Mechanism of Formation of Amorphous Silica Inclusion in Silicon Deoxidized Copper

Kyoko WASAI and Kusuhiro MUKAI

Dept. of Materials Science and Engineering, Kyushu Institute of Technology, Sensui, Tobata-ku, Kitakyushu 804–8550 Japan.

(Received on July 1, 2002; accepted in final form on November 18, 2002)

To investigate the formation mechanism of secondary amorphous silica inclusion in iron and copper, silicon-deoxidation experiment of copper at 1 423 K was performed.

In the copper quenched into water after deoxidation, three types of secondary amorphous silica inclusions (pinecone-like inclusion, gourd-shaped inclusion and network-like inclusion) were observed. In the copper cooled ultra-rapidly, fine spherical inclusion and coral-like inclusion, which were secondary and amorphous, were observed.

The experimental temperature of 1 423 K is not only 573 K lower than the melting point of silica but also 20 K lower than the glass transition temperature of silica (1 443 K). Therefore, the presence of secondary amorphous silica inclusion should be strong evidence of the formation of liquid silica during cooling of the copper without temperature rise. It would also support the formation of secondary liquid silica inclusion in the iron alloy.

Consideration based on Ostwald’s Step Rule indicated that liquid silica inclusion could be formed from the supersaturated state of copper.

KEY WORDS: inclusion; secondary inclusion; amorphous silica; silicon deoxidation; copper; Ostwald’s Step Rule.

1. Introduction

In aluminum-deoxidized iron alloy, not only the stable α phase but also unstable δ, γ, κ and θ phases of alumina inclusion have been observed. Similarly, amorphous silica and unstable silica inclusion have been observed in silicon-deoxidized iron although cristobalite is the stable form of silica at steelmaking temperatures. Why the unstable aluminas and silicas were formed under steelmaking condition has been unclear. Recently, secondary inclusions of δ and γ-alumina, and amorphous silica inclusion were observed in aluminum-deoxidized iron at 1 873 K by the present authors. Analyses on the basis of Ostwald’s Step Rule showed that the nucleation of unstable alumina could occur from the supersaturated state of liquid iron. The analyses also indicated the possible formation of liquid alumina inclusion from the supersaturated state of liquid iron. Through a similar mechanism for the unstable and liquid alumina formation, the unstable and liquid silica inclusions would be formed.

Liquid silica easily transforms into amorphous silica with cooling. Therefore, the presence of amorphous silica is strong evidence of the formation of liquid silica. Seeing that the steel making temperatures around 1 873 K are only about 120 K lower than the melting point of silica (1 996 K), the liquid silica inclusion might be formed through melting of silica deoxidation product immediately after silicon-deoxidation due to the heat of formation evolution. However, amorphous silica inclusion was observed by the present authors in the solidified iron that was deoxidized by aluminum and maintained at 1 873 K for 60 min after deoxidation. There was no silica source other than silica impurity in alumina crucible in which the liquid iron alloy was charged. The silica impurity in the alumina crucible should have been dissolved into the liquid iron. However, after the dissolution of the silica, subsequent solidification of solid silica inclusion in the iron, and its melting and solidifying to provide the final amorphous silica inclusion, could not happen at constant temperature of 1 873 K. Therefore, liquid silica inclusion was probably formed directly in the liquid iron alloy during cooling without temperature rise, and subsequently, solidified as the secondary amorphous silica inclusion. Still, at the current stage, clear evidence of the formation of secondary liquid silica inclusion as well as that of secondary liquid alumina inclusion is not obtained. Thus, an experiment of silicon-deoxidation for copper at 1 423 K was performed in the present study. The melting point of copper is considerably lower (1 356 K) than that of iron. The temperature of 1 423 K is 573 K lower than the melting point of silica and 20 K lower than the glass transition temperature of silica (1 443 K). Further, copper is a good heat conductor. If amorphous silica inclusion was observed in the copper, it would be satisfactory evidence of the formation of liquid silica without temperature rise. It would also support the formation of secondary liquid silica and alumina inclusions in iron alloy.
2. Experimental Method

2.1. Preliminary Experiment

Mixed acid of nitric acid and hydrochloric acid (HCl: HNO₃ = 10: 10: 2) was used for dissolution of the copper samples for preparation of TEM specimens. However, silicon in the copper might form amorphous silica during dissolution process into the mixed acid. One of the authors have ever experienced the formation of amorphous silica small particles during dissolution of iron (a few mass% silicon) into the mixed acid. A small quantity of silicate (Si(OH)₄) would be formed from a reaction between silicon and the mixed acid during the dissolution process of the sample and the silicic acid would transform into the amorphous silica particles through gelation and drying. In addition, the electrolytic copper (99.9 mass% Cu, 0.0017 mass% O, 0.0104 mass% Si) used in the present experiment might contain amorphous silica inclusion. Therefore, following preliminary experiments were performed in order to distinguish the amorphous silica inclusion formed in the copper sample from the amorphous silica particle formed during acid-dissolution process and the silica inclusion contained in the electrolytic copper.

(1) Commercially available silicon standard solution for atomic absorption analysis (1 mg Si/ml, KOH solution of K₂SiO₃) of 1 ml was filtered.

(2) The silicon standard solution of 1 ml was added to the mixed acid (10 ml HCl + 10 ml H₂O₂ + 2 ml HNO₃), heated and filtered.

(3) The electrolytic copper of 1 g was heated in the mixed acid and dissolved into the acid and filtered.

(4) The electrolytic copper of 1 g and the standard silicon solution of 1 ml were heated in the mixed acid, dissolved and filtered.

The filter used in the experiments from (1) to (4) was the polycarbonate filter with 0.1 μm pore diameter. The deposit on the filter was observed by TEM. Hereafter, each preliminary experiment from (1) to (4) is referred to as Preliminary Exp. (1), Preliminary Exp. (2) and so on.

2.2. Experimental Procedure of Silicon-deoxidation

Details on experimental apparatus (furnace and twin rollers etc.) were the same as that described in the previous report.7) A copper specimen, in which copper oxide (Cu₂O) was buried, was charged in a crucible made of transparent polycarbonate (13×10×500 mm or 13×10×1000 mm) and maintained at 1423 K for 60 min in order to dissolve the copper matrix (about 6 g). The copper sample was dripped, by increasing argon pressure, through the bottom aperture onto twin rollers rotating at high speed (3 100 rpm), between which the sample was sandwiched and press to solidify instantly (ultra rapid cooling).7) The sample in the longer crucible (13×10×1000 mm) with no aperture was lowered for the bottom of the crucible to be quenched into water in a vessel equipped under the furnace, in which water was introduced just before the quenching (quenching into water).7) The cooling rate that could be achieved with the ultra-rapid cooling method is probably about 10⁵ K/s and the rate by the water quenching method is less than it.7)

From the sample quenched into water, the top and bottom parts, and peripheral part that had been in contact with the crucible wall, were cut off in order to remove primary deoxidation product, which have floated up to the upper part of the sample or adhered to the wall. The remaining copper specimen was used for TEM observation. The oxygen content of the sample quenched into water was determined by inert-gas fusion-infrared absorptionmetry (LECO, TC136), although oxygen analysis of the sample cooled ultra-rapidly could not be performed because of thin small ribbon-like shape of the sample.

2.3. Preparation of Specimen for TEM

Filter Replica Method7) was used for preparation of specimen for TEM observation. For the TEM specimen of the Preliminary Exp. (1), the polycarbonate filter was soaked in hydrochloric acid before filtration, because, without this process, the filter covered with carbon film often shrank immediately after soaking into chloroform.

3. Experimental Results and Discussion

3.1. TEM Observation*

Amoeba-like particles of amorphous silica was observed on all the filters used in Preliminary Exp. from (1) to (4) (Sec. 2.1). However, there were fewer particles in Preliminary Exp. (1) and (3) than the particles in Preliminary Exp. (2) and (4). In Preliminary Exp. (1), the mixed acid was not added to the standard silicon solution. In Preliminary Exp. (3), the silicon amount in the electrolytic copper is less than that in the standard solution of 1 ml. Thus, the fewer particles were formed in Preliminary Exp. (1) and (3). Consequently, it is clear that the mixed acid reacts with a small amount of silicon in copper or in the standard silicon solution to form amoeba-like particles of amorphous silica. Figures 1(a), 1(b), and 1(d) show the TEM images of the amoeba-like particles of amorphous silica observed on the filters. In Fig. 1(d), which shows an amoeba-like particle of amorphous silica in the Preliminary Exp. (4), square-shaped inclusions containing aluminum buried in the amorphous silica were observed. During dissolution process into the acid, the square-shaped inclusions having been contained in the electrolytic copper would be surrounded by a gel of silicic acid formed by the reaction between silicon and the mixed acid, and the gel would be transformed into the amorphous silica by drying. An amoeba-like particle in Fig. 1(b) in Preliminary Exp. (3), is a little different from

* In the TEM photograph from Fig. 1(a) to Fig. 3(b), the dark grey and black parts show the amorphous silica on the light grey carbon film. The carbon film often has creases, rents and holes as shown in Figs. 1(a), 1(b), 1(c), and 2(c). The holes of the carbon film originate in pores of polycarbonate filter.
the others in Figs. 1(a), 1(c) and 1(d). It seems amoeba-like but also seems an agglomeration of small particles of amorphous silica. It would be an agglomeration of small amorphous silica formed by the reaction between the mixed acid and silicon in the electrolytic copper, or it might be composed of small amorphous silica inclusions in the electrolytic copper bound together during dissolution.

In the copper sample deoxidized with silicon and quenched into water, three types of amorphous silica inclusions were observed; the pinecone-like inclusion (Figs. 2(a), 2(b)), gourd-shaped inclusion (Fig. 2(b)) and network-like inclusion (Fig. 2(c)). Amoeba-like particles of amorphous silica except a particle of amorphous silica similar to that in Fig. 1(b) were not found in the sample quenched into water.

In the sample deoxidized with silicon and cooled ultra-rapidly, the fine spherical inclusion and coral-like inclusion (Figs. 3(a), 3(b)) were observed. The coral-like inclusion would be a fragment of the network-like inclusion. Fine amoeba-like particles of amorphous silica were also observed in the sample cooled ultra-rapidly, although the particles were smaller than those observed in the samples of the preliminary experiments shown in Fig. 1. In contrast, as was stated above, few amoeba-like particles of amorphous silica was found in the sample quenched into water. The results would show that the fine amoeba-like particle of amorphous silica observed in the copper cooled ultra-rapid-
ly would be formed by a reaction between the mixed acid and very fine amorphous silica inclusions in copper. The very fine amorphous silica inclusion would form silicic acid through the reaction with the acid, and subsequently agglomerate to form a fine amoeba-like particle of amorphous silica. However, a small number of amoeba-like particles of amorphous silica might form by the reaction between silicon in the copper and the mixed acid. Practically, it is impossible to distinguish the origin of the fine amoeba-like amorphous silica. Therefore, at the present stage, the fine amoeba-like amorphous silica should be counted out of the inclusion in the copper sample.

Spherical inclusion was not observed in the sample quenched into water. Spherical inclusions initially formed in the sample would have time to coalesce and, due to viscosity of liquid silica at lower temperatures, they would form the pinecone-like or gourd-shaped inclusion. Spherical inclusions formed at the last stage of solidification would be pressed by the advanced copper solidification front and gathered at the grain boundary of the copper where they were pressed and solidified into a network-like inclusion connected each other.

The electron diffraction pattern of the amorphous silica inclusion shows halo pattern as shown in Fig. 3(c).

### 3.2. Primary and Secondary Inclusion

In the sample cooled ultra-rapidly, inclusion with larger size than the fine inclusions shown in Fig. 3 was not found. Primary silica inclusion formed at 1 423 K from the deoxidation reaction would float up to the upper part of the sample and subsequently connect each other to become larger cluster of silica. Further, heterogeneous nucleation would occur on the wall of the crucible to grow to primary silica inclusion and, thus, some inclusions in the midst of flotation would be caught by the inclusion grown on the wall. The large cluster and the inclusion grown on the wall could not pass the hole of the crucible. Therefore, the sample cooled ultra-rapidly did not include the large primary inclusions. Primary inclusion in the sample quenched into water should be eliminated because the upper and peripheral parts of the sample were cut off after deoxidation experiment.

The trunk thickness of the network-like inclusion observed in the sample quenched into water are 100–200 nm and that of the coral-like inclusion in the sample cooled ultra-rapidly are 20–40 nm. Therefore, the size of the network-like (coral-like) silica decreased with increasing of the cooling speed. This fact proves that the network-like (coral-like) inclusion should be secondary. On the other hand, the pinecone-like (Figs. 2(a), 2(b)) and gourd-shaped inclusions (Fig. 2(b)) were not observed in the sample cooled ultra-rapidly, which indicates that there was no sufficient time in the sample to grow to the pinecone-like and gourd-shaped inclusions. This result also proves the inclusions to be secondary If they were primary, they should be observed in the sample cooled ultra-rapidly because the sizes were so small to be able to pass the hole of the crucible. Although primary inclusion was not investigated in the present study, the investigation for comparing the primary and secondary inclusions would be necessary in future in order to confirm the formation mechanism of amorphous silica.

### 3.3. Suspension of Fine Primary Silica

The observed inclusions except the amoeba-like inclusion were recognized as secondary inclusions. However, it has been reported that the suspension of fine primary alumina which could not float upward would be present in aluminum-deoxidized iron with excess oxygen beyond the equilibrium value. Also in the silicon-deoxidized copper, there might have been such fine suspension of silica. The fine suspension of silica, if any, might firstly form as liquid silica because of high supersaturation degree of the copper, and the primary liquid silica would immediately transform into amorphous silica. Thus, in the sample cooled ultra-rapidly, there might be the amorphous silica which had been suspended in the liquid copper. However, in the sample quenched into water, the liquid silica formed during cooling would have caught the suspended silica, and through repeated collision and coalescence, it would have grown to the pinecone-like or gourd-shaped inclusion. The proportion of the suspended silica in the pinecone-like or gourd-shaped inclusion could not be known. However, by TEM observation, the pinecone-like or gourd-shaped inclusions were seemed as homogeneous, which indicates that the inclusions were mainly consisted of liquid silica formed during cooling, and finally transformed into amorphous, although the fine suspension of amorphous silica might be buried in the inclusions. Therefore, in the present stage, it would be adequate to classify the inclusions as secondary.

### 3.4. Consideration Based on Ostwald’s Step Rule

In Fig. 4, the two chemical potential differences between quartz and cristobalite ($\mu^0_{\text{quar}} - \mu^0_{\text{cri.}}$), and between liquid silica and cristobalite ($\mu^0_{\text{liq.}} - \mu^0_{\text{cri.}}$), are shown. The chemical potential of cristobalite is shown by a horizontal line of zero in Fig. 4. Cristobalite is the stable silica crystal from 1 079 K to the melting temperature (1 996 K). At the equilibrium state between liquid copper and cristobalite, the $\mu^0_{\text{cri.}}$ is expressed by Eq. (1).

$$\mu^0_{\text{cri.}} = \mu^0_{\text{liq.}} + RT \ln a_{\text{liq.}} + 2(\mu^0_{\text{quar}} + RT \ln a_{\text{quar}})$$

where $\mu^0_{\text{liq.}}$ and $\mu^0_{\text{quar.}}$ are the standard chemical potential of sil-
icon and oxygen in liquid copper, respectively, $a_{Si}$ and $a_{O}$ are the activity of the silicon and oxygen in the equilibrium state, respectively. The $\mu_{SS}^S$, which is the following sum of the chemical potential values of silicon and oxygen in the supersaturated state ($\mu_{SS}^S$ and $\mu_{SS}^O$), is expressed by both the degree of supersaturation (S) and the chemical potential of cristobalite ($\mu_{SS}^O$):

$$\mu_{SS}^S = \mu_{SS}^O + 2\mu_{SS}^O + RT \ln a_{Si}^{SS} + 2(\mu_{SS}^O + RT \ln a_{O}^{SS})$$

(2)

$$\therefore \mu_{SS}^S = \mu_{SS}^O + RT \ln S$$

(3)

$$S = \{a_{Si}^{SS} \cdot (a_{O}^{SS})^2\} / \{a_{Si} \cdot (a_{O}^O)^2\}$$

(4)

where $a_{Si}^{SS}$ and $a_{O}^{SS}$ are the activity products of silicon and oxygen in the supersaturated state, and in the equilibrium state, respectively. Therefore, the degree of chemical potential, $\mu_{SS}^S - \mu_{SS}^O$, equals $RT \ln S$. According to Ostwald's Step Rule,\(^8,12\) a supercooled liquid material, which shows polymorphism, solidifies first as an unstable (metastable) crystal and then gradually transforms into another polymorph with lower chemical potential in a step by step manner. Further, Ostwald pointed out that the supersaturated state creates unstable or metastable states. Therefore, the Step Rule could be applied for the supersaturated state. At 1 873 K, 1 kJ of $\mu_{SS}^S - \mu_{SS}^O$, corresponds to 1.07 in $S$ value. Although the $S$ value is small, the corresponding $\mu_{SS}^S$ value is higher than the chemical potential of liquid silica. Therefore, a little increase of supersaturation degree during cooling of iron would produce liquid silica which solidifies as amorphous. The amorphous silica observed in aluminum-deoxidized iron would be formed by this process. At 1 423 K, 3 kJ of $\mu_{SS}^S - \mu_{SS}^O$, corresponds to 1.29 in $S$. Thus, in the copper, amorphous silica could be formed from the supersaturated state at 1 423 K or from the supersaturated state achieved during cooling.

In the present experiment, the silicon-deoxidized liquid copper maintained at 1 423 K for 1 h would have been in a supersaturated state. Hendry reported that the copper sample in the equilibrium state with silicon from 16 to 121 ppm, contained a few mass ppm oxygen.\(^18\) The oxygen content in copper quenched into water in the present study was 230 mass ppm. Therefore, the silicon-deoxidized liquid copper maintained at 1 423 K for 1 h should have been in a supersaturated state. The degree of supersaturation would increase during cooling further more than the level at 1 423 K. Therefore, liquid silica would be formed from the supersaturated state and solidified into amorphous silica. However the silicon content was not analyzed in the present study. Thus, evaluation of the degree of supersaturation for the copper of 230 mass ppm O for various silicon content might be helpful for deeper discussion.

### 3.5. Evaluation of Degree of Supersaturation

From JANAF Thermochemical Tables,\(^9\) the standard Gibbs free energy of formation of cristobalite can be obtained as follows.

$$Si (l) + O_2 \rightarrow SiO_2 (cri.), \quad \Delta G^o = -909 + 0.175T (kJ/mol)$$

(5)

The standard Gibbs free energy of oxygen dissolution into liquid copper was calculated from the data by Otuka et al.,\(^13\)

$$\frac{1}{2} O_2 \rightarrow O [mass\%], \quad \Delta G^o = -75.5 + 0.01137 (kJ/mol)$$

(6)

The silicon activity coefficient at infinite dilution ($\gamma^o$) was derived as 0.0014 (at 1 423 K) by the calculation based on an ideal associated solution model,\(^14,15\) using the activity data by Bergman et al. at 1 753 K.\(^16\) Thus, $\text{Si (l)} \rightarrow \text{Si [mass%]}$,

$$\Delta G^o = RT \ln \gamma^o \frac{M_{Cu}}{100M_{Si}} = -123 \ (kJ/mol)$$

(7)

From Eqs. (5), (6), and (7).

$$\text{Si [mass%]} + 2\text{O [mass%]} \rightarrow \text{SiO}_2 (cri.)$$

$$\Delta G^o (at \ 1 423 K) = -419 \ (kJ/mol)$$

(8)

which gives the activity product as,

$$a_{Si}^{SS} \cdot (a_{O}^{SS})^2 = 4.3 \times 10^{-16}$$

(9)

For calculating the activity product ($a_{Si}^{SS} \cdot (a_{O}^{SS})^2$) in the supersaturated state, the interaction parameters ($\epsilon_{Si}^{O}, \epsilon_{O}^{O}$) are required. Although no interaction parameter value at 1 423 K is found, a few data at higher temperatures are available,\(^18-20\) which represent a good linear relationship between the reciprocal temperature (Fig. 5). By linear regression analysis, $\epsilon_{Si}^{O}$ can be represented as follows.

$$\epsilon_{Si}^{O} = -4.200 \cdot 10^5/T + 218.5$$

(10)

From Eq. (10),

$$\epsilon_{Si}^{O} = -76.7, \quad \epsilon_{O}^{O} = -135, \quad at \ 1 423 K$$

(11)

A roughly estimated silicon content in the sample quenched into water is around 260 mass ppm by the assumption that the amount of oxygen decrease from 500 to 230 mass ppm in the present study was consumed by the formation of primary deoxidation product of silica. Therefore, the estimated silicon content of 260 mass ppm, oxygen content of 230 mass ppm and interaction parameter values in Eq. (11) yield activity product ($a_{Si}^{SS} \cdot (a_{O}^{SS})^2$) as follows.

![Fig. 5. Interaction Parameters $\epsilon_{Si}^{O}$ reported by Hendrey et al.,\(^18\) Koval' skii et al.,\(^19\) and Sudavtsova et al.\(^20\)](image-url)
where, \( e_{\text{Si}} \) and \( e_{\text{O}} \) were neglected because of the limiting concentration region. From the value of Eq. (12), the degree of supersaturation of about 2500 was derived. In addition, the assumption for the silicon content of the sample to be 400, 300, 200, or 100 mass ppm, yields the activity product as \( 1.2 \cdot 10^{-13}, 3.1 \cdot 10^{-12}, 7.1 \cdot 10^{-11}, \) or \( 1.2 \cdot 10^{-9} \), respectively. Therefore, even the smallest activity product at 400 mass ppm Si gives the supersaturation degree of 280, which proves that the chemical potential of the supersaturated state in the present experiment is considerably high.

The present authors previously reported that the activities in low aluminum and high oxygen region of Fe–Al–O system could not be expressed by the recommended values of interaction parameter which had been measured for the equilibrium state. The interaction parameters in Eq. (10) were derived based on the values in the equilibrium states. Thus, it is uncertain whether the interaction parameters in Eq. (11) is effective in the supersaturated state. However, there is no other method but to use the values in Eq. (11) for the estimation of activities in the present stage. Further investigation for the interaction parameters should be necessary for more precise evaluation of the degree of supersaturation.

4. Conclusion

An experiment of silicon deoxidation of copper at 1423 K was performed in order to investigate the mechanism of formation of amorphous silica inclusion in iron and copper.

(1) Preliminary experiments proved the formation of amoeba-like amorphous silica through a reaction between silicon and mixed acid (HCl : H₂O : HNO₃ = 10 : 10 : 2). The amoeba-like amorphous silica, which might be formed during the preparation process of TEM specimen, has to be counted out of silica inclusion in copper.

(2) In the copper deoxidized with silicon and quenched into water, three types of amorphous silica inclusions (pinecone-like inclusion, gourd-shaped inclusion and network-like inclusion) were observed.

(3) In the copper deoxidized with silicon and cooled ultra-rapidly, the fine spherical inclusion and coral-like inclusion were observed. The coral-like inclusion would be a fragment of network-like inclusion. The fine amoeba-like silica observed in the sample might have been formed by a reaction between very fine secondary inclusions of amorphous silica and the mixed acid.

(4) The pinecone-like, gourd-shaped and network-like inclusions observed in the copper quenched into water, and the fine spherical and coral-like inclusions observed in the copper cooled ultra-rapidly, were classified as secondary inclusion.

(5) From the standpoint of Ostwald’s Step Rule, possible liquid silica formation from copper even in a small degree of supersaturation was shown. The liquid silica inclusion formed from the supersaturated state during cooling should solidify into the inclusions of amorphous silica.

(6) Amorphous silica observed in iron should be formed in similar mechanism as that in the copper.

(7) The evaluated degree of supersaturation for the copper quenched into water indicates the high degree of supersaturated state of the copper, although further investigation for interaction parameters used in the evaluation is necessary.

Acknowledgments

The authors thank Mr. T. Shiraishi for his experimental assistance while an undergraduate at Kyushu Institute of Technology, Ms Umemane, Kyushu Institute of Technology, for her assistance, and the Center for Instrumental Analysis at Kyushu Institute of Technology for the TEM and oxygen analysis.

REFERENCES

1) K. Wasai and K. Mukai: The Final Report of Ultra Clean Steel Research Group, Progress in Research on Ultra Clean Steel—Fundamental and Applied Aspects—, ISIJ, Tokyo, (1999), 3, No. 9511.
2) N. Iwamoto: Tetsu-to-Hagané, 58 (1972), 787.
3) F. Honda and K. Hirokawa: Tetsu-to-Hagané, 60 (1974), 2013.
4) S. Watanabe, K. Takano, K. Moriya, Y. Tu and Y. Shirotani: Tetsu-to-Hagané, 65 (1979), 383.
5) A. Adachi, N. Iwamoto and Y. Ueda: Tetsu-to-Hagané, 51 (1965), 1617.
6) M. Okubo, Y. Miyashita and R. Imai: Tetsu-to-Hagané, 54 (1968), 859.
7) K. Wasai and K. Mukai: ISIJ Int., 42 (2002), 459.
8) K. Wasai and K. Mukai: ISIJ Int., 42 (2002), 467.
9) JANAF Thermochemical Tables, Second Ed., ed. by D. R. Stull and H. Prophet, Horikoshi Laboratory, Tokyo, (1975), 1049.
10) A. Makisima: Kinzoku, 66 (1996), 196.
11) Iwanami’s Dictionary of Physics and Chemistry, 5th ed., CD-ROM, ed. by S. Nagakura et al., Iwanami Shoten, Tokyo, (1999).
12) W. Ostwald: Z. Phys. Chem., 22 (1897), 289.
13) S. Otsuka and Z. Kozuka: Metall. Trans., 12B (1981), C32.
14) K. Wasai and K. Mukai: J. Jpn. Inst. Met., 45 (1981), 593.
15) K. Wasai and K. Mukai: J. Jpn. Inst. Met., 46 (1982), 266.
16) C. Bergman, R. Chastel and J.-C. Mathieu: J. Chem. Thermodyn., 18 (1986), 835.
17) G. I. Batalin and V. S. Sudavtsova: Izv. Akad. Nauk SSSR, Neorg. Mater., 18 (1982), 155.
18) Alan Hendry and H. B. Bell: Trans. Inst. Min. Metall., 83 (1974), C10.
19) I. M. Koval’skii, I. F. Khudyakov and E. I. Eliseev: Izv. VUZ. Tsvett. Metal., (1985), No. 4, 29.
20) V. S. Sudavtsova, G. I. Batalin and V. M. Ilyushenko: Russ. J. Phys. Chem., 59 (1985), No. 6, 876.
21) K. Wasai and K. Mukai: Metall. Mater. Trans. B, 30B (1999), 1065.
22) O. Repetylo, M. Olette and P. Kozakevitch: J. Met., 19 (1967), 45.
23) L. E. Rohde, A. Choudhury and M. Walthier: Arch. Eisenhüttenwes., 42 (1971), 165.