NOVEL TECHNOLOGY TO PRODUCE FERROMANGANESE ALLOY FROM STEELMAKING SLAG

[1]Sun-Joong Kim, [2]Hiroyuki Shibata, [3]Shin-ya Kitamura, [4]Katsunori Yamaguchi

[1]JSPS Postdoctoral Fellow, IMRAM, Tohoku University, 2-1-1 Katahira, Aoba-ku,
Sendai 980-8577, Japan, e-mail: ksjoong@mail.tagen.tohoku.ac.jp
[2]IMRAM, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
e-mail: shibata@tagen.tohoku.ac.jp
[3]MRAM, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
e-mail: kitamura@tagen.tohoku.ac.jp
[4]Iwate University, 4-3-5 Ueda, 020-8511, Morioka, Japan, e-mail: benko@iwate-u.ac.jp

ABSTRACT

Manganese is an important alloying element for the production of high-grade steel. In Japan, the total amount of Mn disposed of annually in steelmaking slag is close to the amount of imported Mn. Therefore, steelmaking slag can be considered as a Mn resource. Although ferromanganese alloys can be produced by the reduction of steelmaking slag, P content in the product is too high and Mn content is too low, preventing the use of these alloys for the steelmaking process.

The separation of P from Mn and increase in the Mn/Fe ratio is thermodynamically possible via the formation of liquid sulfide (matte). High-purity ferromanganese alloys can be obtained by the desulfurization (oxidation) of the formed sulfide.

A fundamental experiment to clarify the distributions of Fe, Mn, Ca, and P between matte and steelmaking slag was conducted, and it was found that P was not distributed in matte. Moreover, the separation of P from Mn was confirmed.

KEYWORDS: *Recycling, sulfurization, steelmaking slag, matte, manganese, phosphorus.*

1. INTRODUCTION

The properties of steel products are improved by the addition of appropriate alloying elements. Recently, owing to the growing demand for high-grade steel products, the quality of steel products has become significantly dependent on the value of the alloying elements.

Manganese is an important alloying element for high-grade steel. Nowadays, Mn is not only used in the production of heavy plates and pipes but also added to various grades of coils and sheets. This is because the demand for steel with high tensile strength for automobile use has increased. Changes in the consumption of Mn in Japan are shown in figure 1. An increasing trend can be seen in this figure. In particular, the consumption of metallic Mn, which has a low P content, is increasing greatly. In Japan, approximately 440 kton of manganese is imported annually, and more than 95% of this amount is consumed as an alloying metal for steel. Therefore, Mn has been designated as a national stockpile element in Japan to stave off a potential delay in its supply to domestic steel producers. Despite the importance of this element, no attempts have been made to establish a reliable supply of Mn through effective Mn recycling processes.

Japan has a domestic source of Mn, namely, steelmaking slag. Mn contained in Fe ore is reduced in a blast furnace, and Mn content in the hot metal is approximately 0.3%. Almost all Mn in the hot metal is oxidized in a BOF and discarded as slag. After tapping steel from the BOF, imported ferromanganese alloys are added in the secondary steelmaking process. Based on the mass flow of Mn in Japan [1], as the input, about 440 kton Mn was imported as a raw material or product of Fe–Mn alloy and about 255 kton Mn was imported as Fe ore. As the output, only 353 kton Mn was used as an alloying element in steel and about 520 kton were disposed as slag. This observation indicates that the total amount of Mn disposed of annually in steelmaking slag is close to the amount of Mn imported.

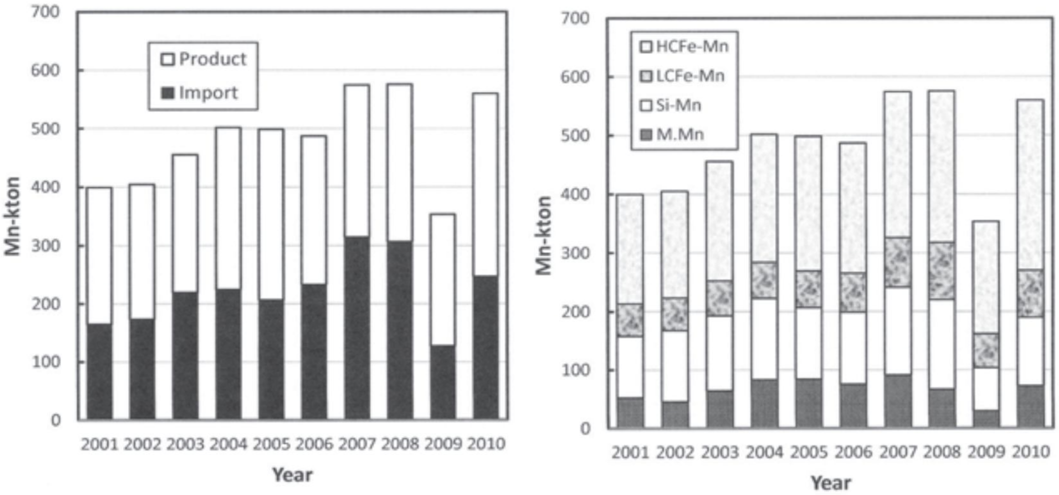


Figure 1: Trends in the annual consumption of Mn in Japan

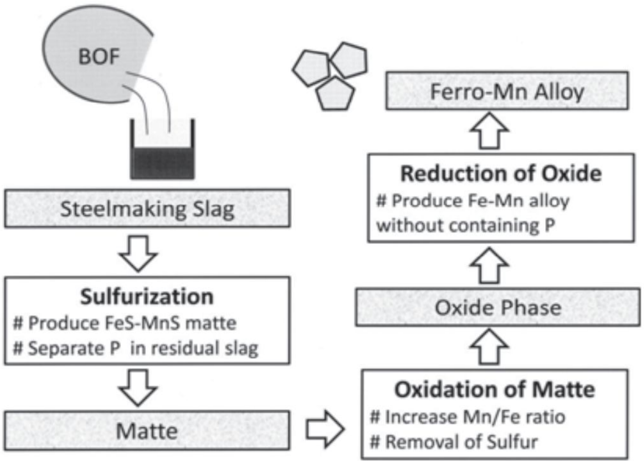


Figure 2: Schematic for recycling of Mn from steelmaking slag [5]

Therefore, steelmaking slag is considered to be a valuable source of Mn. Although ferromanganese alloys can be produced by the reduction of steelmaking slag, the alloys thus produced are not suitable for the steelmaking process because the P content in these alloys is too high and the Mn content is too low. From mass balance calculations, the Mn content is found to be less than 20% while the P content is found to reach up to 7% by a simple reduction process.

We have proposed a novel recycling process for recovering Mn from steelmaking slag [2-6]. figure 2 shows a schematic of the proposed process. First, steelmaking slag is sulfurized to separate P from Mn because MnS is preferentially formed in the liquid sulfide phase (matte). In this step, P remains as an oxide. The next step is to oxidize the separated matte to form a Mn-enriched oxide phase. In this step, the Mn/Fe ratio increases in the oxide phase. This oxide phase is then reduced by C, and an Fe–Mn alloy with ultralow P content is obtained.

In this paper, the results of fundamental experiments to determine the equilibrium distributions of P, Mn, Fe, and Ca between slag and matte will be summarized. On the basis of obtained results, a simple study on the Mn yield and quantity of the produced Fe–Mn alloy is formulated.

2. EXPERIMENTAL METHOD

A furnace equipped with a Kanthal Super heating element and an alumina reaction tube was used. Approximately 5 g of slag was charged on approximately 5 g of matte in a fused magnesia crucible. The slag and matte were prepared by mixing reagents in an appropriate ratio. In order to obtain a liquid sulfide phase at 1673 K, the MnS:FeS ratio in the matte was set at 2:8. The effect of (CaO + MgO)/SiO_2 on Fe, Mn, Ca, and P distributions was investigated by changing the partial pressures of sulfur gas (P_{S2}) and oxygen gas (P_{O2}). Preliminary experiments confirmed that the reaction achieved equilibrium after 24 h when the Mn and Fe distributions between the matte and slag became constant. The sample was heated at 1673 K under a suitable CO/CO_2/SO_2 atmosphere in a furnace. The equilibrium relation between P_{S2} and P_{O2} was calculated using the equilibrium relations of the following equations:

$$2\,CO(g) + O_2(g) = 2\,CO_2(g) \tag{1}$$

$$1/2\,S_2(g) + O_2(g) = SO_2(g) \tag{2}$$

The MgO crucible with the sample was removed from the furnace after 24 h and was then quenched in water.

The amounts of Fe, Mn, Mg, Ca, and P in the slag were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the Si content in the slag was measured using ICP-AES and a gravimetric method with alkali-fusion. The microstructures and compositions of the matte and slag were observed using an electron probe microanalyzer (EPMA). The S content in the slag was determined using infrared absorption spectroscopy (IR).

3. EXPERIMENTAL RESULTS [3,4]

3.1. Separation of P from Mn

Figure 3 shows the typical microstructure of matte after the experiment. Many oxide particles were observed in the matte that was recognizable as suspended slag particles because their compositions were similar to those of slag. The correct matte composition was then calculated by subtracting the composition of each element in the suspended oxide from the total amount of that element in the matte obtained by chemical analysis.

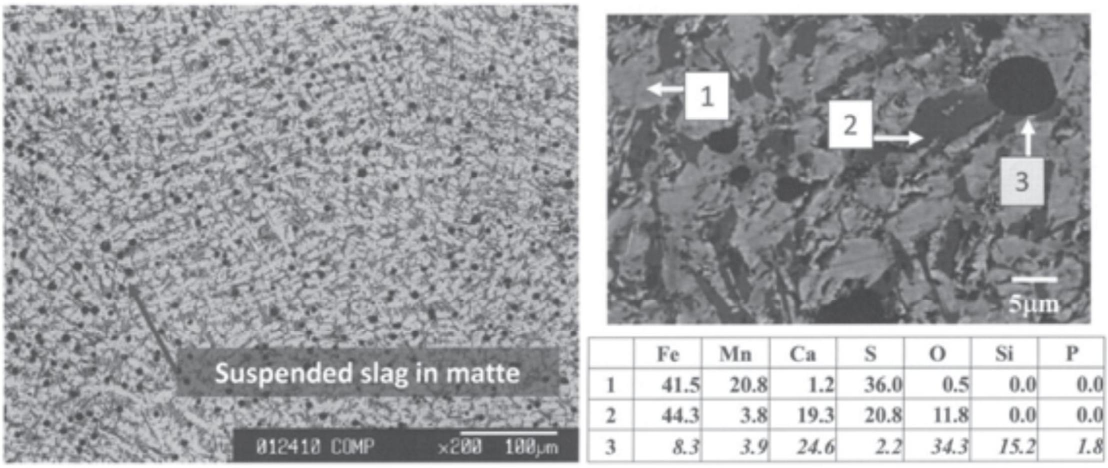
$$\{M\}_{analyzed} = \{M\}_{Matte} + \{M\}_{SP} \tag{3}$$

where $\{M\}_{analyzed}$, $\{M\}_{Matte}$, and $\{M\}_{SP}$ are the concentration of element M obtained by chemical analysis, true concentration of M in the matte, and concentration of M due to the suspended slag, respectively.

The suspended amounts of oxide particles were calculated using the Si content which was obtained by the chemical analysis of the matte, because the true Si content in the matte is negligible and the analyzed value is attributed to the suspended slag particles.

$$\{Si\}_{analyzed} = \{Si\}_{SP} = W_{SP} \times (Si)_{SP}/100 \tag{4}$$

where $\{Si\}_{analyzed}$ and $\{Si\}_{SP}$ denote the Si content obtained by chemical analysis and the Si content due to the suspended slag particles, respectively, W_{SP} is the amount of the suspended slag particles, and $(Si)_{SP}$ is the Si content in the suspended oxide particles.



	Fe	Mn	Ca	S	O	Si	P
1	41.5	20.8	1.2	36.0	0.5	0.0	0.0
2	44.3	3.8	19.3	20.8	11.8	0.0	0.0
3	*8.3*	*3.9*	*24.6*	*2.2*	*34.3*	*15.2*	*1.8*

Figure 3: Typical microstructure of matte phase

Figure 4 shows the relation between the true concentration of P in matte obtained using eq. (3) and the matte composition. It is clear that most of the true values were close to zero. This observation indicates that the P content measured by chemical analysis was due to the suspended slag particles in the matte and the sulfurization of molten slag can separate Mn from P.

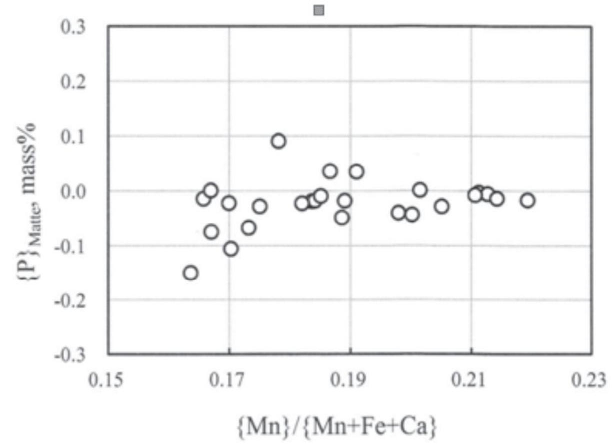


Figure 4: Relation between the true concentration of P in matte and matte composition

3.2. Distributions of Mn and Fe between Slag and Matte

In this paper, the experimental results for log P_{O2} values of -9.9 and -11 and log P_{S2} values of -1.4 and -1.9 are summarized. Figure 5 shows the effect of slag basicity on the Fe, Mn, and Ca content in matte at 1673 K. The Ca content was low although it increased slightly with an increase in the slag basicity. Therefore, the matte can be considered to be a FeS–MnS binary system. The Mn content in matte was almost constant even when the slag composition was changed. Figure 6 shows the effect of slag basicity on the distribution ratios of Fe and Mn.

$$L_{Mn}^{(M/S)} = \{\%Mn\}_{Matte}/\{\%Mn\}_{Slag} \tag{5}$$

$$L_{Fe}^{(M/S)} = \{\%Fe\}_{Matte}/\{\%Fe\}_{Slag} \tag{6}$$

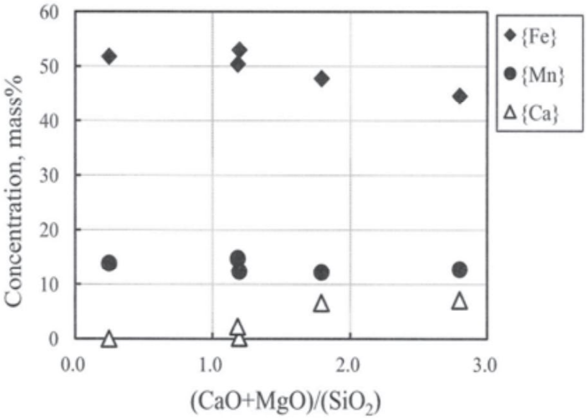


Figure 5: Effect of slag basicity on Fe, Mn, and Ca content in matte

The distribution ratios of Fe and Mn increased with an increase in the slag basicity. When slag basicity was 2.7, $L_{Mn}^{(M/S)}$ increased to 22 and this value is greater than $L_{Fe}^{(M/S)}$. This result indicates that when steelmaking slag is sulfurized, most of the Mn in the slag transfers to the matte because the basicity of steelmaking slag is greater than 2.5.

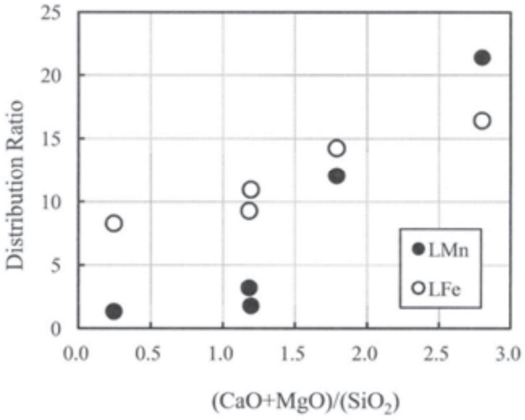


Figure 6: Effect of slag basicity on Fe and Mn distribution ratios

4. STUDY OF FE–MN ALLOY PRODUCTION PROCESS [6]

From the fundamental experiments, it was clarified that the sulfurization of molten slag can separate Mn from P. By a simple mass balance based on experimentally obtained distribution ratios, the Mn yield and Mn content in the matte were evaluated.

The mass balance of an element M between the matte and slag can be derived as follows:

$$\Delta M = W\_M_{Slag}^{Input} - W\_M_{Slag}^{Output} \tag{7}$$

where $W\_M_{Slag}^{Input}$ and $W\_M_{Slag}^{Output}$ are the weights of M in the input slag (before sulfurization) and the output slag (after sulfurization), respectively; ΔM is the weight of M that is transferred from the slag to the matte, i.e., ΔM is equal to the weight of M in the matte. When the matte is assumed to be an FeS–MnS binary system, the mass balance equations can be obtained as follows:

$$\frac{\Delta Fe}{(\Delta Fe \cdot C_{\mathrm{FeS}} + \Delta Mn \cdot C_{\mathrm{MnS}})} = L_{\mathrm{Fe}}^{(\mathrm{M/S})} \cdot \frac{(W.Fe_{\mathrm{Slag}}^{\mathrm{Intput}} - \Delta Fe)}{W_{\mathrm{Slag}}^{\mathrm{Intput}} - (\Delta Fe \cdot C_{\mathrm{FeO}} + \Delta Mn \cdot C_{\mathrm{MnO}})} \tag{8}$$

$$\frac{\Delta Mn}{(\Delta Fe \cdot C_{\mathrm{FeS}} + \Delta Mn \cdot C_{\mathrm{MnS}})} = L_{\mathrm{Mn}}^{(\mathrm{M/S})} \cdot \frac{(W.Mn_{\mathrm{Slag}}^{\mathrm{Intput}} - \Delta Mn)}{W_{\mathrm{Slag}}^{\mathrm{Intput}} - (\Delta Fe \cdot C_{\mathrm{FeO}} + \Delta Mn \cdot C_{\mathrm{MnO}})} \tag{9}$$

where $W_{\mathrm{Slag}}{}^{\mathrm{Input}}$ is the weight of the input slag; C_{FeO} and C_{MnO} are the stoichiometric constants used to convert the weight percents of FeO and MnO to those of Fe and Mn, respectively; and C_{FeS} and C_{MnS} are the stoichiometric constants used to convert the weight percents of Fe and Mn to those of FeS and MnS, respectively.

The Mn yield and Mn ratio were determined using the following equations:

$$\text{Mn yield}(\%) = {W.Mn_{\mathrm{Matte}}} \Big/ {W.Mn_{\mathrm{Slag}}^{\mathrm{Intput}}} \times 100 \tag{10}$$

$$\text{Mn ratio}(\%) = {W.Mn_{\mathrm{Matte}}} \Big/ {(W.Mn_{\mathrm{Matte}} + W.Fe_{\mathrm{Matte}})} \times 100 \tag{11}$$

By using the relation between the slag basicity and $L_{Mn}{}^{(M/S)}$ or $L_{Fe}{}^{(M/S)}$ at 1673 K, the Mn yield and Mn ratio were calculated, assuming that the FeO and MnO content in the steelmaking slag were 25 and 10 mass %, respectively.

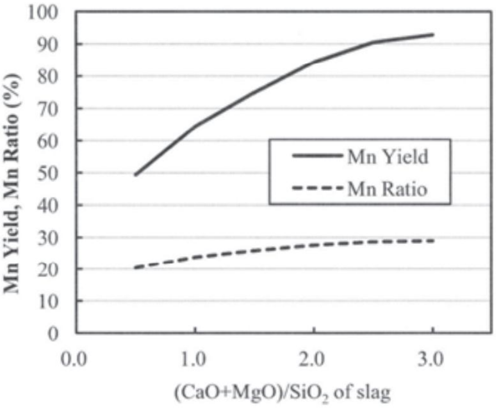


Figure 7: Relation of slag basicity with Mn yield and Mn ratio during the sulfurization process

Figure 7 shows the calculation results. With an increase in the slag basicity, the Mn yield increases, and when the basicity is larger than 2.5, the Mn yield becomes greater than 90%. Therefore, most of the Mn contained in the steelmaking slag is sulfurized under this condition. However, for all values of the slag basicity, the Mn ratio is less than 30%. As this ratio is too low for the production of Fe–Mn alloys, another process is required to increase the Mn/Fe ratio. Therefore, the author has proposed the oxidation process of the matte. From figure 6, it can be deduced that when the matte, which is produced by the sulfurization of steelmaking slag, is oxidized to form a new oxide phase with low basicity, most of the Mn in the matte transfers to the oxide phase as $L_{Mn}^{(M/S)}$ is small. On the contrary, the amount of Fe that transfers to the oxide phase is lower than that of Mn as $L_{Fe}^{(M/S)}$ is greater than $L_{Mn}^{(M/S)}$. On the basis of this principle, it is possible to produce CaO–SiO_2–MnO–FeO oxide with low basicity and high MnO/FeO ratio from matte.

A schematic of the proposed novel recycling process for recovering Mn from steelmaking slag is shown in figure 3. First, the steelmaking slag is sulfurized to separate P from Mn because MnS is preferentially formed in the liquid sulfide phase (matte). In this step, P remains as an oxide and most of the Mn transfers to the matte phase because the basicity of the steelmaking slag is large. The next step is to oxidize the separated matte and form a Mn-enriched oxide phase. In this step, the Mn/Fe ratio increases in the oxide phase because of the use of oxides with low basicity. This oxide phase is then reduced by C and an Fe–Mn alloy with ultralow P content is obtained.

5. CONCLUSIONS

Mn is an important alloying element for the production of high-grade steel. In Japan, the total amount of Mn disposed of annually in steelmaking slag is close to the amount of imported Mn. Therefore, steelmaking slag can be considered to be a resource of Mn. Although ferromanganese alloys can be produced by the reduction of steelmaking slag, P content in the product is too high and Mn content is too low, preventing the use of these alloys for the steelmaking process.

A fundamental experiment was conducted to clarify the distributions of Fe, Mn, Ca, and P between the matte and steelmaking slag. It was found that P was not distributed in the matte and the separation of P from Mn was confirmed. As the Ca content in the matte was low, the matte can be considered to be a FeS–MnS binary system. The distribution ratios of Fe and Mn increased with an increase in slag basicity, and when slag basicity was 2.7, the distribution ratios of Mn increased to 22, which was greater than the distribution ratio of Fe. This observation indicates that when steelmaking slag is sulfurized, most of the Mn in slag transfers to the matte.

By a simple mass balance based on experimentally obtained distribution ratios, the Mn yield and Mn content in the matte were evaluated. The results showed that when the basicity was more than 2.5 during the sulfurization process, the Mn yield was greater than 90%. However, for all values of the slag basicity, the Mn content in the matte was not high. To increase the Mn/Fe ratio, the oxidation of matte is necessary. By the oxidation of matte, a new oxide phase with low basicity and a high MnO/FeO ratio is formed.

A novel recycling process for recovering Mn from steelmaking slag is proposed. In this process, steelmaking slag is first sulfurized to separate P from Mn because MnS is preferentially formed in the liquid sulfide phase (matte). In this step, P remains as an oxide and most of the Mn transfers to the matte phase. The next step is to oxidize the separated matte to form a Mn-enriched oxide phase. In this step, the Mn/Fe ratio increases in the oxide phase. This oxide phase is then reduced by C and an Fe–Mn alloy with a ultralow P content is produced.

6. ACKNOWLEDGEMENT

The authors appreciate the financial support from the Japan Society for the Promotion of Science (21360367), a Grant-in-Aid for Scientific Research (B), the Sumitomo Foundation, and the Steel Industry Foundation for the Advancement of Environmental Protection Technology.

7. REFERENCES

[1] K. Nakajima, K. Yokoyama and T. Nagasaka: ISIJ Int., 2008, vol. 48, no. 48, pp. 549-553.

[2] S.-J. Kim, T. Hotta, H. Shibata, S. Kitamura and K. Yamaguchi: Proceedings of the 6th European Slag Conference, Spain, Madrid, 2010, Euroslag Publication, No. 5, pp. 183.
[3] S.-J. Kim, H. Shibata, N. Maruoka, S. Kitamura and K. Yamaguchi: High Temp. Mater. Proc., 2011, vol. 30, no. 4/5, pp. 425- 434.
[4] S.-J. Kim, H. Shibata, J. Takekawa, S. Kitamura, K. Yamaguchi and Y.-B. Kang: Metall. Mater. Trans. B, 2012, vol. 43, pp. 1069-1077.
[5] S.-J. Kim, S. Kitamura, T. Hotta, H. Shibata and K. Yamaguchi: Proceedings of Fray International Symposium, Cancun, Mexico, 2011, CD-ROM.
[6] S.-J. Kim, H. Shibata, S. Kitamura and K. Yamaguchi: Proceedings of High Temperature Processing Symposium 2013, Swinburne Univ., Melbourne, Australia, 2013.