

Removal Rate of Phosphorus from Molten Silicon

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Abstract. An electron beam melting technique under high vacuum is known to be effective for the removal of phosphorus from silicon, however, the rate of removal is not yet adequate. In order to improve the removal rate, the effects of four experimental factors on this rate were investigated. Raising temperature of the surface of molten silicon provide effective, neither residual gas pressure in a vacuum chamber nor stirring molten silicon improve the rate, while supplying reactant gas to molten silicon had some effect.

Keywords. Silicon, phosphorus, electron beam, solar cell.

1 Introduction

High purity silicon for solar cells, namely solar grade silicon (SOG-Si), has been commercially supplied mainly from off-grade high purity silicon in the semiconductor industry. Production of solar cells has increased rapidly in recent years, and shortage of SOG-Si has become a serious problem, so that a new process which can produce SOG-Si economically is required. Numerous approaches have been made in an attempt to produce a resource of low cost SOG-Si from metallurgical-grade silicon (MG-Si). [1, 2]

An electron beam melting technique under high vacuum is known to be effective for the removal of phosphorus from molten silicon. In this process, phosphorus vaporizes preferentially and can be removed from molten silicon because the vapor pressure of phosphorus is higher than that of silicon. [3–7] Suzuki et al. [3] reported that the concentration of phosphorus in MG-Si was decreased from 32 to 6–7 mass ppm with 1 hour of vacuum treatment. Ikeda and Maeda [4] decreased phosphorus in MG-Si to 3 mass ppm within 30 min by electron beam melting under 10^{-2} Pa, while Yuge et al. [5] reported that the phosphorus content in MG-Si decreased less than 0.1 mass ppm with 2 hours of vacuum refining. Hanazawa et al. [6] reported that the

phosphorus content decreased to 0.1 mass ppm by industrial scale electron beam melting, and Miyake et al. [7] found phosphorus decreased from about 200 to about 1 mass ppm after 1 hour under low vacuum. The removal rate of phosphorus from molten silicon by any of these processes, however, is insufficient.

The above researchers also mentioned factors that affect the removal rate. Suzuki et al. [3] and Yuge et al. [5] reported the rate of phosphorus removal was increased by raising the temperature of molten silicon. Yuge et al. [5] and Hanazawa et al. [6] implied that a high vacuum degree improved the removal rate of phosphorus from molten silicon. Ikeda and Maeda [4] reported that addition of silica during melting by an electron beam also increased the removal rate. To improve this rate by the electron beam melting technique, the effects of the following four experimental factors were investigated.

2 Experimental Procedure

The electron beam melting apparatus is shown in Figure 1. The maximum power of the electron beam gun is 8 kW, and this gun generates an electron beam with a thermal electron from a tungsten filament, which is reference to as a filament type EB in this research. Volume of the chamber is 0.06 m^3 , and the inside of the chamber is evacuated by a rotary pump ($65 \text{ m}^3 \cdot \text{hour}^{-1}$), a mechanical booster pump ($253 \text{ m}^3 \cdot \text{hour}^{-1}$) and a turbo molecular pump ($3600 \text{ m}^3 \cdot \text{hour}^{-1}$). An orifice and a small turbo molecular pump ($180 \text{ m}^3 \cdot \text{hour}^{-1}$) are installed in the electron beam gun for differential evacuation to maintain a vacuum degree around the gun of under 10^{-2} Pa during experiments. A water-cooled copper crucible 60 mm in diameter is placed on the bottom of the chamber, in some experiments, silicon was melted in the crucible. In addition, a graphite crucible was used in order to raise temperature of molten silicon. The graphite crucible within silicon was placed on the water-cooled copper crucible, and the silicon was melted in this graphite crucible.

About 40 g of phosphorus-doped high purity silicon was melted by electron beam under high vacuum, under 10^{-2} Pa. The melting time of zero was defined as that at which the silicon was completely melted in the crucible. A gas could be blown onto the melting surface or injected to the molten silicon. Gases were controlled by a mass flow controller and introduced from a nozzle as illustrated in Figure 1.

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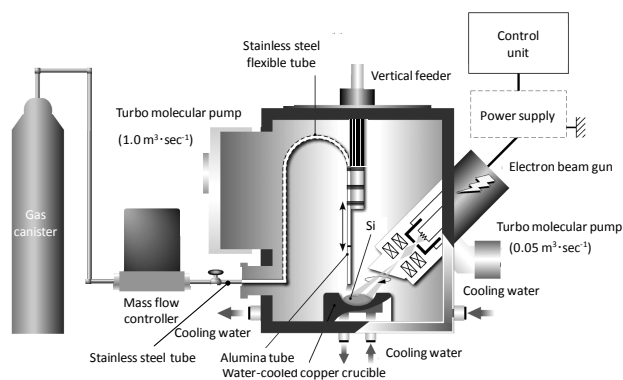


Figure 1. Electron beam melting apparatus with gas supplying system.

A gas-discharge electron beam gun, referenced to in this study as a gas-discharge EB, was also used in some experiments. This gun generates an electron beam with electrons of glow discharge. Details of the gun are described elsewhere. [7] The gun can generate an electron beam in the chamber of ca. 1 Pa in residual gas pressure, which is higher than that of a filament type EB. The dimensions of the chamber and water-cooled copper crucible are almost the same as those of a filament type EB apparatus. The chamber was vacuumed by only a rotary pump and a mechanical booster pump.

After electron beam melting, the center part of the button silicon, ca. 5–10 g, was cut out and dissolved in a mixture of H_2SO_4 , HNO_3 and HF . Then, the concentration of phosphorus in the specimen was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.1 Effect of Temperature on the Removal Rate

Removal rates under three conditions over a larger temperature range than those in previous studies were investigated here. Silicon was melted by an electron beam with 2.6 kW generating power with filament type EB in a water-cooled copper or a graphite crucible. The graphite crucible was used on the water-cooled copper crucible which was placed in the vacuum chamber. Melting by a 4.8 kW electron beam in the graphite crucible with filament type EB was also examined. Temperature of the surface of molten silicon under each condition was measured by a two-color optical pyrometer, which was calibrated using melting points of silicon, iron, titanium and niobium. Temperature of the midpoint between the part irradiated by electron beam and the edge of molten silicon was regarded as the mean temperature.

2.2 Effect of Residual Gas Pressure in a Chamber on the Removal Rate

To investigate the effect of residual gas pressure in the vacuum chamber, two types of EB guns were used; the filament type EB, and the gas-discharge EB. Both can generate an electron beam under 10^{-2} or in ca. 1 Pa, respectively. Silicon was melted in a water-cooled copper crucible with the gas-discharge EB at power of 4.8 kW. Temperature of the surface of molten silicon during melting was measured by the two-color optical pyrometer.

2.3 Effect of Stirring Molten Silicon on the Removal Rate

It remains possible that stirring molten silicon improves the removal rate. Injection of an inert Ar gas at $20 \times 10^{-6} \text{ m}^3/\text{min}$ in a standard state into molten silicon allowed the silicon to be stirred. The silicon was melted by 4.8 kW electron beam in the graphite crucible using the filament type EB, and the removal rate was compared with and without the injection of Ar.

2.4 Effect of Supplying Reactant Gas on the Removal Rate

Ikeda and Maeda [4] reported that addition of silica during melting by electron beam increased the removal rate of phosphorus from molten silicon. Although they did not mention the reason, the removal rate may be improved because the vapor pressure of phosphorus oxide such as PO was higher than that of phosphorus. In this study, a reactant gas was supplied by blowing gas onto the surface of molten silicon or injecting gas into the silicon. 0.1% $\text{O}_2\text{-H}_2$ was used as the reactant gas. $20 \times 10^{-6} \text{ m}^3/\text{min}$ of gas in a standard state was blown or injected to silicon melted by a 4.8 kW electron beam in the graphite crucible. The filament type EB was used in this experiment, and the removal rate was compared with that when gas was not supplied.

3 Results

3.1 Effect of Temperature on the Removal Rate

Figure 2 shows time variation of phosphorus content melted by an electron beam with a 2.6 kW power using a water-cooled copper and a graphite crucible. Temperatures of the surface of molten silicon were 1860 and 1980 K, respectively. Although the initial phosphorus content was ca. 220 ppm, this had already been decreased when the melting time was defined as zero. The content was 87 and 166 ppm with the water-cooled copper and the graphite crucible, respectively, after melting for 1800 sec the content was 2.9 and 0.9 ppm, respectively. Although the carbon dissolved in silicon in the experiments with the graphite crucible, the effect of the carbon on removal rate of phosphorus

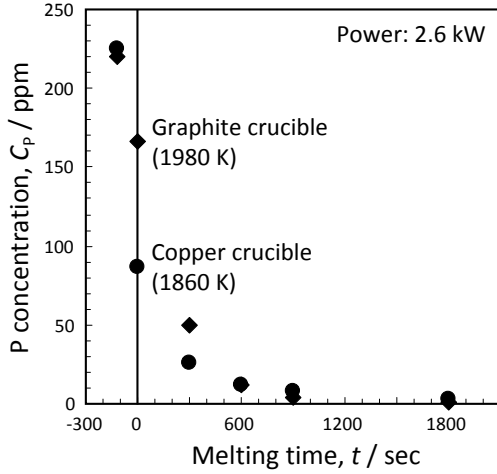


Figure 2. Phosphorus contents as a function of melting time.

from the molten silicon was ignored in this study, since that content was small.

The results were plotted by normalization with phosphorus content at zero in melting time based on the following relation,

$$\ln \frac{C_P(t) - C_P^f}{C_P(0) - C_P^f} = \ln \frac{C_P(t)}{C_P(0)} \quad (1)$$

where $C_P(t)$ and C_P^f were phosphorus content at t in melting time and final phosphorus content at $t = \infty$, which was regarded as zero in this study. (Figure 3)

Since it is safe to say that there is a linear relation between t and $\ln(C_P(t)/C_P(0))$ which was determined by the experimental results, $\ln(C_P(t)/C_P(0))$ can be expressed with an apparent reaction rate constant, K' , as follows:

$$\ln \frac{C_P(t)}{C_P(0)} = -K't. \quad (2)$$

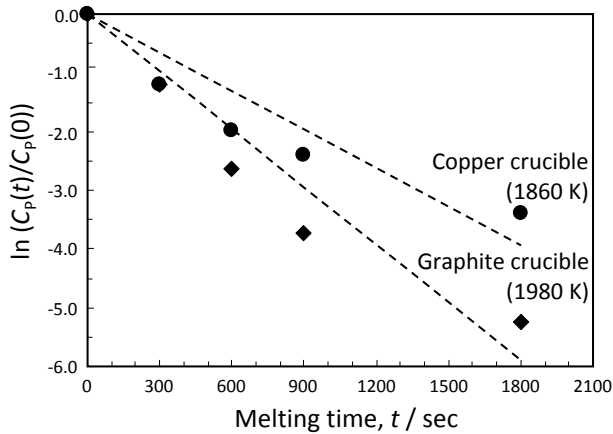


Figure 3. Relation between $\ln(C_P(t)/C_P(0))$ and melting time in water-cooled copper and graphite crucible.

Generally, $\ln(C_P(t)/C_P(0))$ for the first order reaction can be written as equation (3) with an apparent mass-transfer coefficient, k ,

$$\ln \frac{C_P(t)}{C_P(0)} = -k \frac{A}{V} t \quad (3)$$

where A and V are reaction area of silicon melt and volume of silicon melt. Since the relations are similar to each other, k of the removal reaction was calculated using K' :

$$K' = k \frac{A}{V}. \quad (4)$$

In previous studies, k was estimated in the same manner. [4–6] Yuge et al. [5] and Hanazawa et al. [6] also reported the removal reaction was a first order reaction.

As were estimated from the crucible shapes to 1.59×10^{-3} or $1.13 \times 10^{-3} \text{ m}^2$ when the silicon was melting in the water-cooled copper or the graphite crucible, respectively. V s were calculated by the density of silicon and rate of molten silicon as 1.46×10^{-5} and $1.72 \times 10^{-5} \text{ m}^3$. With the water-cooled copper crucible, the rate of molten silicon was 0.85 [4, 7], while with the graphite crucible the rate was equal to 1.0 since the silicon in the crucible was melted completely. Using these values, k s were estimated as 2.0×10^{-5} and $5.0 \times 10^{-5} \text{ m} \cdot \text{sec}^{-1}$. The removal rate of phosphorus from molten silicon is increased by raising the surface temperature of the silicon.

Silicon was also melted by an electron beam with a power of 4.8 kW in the graphite crucible, and the temperature was measured up to 2520 K. Figure 4 shows time variation of phosphorus content normalized with that at zero in melting time, the content was 62 ppm and decreased to 5.2 ppm during the 180 sec. k was estimated to be $2.4 \times 10^{-4} \text{ m} \cdot \text{sec}^{-1}$. These results indicate that the removal rate of phosphorus is increased by raising the surface temperature of molten silicon.

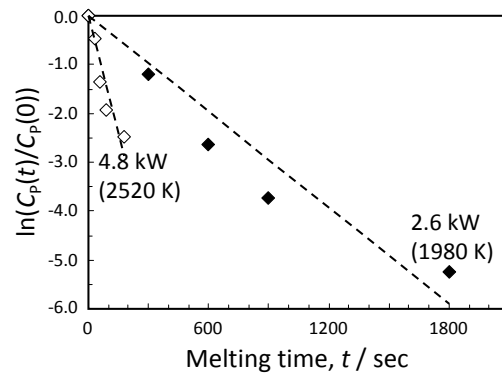


Figure 4. Relation between $\ln(C_P(t)/C_P(0))$ and melting time by 2.6 and 4.8 kW electron beam in graphite crucible.

3.2 Effect of Residual Gas Pressure in a Chamber on the Removal Rate

Silicon was melted in the water-cooled copper crucible with the gas-discharged EB at a power of 4.8 kW. Residual gas pressure in the chamber was around 1 Pa, which is ten times higher than that with the filament type EB. Temperature of the surface of molten silicon was 1840 K. The phosphorus content at zero in melting time was 106 ppm, while at 900 sec was 5.2 ppm.

Figure 5 shows a logarithmic plot of the phosphorus content normalized in the manner mentioned earlier against melting time. k was estimated to be $3.4 \times 10^{-5} \text{ m} \cdot \text{sec}^{-1}$. For comparison, this figure also shows the result with filament type EB at 2.6 kW using the water-cooled copper crucible, where the temperature of molten silicon was 1860 K. If the removal reaction of phosphorus is controlled by diffusion in the bulk gas phase, lower pressure improves the removal rate. However, the removal rate with the gas-discharge EB (ca. 1 Pa) is larger than that by the filament type EB (under 10^{-2} Pa) and this result indicates that the removal reaction is not controlled by bulk gas phase diffusion.

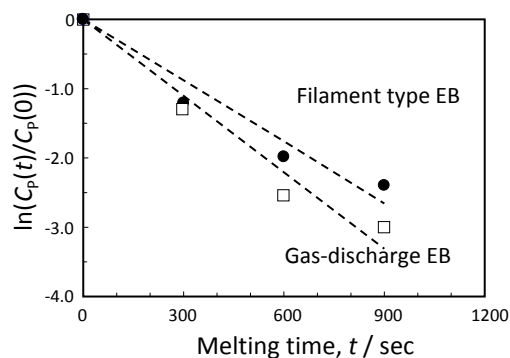


Figure 5. Relation between $\ln(C_P(t)/C_P(0))$ and melting time using filament type and gas-discharge EB.

3.3 Effect of Stirring Molten Silicon on the Removal Rate

Figure 6 shows the results of silicon melted in the graphite crucible with a 4.8 kW electron beam with and without the injection of Ar for comparison. The phosphorus content at zero in melting time was 37 ppm. After melting for 90 sec, the content was 10 ppm. No noticeable difference was observed between these results, indicating that the stirring of molten silicon by injection of Ar was not effective to improve the removal rate.

3.4 Effect of Supplying Reactant Gas on the Removal Rate

Silicon was melted in the graphite crucible with a 4.8 kW electron beam. Temperature at the surface of molten silicon

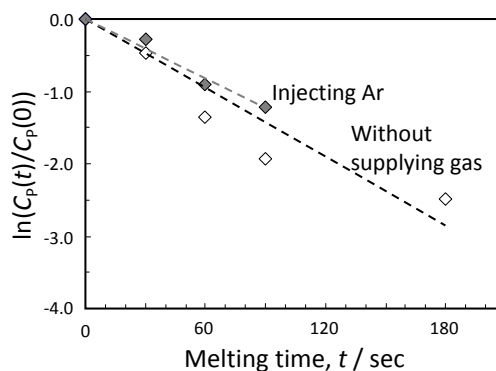


Figure 6. Relation between $\ln(C_P(t)/C_P(0))$ and melting time with and without injection of Ar.

was about 2520 K. Figure 7 shows phosphorus concentration as a function of melting time. The phosphorus content at zero in melting time was 37 ppm. The results were evaluated in the manner described above. After melting for 90 sec by blowing 0.1% $\text{O}_2\text{-H}_2$ gas and 180 sec of injecting the gas to the molten silicon, the contents were 9.4 and 1.5 ppm respectively. Blowing gas was thus not effective in improving the removal rate of phosphorus, and injecting 0.1% $\text{O}_2\text{-H}_2$ gas improved the rate only slightly.

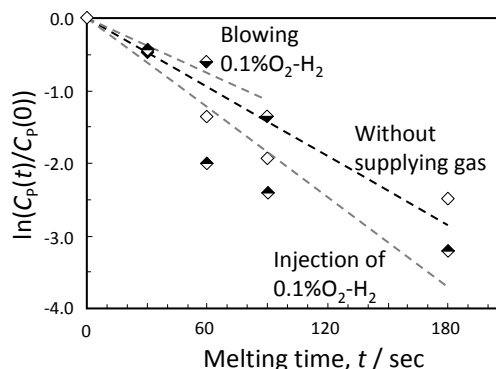


Figure 7. Relation between $\ln(C_P(t)/C_P(0))$ and melting time with blowing and injection of 0.1% $\text{O}_2\text{-H}_2$ gas.

4 Discussion

The apparent mass transfer coefficients against reciprocal of temperature are shown in Figure 8, which is called the Arrhenius plot. Suzuki et al. [3] reported $k = 1.6 \times 10^{-5}$ and $2.0 \times 10^{-5} \text{ msec}^{-1}$ at 1723 and 1823 K, respectively, in vacuum treatment with a high-frequency furnace. Yuge et al. [5] also estimated $k = 1.2 \times 10^{-5}$ and $3.0 \times 10^{-5} \text{ msec}^{-1}$ at 1723 and 1923 K, respectively. The value in this study, $k = 2.0 \times 10^{-5} \text{ msec}^{-1}$ at 1860 K in vacuum treatment by electron beam melting is in very good agreement with their results. Hanazawa et al. [6] reported that k was

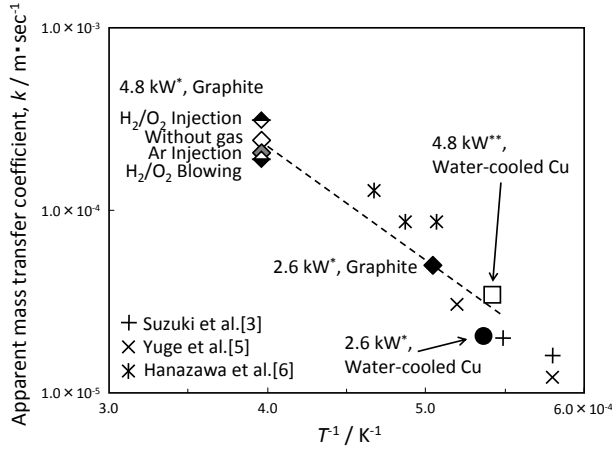


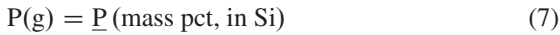
Figure 8. Arrhenius plot of apparent mass transfer coefficient (melted by * filament type EB, ** gas-discharge EB).

$1.0 - 2.0 \times 10^{-4}$ when temperature of the surface molten silicon was 1950–2150 K. By raising the surface temperature of molten silicon from 1860 to 2520 K, k became ten times larger. Therefore this means was found to be most effective in increasing the phosphorus removal rate.

The apparent activation energy in this study was estimated to be about 120 kJ from the slope of this plot. Yuge et al. [5] also estimated the activation energy as 130 kJ, and the values agree well. This is much larger than the value for a reaction controlled by bulk gas phase diffusion (10–70 kJ), but it is close to that for a liquid phase diffusion-controlled reaction (40–150 kJ). [5] This implies the removal reaction was not controlled by bulk gas phase diffusion but by liquid phase diffusion or by a chemical reaction. Since the stirring of molten silicon by injecting Ar gas is not effective in improving the removal rate, the removal reaction is controlled by a chemical reaction. Miki et al. [8] reported the Gibbs energy changes of the following dissolution reactions of phosphorus to molten silicon, and that Henry's law is valid up to around 0.1 mass pct.



$$\Delta G_5^\circ = -139,000 - 43.4T \text{ J (1723–1848 K)} \quad (6)$$



$$\Delta G_7^\circ = -387,000 + 103T \text{ J (1723–1848 K)} \quad (8)$$

Because the Gibbs energies are based on Henrian standard state and mass pct composition coordinate, the vapor pressures of P and P_2 in equilibrium with Si-P alloy can be calculated by the following equations:

$$\Delta G_5^\circ = -RT \ln \frac{f_P \cdot [\text{mass pct P}]}{p_{P_2}^{1/2}} \quad (9)$$

$$\Delta G_7^\circ = -RT \ln \frac{f_P \cdot [\text{mass pct P}]}{p_P} \quad (10)$$

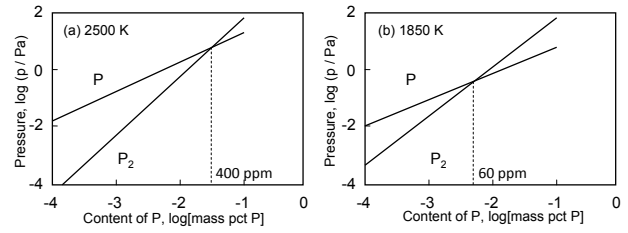


Figure 9. Calculated pressure of P and P_2 at (a) 2500 K (b) 1850 K.

R is the gas constant, f_P is the activity coefficient of phosphorus in liquid silicon relative to 1 mass pct, [mass pct P] is phosphorus content in mass pct, and p_{P_2} and p_P are the partial pressure of P_2 and P, respectively. The phosphorus concentration in this study is lower than 0.1 mass pct, f_P can be assumed to be unity since Henry's law is valid up to around 0.1 mass pct. Figure 9 shows vapor pressure of P and P_2 in equilibrium with Si-P alloy at 2500 and 1850 K calculated using these thermodynamic data. The reaction (7) is dominant at 2500 and 1850 K when phosphorus content is under 400 and 60 ppm, respectively. Therefore, phosphorus was removed by vaporizing as gaseous P in most experimental conditions in this study except the first few minutes in the experiments using the water-cooled copper crucible (1840–1860 K). Therefore, it is presumed that the vaporization reaction of phosphorus in molten silicon as gaseous P controls the removal rate.

5 Conclusions

This study of the removal rate of phosphorus from molten silicon by electron beam melting focused on the effects of four experimental factors; surface temperature of molten silicon, residual gas pressure of the vacuum chamber, stirring of molten silicon, and supplying of reactant gas. The following knowledge was gained.

1. The removal rate of phosphorus increased with raising the surface temperature of molten silicon noticeably.
2. Residual gas pressure in the vacuumed chamber did not affect to the phosphorus removal rate under ca. 1 Pa.
3. Stirring molten silicon also did not improve the removal rate of phosphorus.
4. Injecting 0.1% O_2 - H_2 as a reactant gas to molten silicon improved the removal rate slightly.
5. The removal reaction of phosphorus from molten silicon appeared to be controlled by a chemical reaction.

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References

- [1] K. Yasuda and T. H. Okabe, *J. Japan Inst. Metals*, **74** (2009), 1–9.
- [2] K. Yasuda, K. Morita and T. H. Okabe, *J. MMIJ*, **126** (2010), 115–123.
- [3] Y. Suzuki, K. Sakaguchi, T. Nakagiri and N. Sano, *J. Japan Inst. Metals*, **54** (1990), 161–167.
- [4] T. Ikeda and M. Maeda, *ISIJ Int.*, **32** (1992), 635–642.
- [5] K. Yuge, K. Hanazawa, K. Nishikawa and H. Terashima, *J. Japan Inst. Metals*, **61** (1997), 1086–1093.
- [6] K. Hanazawa, K. Yuge, S. Hiwasa and Y. Kato, *J. Japan Inst. Metals*, **67** (2003), 569–574.
- [7] M. Miyake, T. Hiramatsu and M. Maeda, *J. Japan Inst. Metals*, **70** (2006), 43–46.
- [8] T. Miki, K. Morita and N. Sano, *Metall. Mater. Trans. B*, **27** (1996), 937–941.