Melting Behavior of Siliceous Nickel Ore in a Rotary Kiln to Produce Ferronickel Alloys

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Ferronickel alloys as a nickel source for high alloy steels such as stainless steels are produced from garnierite ores by means of a rotary kiln. That is basically modification of Krupp–Renn process by which clinkers, that are mixtures of ferronickel alloy particles and partially melted slag, can be extracted. It is necessary to have exact knowledge of how the ore is softening with increasing temperature because controlling this behavior is considered to be a key to stable operation.

A study has been carried out to understand the melting behavior of pelletized siliceous nickel ore samples blended with limestone and anthracite heating up to 1300°C. Microscopic observation revealed that mineralogical phases in equilibrium were 2(Mg, Fe)O·SiO2 olivine and (Mg, Fe)O·SiO2 enstatite. It was further found that clear formation of liquid phase composed of CaO–SiO2–FeO–Al2O3–MgO system as a result of assimilation with CaO in the case of ore containing higher Al2O3 and CaO contents with lower MgO/SiO2 ratio. Besides, this type of ore had ability to be molten by itself to generate primary liquid inside the ore. The primary liquid formation could promote assimilation with CaO particles to spread liquid phase causing melting of the ore. Mineralogical phases at 1300°C calculated by thermodynamic software were in good agreement with the experimental results.

In contrast, ore with lower Al2O3 and CaO contents with higher MgO/SiO2 ratio could not generate liquid phase even though limestone was blended. A number of remained CaO particles were observed without assimilating with the ore. It was therefore considered that higher assimilation ability of CaO with ore enhanced liquid formation and that this property was determined mainly by Al2O3 and CaO contents and MgO/SiO2 ratio of the ore.

KEY WORDS: ferronickel; nickel ore; phase analysis; slag; assimilation; melting.

1. Introduction

The demand of austenitic stainless steels is increasing year by year due to their properties representing excellent corrosion resistance, sound ductility in low temperatures and enough resistance in high temperatures. Nickel is an essential element for austenitic stainless steels to keep these properties. There are many resources for nickel such as ferro-nickel alloys, stainless steel scraps, pure nickel and so forth. This study is related to the production of ferronickel alloys. Especially, melting behavior of nickel ores was focused on when extracting ferronickel alloys.

As an extracting method,1,2) ferronickel alloys are produced from siliceous nickel ores by means of a rotary kiln modifying Krupp–Renn process. Siliceous nickel ore is so called garnierite which involves various minerals represented by serpentine, goethite, quartz, talc and other minor ones. Ni2+ ion mainly exists within serpentine substituting Mg2+ ion sites. Raw materials consisting of ground ore, limestone, anthracite, and some auxiliary materials are briquetted with adequate amount of water. They are continuously fed to a rotary kiln in which the stages of drying water, dehydration of serpentine, reduction and partial melting of siliceous ores are passed. Particles of ferronickel alloys, obtained as a result of reduction of Fe and Ni oxides by anthracite, grow during travel countercurrent to the flow of hot gas. Finally, the clinkers, that are mixtures of ferronickel alloy particles and partially melted slag, are discharged from kiln outlet. Thereafter the discharged clinkers are crashed by mill to separate ferronickel alloys and slag by flotation method.

A series of investigations1–6) were previously carried out by Matsumori mainly focusing on how one keeps reduction rate of nickel as high as possible. The investigation revealed what kind of reactions governed in a rotary kiln and how they proceeded. At first, serpentine as a major mineral is dehydrated by hot gas around 600°C followed by the formation of enstatite and forsterite. Nickel and iron oxides form a solid solution in their phases. Around 1000°C nickel oxide is reduced by CO gas as well as iron oxide resulting in the generation of very tiny ferronickel particles. They thereafter grow within the softened magnesia silicate slag that is partially molten in a rotating kiln. A measure of softening behavior of the slag above 1300°C was deter-
mined through the observation of slag formation. Matsumori proposed that the ratio of \((\text{mass}\%\text{Al}_2\text{O}_3/\text{mass}\%\text{CaO})/\text{mass}\%\text{SiO}_2\) was the best measure to express softening behavior. However, the generation of liquid phase in the slag was not fully clarified. The major reason why it was difficult to study was because X-ray diffraction technique was applied to identify most of the mineral phases. It is postulated that generation of a small amount of liquid phase occurs at the initial moment of slag melting. If the slag at this stage is successfully quenched to maintain the phases of both solid and liquid as they are at the operation temperatures, liquid should be solidified as amorphous phase which can not be identified by X-ray diffraction apparatus. As previously pointed out, softening behavior of slag, which strongly is related to the generation of liquid phase, is a key to stable operation.

As explained above, melting behavior of raw materials has not been fully understood so far. The authors have recently tried to clarify how liquid phase generates experimentally. However, some uncertainty was pointed out whether or not the observed mineralogical phase with relatively low melting temperature existed at the experimental temperature. This was because the specimens were not able to be fully quenched.

Thus this study basically aims at understanding the formation mechanism of liquid phase of the ores. Two types of siliceous nickel ore samples blended with limestone and anthracite were heated up to 1300°C in a newly developed vertical furnace equipped with an apparatus accomplishing quench rapid enough. Microstructures were observed to clarify the difference in melting behavior focusing on assimilation of limestone. In addition, phase equilibrium relations of raw materials were calculated using thermodynamic software to verify the experimental results.

### 2. Experimental Details

#### 2.1. Procedure of Heating Ores

Chemical compositions of the ores are listed in Table 1. Ore B contains larger amounts of \(\text{Al}_2\text{O}_3\) and \(\text{CaO}\). \(\text{MgO}/\text{SiO}_2\) ratio of Ore B is lower than that of Ore A. Mineralogically, the ores consist mainly of serpentine, quartz and goethite. These ore samples were well mixed with anthracite as a reductant and limestone as a flux. The ore particle size and mixing ratio of each raw material are provided in Table 2. In some experiments, limestone was not blended to determine the ability of self-melting of each ore. \(A_0\) shown in this table implies stoichiometric mass of anthracite needed for complete reduction of \(\text{Fe}\) and \(\text{Ni}\) in oxides.

### Table 1. Chemical compositions of ore samples (mass%).

| Ore | \(\text{SiO}_2\) | \(\text{Fe}\) | \(\text{Al}_2\text{O}_3\) | \(\text{Ni}\) | \(\text{CaO}\) | \(\text{MgO}\) | \(\text{MgO}/\text{SiO}_2\) |
|-----|-----------------|------|----------------|----|---------|---------|----------------|
| A   | 39.80           | 10.86| 0.52           | 2.42 | 0.10    | 28.30  | 0.71          |
| B   | 45.67           | 19.73| 1.71           | 2.04 | 0.47    | 22.96  | 0.50          |

A pellet contained in a cup assembled by Mo wires was positioned at the center of heating zone hung by a Mo wire in a vertical electric furnace shown in Fig. 1. It was heated according to the heat pattern described in Fig. 2. Namely, a pellet was heated up to 1300°C with heating rate of 5°C/min under an Ar gas atmosphere. It was held for 2 h followed by rapid quenching according to the following procedure. The separator of the bottom room containing water was firstly opened. Then the Mo wire hooked on the...
top lid was disconnected by turning the hook lever. This action allowed the pellet together with the Mo wire to drop into water to be quenched.

2.2. Observation of Microstructure

The samples after dried were infiltrated with epoxy resin not to be broken when polishing because they were very porous. After stiffened, the infiltrated pieces were mounted and polished. Thereafter, the polished specimens were gold-coated to enable observation by a scanning electron microscope (SEM).

2.3. Measurement of Phases

The mineral phases as well as liquid phase were quantitatively analyzed by an EDS (EMAX-7000, HORIBA) equipped with SEM. At first, element distributions were taken by mapping with black and white colors. Coloring treatments for the key elements were performed to visually show the microstructure. The specimens had various phases as explained later in detail. Each phase was quantitatively analyzed. Five points in each phase were randomly chosen for analysis.

2.4. Thermodynamic Calculation

MELTS software (ver. 5.0.0) is developed by Ghiorso in order for mineralogists to predict phase evolution of magma that contains mainly MgO and SiO$_2$. The principal of the program is based on standard free energy change minimization assuming that phases are in equilibrium each other. MELTS is expected to be available for thermodynamic assessment because siliceous nickel ore has components similar to peridotite. Component of the system was adjusted as CaO–SiO$_2$–FeO–NiO–Al$_2$O$_3$–MgO. Oxygen potential of the system was taken to be slightly below the potential of Fe/FeO equilibrium.

3. Results and Discussion

3.1. Microstructure of Ore

Figures 3(a) and 3(b) show the typical microstructures of Ores A and B, respectively. The darker areas correspond to pores while lighter areas are ores that are sintered at 1300°C. Focusing on the state of pores in the pictures, it can be understood that characteristic of the microstructure is significantly different each other. Morphologically the pores of Ore B have round shape while Ore A has angular shape. In porosity size, the pores of Ore B are even larger. Another significant difference was that a number of non-reacted CaO particles identified by EDS still remained in Ore A. This implies that assimilation of CaO with the ore is still in progress. On the other hand, CaO was fully assimilated in Ore B because no CaO particles remained in Ore B at all. Therefore, Ore B appears to be more progressed in sintering state taking porosity state and assimilation of CaO into account.

Furthermore, the size of ferronickel particle was so different. Ferronickel particles observed in the pellets of Ore A and Ore B are shown in Figs. 4(a) and 4(b), respectively. These particles are considered to be reduced by CO gas. Direct reduction by anthracite is considered to be negligible accounting for the distribution of anthracite blended in the pellets. It is apparent that the particle size is even smaller in Ore A than in Ore B. Typically the size in Ore A is submicron while in Ore B they range from submicron to 5 μm.

Figures 5(a) and 5(b) show the typical element distributions of Ores A and B, respectively. The major phases were identified as enstatite, olivine and liquid. The way how to identify these phases is explained later in detail. As mentioned above, the distributions of key elements were colored; red, green and blue correspond to Al, Ca and Mg, respectively. Apparently, only blue areas occupy Ore A, on the other hand, Ore B clearly has two phases that are blue and the mixture of red and green. This implies that phase

Fig. 3. Microstructures of (a) Ore A and (b) Ore B.

Fig. 4. Ferronickel particles of (a) Ore A and (b) Ore B.

Fig. 5. Element distributions of (a) Ore A, (b) Ore B with CaO added (red: Al, green: Ca, blue: Mg).

Fig. 7. Element distributions of (a) Ore A, (b) Ore B with no CaO (red: Al, green: Ca, blue: Mg).
separation of Ore B is more progressed. Table 3 shows the results of quantitative analysis by EDS proving that the blue phases consisting mainly of MgO, SiO₂, and FeO are classified into two kinds of minerals. Referring to the MgO–FeO–SiO₂ phase diagram corresponding to the constituents, the gangue phases enriched with MgO can be identified as (Mg, Fe)O · SiO₂ enstatite and 2(Mg, Fe)O · SiO₂ olivine. It is found that both olivine and enstatite coexists in Ore A while enstatite is dominated in Ore B.

On the other hand, the phase enriched by CaO and Al₂O₃ seen in Fig. 5(b) was considered not to be a compound but most likely glassy. In Table 3, this phase was analyzed as components of CaO–SiO₂–FeO–Al₂O₃–MgO system. This phase was estimated as liquid phase at 1 300°C accounting for the phase diagram along with MELTS calculation explained later. Here, the phase diagram referred to was Al₂O₃–CaO–FeO–SiO₂ system where MgO was counted as CaO, because the corresponding diagram of the above five components was not reported. Summarizing above results, Ore A consists only of the mineral phases of enstatite and olivine while enstatite is dominated in Ore B.

It should be noticed here that 2(Ca, Mg, Fe)O · 2SiO₂ augite phase has not been observed differing from the previous result. Actually this phase was estimated to be formed during cooling of pellets. Thus the present study with rapid quench has successfully proved the estimation.

As mentioned above, appearances of Ore A and Ore B heat-treated at 1 300°C are quite different each other. In particular, assimilation ability of CaO particles with the ore is even higher in Ore B resulting in the formation of a larger amount of liquid phase consisting of CaO–SiO₂–FeO–Al₂O₃–MgO system. The feature in composition of Ore B, larger amount of Al₂O₃ and CaO with lower MgO/SiO₂ ratio, may be related. To fully understand the phase evolution to bring this difference, an appreciable number of experiments have to be performed at various temperatures. That is why thermodynamic calculation has been firstly tried to verify how well the phenomena can be explained.

### 3.2. Thermodynamic Calculation

Figures 6(a) and 6(b) show phase evolutions calculated by MELTS for Ore A and Ore B, respectively. Calculation was carried out under the compositions of the ores (Table 1) in which CaO were added by 28 kg/ore-ton in capital unit. Fe and Ni were given as FeO and NiO, respectively. It is noted that the proportion of Fe–Ni alloy is not described in the figures but its proportion is calculated as 4 mass%.

Validity of the calculation has to be first discussed. When focusing on the liquid phase, generation of liquid starts at about 1 200°C for Ore B that is lower than for Ore A. Here, the liquid phase obtained in the calculation has been CaO–SiO₂–FeO–Al₂O₃–MgO system. In particular, the composition at 1 300°C is quite similar to that of Ore B, which well supports the observation. In addition, the area percent of liquid of 23% in Ore B is larger than 16% in Ore A at 1 300°C consistently with the observation. However, 16% for Ore A appears to be even larger than the observation that shows no liquid formation. This may be attributed to the fact that equilibrium is not attained for Ore A in terms of whole system. Because of the calculation based on equilibrium, complete diffusion of every component including CaO is assumed. In fact, CaO particles are actually left in the specimen due to the lower assimilation ability as shown in Fig. 3(a). According to the calculation of Fig. 6(a) for Ore A, augite should be formed instead of enstatite at the temperatures lower than 1 250°C. Augite has to be formed as a result of assimilation of CaO particles since it is expressed as 2(Ca, Mg, Fe)O · 2SiO₂. As mentioned earlier, however, augite was not observed in Ore A.

Therefore, thermodynamic assessment assuming equilibrium is considered to be effective for the sample, of which equilibrium has been attained, like Ore B. This may also imply that information about relatively lower temperatures...
is somewhat suspicious because of lower reaction rate especially for Ore A with lower assimilation ability.

Further information about the mineralogical phases is available from Fig. 6. For Ore A, the amount of olivine is little bit larger than enstatite at 1300°C. For Ore B, enstatite is dominant with a very small amount of olivine. Approximately, the observed area ratio of enstatite:olivine was 2:3 for Ore A while the ratio was 9:1 for Ore B. Therefore, this tendency of calculation well supports the observation results. This tells us that MELTS program gives us precise information at relatively high temperatures where the system mostly reaches equilibrium.

3.3. Melting Behavior

It can be apparently recognized that assimilation of CaO particles with the ores is a key to melting behavior. Probably primary liquid phases generating internally form inside the ore are the point when considering the experimental result that non-reacted CaO particles are left in Ore A. The extent of formability of internal primary liquid may be in dependent upon the ore composition. Therefore, the experiments without blending limestone were carried out according to the same heat pattern of Fig. 2 to fully understand melting behavior of ores. Figures 7(a) and 7(b) show the element distributions of Ore A and B, respectively. The colors are the same as in Fig. 5. Quantitative analysis of each phase in both ores has been also made as shown in Table 4. Basically the composition of every phase is the same as in Table 3. Due to no addition of limestone, however, CaO content in the red region in Fig. 7(b) is lower than in Fig. 5(b).

Obviously, Ore B has ability to be molten by itself due to the clear formation of silicate liquid phase. As mentioned earlier, the feature in composition of Ore B, which has larger amount of Al₂O₃ and CaO with lower MgO/SiO₂ ratio, strongly affected the formation of primary liquid that internally generates. To assure the experimental results calculation using MELTS was made under the condition of no CaO addition as shown in Fig. 8. One can understand that Ore B can generate liquid phase by itself and the proportion increases with increasing temperature. On the other hand, almost no liquid is generated in the case of Ore A. The calculation result agrees to the observation shown in Fig. 7 very well.

Figure 9 illustrates the proposed mechanism of melting behavior based on the observation for Ore B. It has been confirmed that assimilation behavior of CaO with primary liquid generated internally inside the ore is the key point. Once the primary liquid forms in the ore, it should intimately contact with CaO particles added as a flux. Then liquid phases are connecting each other to spread as is seen in Fig. 5(b). At the same moment, reduction by CO gas simultaneously takes place leading to the formation of tiny

### Table 4. Chemical compositions of the observed phases (mass%).

| Phase | n | MgO | Al₂O₃ | SiO₂ | CaO | FeO | NiO |
|-------|---|-----|-------|------|-----|-----|-----|
| Ore A | Phase 1 | 1 | 32.7 | 1.1 | 59.4 | 0.8 | 5.3 | 0.7 |
|       | 2 | 32.3 | 1.4 | 58.2 | 0.8 | 6.0 | 1.3 |
|       | 3 | 31.3 | 1.1 | 58.4 | 0.0 | 8.2 | 1.0 |
|       | 4 | 25.4 | 0.9 | 55.5 | 0.5 | 16.2 | 1.6 |
|       | 5 | 22.9 | 0.8 | 57.1 | 0.1 | 18.1 | 1.0 |
| Ore A | Phase 2 | 1 | 41.1 | 0.0 | 48.9 | 0.2 | 7.6 | 2.2 |
|       | 2 | 39.5 | 0.0 | 42.4 | 0.2 | 16.9 | 1.0 |
|       | 3 | 30.8 | 0.0 | 39.2 | 0.0 | 29.6 | 0.3 |
|       | 4 | 35.6 | 0.2 | 39.8 | 0.0 | 23.0 | 1.4 |
|       | 5 | 38.8 | 0.7 | 42.9 | 0.0 | 16.5 | 1.4 |
| Ore B | Phase 2 | 1 | 27.9 | 0.9 | 55.4 | 0.3 | 13.2 | 1.3 |
|       | 2 | 28.2 | 1.1 | 57.3 | 0.2 | 12.2 | 1.0 |
|       | 3 | 26.6 | 0.7 | 58.1 | 0.4 | 13.1 | 1.1 |
|       | 4 | 26.2 | 1.3 | 56.5 | 0.2 | 15.0 | 0.8 |
|       | 5 | 28.5 | 1.7 | 56.5 | 0.4 | 10.9 | 2.0 |
| Ore B | Phase 3 | 1 | 37.5 | 0.3 | 41.3 | 0.2 | 19.5 | 1.2 |
|       | 2 | 36.3 | 0.0 | 40.7 | 0.1 | 22.2 | 0.7 |
|       | 3 | 35.7 | 0.0 | 41.2 | 0.0 | 22.9 | 0.2 |
|       | 4 | 37.4 | 0.0 | 40.6 | 0.0 | 21.3 | 0.8 |
|       | 5 | 37.5 | 0.2 | 41.2 | 0.0 | 20.0 | 1.0 |
| Ores | Silicate liquid & olivine or enstatite | 1 | 8.4 | 11.3 | 62.4 | 3.6 | 13.6 | 0.7 |
|       | 2 | 10.2 | 11.2 | 56.3 | 4.4 | 17.6 | 0.3 |
|       | 3 | 11.8 | 10.6 | 54.8 | 4.4 | 18.1 | 0.5 |
|       | 4 | 8.8 | 12.3 | 55.9 | 5.3 | 17.5 | 0.3 |
|       | 5 | 9.0 | 10.9 | 51.7 | 4.2 | 21.5 | 2.7 |
ferronickel particles. They are considered to aggregate by moving and contacting each other through the connected liquid phase in the slag.

This study proved that melting behavior of siliceous Ni ore was quite different depending on the composition. It was confirmed that the behavior was determined mainly by the temperature at which liquid phase started to generate spontaneously inside ore. Therefore engineers should account for these parameters to achieve stable operation because various types of ores are blended and briquetted to feed rotary kilns.

4. Conclusions

Experiments were undertaken by heating the pellets of two types of siliceous Ni ores at 1300°C to understand the effect of ore composition on the melting behavior. Ore A featuring lower Al₂O₃ and CaO contents with higher MgO/SiO₂ ratio was compared to Ore B with vise versa. Thermodynamic calculation by MELTS software developed in the field of magma was tried to predict phase evolution. The following words summarize this study.

(1) It was found in Ore A that the mineralogical phases were identified as 2(Mg, Fe)O·SiO₂ olivine and (Mg, Fe)O·SiO₂ enstatite without forming liquid phase with CaO particles remained.

(2) Contrary, for Ore B, the mineralogical phase was dominated by (Mg, Fe)O·SiO₂ enstatite with a large amount of liquid phase composed of CaO–SiO₂–FeO–Al₂O₃–MgO system. All CaO particles were confirmed to be assimilated with the ore.

(3) Mineralogical phases at 1300°C calculated by MELTS software in the case of Ore B were in good agreement with the experimental results because Ore B attained equilibrium.

(4) In addition, Ore B had ability to be molten by itself to generate primary liquid internally inside the ore while Ore A did not have it.

(5) It was considered that higher assimilation ability of CaO with the ore enhanced liquid formation and that this property was determined mainly by Al₂O₃ and CaO contents and MgO/SiO₂ ratio of the ore.

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