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EFFECT OF FLUX ON THE RECOVERY BEHAVIOR OF VALUABLE METALS DURING THE MELTING PROCESS OF ALUMINUM CAN SCRAP

This study investigated the effect of flux type and amounts on recovery behavior of aluminum alloy during the melting process of Al can scrap. The heat treatment was conducted to remove the coating layer on the surface of can scrap at 500°C for 30 min. The molten metal treatment of the scrap was performed at 750°C in a high-frequency induction furnace with different flux types and amounts. It was observed that the optimum condition for recovery of Al alloy was to add about 3 wt.% flux with a salt and MgCl₂ mixing ratio of 70:30 during melting process. The mechanical properties of recovered Al alloy were about 254.8 MPa, which is similar to that of the virgin Al5083 alloy.

Keywords: Aluminum, Can scrap, Flux, Gas Bubbling Filtration (GBF), Recycling

1. Introduction

Aluminum (Al) is widely used in aviation, automobiles, home appliances, food and beverages industries due to its excellent properties such as light weight, corrosion-resistance, processability, and thermal conductivity. Also, Al has a low melting point that is easy to re-melting and castability, allowing mass production [1-3]. Compared with the extraction of Al from Bauxite, recycling from scrap and waste can result in significant energy savings and lower the cost of the process and the amount of waste [4]. Usually, Al cans are coated with a thickness of about 300 μm on the surface for storage-convenience and protection from oxidation and impurities such as oil, paint, resin, plastic, and lacquer. These coatings must be removed to increase the recovery rate of metal during the recycling process [5,6].

Al is an oxygen-affinity metal, and during the melting process, the molten surface reacts with oxygen, resulting in the formation of dross in the form of oxide [7-9]. Dross is an inevitable byproduct (of 5 to 30 wt.%, depending on melting process) formed from the Al melting process. This dross is disposed of in landfill sites, which is a worldwide problem for dumping costs and environmental pollution [9-11]. Thus, it is necessary to recycling technologies to improve the recovery rate and reduction of dross formation during the melting process of Al scrap.

Therefore, this study investigated the Al alloy recovery behavior with flux type and amounts for minimization of dross formation during the melting process of Al can scrap.

2. Experimental

Al alloy plates left after the tap cutting during the Al can manufacturing process were used in this study. Al can scrap is an Al5182 alloy, consisting of the major elements of Al and Mg, and small amounts of Si, Fe, Cu, Mn, Cr, Zn, and Ti. Al cans are coated inside and outside with polymer resin for content preservation. These coating layers affect to lower recovery rate and increase dross formation during the melting process. To remove the coating layer, The heat treatment condition was determined by Thermogravimetry-Differential Thermometric Analysis (TG-DTA: SDT Q600, TA Instrument), and the thermal analysis was carried out using argon (Ar) atmosphere furnace under 1 ml/min flux and heating rate of 20°C/min. The coating layer removal process was performed at 500°C for 30 min based on the results of the thermal analysis.

The surface of the molten metal reacts with the furnace atmosphere and absorbs moisture, which increases the concentration of hydrogen during the Al melting process. Also, the bubbles

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produce pores during solidification [12-15]. Gas bubbling filtration (GBF) was used to charge a graphite impeller in the molten metal and stirred with Ar gas at 10 l/min and 500 RPM. Degassing was applied to all processes by means of releasing hydrogen gas.

The impurities such as oxide, carbide, fluoride, and inclusion were contained in Al can scrap molten metal, and these impurities affect to lower the grade of Al alloy materials. Thus, the flux treatment was performed to remove the impurities in Al molten scrap. Salt Flux composed of the NaCl and KCl with mixing ratio of 50:50 (DS liquid Co., Ltd.), $MgCl_2$ (purity: 95.21%, powder type, assay: insoluble matter in water, CAS No.7786-30-3_Daejung Chemicals & Metals Co., Ltd.), and NaF (purity: 98%, powder type, CAS No.7681-49-4_Junsei Chemical Co., Ltd.) were selected as the flux types. Salt flux/ $MgCl_2$ and salt flux/NaF were mixed at a ratio of 70:30 to optimize the effect of flux addition. The mixed flux was used as an additive on the GBF treatment during the melting process to evaluate the recovery behavior of Al alloy.

3. Results and discussion

Fig. 1(a) shows the result of TG-DTA of the coated Al can scrap. As shown in Fig. 1(a) a mass change occurred near 100 to 350°C due to the sublimation of moisture on the surface of the Al can scrap and inorganic compounds in the coating

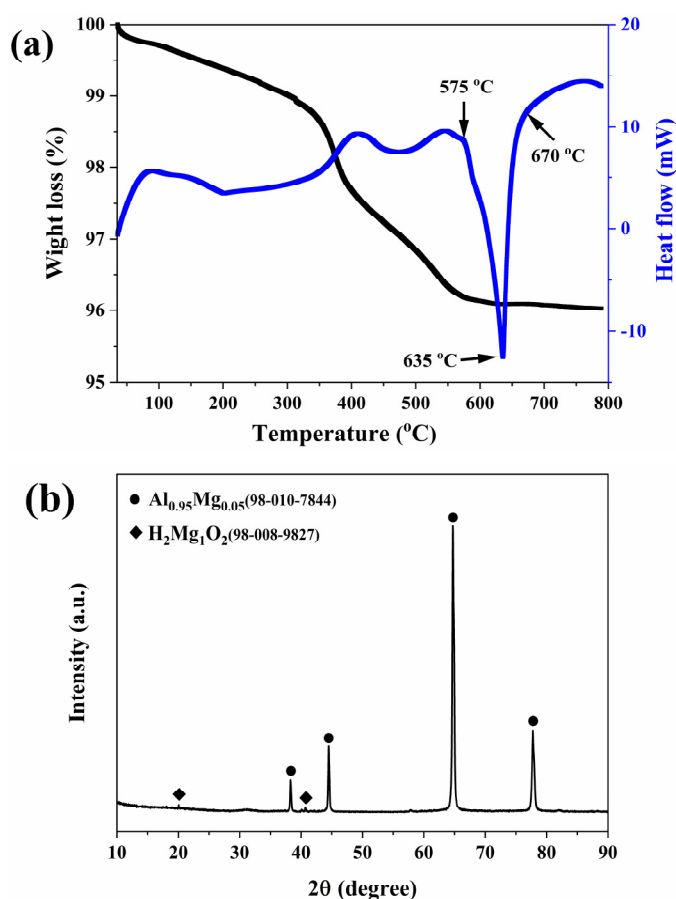
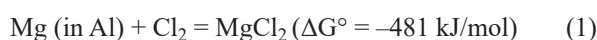


Fig. 1. Result of TG-DTA (a) and X-ray diffraction pattern (b) of aluminum can scrap

layer. A rapid mass reduction was caused by the sublimation of low-temperature organic compounds near 350 to 400°C. High-temperature organic compounds were sublimate at 400 to 550°C, resulting in a mass reduction. The melting of Al can scrap started at 570°C, and the T_m was 635°C. The polymer resin coated Al can scrap on the surface was applied to the heat treatment, and the polymer resin was sublimated at 500°C for 30 min. Fig. 1(b) shows the results of an x-ray diffractometer (XRD: X-ray Diffraction D8 Discover, BRUKER AXS) analysis after the heat treatment of Al can scrap. $Al_{0.95}Mg_{0.05}$ (10-7844), contained in great quantities in the Al can scrap, was the main phase and a trace $H_2Mg_1O_2$ (08-9827) complex oxide phase was detected. It is considered that the magnesium on the scrap surface exposed to the atmosphere was produced by heat-induced oxidation as the coating layer on the surface of the Al can scrap was sublimate.

The Al purification to remove the impurities in molten Al was carried out based on salt flux (NaCl-KCl) or $MgCl_2$ -KCl in the Al alloy melting process. The addition of salt flux to the molten metal was useful for the formation of adequate interfacial energy and aggregation and separation of the impurities. The pure metal was produced by protecting the surface of the molten metal from oxidation and promoting adhesion of the molten drop [16]. Although $MgCl_2$ is expensive, the Al alloy with 2 wt.% < Mg has been widely used due to its high hygroscopic property. In addition, it is useful for the separation of metal and dross lowering the free energy, which reduces the surface tension between metal and dross [16,17]. The chloride-based supporting electrolyte used in the Mg alloy melting process was more stable for the recovery of the high purity of Al metal and removal of Mg, because the Gibbs energy of $MgCl_2$ is lower than that of $AlCl_3$. This means that chloride preferentially reacts with these metal impurities in the injection of chloride to Al containing various metal elements, and fluorine is the same as chloride. Li, Na, K, Ca, Mg, and Ba can be removed by injection of Cl_2 , F_2 , or SF_6 , because these elements form more stable chloride and fluorine than that of Al.

The reaction formula of Mg is as follows [18].



The $MgCl_2$ melts at above 712°C and shows a lower density than Al and is buoyant. It also reacts with Na or Ca existing in the molten metal, producing NaCl or $CaCl_2$ with stable energy, and is removed as dross. The exothermic reaction occurred in the molten metal treatment of NaF, and the liquidity increased due to the temperature of molten metal and heat produced by NaF. At this time, the addition of salt flux promotes separation from the molten metal binding on the oxide surface. It also promotes adhesion, aggregation, and coarsening of oxide. The coarsened oxide containing hydrogen inclusion floats on the surface of the molten metal due to low specific gravity, and is thus easily separated.

The dross, impurities of floated nonmetallic inclusion, and oxide on the surface of the molten metal would be removed through the melt treatment. To compare the effect of the amount of dross with different flux types, the weight of dross derived

from the total 5 kg scrap melting process was calculated, and the result is shown in Fig. 2. The initial scrap was 17 wt.%, and the flux mixed with salt flux and MgCl₂ with ratio 70:30 showed the lowest amount of dross, at 5 wt.%. This confirmed that the mixed flux exhibited remarkable prevention of oxidation and produced light black dross and oxide.

Table 1 shows the results of the chemical composition analysis of Al alloy recovered through the melting process performed using Optical Emission Spectrometer (QBL 750, OBLF spektrometrie) and compared with the composition of Al5083. The chemical composition of the materials proceeded alloy process using the sample with the flux mixed with salt flux and MgCl₂ with ratio 70:30 was similar to that of the Al5083 alloy material.

The fine structure and macroscopic chemical composition analysis of the Al alloy recovered through the melt treatment in the melting process using an Al can scrap were observed by field emission-scanning electron microscope/energy dispersive spectroscopy (FE-SEM/EDS, QUANTA 200F, FEI). Fig. 3(a) shows the fine structure of Al5083 material, and Al-Mg alloy,

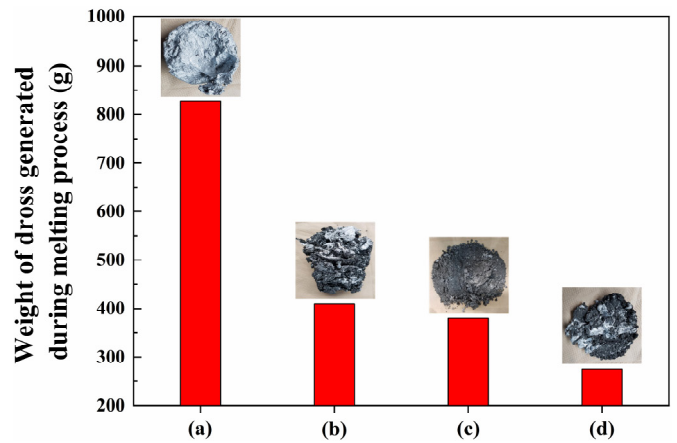


Fig. 2. Amounts of dross after melting process with flux type and mixing ratio

and eutectic phase, Al-Mg-Si-Mn-Fe, were distributed in a matrix structure. Fig. 3(b) shows the fine structure of the sample recovered through the initial scrap melting process. The structure of the sample was similar to Al5083 material and showed a

TABLE 1

Result of composition of recovered metal with flux type and mixing ratio by optical Emission Spectrometer, (wt.%)

Sample name	Al	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
Al 5083	Bal.	0.400	0.400	0.100	0.4-1.0	4.0-4.9	-0.25	0.25	0.15
As-casting	94.69	0.123	0.247	0.061	0.406	4.430	0.028	0.020	0.011
Salt flux	94.96	0.121	0.247	0.034	0.251	4.290	0.046	0.010	0.016
Salt flux(70)/NaF(30)	95.10	0.120	0.286	0.031	0.255	4.110	0.047	0.010	0.016
Salt flux(70)/MgCl ₂ (30)	94.94	0.120	0.281	0.040	0.253	4.360	0.045	0.010	0.017
Salt flux(70)/MgCl ₂ (30)-Alloy and materialization	93.20	0.390	0.390	0.099	0.700	4.560	0.240	0.250	0.160

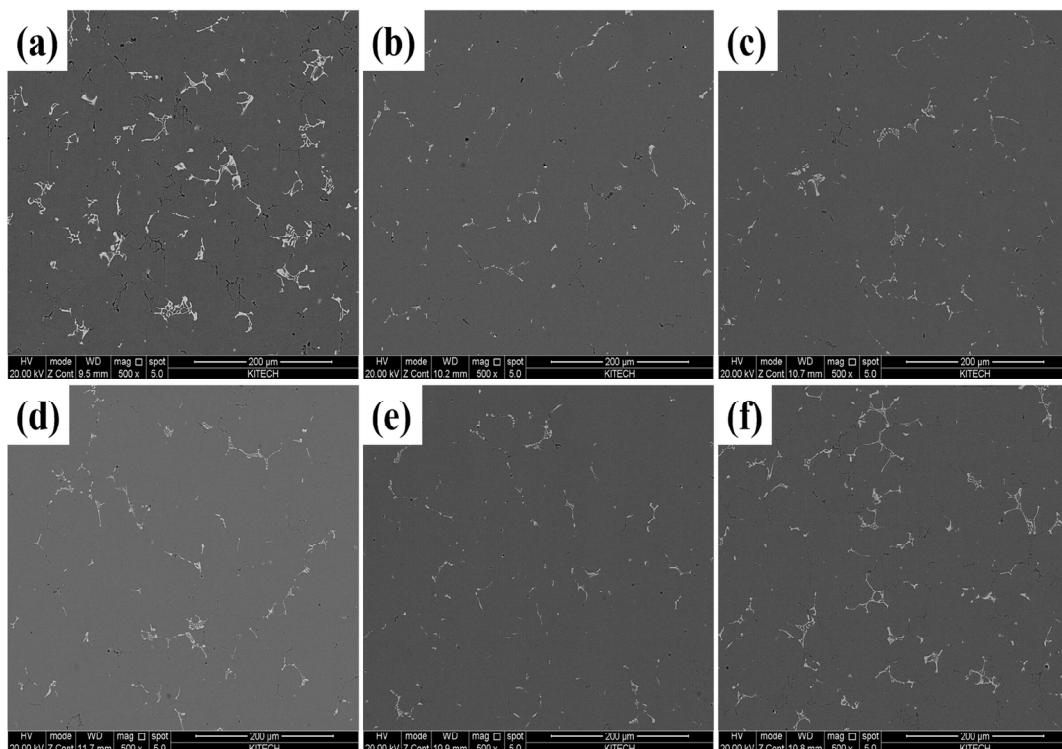


Fig. 3. FE-SEM image of recovered metal with melting process conditions

fine eutectic phase and a small amount compared with Al5083 material. Fig. 3(c)-(e) exhibited the morphological change and fine eutectic phase of Al-Mg-Si-Mn-Fe due to the flux effect. It is considered that the morphological change of the eutectic phase was due to heterogeneous distribution by the flux used in the existing Al can scrap melting process and increased volume fraction by the rapid diffusion of Fe and Mn. Fig. 3(f) shows a sample used in the alloying process of the Al alloy recovered by adding with the flux mixed with salt flux and $MgCl_2$ with ratio 70:30 in the same amount as the Al5083 material. As a result, the fine structures of the Al5083 alloy and the sample were identical, and matrix phase Al-Mg alloy and eutectic phase Al-Mg-Si-Mn-Fe showed a homogeneous distribution similar to Al5083 material.

The results of density and hardness of the recovered Al alloy with flux type are shown in Fig. 4, and the analysis was performed based on the density and hardness of Al5083 alloy. The density was calculated using Archimedes' principle, and it was considered that low density was due to a large amount of hydrogen gas in the initial scrap molten metal. In addition, this means that the alloy used in the alloying process of the Al alloy recovered by adding the flux mixed with salt flux and $MgCl_2$ with ratio 70:30 showed density similar to Al5083 alloy material due to sufficient removal of impurity and hydrogen gas. Hardness was measured using the Rockwell hardness test C scale (HRC), and the correlation with density was confirmed. The alloy used in the alloying process of the Al alloy recovered by adding the flux mixed with salt flux and $MgCl_2$ with ratio 70:30 showed the hardness similar to the Al5083 alloy material. This confirmed that the pore and impurity in the recovered Al alloy affect density and hardness, and the two factors showed a positive correlation.

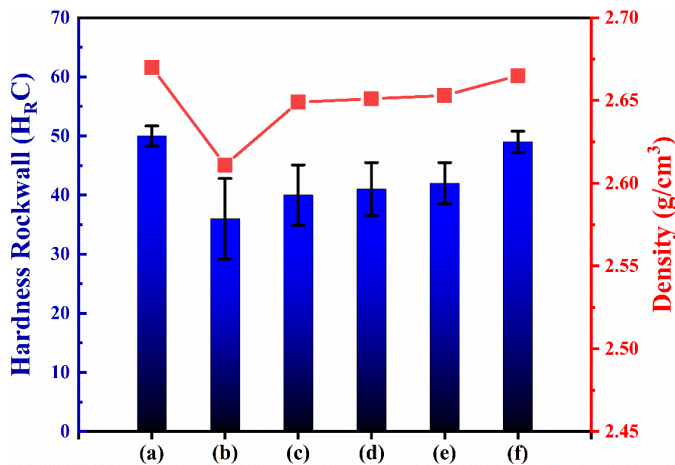


Fig. 4. Results of tension test of recovered Al metal with melting process conditions

Tensile tests were performed using the test pieces produced through each melting process. The recovered Al alloy test piece was produced as a proportional test piece based on the ASTM E8E8M standard, and a tensile test was performed under the ASTM B557-15 standard for tensile strength and elongation

evaluation. Fig. 5 shows a negative correlation between tensile strength and elongation. The alloy used in the alloying process of the Al alloy recovered by the flux mixed with salt flux and $MgCl_2$ with ratio 70:30 showed tensile strength and elongation similar to those of Al5083 alloy. The materialized Al showed similar results in the mechanical test. Therefore, the Al alloy recovered through the recycling process using the Al can scrap could be available as material and components.

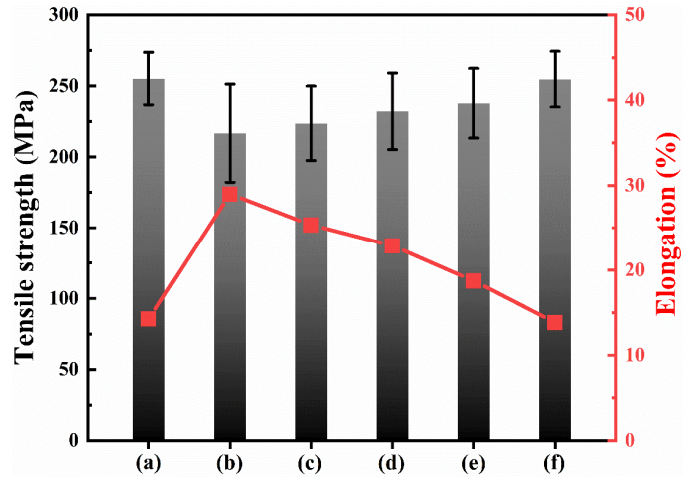


Fig. 5. Results of hardness test (H_{RC}) and density of with melting process conditions

4. Conclusions

This study investigated the recovery of Al alloy with the melt treatment during the melting process using an Al can scrap and compared mechanical properties. The results were as follows.

1. The polymer coating layer of the scrap surface can be removed by heat treatment at $500^{\circ}C$ for 30 min.
2. The samples that underwent the alloy process after the melt treatment using the flux mixed with salt flux and $MgCl_2$ with ratio 70:30 showed sufficient removal of impurities and hydrogen gas. Its density was calculated as near the true density of Al5083 alloy, and the Rockwell hardness test also showed a similar tendency. The positive correlation between the two factors was confirmed.
3. The results of the mechanical test of Al alloy with flux mixing ratio and melting condition revealed that the samples that underwent the alloy process with the flux mixed with salt flux and $MgCl_2$ with ratio 70:30 showed remarkable properties such as 254.8 MPa tensile strength and 13.8% elongation, which were similar to the mechanical properties of Al5083 alloy materials.

Acknowledgments

This work was supported by the Technology Innovation Program (or Industrial Strategic Technology Development Program-Development of Material

Component Technology) (20011183, Commercialization and development of new design on turbulent high temperature melting furnace (2000 ton /y pilot scale) and separation/recovery of valuable metals from end of life xEV/ESS battery pack. (funded by the Ministry of Trade, Industry & Energy, Korea)

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