Rate of Melting of Partly Reduced Iron Pellets into Iron Melt*

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Synopsis

The rate of melting of partly reduced iron pellets into iron melt was determined by measuring the amount of CO gas evolved. The effect of composition of pellets as well as those of temperature and carbon content of iron melt on the melting rate have been investigated. The following results were obtained:

(1) The apparent activation energy for melting of reduced iron pellets containing 0, 10, 20 and 40% Fe_2O_3 was 33 kcal/mol.

(2) Without the presence of molten slag on the iron melt, the maximum melting rates of pellets containing 10, 20 and 40% Fe_2O_3 were determined by using the iron melts of about 3.3, 3.0 and 2.5% carbon, respectively.

(3) The melting rate was proportional to -0.5 power of the Fe_2O_3 content in the range of 15~60% Fe_2O_3 . The rate was larger than the value at 2~10% Fe_2O_3 and was smaller than the value above 70% Fe_2O_3 .

(4) By the addition of 2 to 5% of CaO , CaCO_3 or C the melting rate of pellets was increased, while it was decreased markedly by the addition of Al_2O_3 or SiO_2 . In the cases of simultaneous addition of CaO and SiO_2 ($\text{CaO}/\text{SiO}_2=1$) and addition of pre-fused slag having low melting point, the melting rate was slightly decreased, but their contents in pellets should be below 15%.

I. Introduction

The research work on the continuous iron- and steel-making process from directly reduced iron or pre-reduced iron ore (called reduced iron hereafter) has been carried on at NRIM since 1974. It was shown that the melting rate of reduced iron pellets with high reduction degree into iron melt was greatly affected by the residual oxygen content, content and composition of gangue in pellets, carbon content and temperature of iron melt.¹⁻⁴⁾

In this report, the melting rate of partly reduced iron pellets into iron melt has been determined by measuring the amount of CO gas evolved by the reduction of iron oxide in pellets with carbon in the iron melt. The effects of the above mentioned factors on the rate of melting have been investigated.

II. Experimental

Figure 1 shows a schematic diagram of the experimental apparatus with a Tammann furnace for controlled atmospheric melting. Volume of CO gas evolved was measured by an integrating gas meter. Because the measurable range of this meter was 5 to 300 l/h, nitrogen gas was flowed at the rate of 60 l/h in order to detect the end of reduction.

By the combined use of the electric power source equipped with silicon circuit rectifiers and the temperature controller with a PR-6/30 thermocouple, the iron melt was kept at a pre-determined temperature

within $\pm 5^\circ\text{C}$. The temperature of iron melt was also measured with a Pt-Pt/Rh thermocouple immersed into the melt.

The Fe-C alloy used was prepared by melting the mixture of electrolytic pure iron and electrode carbon powders in a graphite crucible with an induction furnace. A graphite or a alumina crucible was used for the preparation of iron melts of saturated carbon and various carbon contents. Crucibles were of 55 mm ID and 190 mm long. Weight of the iron melt used was about 1.5 kg whose volume was about a half of the crucible. Carbon content of the iron melt was determined by the chemical analysis of sample sucked up with quartz tube.

Partly reduced iron pellets of cylindrical shape were made by pressing the mixture of Hōganās iron powders, Fe_2O_3 [special grade chemical reagent (C.A.)] and other additives in a die with a 60-t oil press. The weight, the horizontal sectional area and the forming pressure of pellets were 70 g, 7 cm^2 and 4 t/cm^2 , respectively. Pulverized additives were Al_2O_3 (first grade C.A.), CaCO_3 (first grade C.A.), CaO (95.2% CaO), SiO_2 (99.8% SiO_2), electrode carbon (98% C) and prefused slag (43% CaO , 48% SiO_2 , 9% Al_2O_3). Contents of Fe_2O_3 and additives were 10–20–40% and 2–5–10%, respectively. Density of pellet was calculated from the weight and the height measured by a direct-vision balance and a micrometer, respectively.

The experimental procedure was as follows: Fe-C alloy was melted in a nitrogen atmosphere and held at an experimental temperature for 30 min. The surface of the iron melt was cleaned by scraping and then Fe_2O_3 was added. After stirring of the iron melt, samples for chemical analysis were taken out

Fig. 1. Schematic diagram of experimental apparatus

* Originally published in *Tetsu-to-Hagane*, **65** (1979), 195, in Japanese. English version received December 11, 1978.

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by suction. From 5 min after closing the window of furnace, the flow rate of nitrogen gas was recorded every 30 sec for 2 min. A pellet previously charged in the apparatus was dropped onto the melt. From that moment, the gas flow rate was recorded every 5 sec. Volume of CO gas evolved was obtained by subtracting the nitrogen gas flow rate from the gas flow rate measured. The time required for melting of pellets was determined on the basis of the diagrams showing the relation between the amount of CO gas evolved and the elapse of time. The melting rate (g/sec) was obtained by dividing 70 g by the time required for melting (sec).

The reproducibility was determined by the results of repeated runs at each experimental condition.

III. Results

Figure 2 shows the dependence of the amount of CO gas evolved on the content of Fe_2O_3 in pellets added onto the iron melt saturated with carbon at 1520°C . The maximum CO gas evolving rate (Nm^3/sec) increased with increasing content of Fe_2O_3 except for 5% Fe_2O_3 . For 5% Fe_2O_3 the melting rate was very rapid, and at the same time, the gas evolving rate was also very rapid. Volume of CO gas evolved reached almost to the theoretical value for pellets of 2~40% Fe_2O_3 , but for pellets of 50~70% Fe_2O_3 the value obtained was slightly lower than the theoretical one. This was confirmed to be due to the CO_2 gas simultaneously evolved in a small quantity when the CO gas evolving rate was very rapid. That is, the amount of CO_2 gas evolved was about 1% according to the measurement by a simple CO_2 gas meter with the accuracy of 0.5% for the pellet of 70% Fe_2O_3 , although CO_2 gas could not be detected for pellets of 2~30% Fe_2O_3 .

Figure 3 shows the effect of the Fe_2O_3 content in pellets on the time necessary for melting into the iron melt saturated with carbon at 1520°C . The melting rate showed a maximum at about 2% Fe_2O_3 and decreased linearly with increasing content of Fe_2O_3 in the range of 15~60% Fe_2O_3 . The melting rate of pellets containing above 70% Fe_2O_3 seemed to decrease markedly.

Figure 4 shows the dependence of the time necessary for melting on the temperature of iron melt saturated with carbon and on the Fe_2O_3 content in pellets. The melting rate increased with increasing temperature and with decreasing content of Fe_2O_3 . However, it is shown that the rate at 1620°C is nearly the same as that at 1570°C .

Figure 5 shows the dependence of the amount of CO gas evolved on the temperature of iron melt saturated with carbon and on the Fe_2O_3 content in pellets. The maximum CO gas evolving rate increased with increasing temperature and with increasing content of Fe_2O_3 .

Figure 6 shows the dependence of the time necessary for melting on the carbon content in iron melt at 1520°C and on the Fe_2O_3 content in pellets. The melting rate of pellets without Fe_2O_3 increased with increasing carbon content. But the melting rates of

Fig. 2. Dependence of CO gas evolved on Fe_2O_3 content in pellet added onto iron melt saturated with carbon at 1520°C .

Fig. 3. Effect of Fe_2O_3 content in pellets on their time for melting into iron melt saturated with carbon at 1520°C .

Fig. 4. Dependence of the time for melting on temperature of iron melt saturated with carbon and on Fe_2O_3 content in pellets.

pellets containing 10, 20 and 40% Fe_2O_3 showed maxima at about 3.3, 3.0 and 2.5% C, respectively. The rate decreased remarkably for the iron melt of less than 1% C. The rates measured in Al_2O_3 crucibles for the samples of high carbon contents were rather lower than those obtained in graphite crucibles.

Figure 7 shows the dependence of the amount of

Fig. 5. Dependence of CO gas evolved on temperature of iron melt saturated with carbon and on Fe_2O_3 content in pellets

Fig. 6. Dependence of the time for melting on carbon content in iron melt at 1520°C and on Fe_2O_3 content in pellets

Fig. 7. Dependence of CO gas evolved on carbon content in iron melt at 1520°C and on Fe_2O_3 content in pellets

CO gas evolved on the carbon content in iron melt at 1520°C and on the Fe_2O_3 content in pellets. The CO gas evolving rate fluctuated widely in the region of low carbon content as in the case of the pellet of $40\%\text{Fe}_2\text{O}_3$ for the iron melt of $1.6\%\text{C}$.

Figures 8 to 12 show the effects of CaO, CaCO_3 , carbon, CaO- SiO_2 mixture ($\text{CaO}/\text{SiO}_2=1$), prefused slag, SiO_2 and Al_2O_3 in pellets on the time necessary for melting into the iron melt saturated with carbon at 1520°C , respectively. With increasing CaO, CaCO_3 or carbon content, the melting rate increased, showed maxima and then decreased, as shown in Fig. 8 to 10. In the case of CaO- SiO_2 mixture or slag, the melting rate decreased it slightly as shown in Fig. 11, but for SiO_2 or Al_2O_3 decreased markedly as shown in Fig. 12. The pellets containing more than

Fig. 8. Effect of CaO and Fe_2O_3 content in pellets on their time for melting into iron melt saturated with carbon at 1520°C

Fig. 9. Effect of CaCO_3 and Fe_2O_3 content in pellets on their time for melting into iron melt saturated with carbon at 1520°C

Fig. 10. Effect of carbon and Fe_2O_3 content in pellets on their time for melting into iron melt saturated with carbon at 1520°C

Fig. 11. Effect of (a) flux, (b) slag and Fe_2O_3 content in pellets on their time for melting into iron melt saturated with carbon at 1520°C flux ($\text{CaO}/\text{SiO}_2=1$)

Fig. 12. Effect of (a) SiO_2 , (b) Al_2O_3 and Fe_2O_3 content in pellets on their time for melting into iron melt saturated with carbon at 1520°C

5% Al_2O_3 floated on the iron melt for more than 10 min keeping cylindrical shape. The CO gas evolving rate of pellets containing 2% Al_2O_3 fluctuated widely for the elapse of time similarly to the case of iron melt of low carbon content.

IV. Discussion

It is considered that the kinetics of melting of a partly reduced iron pellet into iron melt consists of the following four main processes: (1) the heat transfer from the iron melt to the pellet, (2) the transfer of carbon from the iron melt to the melting interface, (3) the transfer of iron from the pellet to the iron melt, and (4) the reduction of iron oxides in the pellet by carbon in the iron melt. Processes from (1) to (3) are similar to those for melting of steel scrap in an iron bath and for a highly reduced iron pellet on the iron melt.⁵⁻¹³⁾ In this research, the process of (4) is considered to play an important role.

Researches on the reduction of iron oxides by carbon in iron melt reported so far are as follows: Dancy¹⁴⁾ reported that there was a pressure increase from 100 mm Hg when iron oxides (FeO , Fe_3O_4) weighing 0.5 g were dropped onto the carbon saturated iron melt weighing 50 g in a rotating MgO crucible, and that the apparent activation energies obtained by neglecting the area of the reaction interface were 43 and 37 kcal/mol for FeO and Fe_3O_4 , respectively. MacRae¹⁵⁾ obtained the pressure increase from 2 torr to 600 torr when Fe_2O_3 sample of cylindrical shape weighing 3 g was dropped onto the carbon saturated iron melt weighing 600 g in a graphite crucible. The apparent activation energies obtained by neglecting the area of the reaction interface were 27 and 44 kcal/mol for 60 and 480 torr, respectively. Since the melting rate and the apparent activation energies changed with the variation of initial pressure, the rate was considered to be determined by the mixed steps of complex chemical reactions and diffusion processes. Lloyd *et al.*¹⁶⁾ reported that a pressure increase from 200 to 300 mmHg was observed when Fe_2O_3 weighing 0.710 g was dropped onto the iron melt weighing 180 to 200 g in an Al_2O_3 crucible. Measuring the area of reaction interface between the iron oxide assumed to be liquid and the iron melt with a planimeter, the activation energy of 56 kcal/mol was obtained. The rate determining step of the process was considered to be the diffusion of carbon in the case of the iron melt below 0.2wt%C and the mixed step of the diffusion of carbon and the chemical reaction for the iron melt of 0.2wt%C or above. Because the rate of preheated sample was almost the same as that of cold one, and because the activation energy of the process was higher than that of the heat transfer, the heat transfer was not considered to be the rate determining step.

In this experiment, it was observed that pellets of 40% Fe_2O_3 reacted with carbon in iron melt in the solid state. Therefore, it was impossible to measure the area of reaction interface from the top. Accordingly, the apparent activation energies were obtained by neglecting the area of the interface. Figure

13 shows the relation between $\log v$ and $1/T$, where v is the melting rate (g/sec) calculated from the weight of pellets (70 g) and the time necessary for melting (sec), and T is the temperature of iron melt ($^\circ\text{K}$). The same apparent activation energy of 33 kcal/mol was obtained for pellets containing 0, 10, 20 and 40% Fe_2O_3 . This value can be regarded as nearly the same as that obtained by Dancy or MacRae. Though the activation energy for a pellet containing 0% Fe_2O_3 was the same as that for a pellet containing 40% Fe_2O_3 , the melting rate of a pellet containing 0% Fe_2O_3 was confirmed to be rate-determined by the heat transfer. That is, in order to confirm the result obtained by Lloyd *et al.* that the reduction rate was not rate-determined by the heat transfer, the melting rate was measured after pellets had been preheated to the temperature of melting. Namely, the pellets were suspended by a Pt wire of 0.5 mm diameter just above the iron melt for 10 min. The iron melt was saturated with carbon and its temperature was 1520 $^\circ\text{C}$. The times necessary for melting of pellets containing 0, 10, 20 and 40% Fe_2O_3 were 13, 65, 95 and 125 sec, respectively. The melting rate of pellets containing 0% Fe_2O_3 increased remarkably, but the increment of the melting rate of pellets containing Fe_2O_3 was at most 10%. Therefore, as reported by Lloyd *et al.*,¹⁶⁾ the melting rate of pellets containing Fe_2O_3 was not rate-determined by the heat transfer.

On the other hand, because the iron melt used was saturated with carbon and was stirred by CO bubbles, and because the activation energy for the diffusion of carbon in the carbon saturated iron melt was much lower than 33 kcal/mol, the diffusion of carbon in iron melt can not be considered to be the rate determining step. Accordingly, the reduction would be remained as the rate determining step for pellets containing Fe_2O_3 . The difference between the apparent activation energy obtained in this research work and the true one obtained by Lloyd *et al.*¹⁶⁾ may be attributable to the evaluation of area of the reaction interface. This must be confirmed by detailed experiments in future.

Figure 14 shows the relation between $\log v$ and $\log (\% \text{C in iron melt})$, where v is the melting rate mentioned above. Below the carbon per cent of the maximum melting rate, the melting rate is propor-

Fig. 13. Relation between $\log v$ and $(1/T)$

Fig. 14. Relation between $\log v$ and $\log (\%C \text{ in iron melt})$

tional to 0.96 and 2.4 powers of the carbon per cent for pellets containing 0, 10, 20 and 40% Fe_2O_3 , respectively. The proportionality of the melting rate of pellets containing 0% Fe_2O_3 to the carbon content is similar to that of the melting of steel scrap into Fe-C alloy bath.⁵⁻¹³⁾ On the other hand, the proportionality of the melting rate of pellets containing Fe_2O_3 to 2.4 powers of the carbon content is considered to be due to the reduction of iron oxide. At the carbon per cent of the maximum melting rate, the stirring of the iron melt by CO bubbles was so vigorous that the iron melt was frequently spurted from the crucible. The reason why vigorous stirring is taken place is not known yet. Above the carbon per cent of the maximum melting rate, the melting rates of pellets containing 0, 10, 20 and 40% Fe_2O_3 were proportional to about 0, -2.6, -1.9 and -1.1 powers of the carbon per cent, respectively. But the reason that the proportionality is valid is not clarified either.

Figure 15 shows the relation between the Fe_2O_3 content in pellets and the melting rate into iron melt saturated with carbon at 1 520°C. The melting rate is proportional to -0.5 power of the Fe_2O_3 content of pellets in the range of 15% to 60% Fe_2O_3 . A remarkable increase in the rate at 2~10% Fe_2O_3 would be due to the stirring by CO bubbles. A decrease in the melting rate of pellets containing above 70% Fe_2O_3 may be due to the decrease in the reaction rate of liquid iron oxides.¹⁵⁾

Figure 16 shows the effect of additives in pellets on the heat required for melting at 1 520°C. The heat was obtained by the thermodynamic and thermochemical calculations.^{17,18)} CaO , SiO_2 or Al_2O_3 increase the heat and CaO-SiO_2 mixture decreases it slightly. By adding 10% of CaCO_3 or carbon, the heat is increased about 20%. In the case of 2 to 5% addition of CaO , CaCO_3 or carbon, the melting rate and the heat are also increased. Therefore, the heat has a little effect on the melting rate.

The increase of the melting rate by the addition of CaO may be the same as that reported by Takahashi *et al.*¹⁹⁾ The increase of the melting rate by the addition of CaCO_3 would be attributable to the stirring by CO_2 gas bubbles brought about by the decomposition of CaCO_3 . The increase of the melting rate by

Fig. 15. Relation between Fe_2O_3 content in pellets and their melting rate into iron melt saturated with carbon at 1 520°C

Fig. 16. Effect of additives in pellets on their heat required for melting

the addition of carbon would be due to the formation of eutectic of Fe-4.3% C and the reaction between solid Fe_2O_3 and solid carbon. In order to produce pellets of high melting rate practically, the followings should be taken into consideration. Because of the reaction of CaO in pellets with moisture and CO_2 in air, the pellets collapsed in a few days. Therefore, in order to increase the rate, CaCO_3 should be added instead of CaO . Addition of 5% CaCO_3 would be proper as it does not increase the heat required for melting greatly. Because the pellets added 5% C decreased their strength markedly, the addition of 3% C would be proper.

Though CaO-SiO_2 mixture or prefused slag had a little effect on the rate in the range up to 10% addition, the pellets were wetttable by the iron melt when the molten slag was not present on the iron melt. Therefore, the apparent melting rate was considered to decrease slightly because the area of melting interface increased. When the addition of slag was more than 15%, Fe_2O_3 would melt into the molten slag. As a result of this the melting rate would be decreased remarkably.

The reason why Al_2O_3 or SiO_2 decreased the rate extremely would be due to the formation of the slag

of a high melting point at the melting interface as reported in the previous report.²⁾

Fluctuations of the CO gas evolving rate at low carbon content in iron melt would be due to the stagnation of the reaction owing to the lack of carbon transfer. On the other hand, fluctuations of the CO gas evolving rate of pellets added 2%Al₂O₃ would be due to the accumulation of Al₂O₃ at the melting interface.

Philbrook *et al.*²⁰⁻²²⁾ reported that the reduction of iron oxide in molten slag was very slow. The molten slag is necessary to stabilize the arc when pellets are melted in an arc furnace. Therefore, the research into the effect of molten slag upon the melting rate of reduced iron pellets into iron melt is very important, and will be carried out in future.

V. Conclusion

The rate of melting of partly reduced iron pellets made of iron powders, Fe₂O₃ powders and pulverized additives was determined by measuring the amount of CO gas evolved. The effects of the composition of pellets as well as temperature and carbon content of iron melt on the rate of melting have been investigated. The following results were obtained:

(1) The apparent activation energy for melting of reduced iron pellets containing 0, 10, 20 and 40%Fe₂O₃ was 33 kcal/mol. The rate determining step is considered to be the heat transfer and the reduction of pellets charged with and without Fe₂O₃.

(2) When molten slag was not present on iron melt, the maximum melting rate of pellets containing 10, 20 and 40%Fe₂O₃ were determined by using the iron melts of about 3.3, 3.0 and 2.5%C.

(3) Below the carbon content which showed the maximum melting rate, the melting rate was proportional to 0.96 and 2.4 powers of the carbon content for pellets charged with and without Fe₂O₃.

(4) The melting rate of pellets into the iron melt saturated with carbon at 1520°C was proportional to -0.5 power of the Fe₂O₃ content in the range of 15 to 60%Fe₂O₃. The rate was greater than the value at 2 to 10%Fe₂O₃ and was smaller than the value in the range above 70%Fe₂O₃.

(5) By the addition of 2 to 5% of CaO, CaCO₃ or carbon, the rate of melting was increased, while it was decreased remarkably by the addition of Al₂O₃ or SiO₂. In the cases of simultaneous addition of

CaO and SiO₂ (CaO/SiO₂=1) and addition of pre-fused slag having low melting point, the rate was slightly decreased in the range up to 5%, but their contents in pellets should be below 15%.

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