Recovery of Molybdenum from Copper Slags

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Slags as the by-product of copper making have been produced in large amounts in Chile, and about 5 million tons of slags are estimated to be disposed every year and about 50 million tons have been already accumulated near the mine site. Typical Chilean copper slag contains about 0.3 mass% Mo which is the same to the grade of primary mine production of molybdenite and the copper slags also contain about 40 mass% of Fe and 1 mass% Cu. Recovery of Mo from Chilean copper slags is quite attractive to secure a stable Mo supply. The feasibility of the recovery of Mo from copper slags as Fe–Mo alloys by carbothermic reduction is investigated in the present study. Mo in the copper slag is found to be fully recovered as Fe rich Fe–Mo alloy. The recovered alloy contains about 0.60 mass% Mo and 2.4 mass% Cu. To use the recovered Fe–Mo alloy effectively in the special steel industry, which is the most important market for molybdenum, Cu in the produced Fe–Mo alloy is successfully decreased from 2.4 mass% to 0.1 mass% by using FeS–Na₂S flux. Thus, Mo recovery from Chilean copper slag can be promising.

KEY WORDS: copper slag; Mo recovery; Fe–Mo alloy; Cu removal.

1. Introduction

Mo as well as Ni and Cr is an essential element for improving the strength and corrosion resistibility of various special steels due to its high melting point, high strength, high toughness, high electrical and thermal conductivities and reasonable ductility so as to form into wires and sheets. The worldwide demand of Mo is increasing not only for the usage in steel industry but also in many fields as a resource of dye, several non-ferrous alloys and lubricant (MoS₂), and its application is now extended to electronics industry. Recently, Mo demand is increasing with the current increase of the special steel production. However, the mining sites of Mo are localized at China, Canada and several South America countries, and sometimes its price had soared due to the shipping difficulties in these countries. Furthermore, the lack of the roasting capacity itself in these countries becomes clear recently so that the international price of Mo steeply rose several times. Namely, the current Mo supply system is quite unstable due to these several reasons. Therefore, the secured stable Mo resource is strongly asked for. To take into account these problems, we pay attention to a huge amount of the wasted copper slags in Chile as a new Mo resource.

Recently, more than 30% of Cu in the world is produced in Chile. The content of Cu in Chilean ore is, however, as low as to be less than 1 mass%. Therefore, the huge amounts of slags are also produced at the Cu refining sites and most of them have been just disposed near the refining sites, and about 5 million tons of Cu slags are continuously disposed every year and about 50 million ton of slags are expected to be already accumulated in Chile. These accumulated slags will soon become big economical, social and environmental burden and it is strongly asked to find the effective treatment of these slags. Several studies have been carried out in Chile^{1–4)} to meet these demands. In their studies, Fe₃O₄ coexisted with Mo are concentrated by using magnet separation for the crushed Cu slag. The concentrates are subjected to hydrometallurgical process to recover pure Mo. At this moment, the recovery fraction of Mo is found to be less than 30%. Further improvement of the process must be required. Differed from their approaches, the pyro-metallurgical recovery of Mo has been investigated in the present study.

The Chilean Cu slag produced after the matte making contains 30–40 mass% of T. Fe, 35–40 mass% SiO₂, less than 10 mass% of Al₂O₃ and CaO, about 1 mass% of Cu and 0.3 mass% of Mo. It also contains Au and Ag of about

Table 1. Chemical composition of Chilean copper cleaning slag.

Elements	Unit	Content
Al ₂ O ₃	mass%	3.4
CaO	mass%	1.1
Cu	mass%	1.1
T.Fe	mass%	43.4
Fe ₃ O ₄	mass%	8.4
SiO ₂	mass%	30.7
Mo	mass%	0.3
As	mass ppm	100
Bi	mass ppm	<1
Ni	mass ppm	12.0
MgO	mass%	0.8
Pb	mass ppm	264
S	mass%	0.5
Sb	mass ppm	240
Ag	mass ppm	>5

0.05 g and 2 g per 1 ton of the Cu slag, respectively. Generally speaking, the grade of the non-ferrous ore is quite low. For example, Mo content as MoS₂ of Mo ore is about 0.6% (0.36 mass% as metallic Mo) and Au content is about 10 g/t-ore. Namely, the Mo content in the disposed Chilean Cu slag is comparable to the high grade Cu ore and can be economically beneficial to recover Mo from the Cu slag, if possible. Differed from the general Mo mine development, it is not necessary to construct the infrastructure for the mining, since Cu slag is simply disposed and accumulated near the refining site. Namely, the Mo resource is easily obtained by open-cut mining of the accumulated Cu slag without extra mining facilities.

There have been many studies of Mo recovery from chemical and industrial wastes, however, few studies of Mo recovery from Cu slags were carried out.^{5–11)} Most of these studies mainly focused on the hydrometallurgical approach that required the precise control of pH, density of Mo solution, and operation temperature as well as Mo dissolution facilities. In the present study, the recovery of Mo as Fe–Mo alloy by the carbothermic reduction of molten Cu slags has been investigated since Mo is mainly used as a resource for Fe–Mo ferroalloy that is used to improve the steel's mechanical properties.

This study focused on the Mo recovery from the Cu removed cleaning slag in the cleaning furnace after the matte making and matte refining process. The composition of the slag after the cleaning is shown in **Table 1**. The P_{S_2} – P_{O_2} diagram of M (M=Cu, Fe, Mo, Pb, As, Sb)–S–O system at 1 300 K is shown in **Fig. 1**. The location of the investigated slag in the present study in Fig. 1 is indicated as (b). It was formed after two treatments for the Cu slag. The first slag was produced by separating matte in the matte-making process. The final slag (b) was produced by further removal of the residual matte in the cleaning furnace. In the matte making process, Mo and Fe are existed as oxides in the slag since the P_{S_2} and P_{O_2} is controlled to produce matte. Cu is mainly existed as sulfide and some amounts may be as oxide.

Fig. 1. P_{S_2} – P_{O_2} phase stability diagram for the ternary Metal–S–O system at 1 300 K. **Fig. 2.** P_{S_2} – P_{O_2} phase stability diagram for the ternary Metal–S–O system at 1 773 K.

Under the condition for the reduction of the cleaning slag by carbon at high temperature, the partial pressure of CO gas will be 1 atm and the activity of carbon will be unity. The carbon oxidation reaction is expressed by

$$\Delta G^0 = -221\,840 - 178.01T \text{ (J)}^{12)} \quad (2)$$

From Eq. (2), the equilibrium $\log(P_{O_2})$ at 1 773 K is calculated to be -15.83 . As shown in **Fig. 2**, Fe, Cu and Mo can be existed as metallic form under this P_{O_2} condition. Namely, oxides of Fe, Cu and Mo can be fully reduced to metals by the carbothermic reduction of the Cu slag at high temperature. The behaviors of Pb, As and Sb as shown in Figs. 1 and 2 will be discussed in 3.3.

Since 80% of Mo demand is for the Fe–Mo alloy production in the steel industry, the recovery of Mo as Fe–Mo alloys can be beneficial as well as pure metallic Mo. Fe and Mo form stable Fe–Mo solid solution. Thus, Mo can be concentrated into the produced Fe phase during the carbothermic reduction process of Cu slag, and recovered as Fe–Mo alloy.

2. Experimental and Analysis

2.1. Experimental Procedure

As shown in Table 1, the actual Chilean slag contains a

lot of minor elements. To simplify the reaction phenomena, the slag without these minor elements were prepared by using chemical agents. The composition was shown in **Table 2**. The reduction experiments were carried out by using both of them. Since it was found that there was negligible difference of the reaction behavior between them, the simulated slag was mainly used in this study.

For the energy saving, the reduction process at lower operating temperature is preferable. In the present study, however, the reduction was carried out at the temperature high enough to promote the effective metal-slag separation. To lower the melting point of the formed slag after the reduction, the appropriate amounts of CaO and Al_2O_3 powder were added to the Cu slag to adjust the final slag composition to the eutectic composition (40 mass% SiO_2 –48 mass% CaO–12 mass% Al_2O_3) of CaO– Al_2O_3 – SiO_2 ternary system. The carbothermic reduction experiment of the Cu slag was carried out by using a graphite crucible at 1 733, 1 773 and 1 823 K.

The experimental apparatus is schematically shown in **Fig. 3**. The Cu slag was charged into the graphite crucible (I.D 25 mm and O.D 30 mm and height 80 mm) and the reduction was carried in the electric resistance furnace. In the preliminary experiments, it was found that the rapid heating of the sample made the sample spread out from the crucible by the violent CO gas evolution. To avoid this problem, the crucible was gradually lowered at the rate of 10 mm/30 min for 2 hrs during the temperature range between 1 423 K and 1 523 K. After the confirmation of the slag volume decrease due to the full melt of the sample, the crucible was quickly lowered at the pre-fixed position. After the reduction, the crucible was taken out from the furnace and

quenched by using He gas injection on it.

2.2. Chemical Analysis

The amounts of Fe, Cu, Mo, Si, Al and Ca contents in the metal and slag phases after the reduction were analyzed by using ICP method. Appropriate amounts of small pieces were cut from the solidified samples and these pieces were crushed and then dissolved in Aqua regia. In advance, the approximate content of each component was examined in the preliminary experiments. Based on these contents, the standard solutions were prepared by dissolving almost the same amount of contents. The background intensity of the solutions is adjusted by adding the same amount of HCl and HNO_3 used for dissolving the sample. The slag was not fully dissolved in Aqua regia due to the large amount of SiO_2 . Thus, another method was applied. At first, the slag (0.1 g) was dissolved into the mixture of HCl (15 ml) and ion exchange water (15 ml) and then the solution was filtered into a measuring flask (250 ml). After the filtration, the residue with the filter was put into a Pt crucible with the mixture of $\text{Na}_2\text{B}_4\text{O}_7$ (0.5 g) and Na_2CO_3 (0.5 g), and was heated to melt. The remained in the Pt crucible was again dissolved into the mixture of HCl (15 ml) and ion exchange water (15 ml) and then filtered into the measuring flask (250 ml). The same process was repeated again for the residue with the filter, and finally the content in the measuring flask was analyzed. The contents of S and C were measured by using the combustion infrared detection method. In this analysis, the sample (2 g) was combusted with Sn tip (1 g) and the combustion improver (1.5 g).

3. Results and Discussion

3.1. Reduction Experiments at High Temperature

The results of the carbothermic reduction at high temperature were shown in **Figs. 4** and **5**. As shown in **Fig. 4**, Fe and Cu contents in the slag phase at 1 733 K are as relatively high as 4.35 and 0.066 mass% respectively. At 1 823 K, however, these were found to be as low as 1.0 mass% and 0.02 mass%. At these temperatures, most of Fe_2O_3 and Cu_2O were reduced to metals by the reduction process and distributed into metallic phase. As shown in **Fig. 5**, and Mo content in the metallic phase was found to be about 0.60 mass%. Mo content in the slag phase was not detected by the analysis.

About 2.3 mass% of Cu, however, was existed in the

Table 2. Chemical composition of the simulated copper slag.

Elements	Unit	Simulated slag
Al_2O_3	mass%	3.4
CaO	mass%	1.1
Cu	mass%	1.1
T. Fe	mass%	43.4
Fe_3O_4	mass%	8.4
SiO_2	mass%	30.7
Mo	mass%	0.3

Fig. 3. Schematic of experimental apparatus.

Fig. 4. Equilibrium contents of Cu and Fe in slag phase after the reduction treatment as a function of temperature.

Fig. 5. Equilibrium contents of Cu, Mo, S and Si in Fe phase after the reduction treatment as a function of temperature.

metallic phase as shown in Fig. 5. This Cu content in metallic phase is too high to use as the resource of Fe–Mo alloy. Namely, de-Cu treatment for the produced Fe–Mo alloy must be carried out. The metallic phase also contains C of about 4.5 mass% and Si of about 0.1 mass% that was produced by the reduction of SiO_2 in slag.

3.2. De-copper Experiment

A number of investigations for Cu removal in steel scrap have been carried out. The process using sulfide fluxes is considered to be the most possibly acceptable for the industrial purpose. One of the authors already investigated Cu removal by using sulfide based flux from carbon saturated liquid iron.^{13,14} In this study, by using the same flux, the possibility of Cu removal in Mo contained Fe–C melt was investigated. Differed from the previous works,^{13,14} there are some chances of Mo sulfide formation since the flux contains S.

3.2.1. Experimental Conditions

Alloys with the same composition produced in the slag reduction were prepared for the study of the de-Cu process. The de-Cu experiments were carried out by using the prepared alloy (15 g) with the mixture (15 g) of FeS and dried Na_2S in a graphite crucible. The experimental temperature was fixed to 1673 K as the same to that of Wang *et al.*^{13,14} In the preliminary experiments, it was found that the content of each element in the melts did not change with time after 1 hr. Thus, it was assumed that the equilibrium condition was practically established within about 1 hr. Thus, after reaching the equilibrium, the sample was removed from the furnace and gas quenched by injecting He. Then, the compositions in the metallic and flux phases were analyzed.

3.2.2. Results of de-Copper Experiments

The Cu and S contents in the liquid Fe alloy and the partition ratio (L_{Cu}) with time are shown in Fig. 6. L_{Cu} is defined by

$$L_{\text{Cu}} = (\text{mass\% Cu})_{\text{flux}} / [\text{mass\%Cu}]_{\text{iron alloy}}$$

The partition ratio is found to be more than 20. As shown in Fig. 6, L_{Cu} increases with Na_2S in FeS– Na_2S flux up to about 35%, but L_{Cu} starts to decrease with more than that value. It is also found that the S content in liquid Fe decreases

Fig. 6. Effect of Na_2S content in FeS– Na_2S flux on L_{Cu} and S content in liquid Fe at 1673 K.

Fig. 7. SEM image of Fe phase after the copper removal treatment.

es with increase of Na_2S in the flux. The Cu content in Fe is found to be about 0.1 mass%. It was also found that the Mo content (about 6.5 mass%) in the melt was did not change during de-Cu process. Namely, Mo loss during de-Cu process was negligibly small. As shown in Fig. 6, the present results show the reasonable agreement with the results by Wang *et al.*,^{13,14} except the S content in Fe. Our results show rather higher concentration than theirs.

The SEM image of the metallic phase after the de-Cu treatment was shown in Fig. 7. It shows FeS particles suspension. This can be the main reason of the higher S content than that of Wang *et al.*^{13,14} Since they used an induction furnace, the dispersed FeS particles could collide each other to agglomerate due to the stirring flow driven by magnetic force and they moved to the surface and trapped by the flux and removed from the metal phase. Therefore, the S content in the present study will be decreased by removing this suspended fine FeS particles. There must be a reaction between the melt and the FeS particles. But the contribution of FeS to the equilibrium values may be negligible since their amount is quite small compared with that of the flux.

The potential diagram for M (metals)–S–O system at 1673 K is shown in Fig. 8. The liquid Fe and molten FeS phases are coexisted during the de-Cu process. Under the conditions of P_{S_2} and P_{O_2} during de-Cu treatment, Cu_2S can be the stable phase and the metallic Mo is the stable phase but not MoS_2 . Namely, Cu in the metal phase will be sulfurized and move to the flux, however, Mo cannot be sulfur-

Fig. 8. P_{S_2} - P_{O_2} phase stability diagram for the ternary Metal-S-O system at 1673 K.

ized and remained in the metallic phase. As a results, Cu partition ratio becomes larger and Mo partition ratio smaller under the present experimental condition and Mo loss in the alloy can be negligible.

3.3. Behaviors of Other Metallic Elements in Slag

As shown in Fig. 1, FeS in Cu ore concentrate is removed by oxidation at the point (b) to make matte. The formed slag at (b) is transferred to the cleaning furnace, and CuS is recovered by the separation from the slag. In the matte making process ((a) to (b)), Pb, As and Sb can exist as metals as well as oxides from the results shown in Fig. 1. The $\log(P_{O_2})$ in the carbothermic reduction process of Cu slag was already calculated to be -15.83. Under this P_{O_2} condition, metallic phase is stable for all elements of Pb, As and Sb as shown in Fig. 2. Thus, if these elements are assumed to be distributed as oxides (PbO, As_2O_3 , and Sb_2O_3) in the slag, they are certainly reduced to metallic Pb, As and Sb.

As already mentioned, the recovered metal phase was subjected to the de-Cu treatment. As shown in Fig. 8, the stable phase of Pb, As and Sb is the metallic phase but not sulfides under the present de-Cu condition. Namely, Pb, As and Sb cannot be converted into sulfides and remained in the metal phase during the de-Cu process.

PbS is assumed to be oxidized to PbO during matte making process, and small amount of PbO is partitioned to the slag phase, however, this PbO will be reduced in the carbothermic reduction process based on the reaction (3);

$$\Delta G^0 = 73\,520 - 158.79T \text{ (J)}^{(12)} \dots\dots\dots (4)$$

Under the reduction condition of $a_C = 1$ and $P_{CO} = 1$, $\log(a_{Pb}/a_{PbO})$ at 1773 K is calculated to be 6.13. The terms of a_C , a_{Pb} and a_{PbO} are the activities of carbon, Pb and PbO, respectively. Namely, a_{Pb} is almost million times larger than a_{PbO} . Even if PbO is existed in slag it can be certainly reduced to metallic Pb. When Pb exists in Fe-Mo alloy, PbS might be formed during de-Cu process by the reaction (5);

$$\Delta G^0 = 82.92 + 27.44T \text{ (J)}^{(12)} \dots\dots\dots (4)$$

At the reduction temperature of 1673 K, ΔG^0 is positive of

Fig. 9. Variation of slag weight before and after the reduction process.

46 396 (J). It means that the reaction (5) will shift to left-hand side. Thus, Fe is preferentially sulfurized and dissolved into the flux phase. Correspondingly, Pb can be stayed in the metal phase during the de-Cu treatment. Namely, PbO in slag in the matte making process will be fully reduced in the carbothermic reduction process and partitioned into metal phase. This portioned Pb will continue to stay in the metal phase even after the de-Cu treatment. Based on these discussion, it was confirmed that the precise P_{O_2} control is certainly required to avoid the formation of oxides of the elements (Pb, As and Sb) during the matte making process. Take into account of the current industrial process, however, it will be quite difficult to precisely control the atmosphere of the actual process at this moment. The further development of the atmosphere control technology is certainly required.

3.4. Change of Slag Volume during the Reduction

As already mentioned, very few Fe and Cu are remained in the slag phase after the Cu slag reduction. The slag after the reduction is consisted of 40 mass% SiO_2 , 48 mass% CaO and 12 mass% Al_2O_3 . Since this composition is very close to that of Portland and alumina cements, the slag after the reduction may possibly be used as an alternative cement resource. From this view point, the amounts of the produced slag after and before the reduction are evaluated and the result is shown in Fig. 9. The main components of the slag before the reduction are SiO_2 and iron oxides. Through the reduction, iron oxides and MoO_2 are reduced to metals and they are recovered as Fe-Mo alloy. About 60 mass% of slag weight is decreased by this reduction process. Most of SiO_2 was not reduced and stayed in the slag. The amounts of CaO and Al_2O_3 in the slag are increased since about 35 mass% of CaO and Al_2O_3 were added to the Cu slag to adjust the slag composition before the reduction. Since Fe_2O (about 60 mass% of slag weight) were reduced during the reduction process, about 25% of the slag weight was decreased. The final slag weight is decreased to about 75 mass% of the initial Cu slag. Thus, by considering the accumulated Cu slag, the Cu slag can be reused as a huge amount of the industrial cement resource.

These results simply indicated that not only Fe-Mo alloy can be possibly recovered from the Cu slag but also the slag after the reduction can be effectively used as the alternative cement resource by applying the carbothermic reduction process at high temperature to the accumulated huge amount

of Cu slag in Chile.

3.5. Economical Merit of the Industrial Implementation of the Reduction Process

The flow chart of the proposed process in the present study is shown in **Fig. 10**. The main product of this process is Fe–0.65%Mo–4.5%C. It can be used as a high carbon Mo ferroalloy. Based on the application, however, the decarburization of the melt will be carried out if necessary. Along with the Fe–C–Mo alloy production, Cu removed flux was also produced as a by-product. Unfortunately, the effective use or after-treatment of this flux such as the recovery of Cu is not yet clear at this moment. The further research work must be carried out for this. By applying the proposed process to the Chilean Cu slag of about 5 million ton/year, about 2 million ton/year of Fe–0.60 mass% Mo alloy can be recovered. This amount corresponds to about 10% of the worldwide production of Mo and possibly contributes to stabilize the international Mo market.

In the steel industry, Fe–Mo alloys with about 10 mass% Mo was generally used as a Mo additives. The recovered Fe–Mo alloys in the present study only contains about 0.6 mass% of Mo. As a result, the recovered Fe–Mo alloys can be used only to produce low Mo alloy steel at this moment. To increase the economical values of the Chilean Cu slags and extend their effective usage, further development of the recovery technology of high Mo content Fe–Mo alloy from Cu slags is certainly required.

Along with the Mo recovery, about 3.5 million ton/year of the CaO–SiO₂–Al₂O₃ slags without metallic elements are produced after the carbothermic reduction and they can be substituted for the cement resource alternative. Namely, huge economical benefit is expected once this process is in practice.

Fig. 10. Flow chart of the proposed process in the present work.

4. Conclusions

In the present study, Mo recovery as Fe–Mo alloys from Cu slag has been investigated by taking into account that Mo is mainly used for the resource for Fe–Mo alloy. The Chilean Cu slag with the addition of an appropriate amount CaO and Al₂O₃ was reduced in the graphite crucible and the following results are obtained;

(1) It is confirmed that Fe–0.60 mass% Mo alloy with low Cu content can be produced from the Chilean Cu slag by applying (1) the carbothermic reduction of the Cu slag with the addition of CaO and Al₂O₃ powders, and (2) the de-Cu treatment of the produced Fe–Mo alloy by using FeS–Na₂S flux.

(2) MoO₂ in the Cu slag was almost fully reduced and concentrated in the Fe-rich phase by the carbothermic reduction. In the de-Cu treatment for the produced Fe–Mo alloy, Mo in the molten Fe–Mo alloy is not converted to a sulphide but remained in the metallic phase. Namely, it is possible to recover Mo with high efficiency since Mo loss during the de-Cu processing is negligibly small.

(3) The Cu slag after the reduction mainly consists of SiO₂, Al₂O₃ and CaO with the negligibly small amount of Fe and Cu. The accumulated Chilean Cu slag can be effectively used as an alternative resource of cement since the slag composition after the carbothermic reduction is almost the same to that of the conventional cement.

REFERENCES

- 1) C. Gonzalez, P. Parra, A. Klenovcanova, I. Imris and M. Sanchez: *Scand. J. Metall.*, **34** (2005), 143.
- 2) F. Parada, R. Parra, T. Waranabe, M. Hino, J. Paracios and M. Sánchez: *Proc. 8th Int. Conf. on Molten Slags, Fluxes and Salts, MOLTEN 2009*, ISS, Warrendale, PA, (2009), 1273.
- 3) D. Busolic, F. Parada, R. Parra, E. Urdy, J. Paracios, M. Hino, F. Cox, A. Sanchez and M. Sanchez: *Proc. 8th Int. Conf. on Molten Slags, Fluxes and Salts, MOLTEN 2009*, ISS, Warrendale, PA, (2009), 621.
- 4) D. Busolic, F. Parada, R. Parra, A. Ulloa, J. C. Carrasco, J. Paracios, A. Reghezza, C. Cablero, J. Zunidga and M. Sanchez: *Proc. 8th Int. Conf. on Molten Slags, Fluxes and Salts, MOLTEN 2009*, ISS, Warrendale, PA, (2009), 1281.
- 5) P. K. Tripathy and R. H. Rakhasia: *Miner. Process. Extr. M.*, **115** (2006), 8.
- 6) T. Darjaa, T. H. Okabe, Y. Waseda and Y. Umetsu: *J. MMIJ*, **116** (2000), 203.
- 7) K.-H. Park, B. R. Reddy, D. Mohapatra and C.-W. Nam: *Int. J. Miner. Process.*, **80** (2006), 261.
- 8) T. N. Angelidis, E. Tourasanidis, E. Marinou and G. A. Stalidis: *Resour. Conserv. Recy.*, **13** (1995), 269.
- 9) B. B. Kar: *Int. J. Miner. Process.*, **75** (2005), 249.
- 10) B. B. Kar, B. V. R. Murthy and V. N. Misra: *Int. J. Miner. Process.*, **76** (2005), 143.
- 11) T. R. Mankhand and P. M. Prasad: *Metall. Trans. B*, **13B** (1982), 275.
- 12) NIST-JANAF Thermochemical Tables, 4th ed., ed. by M. W. Chase, Jr., American Institute of Physics, College Park, MD, (1998).
- 13) C. Wang, T. Nagasaka, M. Hino and S. Ban-Ya: *ISIJ Int.*, **31** (1991), 1300.
- 14) C. Wang, T. Nagasaka, M. Hino and S. Ban-Ya: *ISIJ Int.*, **31** (1991), 1309.