

the interface and did not show any signs of dissolution into the slag that was saturated with respect to alumina. Hence, it could be speculated that these inclusions are either alumina or rich in alumina.

The only inclusions that were observed to separate across the interface were type B inclusions, which generally traveled along the metal meniscus and gradually emerged on the slag side, as shown in Figure 2. As can be seen in Figures 2(b) and (c), the process caused the interface to be stretched to such an extent that the final separation from the interface caused a wave that pushed away the adjacent inclusions. The separation phenomenon in this case is shown schematically in Figure 3. An average of 3 to 4 seconds elapsed from the moment that the inclusion could be first observed to the point that it separated from the interface. If a type B inclusion would rise directly to the interface at the center of the meniscus, it could be seen at the interface for 1 to 2 seconds after which it would disappear from the screen, presumably separating into the slag. Thus, liquid inclusions can separate at a slag-metal interface but only after a significant rest time at the interface.

On a very few occasions, the inclusion was observed to re-emulsify into the metal. In such cases, there was no disturbance on the adjacent inclusions, suggesting that the inclusion had not separated enough to stretch the liquid film.

Aside from the inclusion separation, four types of inclusion interactions were observed on the slag side of the interface:

- (1) type B inclusions would occasionally attract and absorb type C;
- (2) type C inclusions would attract one another and form agglomerates (Figures 4(a) through (d));
- (3) type D inclusions would cluster but not agglomerate; and
- (4) if a type C inclusions were in the vicinity of a type D inclusion, it would remain near it.

The attraction between type C inclusions was strong enough to counter the fluid flow along the meniscus caused by buoyancy. The attractive force had a range of 100  $\mu\text{m}$ . At a distance of 40  $\mu\text{m}$ , the particle slowed down and the final approach was at a much slower rate. It is expectable that at these distances, capillary effects due to the meniscus deformation are responsible for the attraction between the inclusions. At smaller distances, repulsive double layer force and attractive Van der Waals force at the interfaces<sup>[3]</sup> may cause the inclusions to either coalesce, cluster, or remain separated. Figure 5 shows the separation distance with time for two cases where an inclusion approached and finally attached itself to another agglomerated particle. The decrease in distance with time can be used to evaluate the net attractive force acting on the particle approaching an agglomerate. This force was estimated to be between  $10^{-15}$  and  $10^{-16}$  N when using a density of  $3 \text{ g} \cdot \text{cm}^{-3}$  for the inclusion and assuming a spherical particle shape. This is within the same range as the capillary forces reported by Yin *et al.*,<sup>[4]</sup> who observed the long-range attraction between particles on the surface of molten steel in contact with argon. Type C inclusions would remain and agglomerate at the slag side of the interface and were never observed to dissolve into the slag. If the type C inclusion were alumina-rich solid particles, this would be expected as the slag was

most likely saturated with alumina from the crucible. This suggests that agglomeration of alumina can occur at slag-metal interfaces when the slag is saturated with respect to alumina or the alumina dissolution rate is low.

In the current article, inclusions at a slag metal interface were observed for the first time *in situ* with a scanning laser microscope. The separation across the interface into the slag was only observed for one of the four observed types of inclusions (type B). Agglomeration of solid inclusions and liquid inclusions capturing solid ones was seen to occur at the interface.

These results suggest that the rest time for inclusions at slag metal interfaces depends considerably on the inclusion type and may be quite long in industrial vessels such as ladle, tundish, and mold. It is thus important to tailor the inclusions not only with respect to subsequent rolling operations but also with respect to achieving a rapid separation across the interface. The inclusions that do separate relatively rapidly do so depending on the curvature of the meniscus. If they hit the interface at a highly curved surface, then they travel upward along the meniscus and separate or occasionally get re-entrained at the top of the meniscus.

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## Effect of Temperature on Cementite Formation by Reaction of Iron Ore with $\text{H}_2\text{-CH}_4\text{-Ar}$ Gas

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Temperature strongly affects cementite formation and its stability.<sup>[1,2,3]</sup> This article reports experimental results on cementite formation by reaction of iron ore with  $\text{CH}_4\text{-H}_2\text{-Ar}$  gas in the temperature range 600 °C to 925 °C.

Experiments on iron ore reduction/cementation were conducted in a laboratory fixed bed reactor. Gas mixture was prepared from purified methane, hydrogen, and argon (35 vol pct  $\text{CH}_4$ , 55 vol pct  $\text{H}_2$ , and 10 vol pct Ar). The total gas flow rate was maintained at 1000  $\text{cm}^3/\text{min}$ . The size of iron ore (Mt Whaleback, Western Australian) was 0.35 to

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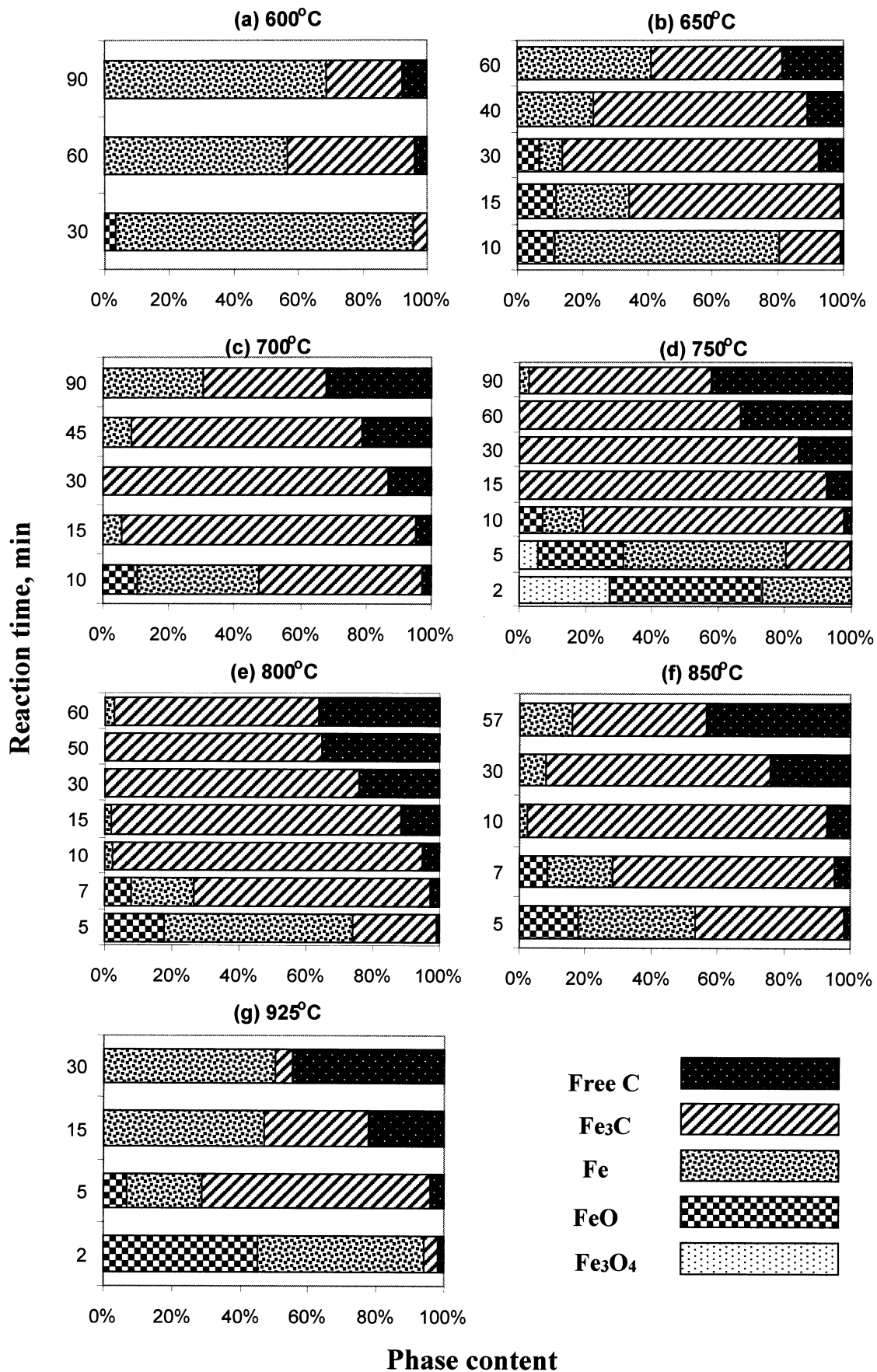


Fig. 1—(a) through (g) Phases formed in the iron ore reduction/cementation process using Ar-CH<sub>4</sub>-H<sub>2</sub> gas mixture (35 vol pct CH<sub>4</sub>, 55 vol pct H<sub>2</sub>).

**Table I. Chemical Composition of Iron Ore, Weight Percent**

T.Fe	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P	Mn	S
62.7	89.56	4.81	2.61	0.08	0.087	0.04	0.026

0.5 mm. Two-gram samples of iron ore were used in all experiments. The composition of iron ore is given in Table I. A sample was heated in argon atmosphere in the reactor to a required temperature. When temperature was stabilized, reaction gases were introduced to the reactor. Reaction time varied from 2 to 120 minutes. After reaction, a sample was quenched and subjected to the x-ray diffraction and Mossbauer spectroscopy analyses. Carbon content was determined by the combustion method.

The following phases were identified in samples after reduction/cementation: Fe<sub>3</sub>O<sub>4</sub>, FeO, Fe, Fe<sub>3</sub>C, and free C. Their proportions depend on the reaction time and temperature, as illustrated in Figure 1. The cementite fraction, defined as the molar fraction of iron in cementite, is plotted as a function of reaction time at different temperatures in Fig. 2.

At 600 °C, iron ore was completely reduced in about 30 minutes, but the rate of cementite formation at 600 °C was rather slow (Figure 1(a)). The proportion of cementite in a sample after 30 minutes reaction was only about 4 wt pct. Cementite concentration increased to 40 wt pct with increasing reaction time to 60 minutes. However, further increase in the reaction time to 90 minutes resulted in a partial decomposition of cementite. Its concentration went down to about 24 wt pct.

Rate of cementite formation increased with temperature. Cementite content in a sample reacted at 650 °C for 30 minutes was found to be 80 wt pct. Reaction at 700 °C produced 87 wt pct cementite for the same reaction time. However, further exposure of reduced samples to CH<sub>4</sub>-H<sub>2</sub>-Ar gas resulted in partial cementite decomposition (Figures 1(b), and (c)). Remarkably, the rate of cementite decomposition at 650 °C was faster than that at 700 °C (Figure 2).

At 750 °C and 800 °C, iron oxides were completely converted to cementite in only 15 minutes. Cementite formed at these temperatures was relatively stable. Cementite exposed to the reducing and carburizing gas was stable for about 60 minutes at 750 °C and 50 minutes at 800 °C (Figures 1(d) and (e)). Further increases in exposure time caused slow cementite decomposition (Figure 2).

Increase in temperature from 800 °C to 850 °C and further to 925 °C accelerated the initial rate of cementite formation. Thus, after 5 minutes of reaction, the content of cementite in the sample was 45 wt pct at 850 °C and 67 wt pct at 925 °C. This concentration increased to above 90 wt pct after 10 minutes of reaction at 850 °C. However, at such high temperature, cementite started to decompose rapidly with further exposure to CH<sub>4</sub>-H<sub>2</sub>-Ar gas (Figure 1(f)). At 925 °C, the decomposition process started after 5 minutes of reaction and was faster than that at 850 °C (Figure 2).

Increase in temperature increased the rate of cementite formation in the temperature range 600 °C to 925 °C

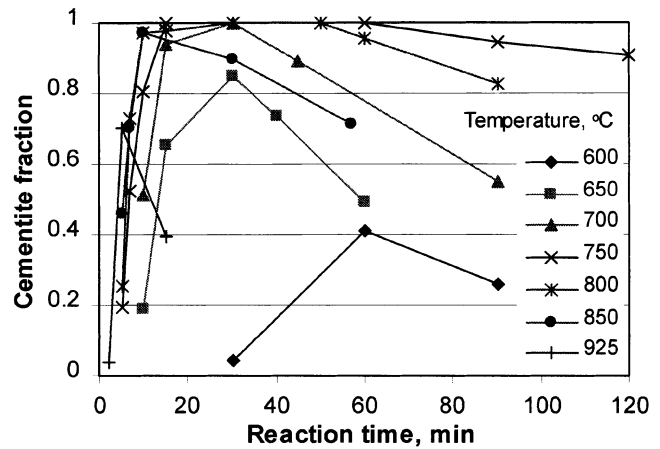


Fig. 2—Cementite fraction as a function of reaction temperature and time (CH<sub>4</sub>-H<sub>2</sub>-Ar gas composition: 35 vol pct CH<sub>4</sub>, 55 vol pct H<sub>2</sub>, and 10 vol pct Ar).

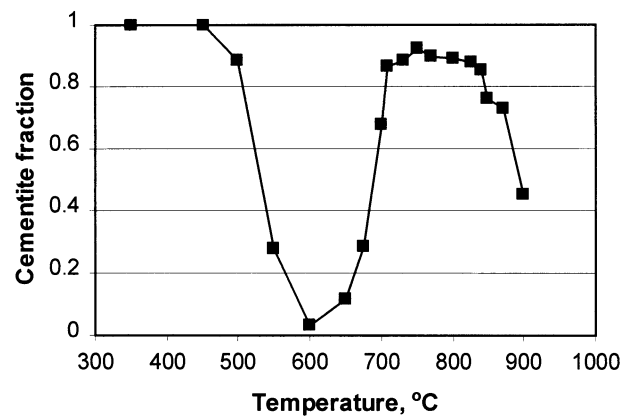


Fig. 3—Cementite fraction in a sample after 1 h exposure to argon at different temperatures.

examined in this work. However, cementite decomposition as a function of temperature exhibited a complex behavior. Increasing temperature increased the rate of cementite decomposition in the temperature range 750 °C to 925 °C. However, in the temperature range of 650 °C to 750 °C, the rate of cementite decomposition decreased with increasing temperature (Figure 2). Cementite formed under conditions employed in this work was most stable at 750 °C. This agrees with results obtained by Nakagawa *et al.*<sup>[3]</sup>

Mechanism of cementite decomposition in the gas atmosphere with high carbon activity was proposed by Grabke and Muller-Lorenz<sup>[4]</sup> and Grabke<sup>[5]</sup> in their study of iron dusting. In accordance with this mechanism, exposure of metallic iron to gas with high carbon activity results in supersaturation of iron-carbon solution and cementite formation. A further carbon ingress slows down because of low diffusivity of carbon in cementite.<sup>[4]</sup> Carbon is accumulated on the cementite surface, decreasing the activity of carbon on the surface and causing cementite decomposition.

Effect of temperature on cementite decomposition was examined further in the following experiments. Iron ore was reduced and carburized to cementite at 750 °C in 15

minutes using gas consisting of 35 vol pct methane, 55 vol pct hydrogen, and 10 vol pct argon. Then temperature was changed in the range of 350 °C to 900 °C, and gas was switched to argon. The sample was exposed in the argon atmosphere for 60 minutes. The cementite fraction obtained after decomposition as a function of temperature is given in Figure 3. It should be mentioned that a temperature change from 750 °C to another value in the range of 350 °C to 900 °C took about 15 minutes. Therefore, during those 15 minutes, experimental conditions were nonisothermal. It is seen from Figure 3 that cementite was stable at temperatures below about 500 °C. The rate of cementite decomposition increased with increasing temperature from 500 °C to 600 °C and decreased with further increase in temperature to about 750 °C. In the temperature range of 750 °C to 825 °C, the rate of cementite decomposition increased slightly with increasing temperature. With further increase in temperature above 825 °C, the rate of cementite decomposition increased quickly. In accordance with the iron-carbon phase diagram, at temperature above 727 °C,

cementite decomposes to austenite and graphite, while below this temperature, ferrite is formed. Rates of cementite decomposition into austenite-graphite and ferrite-graphite are expected to be different, which may be the main reason for a complex change in the rate of cementite decomposition with temperature.

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