Reduction Kinetics of Zinc Powder from Brass Converter Slag by Pyrometallurgical Method Using Hydrogen Gas[†]

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Abstract

A pyrometallurgical reduction process for the recovery of copper and zinc from brass secondary slag (BSS) was studied. Specifically, the effect of reduction temperature and time on the conversion to metallic phases was investigated. The brass secondary slag was characterized by X-ray diffraction, inductively coupled plasma-atomic emission spectrometry, automatic elemental analysis, thermogravimetric analysis, and field emission scanning electron microscopy. A two-step reduction of BSS was identified. The step 1 comprised the reduction of ZnO, while the step 2 featured the reduction of ZnO·Al₂O₃. Furthermore, the application of a first-order reaction model with Arrhenius analysis, indicated a conversion of ZnO to Zn(g) that had a rate constant increasing from $1.4 \pm 0.13 \times 10^{-3} \text{ s}^{-1}$ at 900 °C to $2.18 \pm 0.15 \times 10^{-2} \text{ s}^{-1}$ at 1050 °C. This reaction had an activation energy of $233.2 \pm 26.1 \text{ kJ/mol}$. Secondly, the conversion of ZnO·Al₂O₃ to Zn(g) and Al₂O₃ increased from $1.54 \pm 0.21 \times 10^{-5} \text{ s}^{-1}$ at 900 °C to $1.09 \pm 0.19 \times 10^{-3} \text{ s}^{-1}$ at 1050 °C, and the activation energy was $376.7 \pm 22.4 \text{ kJ/mol}$. This reaction mechanism and its associated kinetic data can be applied to optimize the operation conditions of recycling processes for Cu-containing wastes.

Keywords: pyrometallurgy, copper converter slag, kinetic analysis, zinc powder

1. Introduction

Copper and zinc are important base metals required for various applications in metallurgical and chemical industries. The annual global output of copper and alloy products represents around 16.1 million tons, of which about 15.3 million tons (75–80 %) originate from refined copper, while about 4.2 million tons (20–25 %) are derived from direct melt scrap (Moskalyk P.R. and Alfantazi A.M., 2003).

However, the increasing worldwide demand for zinc and copper has necessitated intensive studies into the recovery and extraction of these metals from different sources (Rudnik E. et al., 2009). Some of these metals are

recovered from different secondary slags, e.g., brass dross, brass ash, and flue dusts in electric furnaces. These brass secondary slags (BSS) are by-products obtained during brass scrap smelting and crushing of brass slag. It has been estimated that for every tons of copper production about 2.2 tons of slag are generated, so that 24.6 million tons of slag result from world copper production every year (Gorai B. et al., 2003).

BSS usually contains Cu, Zn, and other minor elements such as Pb, Fe, Ni, Si, and Sb (Jha M.K. et al., 2001). However, these slags contain different level of impurities depending on source. Recovery and extraction of these metals is necessary and important from both economic and environmental viewpoints.

In industries, various methods are used to extract metals from BSS. One of these, the hydrometallurgical process, is used to recover and recycle metals from BSS using different leaching agents, including sulfuric acid (Anand S. et al., 1983), hydrochloric acid (Sharma K.D. and Row B.R.L., 1985), cyanide (Anand S. et al., 1980) acetic acid (Altundogan H.S. and Tumen F., 1997), and ammonia (Sukla L.B. et al., 1986). However, the use of leaching agents is harmful to the human body and can cause environmental pollution.

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These drawbacks can be overcome using pyro-metallurgical smelting to recover Cu and Zn from BSS. The top submerged lance (TSL) process is a typical pyro-metallurgy method that was commercialized and researched to improve recovery efficiency. The TSL process provides highly efficient mixing and a heat source for reaction, due to combustion of the fuel and oxygen-mixed gas with the BSS. Moreover, TSL process can easily remove the impurities that are generated through the formation of slag in the upper furnace (Bakker M.L. et al., 2011).

However, it is difficult to directly feed certain raw materials that are fine dusts to a TSL furnace because of dust-scattering during the injection step. To solve this problem, the density of the BSS can be increased during the reduction process using a fluidized bed reactor. This is done in a stage prior to the TSL furnace, and can be effective for increasing process throughput. The reduction rate and reaction mechanism of BSS are very complex to determine because such slags can contain mixtures of copper, zinc, and various elements. Therefore, further research into the thermodynamics and reaction kinetics of BSS recovery processes is necessary to optimize process conditions in fluidized bed reactors.

The aim of this work is to determine the activation energy and reaction mechanism of BSS reduction by applying a pyro-metallurgical method using different reduction gas. Firstly, different parameters affecting the reduction ratio, such as reduction temperature and reduction time, were investigated. Then, based on the results of the reduction, the activation energy and reaction mechanism of BSS were determined using the Arrhenius equation (Igor I. K., 2008).

2. Experimental

The BSS that was used in this experimental was taken from the brass smelter of SEOWON CO. LTD in South Korea. The BSS sample was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, ARL 3410, Switzerland) and X-ray diffraction (XRD, Siemens D-5000, Germany). The carbon concentration of the BSS sample was determined by an automatic elemental analyzer (AEA, Flash EA 1112 series, Thermo Fisher Scientific, U.S.A.). The extent of reduction of the BSS sample was estimated by a simultaneous thermogravimetric analyzer (TGA, TA SDT model 2060, TA Instruments, U.S.A.), under a flow of 5 % H_2 + 95 % N_2 , at a flow rate 100 cm^3/min . The sample was heated to 850 °C at a heating rate of 5 °C/min.

The reduction of the BSS sample was carried out under a hydrogen atmosphere in a horizontal alumina tube furnace. The hydrogen flow rate was fixed at 100 cm^3/min in all experiments. The respective effects of reduction tem-

perature and time on the reaction rates of the brass secondary slags were investigated. Specifically, the reduction temperature was varied from 900 to 1050 °C, and the reduction time was varied from 10 to 480 min. Each sample of BSS, weighing 15 g, was placed in an alumina crucible and then put in the tube furnace. Then, the samples were heated to the desired reduction temperature at a heating rate of 5 °C/min. Finally, the samples were cooled in the furnace.

After reduction, phase analysis of the reduction products was performed by X-ray diffraction, using Cu $K\alpha$ radiation (40 kV, 30 mA) at step size increments of 0.1°. The microstructures of the reduction samples were observed using a field emission scanning electron microscopy (FE-SEM, JSM 6330F, Jeol, Japan). The respective chemical compositions of copper and zinc were analyzed using energy-dispersive X-ray spectroscopy (EDS, INCA, Oxford, U.K.).

3. Results and discussion

3.1 Characteristic of BSS

The chemical composition of the BSS sample used in this study is presented in **Table 1**, as determined by ICP-AES and AEA. ZnO and CuO were identified by X-ray diffraction analysis as major components in the BSS, whereas Zn-spinel ($ZnO \cdot Al_2O_3$) and Al_2SiO_4 were detected as a minor component, as shown in **Fig. 1**. **Fig. 2a** shows all the morphological features of the initial BSS sample. The latter consisted mainly of well-distinguishable, submicron-sized ZnO particles (**Fig. 2b**). The BSS samples were also leached with $HNO_3 + HCl$ (3M: 1M) to measure the other impurities. Bright particles indicate aluminum and silicon compounds, whereas other particles indicate silicon dioxide (**Figs. 2c, d**).

The thermogravimetric curve of the reduction process, which was recorded during a linear program at a constant heating rate, is shown in **Fig. 3**. As shown in **Fig. 3**, the TGA curve of the initial sample reveals two major weight losses: one has a monotonous weight decrease of 1.3 % in the range of 50–760 °C, and the other is very rapid and occurs at 760 °C with approximately 1.4 % weight loss. The first weight loss is possibly related to the combustion of impurities, evaporation of water, and a chemical reaction between carbon in the BSS sample (2.2 mass% in

Table 1 Chemical composition of the initial brass secondary slags (mass%)

Cu	Zn	Si	Al	Pb	Fe	Mn	C	Other
14.74	70.54	3.92	5.7	1.01	0.74	0.32	2.2	0.83

Table 1) and hydrogen gas. The other weight loss (1.4 %) is due to the reduction of zinc oxide in the BSS sample to zinc gas phase, by hydrogen gas (Gioia F. et al., 1977).

3.2 Reduction mechanism of BSS

Fig. 4 shows the XRD patterns of BSS samples prior to and after reduction at various temperatures (900–1050 °C) for varying reaction times (10–480 min). Generally, XRD patterns for reductions at the four temperatures are similar, with the exception of time-scale, indicating that the same reduction mechanism prevails in the range of 900–1050 °C. These results suggest a stepwise reduction

mechanism of BSS with hydrogen gas. Thus, based on these XRD results, a two-step reaction was identified. The main reactions at each step are as follows: Step 1 is the ZnO reduction (Eqn. 1), and step 2 is the ZnO·Al₂O₃ reduction (Eqn.2).

The morphology changes in the BSS samples versus the reduction times at 1050 °C are shown in **Fig. 5**. It is seen that the initial fine ZnO powder is aggregated at the

Fig. 1 X-ray diffraction pattern of initial BSS sample.

Fig. 3 TGA analysis of the BSS sample in mixed gas (5 % H₂ + 95 % N₂).

Fig. 2 SEM morphologies of BSS samples: a) whole morphological features of the initial samples, b) the submicron-size ZnO, c) after ZnO leaching with HCl + HNO₃, and d) EDS analysis results.

initial stage of the reaction, after which the $[\text{ZnO} \cdot \text{Al}_2\text{O}_3 / \text{Cu}]$ mixture forms a more dense structure as shown in **Figs. 5a, b**, respectively. The amount of ZnO powder decreased with increasing reduction time because Zn evaporated after reduction by hydrogen gas according to Eqn. 1. Also, it should be noted that Cu powder, having spherical particles of $\sim 1 \mu\text{m}$, appeared after removal of the ZnO at 120 min of the reaction time. Furthermore, there was no significant change in the shape or particle size of the Cu particles, even after 480 min.

Fig. 4 XRD patterns of BSS, prior to, and after, hydrogen reduction at 1000 °C for various times.

The distilled Zn was recovered as metallic Zn in the cold zone of the alumina tube, as shown in the inset of **Fig. 6a**. In the cold zone, it was condensed and formed Zn powder immediately. The latter had spherical particles with a size range of approximately 1–6 μm . The XRD pattern confirms that the recovered powder is composed of pure Zn, without any other components. This is due to much difference in evaporation temperature between Zn (907 °C) and Cu (2562 °C), SiO₂ (2950 °C), Al₂O₃ (2977 °C) and CuO (2000 °C), respectively.

From the XRD and SEM data, the process of Cu reduction from BSS comprises several stages. The first step is the conversion of brass to Cu with distilled Zn. According to previous research, the brass is generated by the reaction of CuO and ZnO with hydrogen gas at above 600 °C (Kappenstein C. et al., 1996). The concentration of Zn in brass decreased with increasing reduction temperature and times. This was due to loss of Zn by distillation from the brass during the first step. **Fig. 7** shows the respective concentrations of Cu and Zn in brass as a function of reduction temperature and reaction time. Here, Cu concentration increases with reduction time; moreover, the rate of increase of Cu concentration is reduced with decreasing reduction temperature as shown in **Fig. 7a**.

The Cu concentration increase is attributed to not only reduction of CuO but also evaporation of reduced Zn. The contribution of Zn is presented in **Fig. 7b**, where Zn concentration linearly decreases in the early of the reaction time at most of the reduction temperature. In the case of

Fig. 5 The morphology change in BSS versus hydrogen reduction times at 1050 °C: a) 10, b) 60, c) 120, and d) 480 min.

Fig. 6 a) Metal zinc powders recovered from ZnO in BSS at the cold zone of furnace, b) morphology of metal Zn powder, and c) XRD pattern of metal Zn powder.

reactions performed at 1000 °C and 1050 °C, all Zn is eliminated by 480 min and 360 min, respectively. Lastly, a significant amount of Zn remained in the Cu phase at 900 °C for all reduction times.

3.3 The kinetics analysis of BSS

In order to understand the reduction mechanism for BSS, a series of kinetic analyses were performed. For this, the extent of BSS reduction was integrated with respect to time and plotted cumulatively as a reaction ratio (α). The reaction ratio was defined as 0 before the reaction and 1 when it was completed. The rate of each reaction was expressed as a function of Arrhenius parameters with reaction model in Eqn. 3:

$$d\alpha/dt = k(T)f(\alpha) \quad (3)$$

where $d\alpha/dt$ is the reaction rate, α the reaction ratio, $k(T)$ is the temperature-dependent rate constant, t is the time, T is temperature, and $f(\alpha)$ is the differential form of the reaction model (Santosh K.U., 2006). We used the first-order reaction model $f(\alpha) = 1 - \alpha$ for this reaction. This model is applicable to a wide range of solid-state reactions: Reactant(s) $\rightarrow$ Product(s) + Gas (g) (James E.H., 2007). For the purpose of this kinetic analysis, the residual mass at various reduction times was expressed as the reaction ratio (α), by means of Eqn. 4:

$$\alpha = (M_0 - M_t)/M_0 \quad (4)$$

where M_t represents the mass of the sample at a reduction time t and M_0 is the initial mass of the sample. Therefore, a more general form of the first-order reaction equation can be written as follows:

$$-\ln(1 - \alpha) = k(T) t \quad (5)$$

Fig. 7 Concentration change of Cu and Zn in brass by Zn vaporization according to reduction times and temperature: a) Cu, and b) Zn.

Thus, by plotting $-\ln(1 - \alpha)$ versus t , the rate constant (k) can be determined from the slope and intercept of the fitted straight line. Values for the rate constant (k) calculated for α , in the range 0.2–1, are given in **Table 2**. The transformation step 2 is not as rapid as step 1, although the amount of $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ is relative small. Specifically, the rate constant of step 1 increases from $1.4 \pm 0.13 \times 10^{-3} \text{ s}^{-1}$ at 900 °C to $2.18 \pm 0.15 \times 10^{-2} \text{ s}^{-1}$ at 1050 °C. Meanwhile, the rate constant of step 2 increases from $1.54 \pm 0.21 \times 10^{-5} \text{ s}^{-1}$ at

Table 2 Summary of rate constants k of BSS sample reduction at different temperature and step

	STEP 1 (s^{-1})	STEP 2 (s^{-1})
900 °C	$1.4 \pm 0.13 \times 10^{-3}$	$1.54 \pm 0.21 \times 10^{-5}$
950 °C	$5.52 \pm 0.72 \times 10^{-3}$	$5.61 \pm 0.68 \times 10^{-5}$
1000 °C	$1.16 \pm 0.24 \times 10^{-2}$	$3.45 \pm 0.52 \times 10^{-4}$
1050 °C	$2.18 \pm 0.15 \times 10^{-2}$	$1.09 \pm 0.19 \times 10^{-3}$

900 °C to $1.09 \pm 0.19 \times 10^{-3} s^{-1}$ at 1050 °C. The temperature-dependence of the rate constant is traditionally described by the Arrhenius law:

$$k(T) = A \exp - (E_a/RT) \quad (6)$$

In Eqn. 6, A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant. Rewriting Eqn. 6 (Jelic D. et al. 2011),

$$\ln k = \ln A - (E_a/RT) \quad (7)$$

The activation energies (E_a) calculated for steps 1 and 2 are 233.2 ± 26.1 and 376.7 ± 22.4 kJ/mol, respectively, as shown in **Fig. 8**. The significant coefficients of determination (R^2) of the activation energy indicated 0.963 and 0.989 as confidence level, respectively. The reaction mechanism, deduced from the kinetic data, is depicted graphically as shown in **Fig. 9**. In step 1, the reductions of CuO and ZnO begin at 500 °C and 600 °C, respectively. ZnO starts to evaporate as soon as it is reduced to the metallic phase, due to its high vapor pressure, and this evaporation is the main cause of the weight loss in this reaction system. In the temperature up to 600 °C, Cu forms a brass phase with Zn, whereas the brass phase decomposes into solid Cu and Zn vapor at 900 °C, which is step 2. It should be noted that ZnO in the ZnO·Al₂O₃ spinel phase is also reduced in this step; hence, Cu, SiO₂, and Al₂O₃ are the final phase formed in this BSS reduction system. It is supposed that the ceramic impurities are removed by the succeeding smelting process.

4. Conclusion

The reduction kinetics of BSS in a hydrogen atmosphere has been studied at 900 °C to 1050 °C, and for the reduction times between 10 min and 480 min. The characterization of the samples was done by means of SEM and XRD analysis. The results indicated that the reduction of BSS samples was found to occur in a two-step process, with recovery of Zn powder (spherical particles, size: approximately 1~6 μm). The first step involved a rapid transformation of ZnO to Zn (g), whereas the sec-

Fig. 8 Arrhenius plot for the dominant reaction in the range of 900–1050 °C with hydrogen gas: a) step 1 (ZnO reduction); and b) step 2 (ZnO·Al₂O₃ reduction).

ond step involved the slow conversion from ZnO·Al₂O₃ to Zn (g).

A first-order function and Arrhenius analysis were utilized to calculate the rate constants and activation energies for the BSS reduction. In particular, the rate constant for the transformation from ZnO to Zn (g) increased from $1.4 \pm 0.13 \times 10^{-3} s^{-1}$ at 900 °C to $2.18 \pm 0.15 \times 10^{-2} s^{-1}$ at 1050 °C with an activation energy of 233.2 ± 26.1 kJ/mol in step 1. In step 2, the corresponding rate constant for the transformation from ZnO·Al₂O₃ to Zn (g) increased from $1.54 \pm 0.21 \times 10^{-5} s^{-1}$ at 900 °C to $1.09 \pm 0.19 \times 10^{-3} s^{-1}$ at 1050 °C with an activation energy of 376.7 ± 22.4 kJ/mol. It is believed that further understanding of the reaction mechanism observed in this study can contribute to the further optimization of process conditions in fluidized bed reactors.

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Fig. 9 Schematic diagram of BSS samples reduction mechanism between room temperature and 1050 °C with hydrogen gas.

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