

# Viscosity of Liquid Fe-Cu-Si Alloy Formed in New Melting Process for Domestic Waste Incineration Residue

著者	Washizu Toshi, Nagasaka Tetsuya, Hino Mitsutaka
journal or publication title	Materials Transactions
volume	42
number	3
page range	471-477
year	2001
URL	<a href="http://hdl.handle.net/10097/52046">http://hdl.handle.net/10097/52046</a>

# Viscosity of Liquid Fe–Cu–Si Alloy Formed in New Melting Process for Domestic Waste Incineration Residue

Toshi Washizu\*<sup>1</sup>, Tetsuya Nagasaka and Mitsutaka Hino\*<sup>2</sup>

Department of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

A new melting system is being developed to solve the problems in the treatment of ash from municipal waste incinerators. The viscosity of liquid Fe–Cu–Si ternary melt has been measured in the present work by the oscillation crucible technique in the temperature range from 1523 to 1673 K in order to obtain the basic information on the fluidity of the typical alloy system generated in the ash melting furnace. The relation between the viscosity of Fe–Cu–Si ternary alloys and  $1/T$  can be expressed by Arrhenius-type formula in the temperature range from 1523 to 1673 K. Viscosity of the alloy is in the range of 5 to 7 mPa·s in the composition range of 0 ~ 5 mass%Cu and 10 ~ 20 mass%Si at 1723 K. These values are approximately double of that in pure Cu melt at 1723 K. From the result obtained, the appropriate condition is discussed for the operation of the melting furnace for ash from municipal solid waste incinerator.

(Received November 1, 2000; Accepted January 12, 2001)

**Keywords:** viscosity, liquid iron-copper-silicon ternary alloy, oscillating crucible viscometer, melting treatment, ash of municipal waste incinerators, physical property of liquid metal

## 1. Introduction

The amount of municipal waste generated is reaching approximately 50 million-tons per year in Japan. Most of such waste is incinerated and the ash remained after the incineration is buried in the landfill sites. However, the treatment of such huge amount of ash from municipal waste incinerators is facing several problems due to the lack of the landfill sites, secondary pollution by toxic substances and so on. One of the most probable technologies to solve these problem is the new melting system for the ash (Melting Treatment Process for Domestic Waste Incineration Residue, hereinafter MTP) which is recently being developed with coke bed, plasma, arc or electric resistance furnace.<sup>1)</sup> This new process enables to reduce the volume of ash significantly and would be very useful for environmental protection.

The products or residues of MTP are essentially slag and metal, and they are expected as harmless and recyclable. The slag is basically CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>-based oxide mixture which is similar to blast furnace slag, while basicity of the slag is much lower (CaO/SiO<sub>2</sub> = 1 in mass) than that of blast furnace slag and it contains some heavy metal oxides. On the other hand, the metal phase generated in MTP is very complex multi-component alloy as typically shown in Fig. 1 and its composition widely varies depending on the local conditions and season. The metal is generally iron-based metal containing 6 ~ 20 mass%Cu, 4 ~ 10 mass%Si, 1 ~ 4 mass%P *etc.* The sources of Cu, Si and P are mainly lead wire, glass and born contaminated in wastes, respectively. The metal phase may contain 0.4 ~ 2 mass% of C if carbon electrode or coke bed is used for melting. Small amount of many kinds of heavy metals such as Pb, Sb, Ni, Cr *etc.* are also contained. Since the reutilization of these slag and metal is limited only in an aggregate cement mortar, paving materials and so on, the re-

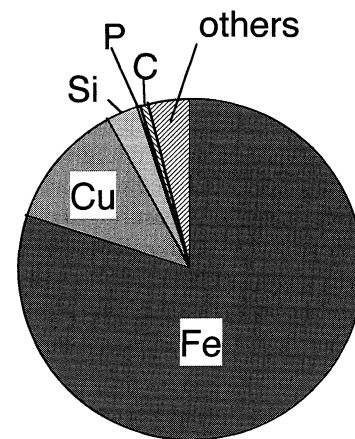


Fig. 1 Typical metal composition formed in the Melting Treatment Process for Domestic Waste Incineration Residue (MTP).

cycling process of these by-products of MTP should also be developed.

It is reported in the operation of MTP plant that there are some problems in MTP reactor such as the difficulty of tapping of slag and metal from the furnace, corrosion and erosion of refractories, penetration of metal through joints of refractory bricks and so on. Most of these troubles would be due to the tendency of two-liquid separation of metal phase. It is known that Fe–Cu system has large metastable miscibility gap in liquid phase.<sup>2)</sup> The phase diagram, physico-chemical properties such as viscosity and enthalpy of metal phase generated in MTP are necessary for better control of MTP operation.

The present authors have mentioned that the metal phase could be approximated as Fe–Cu–Si and Fe–Cu–P ternaries if minor elements less than 2 ~ 3% is ignored, and phase equilibria in both ternary systems in the temperature range from 1523 to 1723 K were first studied in our previous paper.<sup>3,4)</sup> Since the heat content would be closely related to the energy which should be supplied for the melting, the heat contents of liquid iron, Fe–Cu and Fe–Cu–Si alloys were directly

\*<sup>1</sup>Graduate Student, Tohoku University. Present address: Steelmaking Division, Ohita Works, Nippon Steel Corp., Ohita 870-8566, Japan.

\*<sup>2</sup>E-mail: takahino@material.tohoku.ac.jp

determined with the drop calorimeter in our third investigation.<sup>5)</sup> The measured heat content showed reasonable agreement with the predicted using our assessed thermodynamic parameter.<sup>3)</sup>

The present work aims to observe the viscosity of liquid Fe–Cu–Si ternary alloy by oscillating crucible viscometer within the homogeneous liquid region of this ternary system which have been revealed in our previous work.<sup>3)</sup> Viscosity is an important information for the fluidity of metal phase during tapping operation. The appropriate condition for the operation of smelting furnace for ash from municipal solid waste incinerator is also discussed based on the results of the present work.

## 2. Experimental

### 2.1 Principle

There are some experimental techniques to measure the viscosity of liquid alloy. The present work employed a high temperature oscillating crucible viscometer. This technique would be suitable for the liquid metal which has relatively low viscosity. The details of the viscosity determination with this technique have been described elsewhere.<sup>6–8)</sup>

When a rotational oscillation is initially given to the suspended crucible which contains liquid, rotational oscillation would gradually decrease due to the internal friction of liquid. The oscillating crucible viscometer allows to determine viscosity of liquid metal by measuring the period and logarithmic decrement of the rotational oscillation. Roscoe<sup>9,10)</sup> derived eq. (1) as a relation between the period and logarithmic decrement of the rotational oscillation for cylindrical crucible based on the Navier-Stokes' equation.

$$\eta = \left( \frac{I\delta}{\pi R^3 H Z} \right)^2 \frac{1}{\pi \rho \tau} \quad (1)$$

Where,  $\eta$ ,  $I$ ,  $\delta$ ,  $R$ ,  $H$ ,  $\rho$  and  $\tau$  denote viscosity, the moment of inertia of the suspended crucible, the logarithmic decrement of the oscillation, radius of the crucible, height of liquid metal in the crucible, density and oscillation period, respectively. Among these parameters,  $I$ ,  $R$  and  $H$  are determined by the experimental condition, and  $\delta$  and  $\tau$  are measurable values when rotational oscillation is supplied to the viscometer. The parameter  $Z$  is given as eq. (2).

$$Z = \left( 1 + \frac{R}{4H} \right) a_0 - \left( \frac{3}{2} - \frac{4R}{\pi H} \right) \frac{1}{p} + \left( \frac{3}{8} + \frac{9R}{4H} \right) \frac{a_2}{2p^2} - \left( \frac{63}{128} + \frac{45R}{64H} \right) \frac{a_4}{4p^4} \dots \quad (2)$$

where,

$$a_0 = (1 - \Delta) \left[ \frac{\{(1 + \Delta^2) + 1\}^{-1/2}}{2} \right]^{-1/2} - (1 - \Delta) \left[ \frac{\{(1 + \Delta^2) - 1\}^{-1/2}}{2} \right]^{-1/2} \quad (3)$$

$$a_2 = \left[ \frac{\{(1 + \Delta^2) + 1\}^{-1/2}}{2} \right]^{-1/2} + \left[ \frac{\{(1 + \Delta^2) - 1\}^{-1/2}}{2} \right]^{-1/2} \quad (4)$$

$$a_4 = \frac{a_2}{(1 + \Delta^2)^{1/2}} \quad (5)$$

$$p = \left( \frac{\pi \rho}{\eta T} \right)^{1/2} R \quad (6)$$

$$\Delta = \frac{\delta}{2\pi} \quad (7)$$

$$\delta = \ln \frac{A_i}{A_{i+1}} \quad (8)$$

The parameter of  $A_i$  in eq. (8) denotes the amplitude of  $i$ -th period in the measured oscillatory curve with decay.

Figure 2 illustrates the schematic diagram of the system for the observation of logarithmic decrement and period. This equipment is essentially the same with that developed by Ejima *et al.*<sup>6)</sup> The laser beam reflected by the mirror attached on the suspension system is detected by two photo-sensors. The detection limit of the photo-sensor is 1 ms. The time at which the laser beam passes on each photo-sensor is recorded. The true period of oscillation and logarithmic decrement can be determined according to the proposal given by Sato *et al.*<sup>7,8)</sup> with the aid of the personal computer. The viscosity  $\eta$  can be determined by numerically solving eqs. (2) to (8) with the measured values of  $\delta$  and  $\tau$  and other physical values such as the mass and the density of the melt, the inner diameter of the crucible and the moment of inertia of the suspension system. Since no literature information is available for the density of liquid Fe–Cu–Si ternary alloy, its value is estimated by assuming simple additivity of the density of pure liquid Cu and that of liquid Fe–Si binary alloy.

$$\rho_{\text{Fe-Cu-Si}} = \frac{M_{\text{Fe-Si}} X_{\text{Fe-Si}} + M_{\text{Cu}} X_{\text{Cu}}}{M_{\text{Fe-Si}} X_{\text{Fe-Si}} / \rho_{\text{Fe-Si}} + M_{\text{Cu}} X_{\text{Cu}} / \rho_{\text{Cu}}} \quad (9)$$

where,  $M$  and  $X$  mean mass and volume of Fe–Si or Cu, re-

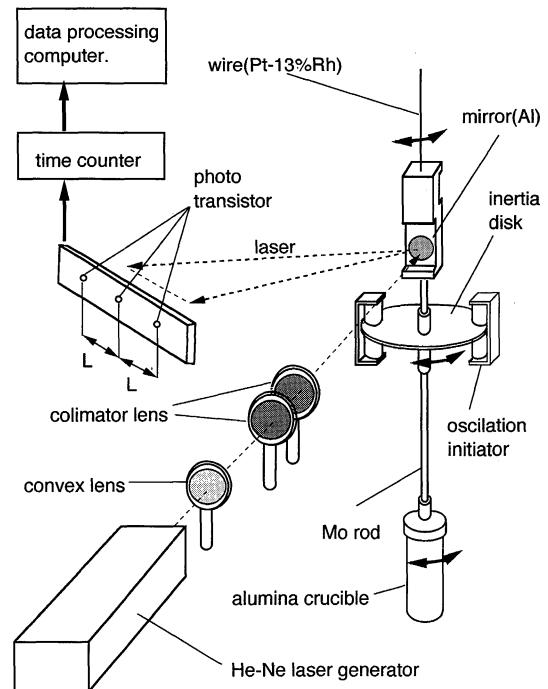


Fig. 2 Schematic diagram of the system for the observation of logarithmic decrement and period in the oscillating crucible viscometer.

spectively. The values of  $\rho_{\text{Fe-Si}}$  and  $\rho_{\text{Cu}}$  in  $\text{g/cm}^3$  are referred from the literatures<sup>11,12)</sup> as follows:

$$\rho_{\text{Fe-Si}} = 7.006 - 0.05248 [\text{mass}\% \text{Si}] - 0.7892 - 5.006 \times 10^{-5} [\text{mass}\% \text{Si}](T - T_L) \quad (10)$$

$$\rho_{\text{Fe-Si}} = 8.75 - 0.657 \times 10^{-3} T \quad (11)$$

where,  $T_L$  denotes liquidus temperature of Fe–Si system (K).

## 2.2 Apparatus

Figure 3 shows schematic drawing of the oscillating crucible viscometer with a cylindrical alumina crucible of 14 mm I.D. used in the present work. This apparatus is the same one which is used by Sato *et al.*<sup>7,8)</sup> The cylindrical crucible containing Fe–Cu–Si melt was connected to an inertia disk and a reflection mirror block with molybdenum rod. All these were suspended by a torsion wire of Pt–13 mass%Rh alloy from the head cone. This torsion wire was preliminary annealed at 1500 K in air. In order to minimize the fluctuation of the shear modulus of the torsion wire with change of surrounding temperature, the water controlled at  $308 \pm 0.5$  K was flown in the reaction chamber around the torsion wire. The inertia disk was made of aluminum, and this disk had the largest inertia moment in the whole suspension system. The pairs of coils above and under the inertia disk were used for supplying the initial torque to the inertia disk electromagnetically. The He–Ne laser beam (power: 1 mW, wave length:  $\lambda = 632.8$  nm) was reflected by a mirror attached on the mirror block, and the reflected light was focused on two photo-sensors which were 1000 mm far from the mirror.

The furnace used was divided into three parts to obtain uniform temperature profile around the crucible. The heating el-

ement of the central part was SiC and those of others were Kantal heater. The temperatures of these three parts were controlled independently with automatic temperature control units. The temperature profile around the crucible was monitored by moving the Pt–13 mass%Rh/Pt thermocouple in alumina sheath tubing. Temperature uniformity around the crucible was kept within 0.5 K at the aimed and was controlled as to be slightly higher at upper part than lower part to prevent the convection current in the melt. Sponge titanium was set just below the crucible as an oxygen getter.

## 2.3 Procedure

The atmosphere in the viscometer was He which has considerably low viscosity, and 5% of  $\text{H}_2$  was added in it to prevent the liquid alloy from oxidation by trace oxygen in He. Weighed electrolytic iron, semiconductor grade of high purity silicon and oxygen free copper at the aimed composition was preliminary melted at 1873 K for 2 hrs in an alumina crucible of 18 mm I.D. with the induction furnace under Ar– $\text{H}_2$  atmosphere. After changing the atmosphere from Ar– $\text{H}_2$  to Ar and keeping the condition for 45 min, the alloy was slowly cooled to the room temperature in the furnace by gradually lowering the induction power. The solidified alloys were machined to be the cylindrical shape of slightly smaller diameter than the inner diameter of the crucible of viscometer (18 mm I.D.). Alloy composition was preliminary determined by the chemical analysis. As it has been reported by the authors,<sup>3)</sup> Fe–Cu–Si system has a large miscibility gap in the liquid phase at high temperature. By taking the phase diagram into account, alloy compositions of the present work were selected in the homogeneous liquid region within the range of the experimental temperature.

After setting the apparatus, the viscometer was filled with purified He– $\text{H}_2$  gas mixtures and was heated to higher temperature than the melting temperature of alloy. After the temperature became stable, several measurements were carried out at least four times at each metal composition and temperature. The viscosities of Fe–Cu–Si melts were measured over the temperature range from the respective liquidus temperature to approximately 1673 K.

Blank test was performed with the empty crucible at the experimental temperature to determine the moment of inertia and the logarithmic decrement as a function of temperature. The values obtained by the blank test were used to correct the parameters obtained in the viscosity measurements.

## 3. Experimental Results and Discussions

### 3.1 Viscosity of liquid Sn

Prior to the measurement of Fe–Cu–Si alloys, viscosity of molten Sn was first measured at 673, 873, 1073 and 1273 K to confirm the reliability and reproducibility of the viscometer. The density of liquid Sn for the calculation of the viscosity was referred after Thresh *et al.*<sup>13)</sup> The result is plotted against the reciprocal temperature in Fig. 4 together with other literature values,<sup>8,14–21)</sup> which shows that the result of the present work is in good agreement with the literature values within the acceptable experimental uncertainty. Therefore, the present viscometer is considered to be reliable at higher temperatures. The regression analysis for the present

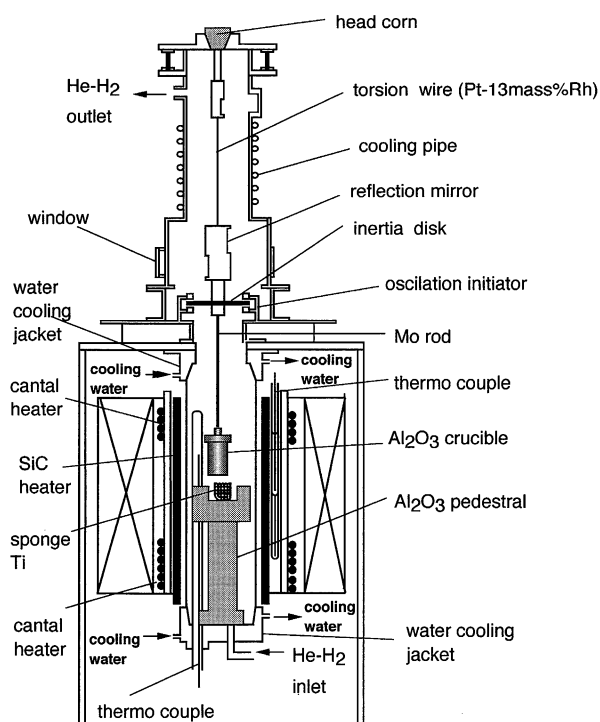


Fig. 3 Schematic illustration of the oscillating crucible viscometer with a cylindrical alumina crucible.

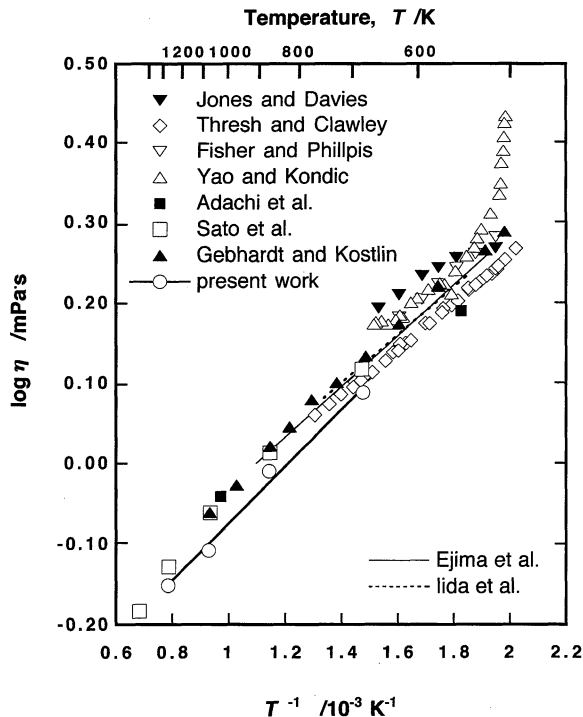


Fig. 4 Viscosity of liquid Sn as a function of  $1/T$ .

results gave the temperature function of the viscosity of pure liquid Sn.

$$\log \eta = -0.4275 + 350.5/T \text{ (mPa}\cdot\text{s)}$$

$$\text{(pure liquid Sn, 675} \sim \text{1275 K)} \quad (12)$$

### 3.2 Viscosity of liquid Fe–Si binary alloy

Viscosity of liquid Fe–Si binary alloys was measured at 9.8, 13.8 and 19.9 mass%Si in the temperature range from 1523 to 1676 K. The results obtained are plotted in Fig. 5 as a function of the reciprocal temperature. Good linear relation was obtained between  $\log \eta$  and  $1/T$  for each alloy. Experimental results in Fe–Si binary system are summarized in Table 1. No significant difference was observed in the dependence of  $\log \eta$  on Si content and temperature within the present experimental range. Figure 6 shows the variation of the viscosity of liquid Fe–Si alloy at 1523 and 1623 K with Si content in the metal which are calculated from the temperature function given in Table 1. Some researchers<sup>22–24)</sup> reported the viscosity of liquid Fe–Si binary alloy. As they are also shown in Fig. 6, their Si content range was very limited up to 6 mass% and the temperature was higher than 1773 K. In addition, there is a significant disagreement on the composition dependence of viscosity in Fe–Si alloy. Contrarily, Sato *et al.*<sup>8)</sup> recently determined the viscosity of liquid Fe–Si alloy up to 25 mass% of Si in the temperature range from 1496 to 1699 with the same oscillating crucible viscometer. Their results at 1623 and 1723 K calculated from its temperature dependence at each alloy composition are plotted in Fig. 6. On the other hand, the viscosity of liquid iron reported in the literature shows considerable disagreement as pointed out by Kawai and Shiraishi.<sup>24)</sup> For example, the viscosity of liquid iron in the available literatures is scattered from 5 to 6 mPa·s near the melting point. The viscosity of pure liquid iron de-

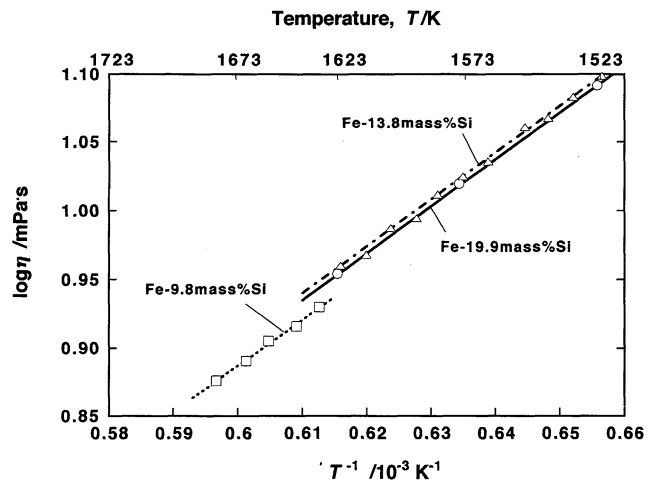


Fig. 5 Viscosity of liquid Fe–Si binary alloy as a function of  $1/T$ .

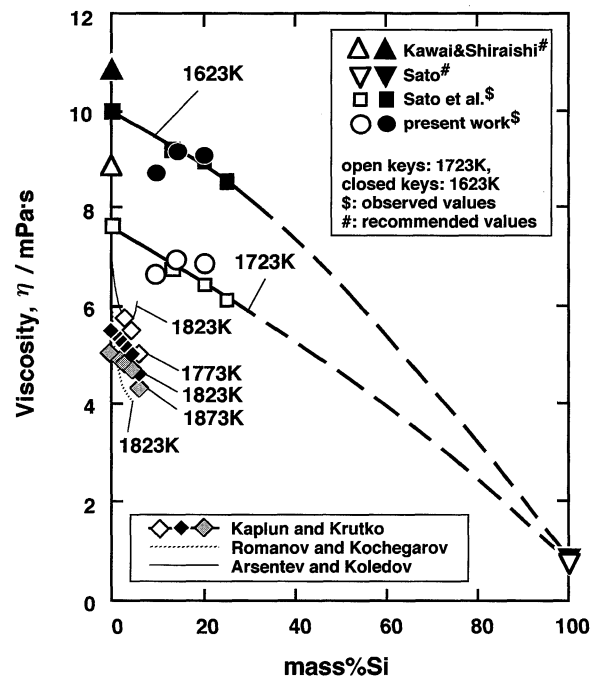


Fig. 6 Effect of Si on the viscosity of liquid iron reported in the literatures.<sup>22–24)</sup>

Table 1 Viscosity of liquid Fe–Cu–Si alloy as a function of temperature.

$\log \eta = A + B/T$ , mPa·s				
Run No.	mass%Cu	mass%Si	A	B
Fe–Si binary				
101	—	19.9	−1.151	3420
102	—	13.8	−1.146	3420
107	—	9.8	−1.129	3360
Fe–Cu–Si ternary				
103	2.3	19.0	−1.332	3617
104	2.1	14.8	−1.300	3587
108	3.2	9.7	−0.946	3088
105	5.3	19.1	−1.030	3062
106	4.8	13.2	−1.042	3200
109	4.5	9.8	−0.882	3098

terminated by Sato *et al.*<sup>8)</sup> is extrapolated to 10.0 and 7.5 mPa·s at 1623 and 1723 K, and they are plotted in Fig. 6 together with the value recommended by Kawai and Shiraishi. Grazov *et al.*,<sup>25)</sup> Kakimoto *et al.*<sup>26)</sup> and Sasaki *et al.*<sup>27)</sup> reported the viscosity of pure liquid Si. Though their values were somewhat scattered and depended on the crucible materials, Sato<sup>28)</sup> recently reviewed the most of available literature values and recommended the following temperature function of the viscosity of pure liquid Si.

$$\log \eta = -0.758 + 874/T \text{ (mPa}\cdot\text{s)}$$

(pure liquid Si) (13)

This value is also plotted in Fig. 6 for the comparison. The addition of Si into liquid iron seems to have considerable effect on the viscosity of liquid iron up to 20 mass% according to the present experimental results. Sato *et al.*<sup>8)</sup> found the decrease of the viscosity with increasing Si content up to 25 mass%. Both data are in excellent agreement each other. Based on the above discussions, the viscosity of Fe–Si alloy is deduced to change as dotted line in Fig. 6 over the entire composition range. Since the viscosity in whole composition range of Fe–Si melt is important when the interaction among the components of alloy is considered, more extensive study in higher Si content should be done in the future.

### 3.3 Viscosity of liquid Fe–Cu–Si ternary alloy

Figures 7, 8 and 9 represent the temperature dependence of viscosity of liquid Fe–Cu–Si alloy at constant Cu and Si contents. Good linear relation was obtained between  $\log \eta$  and  $1/T$  for each alloy composition. Experimental results in Fe–Cu–Si ternary system are also summarized in Table 1. It was seen from Figs. 7 and 8 that the viscosity of the alloy decreased with adding Si at constant Cu content of approximately 2.5 and 5 mass%. It was also observed that the addition of Cu decreased the viscosity of liquid Fe–Cu–20 mass%Si alloy. Effects of Si and Cu addition on the temperature dependence of the viscosity seemed to be small. The apparent activation energy of viscosity was slightly reduced from 64.3 kJ/mol at Cu free to 59.3 kJ/mol at Cu = 4.5 mass% in Fe–10 mass%Si alloy and from 65.5 kJ/mol at Cu free to 58.6 kJ/mol at Cu = 5.3 mass% in Fe–20 mass%Si alloy.

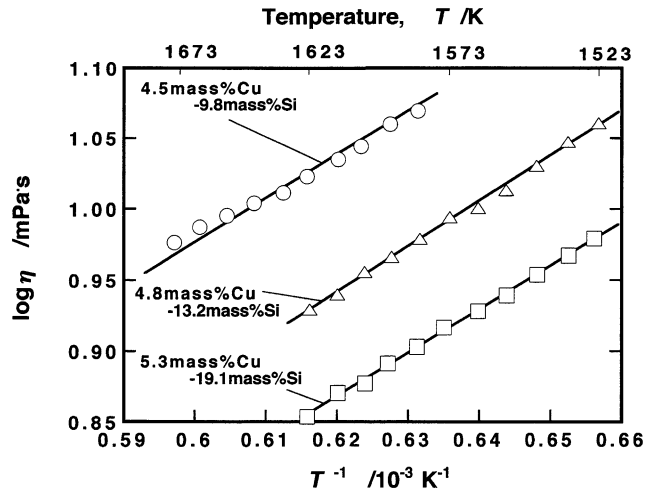


Fig. 8 Viscosity of liquid Fe–5 mass%Cu–Si alloy as a function of  $1/T$ .

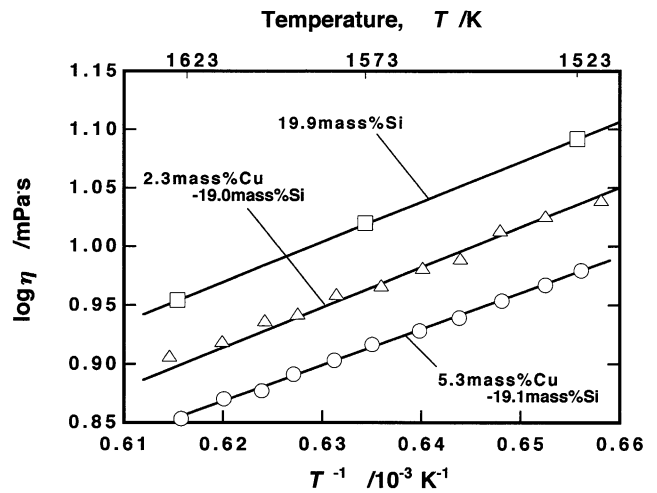


Fig. 9 Viscosity of liquid Fe–Cu–20 mass%–Si alloy as a function of  $1/T$ .

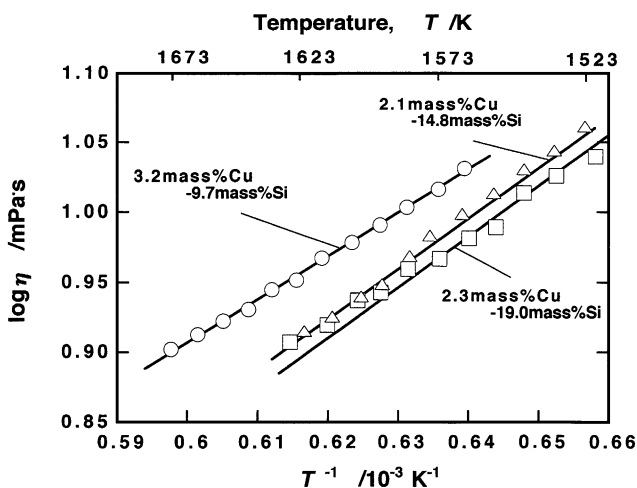


Fig. 7 Viscosity of liquid Fe–2.5 mass%Cu–Si alloy as a function of  $1/T$ .

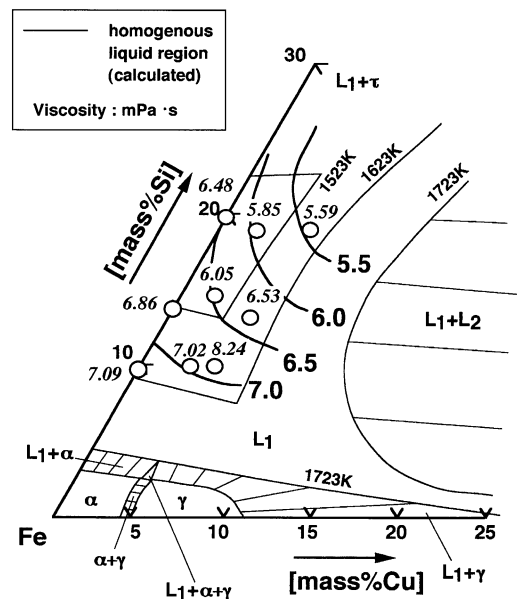


Fig. 10 Iso-viscosity lines in liquid Fe–Cu–Si ternary alloy at 1723 K. Numerical values show the observed viscosity values.

No literature data is available on the viscosity of Fe–Cu–Si system. Iso-viscosity contours of liquid Fe–Cu–Si alloy at 1723 K are estimated by drawing smooth lines through similar viscosity values and they are represented on its phase diagram in Fig. 10 with the observed viscosities. Viscosity of the alloy is in the range of 5.5 to 8.3 mPa·s in the present experimental composition area. Iso-viscosity lines tend to exhibit positive deviation from the simple additivity toward Fe corner.

### 3.4 Consideration on MTP operation

Figure 11 shows phase diagram of Fe–Cu–Si ternary alloy at 1523, 1623 and 1723 K assessed in our previous work.<sup>3)</sup> Typical composition range of metal phase formed in MTP is also super-imposed on these diagrams as shaded area. As indicated in Fig. 11, most of the composition range of metal is on the solid-liquid (( $\alpha$  or  $\gamma$ ) + ( $L_1$  or  $L_2$ )) or liquid-liquid ( $L_1 + L_2$ ) two phase region or liquid-liquid-solid ( $L_1 + L_2 + \alpha$  or  $\gamma$ ) three phase region at the typical operating temperature of MTP, 1523 to 1623 K. A part of the metal composition range would still lie on the two phase region such as  $L_1 + L_2$  range even at higher temperature like 1723 K. However, liquid miscibility gap shrinks significantly with higher temperature as seen in Fig. 11. As pointed out in the previous work, Fe-rich melt is in equilibrium with almost pure liquid Cu, the activity of Cu in two liquid area is as high as almost unity. This would cause the accumulation of liquid Cu phase in the bottom of the MTP furnace and penetration of Cu through joints of furnace refractories even if Cu content is not so high and the metal composition is in the two liquid separation region.

On the other hand, viscosity of liquid Cu at around 1723 K is reported as 3 mPa·s<sup>24)</sup> which is approximately half value of that of homogeneous liquid Fe–Cu–Si alloy in equilibrium with liquid Cu. Therefore, some operating problem could occur in MTP if the formed metal phase was in the two-liquid region. According to such consideration based on the present results, it can be concluded that higher temperature than 1723 K would be favorable for stable operation of MTP. A higher temperature generally lowers the viscosity of liquid metal, and such operation results in the easier tapping of metal phase from MTP furnace.

### 4. Conclusions

The viscosity of liquid Fe–Cu–Si ternary melt (Fe-rich corner) was observed by the oscillation crucible technique in the temperature range from 1523 to 1673 K. The relation between the viscosity of Fe–Cu–Si ternary alloys and  $1/T$  was expressed by Arrhenius-type formula. Iso-viscosity lines in Fe–Cu–Si melt were drawn at 1723 K based on the present experimental data. The numerical values of viscosity were from 5.5 to 7 mPa·s in the composition range of Cu 0 ~ 5 mass% and Si 10 ~ 20 mass% at 1723 K. These values are approximately double of that in pure Cu melt at 1723 K. Higher melting temperature than 1723 K was recommended for the easier tapping in the operation of the melting furnace for ash from municipal solid waste incinerator in consideration of the present work.

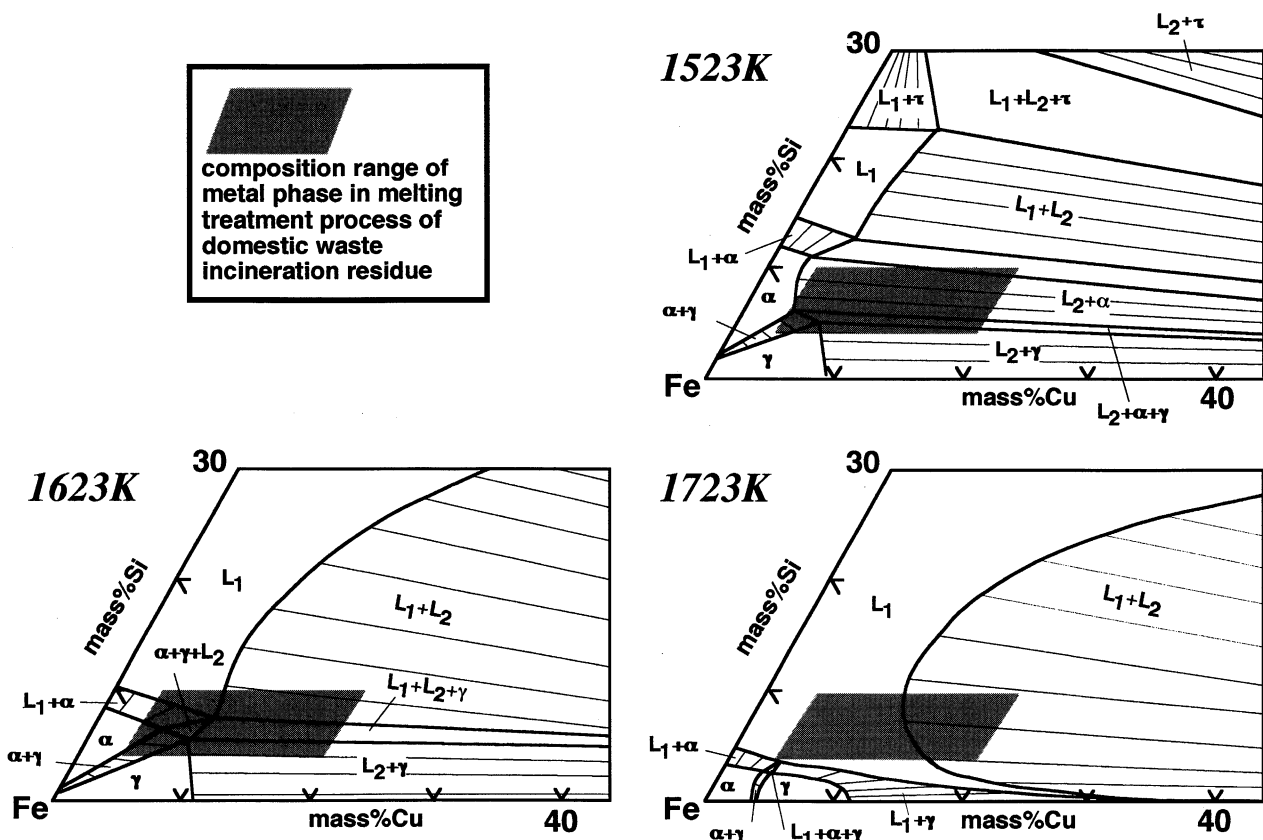


Fig. 11 Composition range of metal phase in the melting treatment process of ash from the domestic waste incineration residue super-imposed on Fe–Cu–Si ternary phase diagrams calculated with the thermodynamic parameters assessed in the previous work.<sup>3)</sup>

## Acknowledgments

The present work was performed with the experimental apparatus in Professor T. Yamamura's laboratory (Department of Metallurgy, Tohoku University). The authors wish to express many thanks to Professors T. Yamamura and Y. Sato for their valuable experimental guidance and comments. They also wish to thank Mr. S. Nozawa (formerly undergraduate student at Tohoku University, now SEGA Enterprises Co. Ltd.) for carrying out the experiments. This work was financially supported by Grant-in-Aid for General Scientific Research (C) in 1995 and 1996 from The Ministry of Education, Science, Sports and Culture of Japan Contract No. 07650864. Partial financial support from Daido Steel Corp. is also gratefully acknowledged.

## REFERENCES

- 1) For example, K. Kinoshita, A. Hayashi, K. Akahide and T. Yamazaki: *Pure Appl. Chem.* **66** (1994) 1295–1300.
- 2) For example, M. Hasebe and T. Nishizawa: *Calphad* **4** (1980) 83–100.
- 3) M. Hino, T. Nagasaka and T. Washizu: *J. Phase Equilibria* **20** (1999) 179–186.
- 4) T. Washizu, T. Nagasaka and M. Hino: *J. Phase Equilibria*, to be published.
- 5) M. Hino, T. Nagasaka and T. Washizu: *Z. Metallknd.*, to be published.
- 6) T. Ejima, Y. Sato, S. Yaegashi, T. Kijima, E. Takeuchi and K. Tamai: *J. Japan Inst. Metals* **51** (1987) 328–337.
- 7) Y. Sato, T. Yamamura, H.-M. Zhu, M. Endo, T. Yamazaki, H. Kato, T. Ejima and G. J. Janz: *Proceedings of the 3rd International Symposium on Carbonate Fuel Cell Technology*, ed. by D. Shores, H. Maru, I. Uchida and J. R. Selman, vol. 93-3 (The Electrochem. Soc., Pennington, NJ, 1993) pp. 416–428.
- 8) Y. Sato, H.-M. Zhu, Y. Kameda, T. Nagasawa and T. Yamamura: *The 17th Japan Symposium on Thermophysical Properties* (The Japan Society of Thermophysical Properties, Tsukuba, 1996) pp. 411–415.
- 9) R. Roscoe: *Proc. Phys. Soc.* **72** (1958) 576–584.
- 10) R. Roscoe and W. Barinbridge: *Proc. Phys. Soc.* **72** (1958) 585–593.
- 11) S. Watanabe and T. Saito: *Trans., JIM* **13** (1972) 186–191.
- 12) O. I. Ostrovskii, V. A. Ermachenkov and V. A. Grigoryan: *Zh. Fiz. Kim.* **56** (1982) 391–393.
- 13) H. R. Thresh, A. F. Crawley and D. W. G. White: *Trans. Met. Soc. AIME* **242** (1968) 819–822.
- 14) E. Gebhardt and K. Kostlin: *Z. Metallknd.* **48** (1957) 636–641.
- 15) W. R. D. Jones and J. B. Davies: *J. Inst. Metals* **86** (1957–58) 164–166.
- 16) H. R. Thresh and A. F. Clawley: *Metall. Trans.* **1** (1970) 1531–1535.
- 17) T. P. Yao and V. Condit: *J. Inst. Metals* **81** (1952–53) 17–24.
- 18) H. J. Fisher and A. Phillips: *J. Metals* **6** (1954) 1060–1070.
- 19) A. Adachi, Y. Ogino and Y. Shiraishi: *J. Japan Inst. Metals* **36** (1972) 927–933.
- 20) T. Ejima, Y. Sato, T. Yamamura, A. Hayashi and T. Yamazaki: *J. Japan Inst. Metals* **54** (1990) 1005–1012.
- 21) T. Iida, T. Sato and N. Ishiura: *J. Japan Inst. Metals* **44** (1980) 443–452.
- 22) T. Saito, K. Nakanishi and Y. Shiraishi: *J. Japan Inst. Metals* **31** (1967) 881–887.
- 23) A. B. Kuplum and M. F. Krutko: *Izv. Akad. Nauk SSSR Met.* (1979) No. 3, 78–80.
- 24) *Handbook of Physico-Chemical Properties at High Temperature*, ed. by Y. Kawai and Y. Shiraishi (The Iron Steel Inst. Jpn., Tokyo, 1988) pp. 93–120.
- 25) V. M. Grazov, S. N. Chizhevskaya and N. N. Glagoleva: *Liquid Semiconductors* (Plenum Press, NY, 1969) pp. 55–83.
- 26) K. Kakimoto, M. Eguchi, H. Watanabe and T. Hibiya: *J. Cryst. Growth* **94** (1989) 412–420.
- 27) H. Sasaki, E. Tokizaki, X.-M. Huang, K. Terashima and S. Kimura: *Jpn. J. Appl. Phys. Pt. 1*, **34** (1995) 3432–3436.
- 28) Y. Sato: Tohoku University (1999) private communication.