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STUDY ON RECOVERY OF VALUABLE METALS IN SPENT LITHIUM-ION BATTERIES BY Al_2O_3-SiO_2-CaO-Fe_2O_3 SLAG SYSTEM

This study investigated the recovery behavior of valuable metals (Co, Ni, Cu and Mn) in spent lithium ion-batteries based on Al_2O_3-SiO_2-CaO-Fe_2O_3 slag system via DC submerged arc smelting process. The valuable metals were recovered by 93.9% at the 1250°C for 30 min on the $20Al_2O_3$-$40SiO_2$-$20CaO$-$20Fe_2O_3$ (mass%) slag system. From the analysis of the slag by Fourier-transform infrared spectroscopy, it was considered that Fe_2O_3 and Al_2O_3 acted as basic oxides to depolymerize SiO_4 and AlO_4 under the addition of critical 20 mass% Fe_2O_3 in $20Al_2O_3$-$40SiO_2$-CaO-Fe_2O_3 (CaO + Fe_2O_3 = 40 mass%). In addition, it was observed that the addition of Fe_2O_3 ranging between 20 and 30 mass% lowers the melting point of the slag system.

Keywords: Spent lithium-ion battery, Smelting, Al_2O_3-SiO_2-CaO-Fe_2O_3, Recovery, Slag

1. Introduction

Lithium-ion batteries (LIBs) are widely used in most portable electronic devices due to their advantages of high current density, high voltage, long lifetime, and low weight [1-2]. Moreover, with the development of new electrode materials, applications of LIBs have extended to the electric vehicles (xEvs) and large-capacity energy storage systems (ESS).

LIBs are composed of various valuable metals such as Co, Ni, Li, Mn, and Cu. Therefore, the use of the valuable metals in increasing with the increasing use of LIBs for xEvs and ESS. Additionally, the amount of waste LIBs generated has increased rapidly.

Landfilling of spent LIBs can result in environmental pollution as well as economic losses because of valuable metals [3-4]. To prevent such problems, it is necessary to develop of recycling technology for spent LIBs.

The recycling process of spent LIBs is divided into hydrometallurgical and pyrometallurgical process. Hydrometallurgical process can recover high-purity valuable metals through electro-winning, electro refining, and solvent extraction after the dismantling-discharge-crushing process of LIBs. However, the use of acid, organic matter, and dismantling-discharge process in hydrometallurgical process increase the cost and complexity of the process [5].

In the pyrometallurgical process, spent LIBs scraps are placed at high temperature. Thereafter, they are reduced, melted, and then concentrated to a metallic state. Usually, compared with the hydrometallurgical process, the pyrometallurgical process has the advantages of flexibility of feed materials and mass treatment of spent LIBs.

The Al_2O_3-CaO-SiO_2 slag system is widely used, in which CaO and SiO_2 is selected as slag former, whereas Al_2O_3 is mainly obtained from the spent LIBs in the pyrometallurgical process [6]. However, the recovery of valuable metals decrease and the cost of the process increase because of the high melting point and high viscosity of the slag system.

Therefore, this study investigated the effect of Fe_2O_3 addition on the recovery behavior of valuable metals (Co, Ni, Mn and Cu) in spent LIBs based on the Al_2O_3-CaO-SiO_2 slag system by DC submerged arc smelting process.

2. Experimental

The cell powder of a spent lithium-ion battery from which Fe and plastic were removed through the discharge-shredding-crushing process was used for reduction smelting. The chemical composition of the cell powder is summarized in Table 1.

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Mass%	Co	Ni	Mn	Li	Cu	Al	Fe	Others
Cell powder	5.15	15.11	4.31	2.97	4.6	8.33	0.12	59.41

The cell powder was calcined at 800°C in an electric furnace to remove organic carbon and then cooled to room temperature. SiO_2, CaO and Fe_2O_3 were added to the cell powder as slag formers according to the Fe_2O_3 experimental range from 10 mass% to 40 mass%. The cell powder was uniformly mixed with the slag formers using a three-dimensional mixer, and the mixture was charged into a graphite crucible. Thereafter, the reduction smelting was carried out by holding for 30 min under the temperature conditions ranging from 1200°C to 1350°C by DC submerged arc smelter.

The chemical compositions of recovered metals obtained after reduction smelting were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES: Jobin-Yvon Model JY-38 plus, Jobin-Yvon Equipment Co., Division' Instruments S.A. France). The structural change of the obtained Al_2O_3-SiO_2-CaO-Fe_2O_3 slag was confirmed by Fourier-Transform Infrared spectroscopy (FT-IR: Nicolet iS 10, Thermo Fisher Scientific), and the melting point of the slag was determined by thermogravimetry-differential thermometric analysis (TG-DTA: SDT Q600, TA Instrument). In addition, the microstructures of the metal were analyzed using Field Emission-Scanning Electron Microscope/Energy Dispersive Spectroscopy (FE-SEM/EDS: QUANTA 200 F, FEI Company).

3. Results and discussion

Fig. 1(a) shows the recovery ratio of the valuable metals (Co, Ni, Cu and Mn) with addition of Fe_2O_3 ranging between 10 and 40 mass% in Al_2O_3-CaO-SiO_2. The reduction smelting process was carried out under certain condition as follows: $20Al_2O_3$-$40SiO_2$ (mass%), CaO + Fe_2O_3 = 40 mass%, smelting temperature 1300°C and holding time 30min. After the smelting process, the target metal was obtained. The chemical composition of metal was quantitatively analyzed by ICP-AES. The recovery ratio was calculated by comparing the amount of metal obtained after smelting to the amount of metal in the charged cell powder by quantitative chemical analysis.

The recovery ratio of valuable metals increases with the addition of Fe_2O_3, but there is no significant effect from 20 mass% to 40 mass% as shown in Fig. 1(a).

The increase in recovery ratio can be explained for the following reason. The Fe_2O_3 has an amphoteric characteristic and its behavior varies depending on the basicity of the slag [7-8]. Usually, the amphoteric oxide acts as an acidic oxide in the high basicity of the slag, whereas it acts as a basic oxide at low basicity. Therefore, the amphoteric oxide acts like a basic oxide as the amount of Fe_2O_3 increases, thereby decreasing the viscosity. SAITO et al. [9] observed that viscosity decreases with the
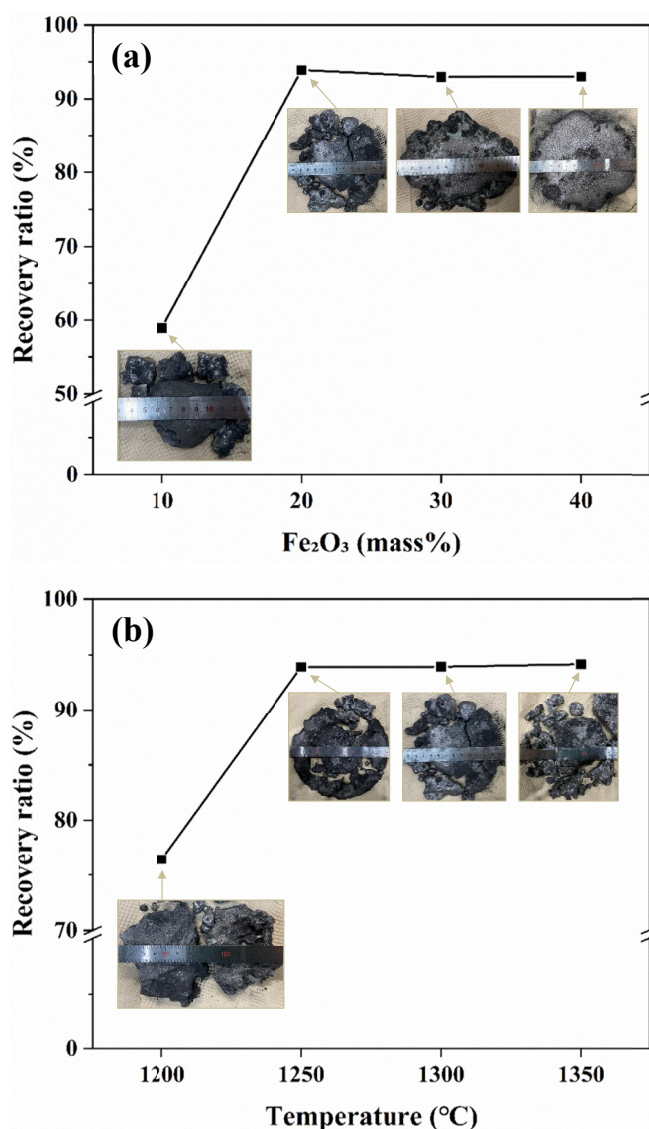

Fig. 1. Effect of recovery ratio of valuable metals (Co, Ni, Cu and Mn) with (a) Fe_2O_3 addition ($20Al_2O_3$-$40SiO_2$ (mass%), CaO + Fe_2O_3 = 40 mass%) at 1300°C for 30 min, and (b) smelting temperature ($20Al_2O_3$-$40SiO_2$-$20CaO$-$20Fe_2O_3$ mass%) for 30 min

addition of Fe_2O_3 in Al_2O_3-CaO-SiO_2 slag system, and it was similar to the result of this study.

Fig. 1(b) shows the effect of the smelting temperature on the recovery ratio of valuable metals from 1200°C to 1350°C. The reduction smelting process was carried out under certain condition as follows: $20Al_2O_3$-$40SiO_2$-$20CaO$-$20Fe_2O_3$ (mass%) and holding time 30min. As shown in Fig. 1(b), the recovery ratio of the valuable metals increases with the smelting temperature and then saturates above 1250°C.

As the smelting temperature increase, the increase of the recovery ratio of valuable metals can be explained by the following equation [10]:

$$\eta = A \cdot \exp(E_v/RT) \tag{1}$$

Where η is viscosity, A (= 4.80×10^{-8}) is a constant, E_v is the activation energy for viscosity, R is the gas constant, and T is the temperature.

Eq. (1) shows that viscosity and temperature are inversely proportional. Thus, the viscosity decreases and the recovery ratio increases with increasing smelting temperature.

As a result of the recovery ratio with the smelting temperature, the valuable metals were recovered by approximately 93.9% at 1250°C for 30 min based on $20Al_2O_3-40SiO_2-20CaO-20Fe_2O_3$ (mass%).

Fig. 2(a) shows the results of structural change for the slag in $20Al_2O_3-40SiO_2-CaO-Fe_2O_3$ (CaO + Fe$_2$O$_3$ = 40 mass%) depending on the Fe$_2$O$_3$ content. The transmittances of Al$_2$O$_3$-SiO$_2$-CaO-Fe$_2$O$_3$ quaternary slag vary significantly depending on the structure of the silicate. Silicate has different structures corresponding to the non-bridging oxygen (NBO) value of 1 to 4, and these structures are observed between 1100 cm^{-1} and 750 cm^{-1} via FT-IR [11,12].
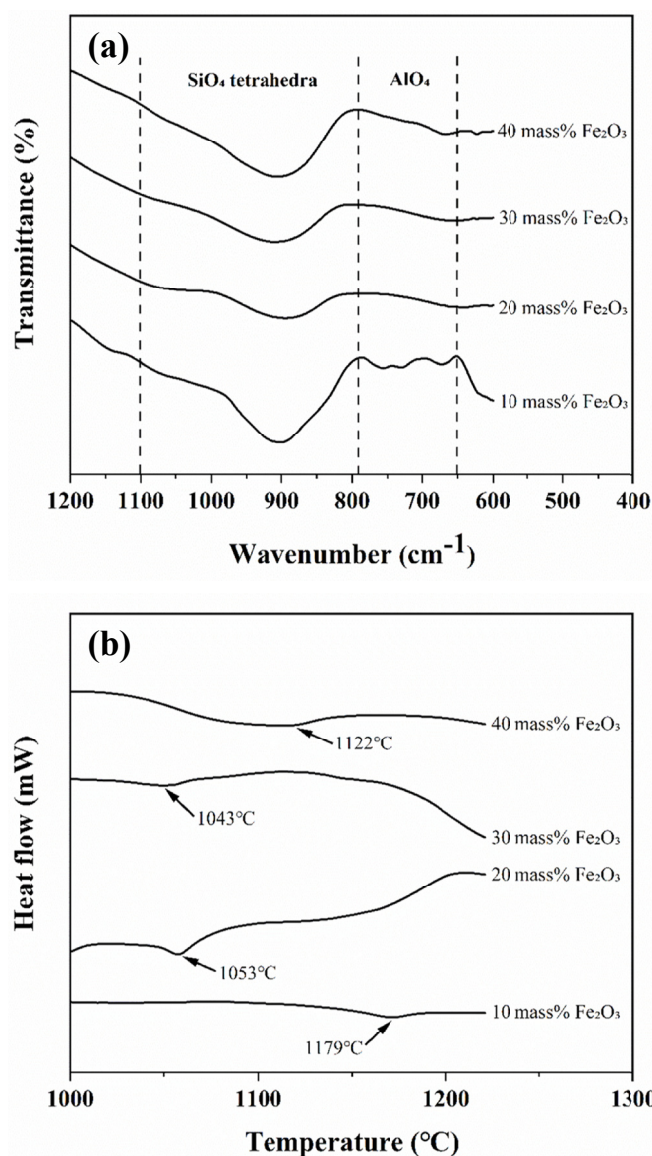

(a)

(b)

Fig. 2. Result of (a) FT-IR and (b) TG-DTA with addition of Fe$_2$O$_3$ in $20Al_2O_3-40SiO_2-CaO-Fe_2O_3$ (CaO + Fe$_2$O$_3$ = 40 mass%)

Fe$_2$O$_3$ and Al$_2$O$_3$ are amphoteric oxide [7,13], which exhibit different behaviors in slag depending on the molar ratio of the

amphoteric oxide to the basic oxide [9]. When 10 mass% of Fe$_2$O$_3$ was added, the amphoteric oxides acted as acidic oxide (network former) and thus forming SiO$_4$ and AlO$_4$ polymers. However, if more than 20 mass% was added, the amphoteric oxides behaved as basic oxide (network modifier) and depolymerize SiO$_4$ and AlO$_4$. However, when Fe$_2$O$_3$ was continuously added, the amount of SiO$_4$ tetrahedral structure tended to increase, respectively. This is because Fe$_2$O$_3$ and CaO have different ion potentials, which can be explained by the following equation [14]:

$$\phi = Z/r \qquad (2)$$

Where ϕ is ionic potential, Z is valence of the ions and r is radius of the ions.

ϕ is the energy required by an atom or molecule to remove an electron and it increase with higher valence or closer distance between ions. That is, Fe$_2$O$_3$ has a higher ionic energy than CaO; therefore, the electrostatic attraction with oxygen is stronger. Although Fe$_2$O$_3$ acts as a basic oxide, the amount of SiO$_4$ tetra-
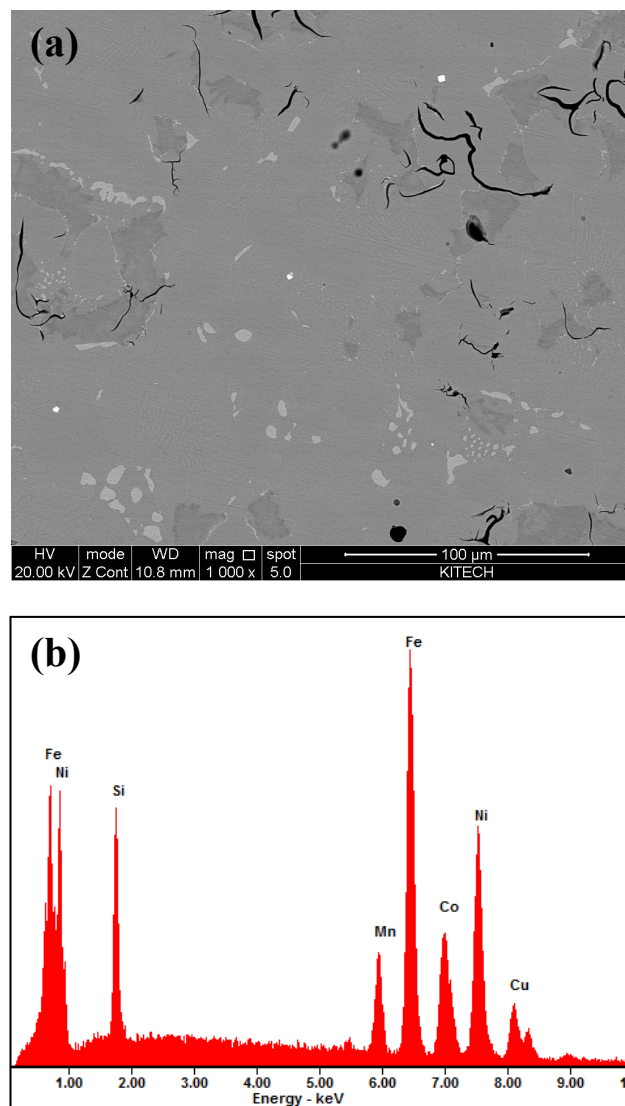

(a)

(b)

Fig. 3. Microstructure (a) recovered valuable metal and (b) EDS spectrum patterns at the condition of $20Al_2O_3-40SiO_2-20CaO-20Fe_2O_3$ (mass%) at 1250°C for 30 min

hedral structure increases because the amount of released free oxygen (O^{2-}) is relatively small compared to CaO, respectively.

The change of the melting point of the slag with addition of Fe_2O_3 is shown in Fig. 2(b). From the result of TG-DTA, the melting points of the slag changed from 1179°C, 1053°C, 1043°C, and 1122°C with addition of Fe_2O_3 between 10 and 40 mass%. Notably, the decrease in the melting point of the slag seems to be the change in the slag composition.

Fig. 3 shows the FE-SEM/EDS analysis of metal produced under optimum processing. As shown in Fig. 3, the recovered metal is composed of Fe, Si, and the valuable metals. When the reduction smelting process was performed at high temperature, some Fe_2O_3 reacted directly or indirectly with carbon and was reduced to metallic Fe [15-17]. The phenomenon in which a part of Fe_nO charged as a slag former was reduced to metal was confirmed in the previous papers [18, 19]. The reduction reaction of Fe_2O_3 is given by Eq. (3) [20]:

$$Fe_2O_3 + 3C + 1/2\ O_2 = 2Fe + 2CO + 2CO_2 \qquad (3)$$

Additionally, Si was produced from the slag former, but it was reduced by reaction with metallic Al in the cell powder. The reaction is given by Eq. (4) [21, 22]:

$$3SiO_2 + 4Al = 3Si + 2Al_2O_3 \qquad (4)$$

4. Conclusions

In this study, the recovery behavior of valuable metals in spent LIBs was conducted by reduction smelting process based on Al_2O_3-SiO_2-CaO slag system with addition of Fe_2O_3 as the melting point and viscosity depressant. The results obtained are as follows.

1. The valuable metals (Co, Ni, Cu and Mn) in spent LIBs were recovered by approximately 93.9% at 1250°C for 30min based on a $20Al_2O_3$-$40SiO_2$-$20CaO$-$20Fe_2O_3$ (mass%) slag system.

2. When 10 mass% of Fe_2O_3 was added, it was observed that the amphoteric oxides (Fe_2O_3 and Al_2O_3) acted as acidic oxides forming SiO_4 and AlO_4 polymers in $20Al_2O_3$-$40SiO_2$-CaO-Fe_2O_3 (CaO + Fe_2O_3 = 40 mass%). However, the amphoteric oxides acted as an basic oxide that depolymerize SiO_4 and AlO_4 polymers when the Fe_2O_3 added was more than 20 mass%.

3. The melting point of the slag was lowered in the range of 20~30 mass% Fe_2O_3 addition to slag. This is attributed to the change in slag composition with the addition of Fe_2O_3.

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