is not fully understood. There is generally no agreement regarding the condition that initiates the phenomenon. The influence of some important parameters on carbon boil, such as the melt sulfur content and temperature, has not been systematically studied. The knowledge of the time for carbon boil occurrence is critical for direct iron smelting processes. If the time spent by the metal droplet in the gas phase exceeds the time required for boil then carbon boil is likely to occur. Therefore an understanding of the carbon boil as function of key parameters could assist with establishing the occurrence of the phenomenon under operating conditions.

The focus of previous investigations on carbon boil was mainly on steelmaking.^{1,3,5–7)} Compared to steelmaking processes, melt sulfur in direct smelting metal is higher and the metal bath is at a lower temperature. Therefore the aim of this investigation is to obtain fundamental understanding of the influence of melt conditions on the carbon boil phenomenon, specifically the influence of melt sulfur and temperature on the occurrence of boil under direct smelting reduction conditions. The time for occurrence of carbon boil has been determined in this study by capturing the time-dependent, *in-situ* images of the metal drops at high temperatures during the metal/gas reaction using a CCD camera and a time/date generator connected to a video recorder.

Fig. 1. Image of sample assembly (front view).

The time of boil was determined to be in the range ~5 to ~20 sec under the conditions of this study, with the reproducibility of ± 0.5 sec for most runs.

2. Experimental

2.1. Experimental Arrangement and Procedure

2.1.1. Experimental Arrangement for Carbon Boil Study

Fe–C–S drops with 4.1 ± 0.2 wt% carbon and different sulfur concentrations were prepared from electrolytic iron (99.98% iron), synthetic graphite (99.999%) and high purity sulfur (99.9%) in a high purity alumina boat using horizontal Super-Kanthal resistance high temperature furnace at 1500°C in argon atmosphere. The carbon and sulfur concentration of the iron–carbon–sulfur alloys was determined by a Leco CS244 carbon and sulfur analyser. A number of samples were also analysed by an independent laboratory to determine the level of impurities present. It was found that the impurity level of both silicon and aluminium was less than 0.01 wt%. Prior to carbon boil runs, experiments were carried out by quenching high and low sulfur content samples after being exposed to the inert atmosphere of argon for an extended period of time in a vertical Super-Kanthal resistance high temperature tube furnace to determine the loss of carbon and sulfur before the introduction of oxidising gases. It was found that the loss of carbon and sulfur was less than 5% of the elemental concentration before the introduction of the oxidising gas under the conditions of this study.

The carbon boil experiments were conducted in a horizontal super-kanthal tube furnace. The inside diameter of the furnace tube was 50 mm. The Fe–C–S drops were placed on alumina substrates and heated in the furnace until the desired temperature was attained under an argon atmosphere to prevent oxidation of the metal sample. Upon the establishment of equilibrium, the oxidising gas mixture was introduced. Two alumina boats used in each experiment were positioned one on top of another in an alumina assembly as shown in Fig. 1. The assembly was used to protect the primary furnace tube from the metal droplets produced as a result of carbon boil phenomenon.

The reaction sequence prior to and during carbon boil was monitored *in-situ* at high temperatures with a television set and video recorder unit connected to a Sanyo hi-resolu-

Fig. 2. Schematic diagram of the carbon boil experimental set-up.

Fig. 3. Schematic diagram of the decarburisation experimental set-up.

tion CCD camera which permitted the capture of time-dependent images of the metal drops. A schematic diagram of the experimental set-up, details inside of the furnace is schematically shown in Fig. 2. After allowing the metal droplet to equilibrate at a desired temperature, the recording was initiated and the oxidising gas was introduced. An on-line date/time generator permitted the monitoring of the *in-situ* reactions as a function of time. The Video recorder can capture 25 images per second. The images are replayed on a TV and a computer screen for further analysis. This arrangement permits the capture of the entire sequence of events leading up to carbon boil and therefore the determination of time for occurrence of boil.

2.1.2. Experimental Arrangement for Decarburisation and Oxygen Absorption Study

Some experimental investigation of carbon and oxygen concentration prior to carbon boil was conducted in a vertical, high-temperature, super-kanthal resistance tube furnace. The Fe-C-S metal drops were placed on an alumina sample holder and suspended by platinum wire in the furnace hot zone as shown in Fig. 3. The samples were then heated under argon atmosphere until a predetermined tem-

Table 1. Experimental parameters for carbon boil and decarburisation study.

	Carbon boil study	Decarburisation study
Gas flow rate (@ 20°C)	11.5 L/min	31.9 L/min
Gas velocity (@ 20 °C)	0.28 m/s	0.28 m/s
Metal carbon content	4.1 ± 0.2%	4.1 ± 0.2%
Metal sulfur content	0.005 - 0.417 wt%	0.01 and 0.29 wt%
Metal temperature	1370 - 1450 °C	1450°C
Metal drop weight	0.50 ± 0.01 g	0.50 ± 0.01 g
Oxidizing gas	40% O ₂ , balance Argon	40% O ₂ , balance Argon

perature was reached. After equilibration, oxidizing gas mixture of 40 % oxygen and argon was passed through the furnace. After exposing the sample to the oxidizing gas for a certain period of time, the gas was switched back to argon. At the same time the sample together with the alumina crucible was pulled to the top space of the furnace tube near the water-cooled cap and allowed to solidify. Samples were collected and analyzed by a LECO TC-136 Oxygen Analyzer.

2.2. Experimental Parameters

In a smelting reduction vessel, 90 % of the droplets generated have diameters between 0.3 and 7.5 mm, or, weighing about 0.2 g for the medium sized droplets.¹⁶⁾ The weight of the droplets used in this experiment is 0.5 g, with diameter of about 6 mm if the droplets are considered to be about a hemisphere on the alumina crucible. Moodie *et al.*¹⁷⁾ have shown in their mathematical model that the absolute velocity of oxidising gas is in order of 10–50 m per second in the smelting vessel, with gas velocity approaching a few hundred meters per second in the vicinity of air nozzle. Such gas velocities are extremely difficult to simulate in laboratory and moreover, the reaction would also be expected to be too rapid for observation and analysis of elements in metallic samples. For above practical reasons, in order to understand the fundamentals of carbon boil phenomenon in the reaction vessel, lower gas velocity of 0.28 m/s was adopted. To compensate for the effect of lower gas velocity on the mass transfer of oxygen in the gas phase, a higher oxygen concentration of 40 % was used instead of air, which is generally used in the smelting vessel. Details of experimental parameters are shown in Table 1. At the gas velocity of 0.28 m/s (at 20°C), it takes approximately 0.2 sec for the oxidising gas to reach the metal sample. This could contribute to the variability in the measurements.

3. Experimental Results

3.1. Carbon Boil Phenomenon—Definition

Some images from a typical sequence of events observed in experiments conducted over a wide range of parameters are shown in Figs. 4–9. The upper and lower metal drops contained 0.124 and 0.343 wt% sulfur, respectively, as shown in Fig. 4. Sparks first emitted at around 3 sec after the oxidising gas was switched on. Then at 4.6 sec in the lower boat increased sparks were released from the drops, accompanied by an increase in metal drop volume which is caused by CO gas formation inside the droplet, as shown in Fig. 5. A further increase in volume was observed at 13.3 sec as shown in Fig. 6, which was followed by carbon boil

Fig. 4. Image taken at time=0 sec.

Fig. 7. Image taken at time=13.9 sec.

Fig. 5. Image taken at time=4.6 sec.

Fig. 8. Image taken at time=16.4 sec.

Fig. 6. Image taken at time=13.3 sec.

Fig. 9. Image taken at time=17.6 sec.

at 13.9 sec, as shown in Fig. 7. The average increase in volume of the droplets was about 50% before carbon boil occurs. Generally, metal density increases after decarburisation, resulting in a decrease in droplet volume. However such change in this study is negligible compared to the volume increase due to gas formation inside the droplet. Figure 8 shows an image taken at 16.4 sec, which illustrates that the metal sample in the upper boat has increased in volume. Excessive spitting of smaller metal droplets in an explosive manner, that is, carbon boil was then observed in the upper boat at 17.6 sec, as shown in Fig. 9.

The occurrence of the carbon boil phenomenon is clearly illustrated by Figs. 7 and 9, at times of 13.9 and 17.6 sec, respectively. The photographs taken prior to the occurrence

of carbon boil show that the drops pass through a series of stages including an increase in drop volume and surface reaction/sparking. The resulting excessive spitting of smaller metal droplets in an explosive manner is then observed, this is referred to as carbon boil. Some remaining material on the crucible after the completion of carbon boil experiments was analysed, and only negligible carbon concentration could be detected.

Based on the observations from this experimental study, the following definition has been adopted for the carbon boil phenomenon: Carbon boil occurs when a subsurface reaction in a metal drop results in the spitting of smaller metal droplets in an explosive manner, such as the reactions shown in Figs. 7 and 9. Therefore, the time for carbon boil

Fig. 10. Influence of melt sulfur content on the time for occurrence of carbon boil at 1410°C.

Fig. 11. Influence of melt sulfur content on the time for occurrence of carbon boil at 1370°C.

to occur is defined in this study as the time required to initiate the phenomenon described above. The occurrence of carbon boil depends on the pressure generated to overcome surface energy and the surface tension. Both these factors are influenced significantly by the melt composition, hence the pressure required for the occurrence of boil could vary within a range of pressures.

3.2. Influence of Melt Sulfur Content and Temperature on Carbon Boil

The influence of the melt sulfur content on the time for carbon boil was investigated by carrying out a number of experiments using Fe-C-S samples with approximately 4.1 wt% carbon and a variable content of sulfur, in the range 0.005 to 0.417 wt%. The metal samples had a weight of 0.50 g. The experiments were conducted at the gas flow rate of 11.5 l/min, that is, a velocity of 0.28 m/s (at 20°C); the gas phase contained 40% oxygen and balance argon; the metal temperature of 1410°C. The experimental results obtained are shown in Fig. 10, in which time for boil is plotted against melt sulfur content. The line is drawn through the data points to illustrate the trend.

Figure 10 shows that the sulfur content has minimal influence on the time for occurrence of carbon boil up to the sulfur content of approximately 0.2 wt%. However, with increasing melt sulfur content beyond this level the time for occurrence of carbon boil is observed to decrease from ~11 sec at 0.15 wt% sulfur to ~6 sec at 0.42 wt% sulfur.

The influence of the melt temperature on the time for occurrence of carbon boil was investigated by carrying out a number of experiments at the three different temperatures of 1370°C, 1410°C and 1450°C. The experimental results at 1410°C are shown in Fig. 10. The results of experiments at 1370 and 1450°C are shown in Figs. 11 and 12, respectively.

Figures 10, 11 and 12 show that when the melt temperature is increased to 1450°C the time for carbon boil increases compared to that at the lower temperatures. The experimental observations revealed that the carbon boil phenomenon at the temperature of 1450°C was relatively less violent compared to the boil which was observed at the lower temperatures of 1370 and 1410°C. This is illustrated by the carbon boil images shown in Figs. 13, 14 and 9, taken at the temperatures of 1370, 1410, and 1450°C, with corresponding melt sulfur content of 0.0385%, 0.159%

Fig. 12. Influence of melt sulfur content on the time for occurrence of carbon boil at 1450°C.

Fig. 13. Image showing carbon boil at 1370°C.

Fig. 14. Image showing carbon boil at 1410°C.

Fig. 15. The influence of both melt sulfur and temperature on the time for occurrence of carbon boil.

Table 2. Carbon and oxygen concentrations of metal droplets after exposing to oxidising gas for different time intervals at 1450°C.

Exposure time second	carbon in metal mass %	oxygen in metal mass %
sample 1(0.01 mass% sulfur)		
0	4.10	0.0018
4	3.31	--
8	2.81	0.0238
13	2.07	0.0242
sample 1(0.29 mass% sulfur)		
0	4.04	0.0018
4	3.46	0.0048
8	2.96	0.0118
13	2.51	0.0199

and 0.124% respectively. At the lower temperatures of 1370 and 1410°C there are significantly more fine droplets released due to carbon boil compared to the higher temperature of 1450°C.

The influence of both melt sulfur and temperature on the time for occurrence of carbon boil is shown by the trend lines in Fig. 15.

3.3. Results of Droplet Decarburisation and Oxygen Content

Table 2 shows the carbon concentration of metal droplets with 0.01% sulfur and 0.29% sulfur after being exposed to oxidising gas with 40% oxygen for different time intervals. Results clearly indicate that the decarburisation rate is depressed with an increased sulfur concentration. This is in agreement with the decarburisation studies reported by Mannion and Fruehan,¹⁸⁾ Belton¹⁹⁾ and Peprika and Skala.²⁰⁾ Only negligible change in sulfur concentration was observed throughout the duration of decarburisation experiment.

The results of oxygen analysis were also presented in Table 2. Effect of sulfur on the variation of oxygen in the metal was not clear because FeO may be generated at the surface in the later period of the reaction. Furthermore, the subsurface reaction results in small FeO or iron droplets being erupted from the sample surface, and these erupted droplets could not be collected and included in the oxygen analyses. The critical condition at which FeO is formed on the surface during the decarburisation of liquid Fe-C-S by carbon dioxide or H₂O could be determined by mutual con-

tribution of liquid phase mass transfer and interfacial kinetics as revealed by Sain and Belton²¹⁾ and Nagasaka and Fruehan.²²⁾ In the previous modeling study by Sun *et al.*²³⁾ where liquid, gas phases mass transfer and interfacial kinetics were included, the FeO was predicted to form at 9–12 sec into reaction under present experimental conditions.

In spite of above 2 mass% carbon present in the liquid, the oxygen reached contents as high as 200–240 ppm. An iron oxide layer was visually observed on the surface of the droplets which had reacted longer than 8 sec. These results were also observed by Sun *et al.*²³⁾ The phenomena indicates that the supply rate of oxygen from the bulk gas is faster than the oxygen consumption rate at the surface by the reaction, $[C] + [O] = CO$, and a portion of the oxygen reaching the surface could dissolve into the bulk metal or react with Fe at the surface to form FeO. The slow rate of decarburization could be due to an insufficient carbon supply at the surface or slow interfacial decarburization. Thus, the diffusion of carbon in the liquid is a possible rate limiting step because slow carbon diffusion from the bulk to the surface would lead to a depletion of carbon at the surface. The fact that the decarburization rate decreased with more sulfur present in the liquid suggests that the interfacial reaction is also a possible rate limiting step, because sulfur, as a surface active element will retard interfacial chemical reactions by occupying interfacial reaction sites. The occurrence of carbon boil also suggests that the liquid phase mass transfer is one of the limiting step, because it allows a concentration gradient of carbon and/or oxygen in metal, resulting in the maximum of internal pressure of CO in the radius direction of the liquid droplet.

The liquid phase mass transfer mechanism is in agreement with many investigations^{1,3)} where the Fe-C drop was allowed to fall through an oxygen column. However, in the investigations^{7,20,24,25)} where levitation technique was adopted, the diffusion in the gas phase was concluded as the rate dominating step for decarburization because of the intensive stirring within drop by magnetic field.

4. Discussion

Molten Fe-C-S drops in the presence of oxidising gases can undergo reactions leading to the generation of gaseous products, such as carbon monoxide. The formation of CO gas occurs according to the following reactions:

When CO gas is formed at the surface of the metal drop (as a result of decarburisation), it is easily liberated into the gas phase without leading to a violent explosive reaction. In this case, sparks tend to be generated as a result of the gaseous products being released from the surface or very close to the surface of the metal drop. In contrast, if the CO gas is generated within the bulk metal, its evolution from the molten drop may result in carbon boil when the internal pressure of CO is high enough to exceed the surface energy of the metal drop. The possible rate limiting steps for the generation of subsurface CO gas are: (i) transfer of oxygen in the gas boundary layer; (ii) oxygen absorption by the metal drop (Eq. (1)); (iii) transfer of oxygen to the reaction

sites within the drop; (iv) transfer of carbon to the reaction sites within the drop; (v) CO formation within the metal drop (Eq. (2)).

The time for occurrence of carbon boil depends on the increasing rate of internal pressure of CO required to overcome surface energy and on the rate of build up of CO gas pressure within the metal drop. The CO gas pressure depends on the concentration of carbon and oxygen in the metal, and other alloying elements which dictate their activity, as well as temperature. During decarburisation, the carbon content of a metal drop depends on a number of factors including the melt sulfur content, temperature, gas velocity and the oxygen partial pressure. The buildup rate of bulk oxygen depends on the difference between the oxygen absorption rate and the rate of consumption of this oxygen at the surface due to decarburisation and iron oxide formation. During oxygen absorption the oxygen content of a metal drop depends on a number of possible factors including the melt sulfur content, temperature, gas velocity and the oxygen partial pressure.

From the above discussions, it could be suggested that carbon boil may not occur under some conditions. For example, if buildup rate of bulk oxygen is slow, the internal CO pressure may not reach high enough value to overcome the surface energy. The internal CO pressure is expected to achieve some maximum value (due to bulk oxygen buildup) and drop off after that (due to lowering of bulk carbon content as a result of decarburisation). The images illustrate that the volume of a metal drop increases with time upon the introduction of oxidising gas mixtures. This occurs due to the sub-surface generation of CO gas, given by Eq. (2). When the internal CO pressure exceeds the surface energy of the metal drop carbon boil occurs, as illustrated by the images. If this is not the case then the CO pressure is eventually expected to decrease with time; in such a case carbon boil is not expected to occur.

4.1. Influence of Melt Sulfur Content on Carbon Boil

Figures 10–12 show that the time for occurrence of carbon boil is only marginally dependent of sulfur content up to a certain sulfur level beyond which increasing melt sulfur content decreases the carbon boil time.

The occurrence of carbon boil is dictated by the internal CO pressure generation and the surface tension of the liquid as explained earlier, which are both dependent on metal sulfur content. Surface tension decreases with increasing melt sulfur content,²⁶⁾ it would be expected that faster occurrence of carbon boil should be observed with increasing melt sulfur, provided that internal CO generation is not retarded as the sulfur is increased.

On the other hand, an increase in metal sulfur contents would decrease the surface decarburization reaction, which allows more buildup of oxygen and less decrease of carbon in the droplet, consequently more buildup of internal CO pressure and less time period would be required for occurrence of carbon boil.

4.2. Influence of Melt Temperature on Carbon Boil

Comparison of Figs. 10, 11 and 12 shows that the time required for occurrence of carbon boil increases as the melt temperature is increased. The effect of the melt temperature

on the boil time may be explained as follows. There are many studies, for example the study by Fruehan *et al.*,²⁷⁾ suggesting that an increase in melt temperature leads to an increase in the rate of decarburisation. Hence, for a decrease in the melt temperature the rate of decarburisation will be slower, resulting in a relatively higher carbon content remaining in the metal after the same time period. The equilibrium constant of Reaction (2) decreases with increasing temperature and internal CO pressure would be decreased with increasing temperature as reported by Sun *et al.*²³⁾ This could result in the carbon boil time to increase with an increase in the melt temperature, which is in accordance with the results obtained. Examination of literature shows that there is no agreement regarding the influence of temperature on surface tension, Keene²⁸⁾ has summarized these studies in the literature, therefore the effect of surface tension is not considered here.

4.3. Factors Influencing on Carbon Boils

As discussed earlier, the occurrence of carbon boil is due to sufficient super-saturation CO pressure to overcome the surface energy. However, both CO pressure and surface tension are influenced by a number of factors. To predict the possibility of occurrence of carbon boil under different specific experimental conditions, the influence of different factors could be included by considering their effect on CO pressure and surface tension.

Carbon boil would likely occur when there is higher internal pressure of CO and lower surface tension. The internal CO pressure and surface tension are influenced by a number of factors including decarburisation, oxygen absorption, sulfur content, temperature, and *etc.* A modeling study has been recently completed by Sun *et al.*,²³⁾ the model developed takes into account the influence of these factors on CO pressure, which is the proposed criterion for the occurrence of carbon boil in this study.

The relationship between CO pressure and metal surface tension, for a given size of the gas bubble is expressed by the equation, as shown below,²⁹⁾

$$P_{CO} = P_0 + \frac{2\sigma}{r} \dots\dots\dots(3)$$

where P_{CO} is the internal pressure, P_0 the atmospheric pressure, σ the surface tension and r is the radius of bubbles formed inside the metal. The radius of bubble formed inside of metal are then given by,

$$r = \frac{2\sigma}{P_{CO} - P_0} \dots\dots\dots(4)$$

The nucleation of a CO bubble, or the carbon boil, is likely to occur when the radius is small. Any factor which reduces the radius, r , would increase the possibility of the carbon boil occurrence. As can be seen from Eq. (4), a smaller r can be obtained by increasing internal pressure of carbon monoxide and decreasing surface tension.

The carbon is lower for runs at low sulfur contents or at higher temperatures, since the decarburization rate increases with reduced sulfur in the liquid or with increasing temperature. Although as mentioned earlier, the effect of sulfur on the variation of oxygen in the metal could not

confirmed from experimental observation, the oxygen is also predicted²³⁾ to be lower for runs at lower sulfur contents or at higher temperature because more oxygen is consumed by the interfacial decarburization. Consequently, internal P_{CO} which is strongly affected by sulfur and temperature, increases with increasing sulfur content and decreases with increasing temperature. The negative temperature dependence of the equilibrium constant of Reaction (2) could be another reason for the decrease of the internal CO pressure with increasing temperature.

The surface tension is sensitive to the sulfur content, and will be reduced by adding small amounts of sulfur. Unlike other systems, the surface tension of Fe–C–S liquid has a positive temperature dependency.²⁶⁾ Surface tension of higher sulfur liquid is lower than that of lower sulfur liquid, and that of a higher temperature is higher than that of a lower temperature.

The effect of sulfur on the carbon boil phenomenon can be interpreted by comparing samples containing different levels of sulfur, but are otherwise essentially the same. As discussed above, the surface tension decreases and internal CO pressure increases with increasing sulfur concentration in the liquid. The lower surface tension and higher internal pressure for higher sulfur sample results in earlier occurrence of carbon boil as seen in Figs. 10–12. Similar reasoning could also be applied for interpreting the effect of temperature by comparing the results of runs where different temperatures were used as shown in Fig. 15. A lower internal P_{CO} for high temperature run than that of low temperature, and the higher surface tension of high temperature run than that of low temperature run results in the occurrences of carbon boil to be delayed at higher temperature.

Although the carbon boil phenomena are qualitatively well explained by this study. The boundary conditions for the boil phenomenon are not yet sufficiently clear to predict the phenomenon on a quantitative basis. There are several aspects which remain unclear in the present study. Firstly, the subsurface CO generation, which will release some carbon and oxygen from inside of the droplet to the gas phase is still not clear enough to be described quantitatively. Secondly, the effects of the turbulence within the liquid drop due to gas bubbles or circulation by the gradient of temperature within the droplet on the liquid mass transfer rate are uncertain. Furthermore, the oxygen supply rate from gas could not be determined precisely after the FeO formation at the liquid surface due to the uncertainty of the reaction area at surface and the oxygen transport rate in the FeO layer. Unless these aspects are clarified quantitatively, the gradients of carbon and oxygen contents, and consequently gradients of P_{CO} and surface tension in the droplet could not be determined for a quantitative discussion of the carbon boil phenomena.

5. Conclusions

The following conclusions could be made from the present investigation.

(1) Under the conditions in this study, the time for occurrence of carbon boil is independent of the sulfur content up to a certain level and then decreased with a further increase in sulfur content. This can be explained on the basis

of dependence of surface tension and CO pressure generated on melt sulfur. The time for boil was in the range ~5 to ~20 sec.

(2) The time for occurrence of carbon boil increases with an increase in melt temperature. This can be explained on the basis of dependence of decarburisation rate and iron oxide formation on temperature. The decarburisation rate is accelerated with temperature, which results in lowering the melt carbon content and oxygen content within a comparable time period as reported by Sun *et al.*²⁵⁾ This lowers the CO pressure generation rate and therefore requires longer time to result in occurrence of carbon boil.

(3) The mechanism for carbon boil involves the supersaturation of a metal droplet with CO gas which attains internal pressures which are sufficient to overcome the surface energy of the molten metal.

(4) The influence of the critical factors dictating the occurrence of carbon boil could be translated into an internal CO pressure generated and surface tension, which is proposed to interpret the occurrence of carbon boil.

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REFERENCES

- 1) P. G. Roddis: *JISI*, **211** (1973), 53.
- 2) N. H. El-Kaddah and D. G. C. Robertson: *Metall. Trans. B*, **9B** (1978), 191.
- 3) L. A. Baker and R. G. Ward: *JISI*, **205** (1967), 714.
- 4) N. H. El-Kaddah and D. G. C. Robertson: *Metall. Trans. B*, **19B** (1988), 831.
- 5) M. Hayer and S. G. Whiteway: *Can. Metall. Q.*, **12** (1973), 35.
- 6) D. G. C. Robertson and A. E. Jenkins: *Heterogeneous Kinetics at Elevated Temperatures*, Plenum Press, New York, (1970), 393.
- 7) P. A. Distin, G. D. Hallett and F. D. Richardson: *JISI*, **206** (1968), 821.
- 8) J. B. See and N. A. Warner: *JISI*, **211** (1973), 44.
- 9) M. Sano, H. Ye-Tao and M. Katoh: *Proc. of the 6th Int. Iron and Steel Cong.*, ISIJ, Tokyo, (1990), 370.
- 10) M. Sano, H. Yetao, T. Sawada and M. Kato: *ISIJ Int.*, **33** (1993), 855.
- 11) T. Emi, W. M. Boorstein and R. D. Pehlke: *Metall. Trans. B*, **5** (1974), 1956.
- 12) T. Emi and R. D. Pehlke: *Metall. Trans. B*, **3** (1975), 95.
- 13) S. K. Vig and W.-K. Lu: *JISI*, **209** (1971), 630.
- 14) L. A. Greenberg and A. McLean: *Trans. Iron Steel Inst. Jpn.*, **14** (1974), 395.
- 15) T. Choh and M. Inouye: *Trans. Iron Steel Inst. Jpn.*, **20** (1980), 768.
- 16) L. Zhang and F. Oeters: *Steel Res.*, **62** (1991), 95.
- 17) J. Moodie, M. Davis and M. Cross: *Proc. 1988 Process Technology Conf.*, ISS, Warrendale, PA, (1988), 55.
- 18) F. J. Mannion and R. J. Fruehan: *Metall. Trans. B*, **20B** (1989), 853.
- 19) G. R. Belton: *Metall. Trans. B*, **24** (1993), 241.
- 20) T. Paprika and J. Skala: *Kovovc Mater.*, **27** (1989), 339.
- 21) D. R. Sain and G. R. Belton: *Metal. Trans. B*, **7B** (1976), 235.
- 22) T. Nagasaka and R. J. Fruehan: *ISIJ Int.*, **34** (1994), 241.
- 23) H. Sun, K. Gao, V. Sahajwalla, K. Mori and R. D. Pehlke: *ISIJ Int.*, **39** (1999), 1125.
- 24) H. Sun and R. D. Pehlke: *Metall. Trans. B*, **23B** (1995), 335.
- 25) H. Sun and R. D. Pehlke: *Metall. Trans. B*, **23B** (1996), 854.
- 26) L. Jimbo, A. Sharan and A. W. Cramb: *Proc. of 76th Steelmaking Conf.*, ISS, Warrendale, PA, (1993), 485.
- 27) R. J. Fruehan, G. R. Belton, F. J. Mannion and Y. Sasaki: *Metall. Trans. B*, **23B** (1992), 45.
- 28) B. J. Keene: *Int. Mater. Rev.*, **33** (1988), 1.
- 29) N. P. Allen: *J. Inst. Met.*, **49** (1932), 317.