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RECOVERY OF VALUABLE METALS IN TIN-BASED ANODIC SLIMES BY CARBOTHERMIC REACTION

ODZYSK CENNYCH METALI ZE SZLAMÓW ANODOWYCH NA BAZIE Sn METODĄ REAKCJI KARBOTERMICZNEJ

This study investigated the recovery of anodic slimes by carbothermic reaction in the temperature range of 973~1,273K and amount of carbon as a function of time. Tin anodic slime samples were collected from the bottom of the electrolytic cells during the electro-refining of tin. The anodic slimes are consisted of high concentrated tin, silver, copper and lead oxides. The kinetics of reduction were determined by means of the weight-loss measurement technique. In order to understand in detail of carbothermic reaction, thermodynamic calculation was carried out and compared with experiments. From thermodynamic calculation and experiment, it was confirmed that Sn-based anodic slime could be reduced by controlling temperature and amount of carbon. However, any tendency between the reduction temperature and carbon content for the reduction reaction was not observed.

Keywords: Tin, anodic slime, carbothermic reduction, carbon, recovery

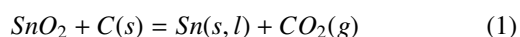
1. Introduction

During the production of tin metal from waste solder concentrates by electrowinning process, tin-based anodic slime are accumulated in the bottom of electrolytic cell and they exhibits a form of oxide which are composed of a relatively silver(Ag), lead(Pb), copper(Cu) and tin(Sn) content.

Considering the depleting reserves of resources for the extraction of metals, recovering process should be establish for secondagy sources such as slag, slime etc. Several method are applied in order to recover the values such as pyrometallurgy, hydrometallurgy and pyro-hydrometallurgy process[1-6].

Usually, the reduction of metal oxides by carbon is an important means of extracting metal value and many researchers have been reported on the carbothermal reduction of metal oxides[7-9].

In the tin smelting processes, the reduction reaction of tin dioxide (SnO₂) by carbon is usually can be represented by Eq. (1) and some researchers reported on the reduction and reaction mechanism of tin oxide (SnO₂) reduced to Sn metal [10, 11].



However, most work in the literature as mentioned above considered about the reduction reaction of pure tin oxide. In general, to satisfy the industrial needs and conditions, slime composed of alloying elements such as silver, lead, copper, tin and their oxides should be considered for reduction reaction.

Therefore, this study investigated the carbothermic reaction phenomena of Sn anodic slime by thermodynamic cal-

ulation using FactSage and the effect of temperature and amount of cokes on the reduction were experimentally investigated by weight loss measurement using thermogravimetric analysis(TGA).

2. Experimental Procedure

The tin-based anodic slimes used in this study were collected in the bottom of the electrolytic cells during the electrowinning of tin from Sungeel Hi-Tech. Ltd., Gunsan, Korea. These samples were classified through a 1.0 mm sieve to remove large inclusions in the slime and rinsed with distilled water and then dried in air. The slime was analyzed for silver(Ag), tin oxide(SnO), tin dioxide(SnO₂), lead oxide(PbO), tin(Sn), Ag₃Sn and Cu by X-ray diffraction pattern (XRD) and the chemical composition by inductively coupled plasma optical emission spectrometer(ICP-OES, model: ICPS-1000IV) was given in Fig. 1 and Table 1. From XRD pattern, it is confirmed that the slime used in this study is mainly composed of SnO and SnO₂. The reductant agent of oxide in slime was chosen as cokes which is consisted of 85 wt.% fixed carbon and 15 % ash with average particle size 1 mm.

TABLE 1
Chemical compositions of Sn anodic slime used in this study by ICP-OES(wt.%)

element	Sn	Ag	Cu	Pb	Bi	O
slime	52.05	12.14	2.98	11.54	0.92	20.37

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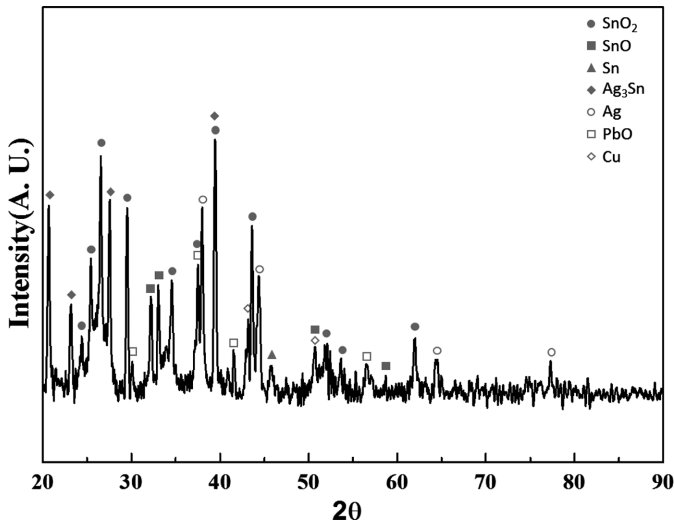


Fig. 1. XRD pattern of Sn-based anodic slime used in this study

Before to determine the amounts of carbon and reduction temperature of anodic slime, thermodynamic calculation was performed for reduction reaction of slime using FactSage. The conditions of thermodynamic calculation are as follows. The total amount of sample is 100gram and carbon is added to sample from 0 to 10gram. We investigated the phase distribution of sample (slime) with amount of carbon at some temperatures.

Based on the amount of carbon obtained from thermodynamic calculation, the sample were prepared by mixing with slime and cokes powder in turbulent mixer in a 1 hr with weight ratio of cokes from 7 to 11 wt.%, respectively.

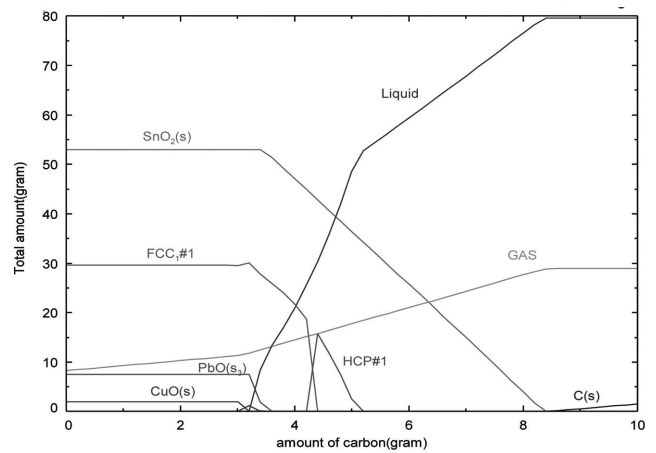
The reduction behaviors were determined by weight loss measurement in a typical TGA analysis(model: STA8000). The TGA was consisted of a recording microbalance from on arm of which a shallow silica tray for sample was suspended by a platinum chain into reactor tube located within vertical tubular furnace. During the experiment, the weight change was continuously recored by microbalance and purged with Ar gas to prevent the leakage of ambient air into the system.

Pyrometallurgical experiments were conducted in a resistant furnace to investigate the metal yield using carbon crucible with various cokes contents and temperature for 2 hours, respectively. The molten metal was poured into steel mold and solidified.

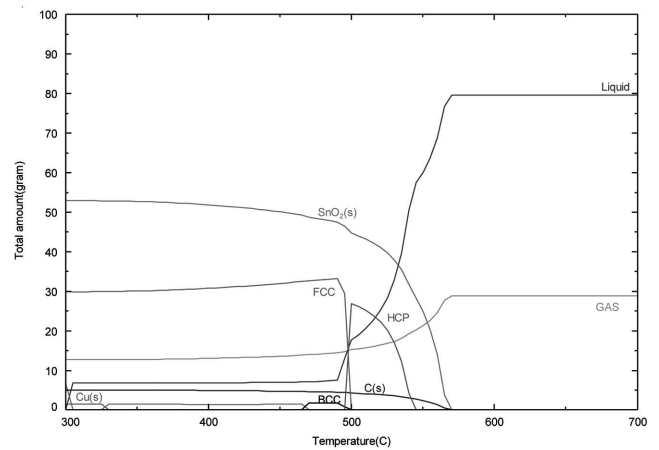
3. Results and discussions

Fig. 2 (a) and (b) show the phase distribution of sample with amount of carbon at 843K (Fig. 2 (a)) and with 8.4 gram carbon according to the temperature (Fig. 2 (b)). According to the thermodynamic calculation results, as shown Fig. 2(a), the reduction reaction of Sn-based anodic slime is finally finished around 843K with 8.4gram carbon (7.7 wt. % of total system). In this temperature, Ag is existed as solid state from 0 to 3 gram carbon and then liquefied. However, Pb and Cu are existed as oxide state from 0 to 3gram carbon and then liquefied. Also, to investigate the temperature dependency of reduction reaction of anodic slime, we carried out calculation of the reduction reaction for slime with 8.4 gram carbon according to the temperature (Fig. 2(b)). With increasing temperature,

reduction reaction of sample is finished at 843K as mentioned above. Ag liquid is formed at 773K and fully liquefied at 818K. Moreover, it is calculated that Pb and Cu are also fully liquefied at 818K, respectively.



(a)



(b)

Fig. 2. (a) Phase distribution of sample with amount of carbon at (a) 843K (b) with 8.4 gram carbon according to the temperature

From these thermodynamic calculation, it could be obtained the amount of carbon needed for reduction of Sn-based anodic slime. These calculation results will be applied on the tin extraction and refining.

On the basis of thermodynamic simulation, the effect of reduction temperature on the carbothermic reduction behavior of slime powder was determined by varying reaction temperature between 873K and 1,273K with fixed cokes content of 9 wt. % using TGA.

Fig. 3 shows the effect of temperature on the reduction rate of Sn-based anodic slime with 9 wt. % cokes expressed for weight loss ($\Delta W/W_0$). In this figure, ΔW is the weight loss of sample and W_0 is the initial weight of sample, respectively.

As shown in Fig. 3, the reduction of samples at the temperature between 873K and 1,073K slightly increased at initial state for 30 min and then keep up about 0.025 during the experiment. However, the weight loss for reduction at 1,273K was rapidly increased to 120 min and was saturated about 0.23.

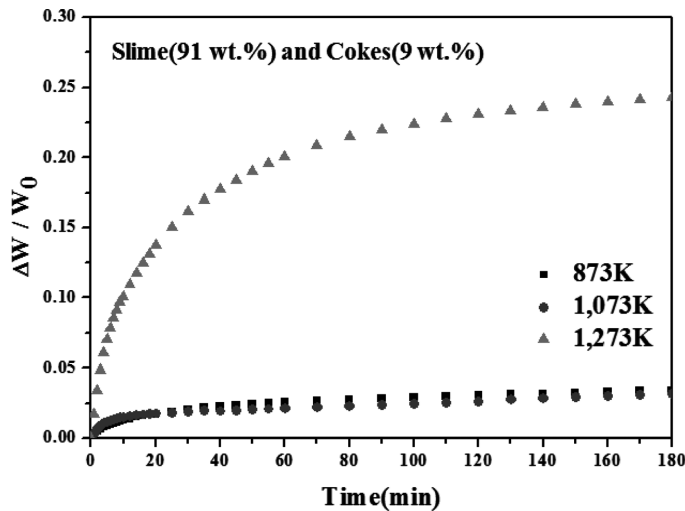


Fig. 3. Effect of temperature on the rate of reduction of Sn-based anodic slime with 9 wt. % cokes

Compared with the thermodynamic calculation and weight loss measurement, the reduction temperature is different. In case of thermodynamic calculation, reduction temperature is 843K. However, in case of experiment, the reduction temperature is between 1,073K and 1,273K. The discrepancy between experiment and thermodynamic calculation is possibly originated from the kinetic factors during reduction reaction.

Fig. 4 shows the results of reduction behavior of Sn anodic slime with reductant contents at 1,273K. As shown in Fig. 4, it is observed that the amount of weight loss ($\Delta W/W_0$) with 9 wt. % cokes is higher than the condition of 7 and 11 wt. % cokes after 180 min, respectively. In the early stage of reduction, slime with 11wt. % cokes shows a higher amount of weight loss than other two slimes. This tendency is kept to 20 min and then amount of weight loss of slime with 9 wt. % cokes is the highest among the three slimes. The amount of weight loss of slime with 7 wt. % and 11 wt. % cokes are similar after 40 min. It means that to obtain the highest metal yield in the slime, specific content of cokes needs at the some reduction temperature. In this study, it is observed that the effect content of cokes to recover Sn slime to metal at 1,273K is 9 wt. %.

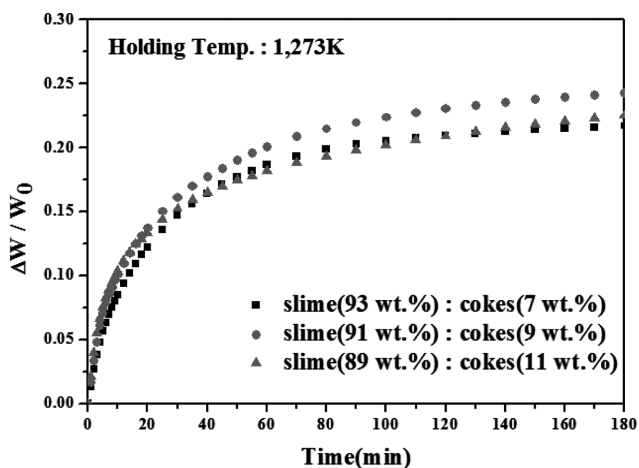


Fig. 4. Effect of amounts of reductant on the rate of reduction of Sn-based anodic slime at 1,273K for 3hr

From the experimental results for reduction, it is considered that the reduction temperature and carbon content are main factors to reduce the Sn anodic slime to Sn metal.

In the previous research, the reduction of stannic oxide (cassiterite) with increasing the amount of carbon decrease the rate of reduction because the increased layer of carbon surrounding the SnO_2 particle and the reduction of SnO_2 with CO does not reach complete equilibrium state[10]. Also, Lucheva et al. reported that the melting of solder dross by carbothermic reduction is often prevented by excess reductant particles [12].

To check the effect of carbon content and reduction temperature on the metal yield at same reduction time, metal yield of slime for 7, 9 and 11 wt. % cokes with different reduction temperature for 2 hrs are compared. As shown in Fig. 5, metal yield of slime with 7 wt. % cokes at 1,173K is higher than that at 1,273K. However, in case of slime with 11wt. % cokes, tendency of metal yield is changed to opposite. Also slime with 9wt% coke shows almost same value for metal yield at 1,173K and 1,273K as shown in Fig.5. Therefore, it was confirmed that the highest yield of Sn-based valuable metal is obtained about 86.6 % when using 9 wt. % cokes in the condition of 1,273K for 2 hrs, but it could not find any tendency with regard to carbon content for the reduction reaction.

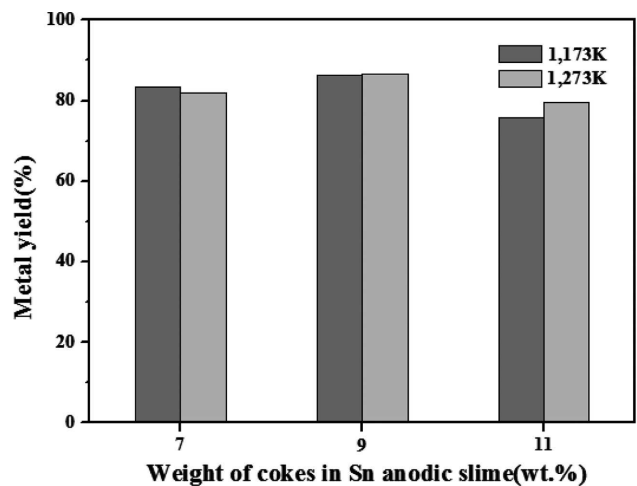


Fig. 5. Effect of amount of cokes and reduction temperature for 2hr on metal yield

4. Conclusions

The recovery of valuable metals in Sn-based anodic slime by carbothermic reduction with cokes was investigated by thermodynamic calculation and TGA analysis. From thermodynamic calculation, various phase distribution with temperature change could be obtained and it was confirmed the amount of carbon needed for reduction of Sn-based anodic slime. In the experiment, it was also confirmed that 9 wt. % cokes is needed to get the highest Sn in the slime at 1,273K. From thermodynamic calculation and experiment, it was confirmed that Sn-based anodic slime could be reduced by controlling temperature and amount of carbon. However, any relationship between the reduction temperature and carbon content for the reduction reaction could not find.

Acknowledgements

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