Chapter

Application of the Aluminothermic Reduction Process for Magnesium Removal in Aluminum Scrap

Rocio Maricela Ochoa Palacios, Citlaly Castillo Rodriguez, Jesus Torres Torres, Perla Janet Resendiz Hernandez and Alfredo Flores Valdes

Abstract

Magnesium is considered as impurity element in aluminum recycled for obtaining some cast alloys, with low concentration Mg, because at 0.1 wt% results in fragility, fractures, and defects. This research applies the aluminothermic reduction process to decrease magnesium content in aluminum cans by adding ZnO, to produce reaction products solid-state (Al_2O_3, MgO and $MgAl_2O_4$), and there is a possibility to obtain Al-Zn alloy. The conditions of the process were, melting temperature (750, 800, 850°C) and stirring velocity (200, 250, 300 rpm). The Mg and Zn contents were measured for chemical analysis and scrap generated from every process was analyzed by X-ray diffraction. The results show how the aluminothermic reduction decreased Mg from 0.93 to 0.06 wt% and increased zinc up to 5.52wt % in the molten metal. Therefore, this process can be used to remove Mg and can also prevent the generation of polluting gases into the environment.

Keywords: aluminum, scrap, aluminothermic, magnesium removal, Al-Zn alloy

1. Introduction

Aluminum alloys are a material required mainly in aerospace and automotive sectors [1]. This has contributed to an increased demand for aluminum and therefore the search for new forms of production. Recycling products have been considered as an alternative source of raw material; however, the secondary aluminum industry is facing up the implementation of different processes to return these materials to everyday life, modifying the mechanical properties according to the type of application to which it will be destined. For this reason, the trend toward metal recycling has increased significantly in recent years, not only because of economic aspects, but also because of the positive impacts on the environment [2–4]. Nevertheless, there is still a lot of development to be done because the industry demands high-quality materials regardless of their origin. For cast alloys, the aluminum scrap must be carefully selected because the impurities degrade the material form that decrease the mechanical properties of the alloys. The most common impurities in recycled alloys are Fe, Si, and Mg in the automotive industry [5, 6]. Different refining processes are used for the removal of magnesium, such as Cl_2 or Fl_2 gas injection, but the processes produce great amounts of HCl gas. Many countries have been forced to regulate this process, while others have banned it due to the high amount of polluting gases that are emitted into the environment [7–9]. Right to this, the industry needs to find new technologies to reduce the magnesium in aluminum scraps, such as the process of compound separation methods or aluminothermic reduction with different oxides [10–13].

This work uses the aluminothermic reduction process with ZnO powder, with the objective of removing the magnesium content in aluminum molten scrap and adding zinc for production aluminum alloys type 700. By implementing this technology, gases can be considerably reduced because the reactions produced in the metal bath can lead to the formation of magnesium products in a solid-state and to be easily removed with the slag.

2. Experimental procedure

The study used aluminum scrap from beverage cans as raw material in the aluminothermic reduction process with ZnO powder as reactive, the composition of both materials were analyzed by atomic emission spectroscopy (AES), the equipment used was SPECTRO model M11, the results are shown in **Table 1**. The beverage cans were melted in 10 kg capacity induction furnace, then, the melted aluminum was degassed using N_2 gas for 10 minutes to obtain secondary aluminum ingots cooled at room temperature. These ingots were cut into pieces of 2 kg to be melted again in a laboratory-scale induction furnace and carried out aluminothermic reduction process using ZnO powder at 750, 800, and 850°C and 200, 250, and 300 rpm of stirring velocities. **Figure 1** shows the induction furnace where the aluminothermic reduction was carried out, (a) top view photography of the furnace, (b) scheme of the interior furnace, and (c) the impeller used during the experimentation. The time of all experiments was given for 60 minutes, taking samples every 10 minutes to measure the magnesium and zinc content by AES. The slag was analyzed by X-ray diffraction (XRD) to analyze reaction product types. Finally, the microstructure of the alloys at the end of the process was analyzed by scanning electron microscopy (SEM).

3. Results and discussion

Figure 2 shows the relationship of the magnesium content measured by AES with respect to the treatment time from 1 to 60 minutes, at 750, 800, and 850°C and

wt. %	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Otros	Al
Aluminum scrap	0.286	0.625	0.188	0.77	0.93	0.022	0.013	0.15	0.017	0.024	96.7
ZnO powder	<0.01	0.02	—	0.01	—	—	—	76.65	—	22.32	96.7

Table 1.
Chemical composition of aluminum scrap and ZnO used by aluminothermic reduction process.

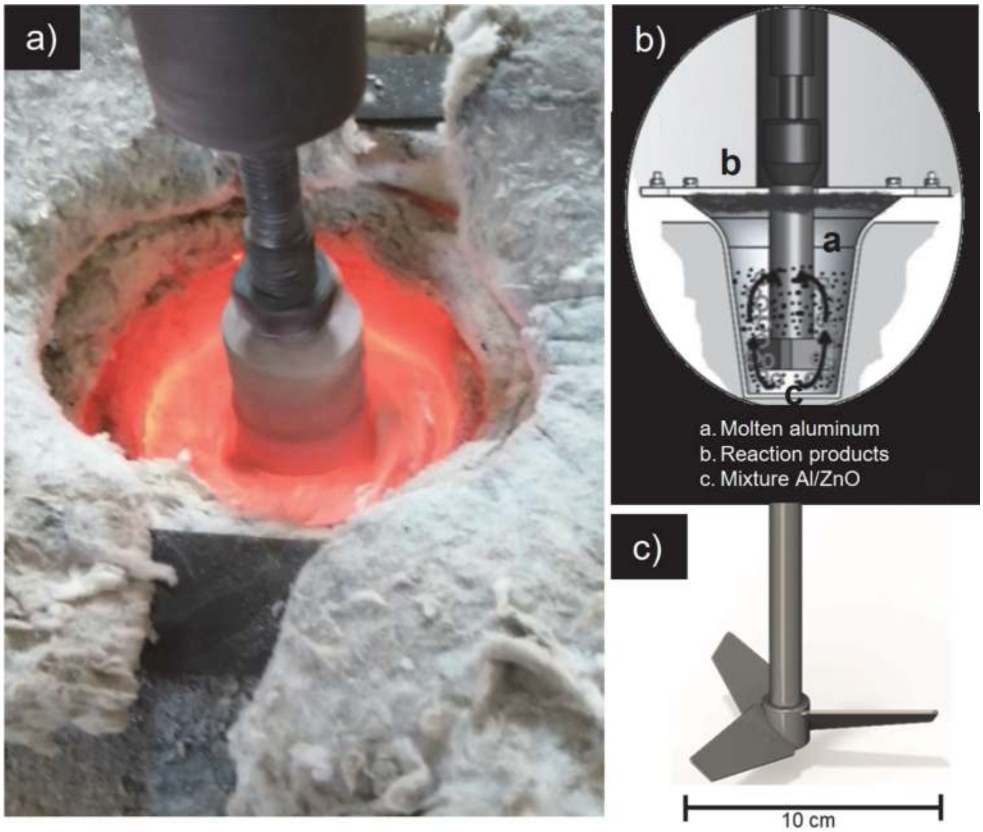

Figure 1.
(a) Top view photography of furnace, (b) scheme of the interior furnace, and (c) the impeller used during the experimentation in aluminothermic reduction process.

stirring velocity of the impeller was 200, 250, and 300 rpm. The results show a significant decrease in magnesium content for all conditions of work. **Figure 3a–c** shows the increase of zinc content in the experiments. Therefore, it can be deduced that the reaction of Eq. (1) governed the process of magnesium removal and zinc added in melted aluminum. The temperature is the variable with the strongest influence on the process, no matter the agitation speed, observing better results at 800 and 850°C, while at 750°C the contents of magnesium and Zn were out the specification for to be used in the automotive industry.

$$1/2\ Al_{(l)} + 1/4\ Mg_{(l)} + ZnO_{(s)} \rightarrow 1/4\ MgAl_2O_{4(s)} + Zn_{(l)}\ \Delta G^0 = -223.99\ kJ \quad (1)$$

Graphics of **Figures 2** and **3** indicate that the processes have an exponential reaction after 20 minutes because this is the time necessary for wettability of the ZnO solid particle with molten aluminum, which allows the reaction to be carried out, where magnesium has an important effect [13, 14]. **Figure 3d** shows the ratio in wt% of magnesium and zinc content at 800°C and 250 rpm, this experiment was more favorable in the present study, because both contents are in the specification for automotive application, giving values <0.06 wt% of Mg and 5.52 wt% of zinc. Other zinc contents obtained were 1.66, 2.3, 2.3, 3.2, and 4 wt%, values used in the aluminum industry in the 700 series alloys. Thus, the reduction process of ZnO powder can remove magnesium and incorporate zinc in molten aluminum.

According to Hashiguchi [15], the change in the magnesium content can also be to the reaction between dissolved magnesium and ambient oxygen gas too, the process is carried out at ambient conditions can be explained by the reaction of

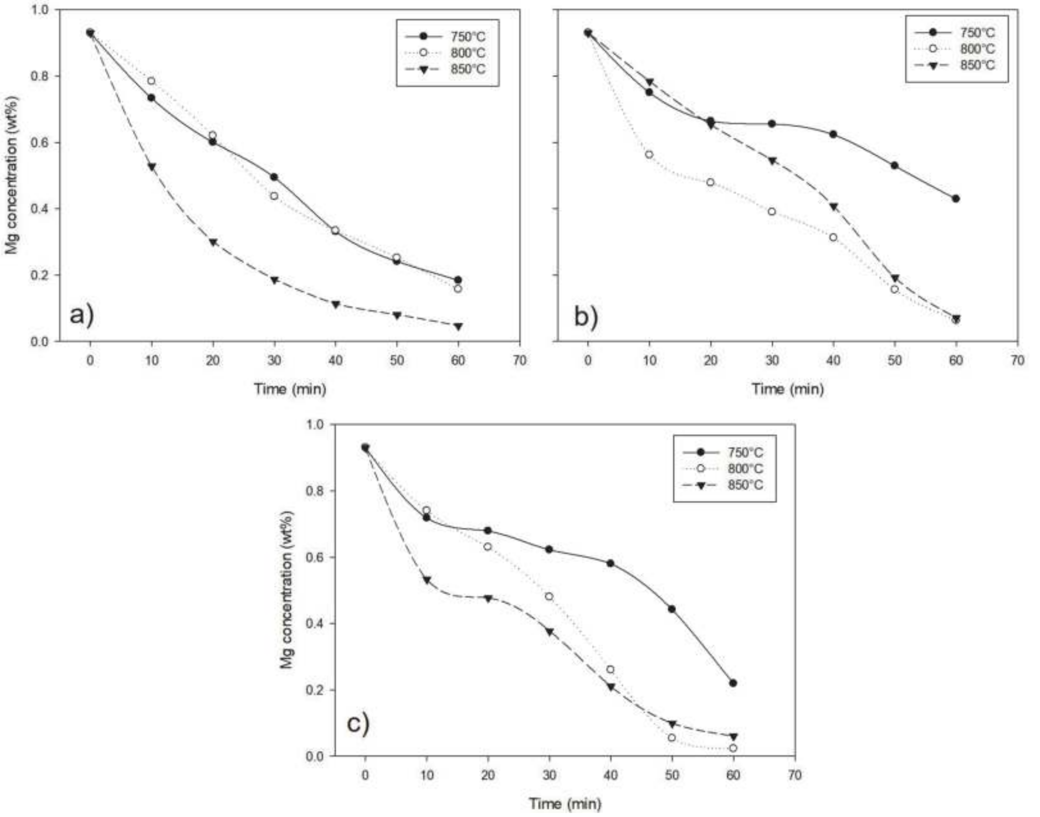

Figure 2.
Relationship between magnesium content and time with respect to temperature and stirring velocity, (a) 200, (b) 250, and (c) 300 rpm.

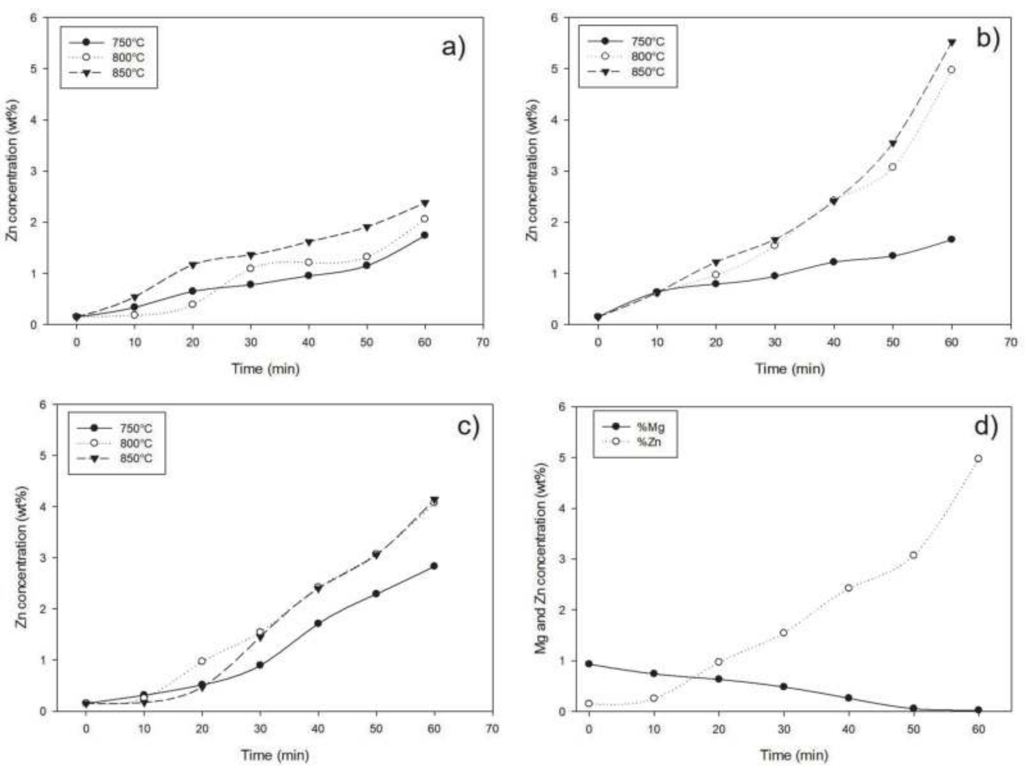

Figure 3.
(a–c) Relationship between zinc content and time with respect to temperature and stirring velocity, and (d) relationship between magnesium and zinc content in molten aluminum at 800°C and 250 rpm.

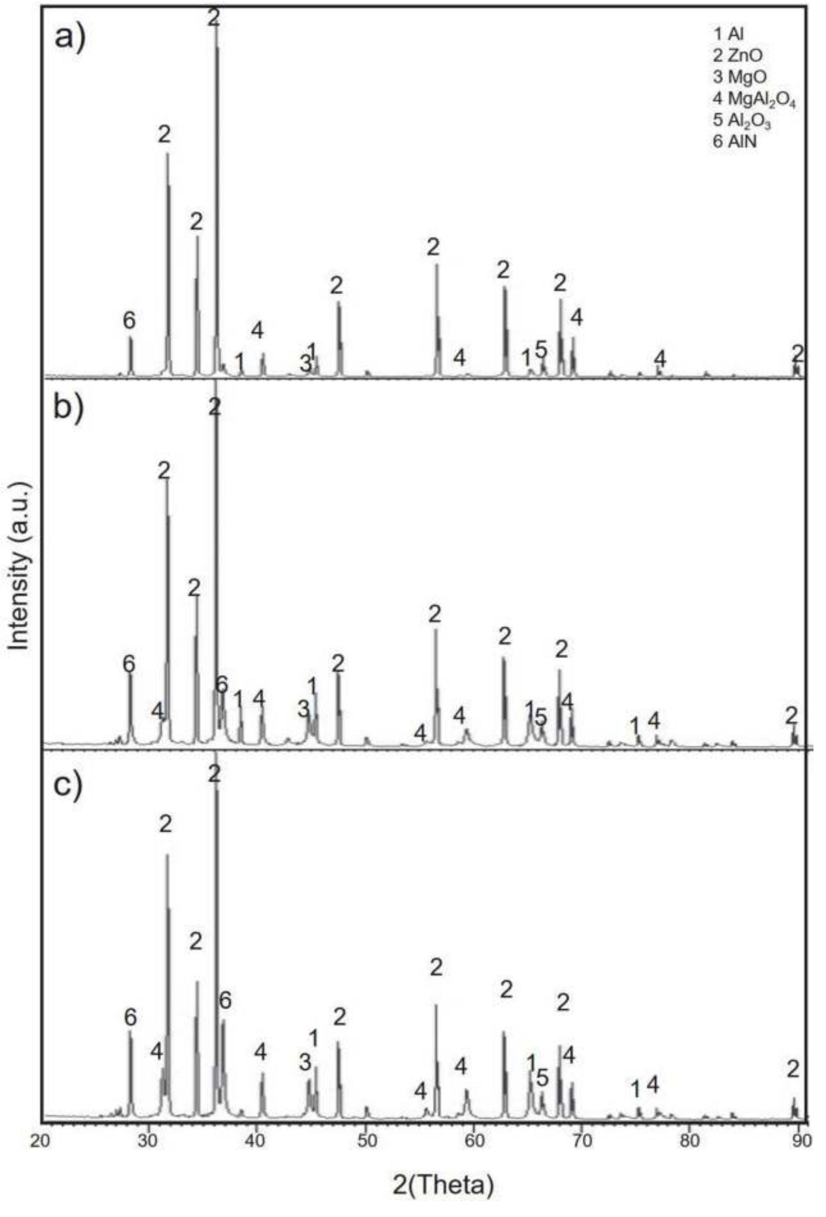

Figure 4.
XRD pattern of the slags produced at 250 rpm and (a) 750°C, (b) 800°C, and (c) 850°C during aluminothermic reduction of ZnO.

Eq. (2). This can be demonstrated by the XRD analysis in **Figure 4**, where the slags obtained in the experiments at 250 rpm and at 750, 800, 850°C are presented, the compounds of these results are $MgAl_2O_4$, MgO, and Al_2O_3. Furthermore, it has been reported that the reactions involved between solid ZnO and molten Al-Mg can be carried out by the Eqs. (1)–(9), values of free energy calculated at 850°C.

$$Mg_{(l)} + O_{2(g)} \rightarrow MgO_{(s)}\ \Delta G^0 = -970.09\ kJ \tag{2}$$

$$4/3\ Al_{2(l)} + O_{2(g)} \rightarrow 2/3Al_2O_{3(s)}\ \Delta G^0 = -882.46\ kJ \tag{3}$$

$$Al_2O_{3(s)} + Mg_{(l)} + 1/2O_{2(g)} = MgAl_2O_{4(s)}\ \Delta G^0 = -1036.56\ kJ \tag{4}$$

$$2/3\ Al_{(l)} + 1/3\ MgO_{(s)} + ZnO_{(s)} \rightarrow 1/3\ MgAl_2O_{4(s)} + Zn_{(l)}\ \Delta G^0 = -220.23\ kJ \tag{5}$$

$$4/3\ Al_{(l)} + 2ZnO_{(s)} = 2/3\ Al_2O_{3(s)} + 2Zn_{(l)}\ \Delta G^0 = -205.82\ kJ \tag{6}$$

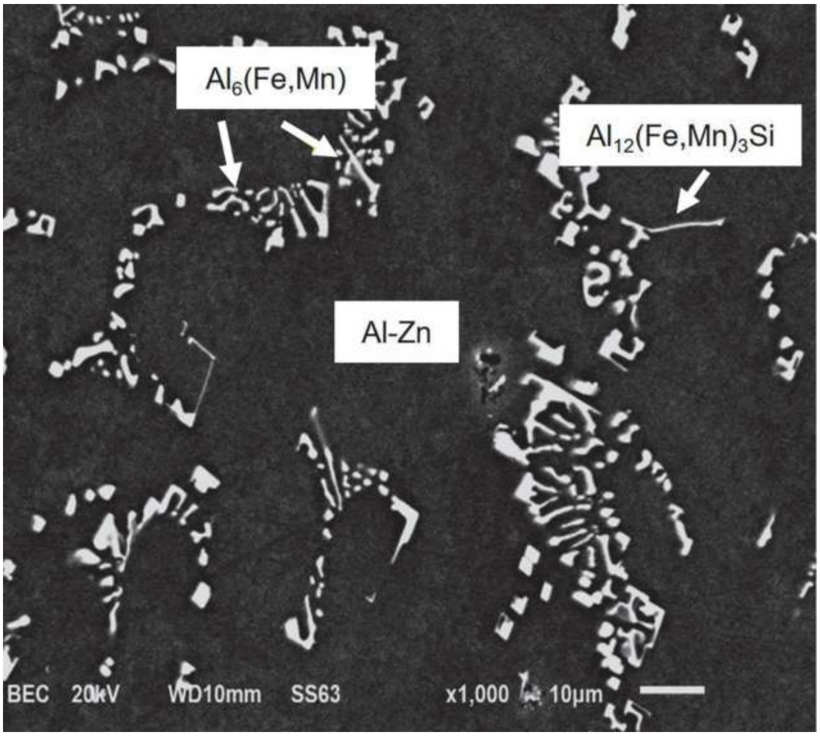

Figure 5.
SEM images of Al-Zn alloys from aluminothermic reduction process at 250 rpm and (a) 750°C, (b) 800°C, and (c) 850°C. (d) Al_6(Fe,Mn) and $Al_{12}(Fe,Mn)_3Si$ phases on Al-Zn matrix.

$$Mg_{(l)} + ZnO_{(s)} \rightarrow MgO_{(s)} + Zn_{(l)}\ \Delta G^0 = -244.91\ kJ \quad (7)$$

$$Al_2O_{3(s)} + 3Mg_{(l)} \rightarrow 3MgO_{(s)} + 2Al_{(l)}\ \Delta G^0 = -117.69\ kJ \quad (8)$$

$$Al_2O_{3(s)} + MgO_{(s)} \rightarrow MgAl_2O_{4(s)}\ \Delta G^0 = -92.02\ kJ \quad (9)$$

According to the free energy values of each reaction calculated at 850°C, the decrease of magnesium and the increase of Zn in the aluminothermic reduction process can be carried out mainly by reactions of the Eqs. (1), (2), and (4)–(7) while Eqs. (3), (8), and (9) are reactions for slag formation.

The beverage cans used in this work were without any type of refining treatment, therefore, the alloy presented higher contents of Fe, Si, Mn. **Figure 5** shows microstructure after the aluminothermic reduction process of secondary aluminum with a matrix rich in zinc and second phases of Al_6(Fe, Mn) and $Al_{12}(Fe, Mn)_3Si$, the first phase with massive blocky morphology due to the content of the Mn in the alloy, according to Liu [16], this element is the one that determines the morphology of this type of intermetallic, while the phase $Al_{12}(Fe, Mn)_3Si$ was presented less quantity, this phase is formed by the cooling rate and diffusion of Si to the Al_6(Fe, Mn). Previous studies [17, 18] indicate that this transformation can also be carried out in processes where there is a loss of magnesium and Si was effective nucleating substrates for the transformation of Al_6(Fe, Mn) to $Al_{12}(Fe, Mn)_3Si$.

4. Conclusion

Magnesium was removed from the aluminum scrap using the aluminothermic reduction process of ZnO powder. The temperatures favored the decrease of magnesium in the metal bath and generated reaction products as $MgAl_2O_4$, MgO, and Al_2O_3 in solid-state, so that this process can help to reduce the emission of polluting gas. Also, the ZnO powder was reduced, and the zinc incorporated into the melted aluminum microstructure of the alloys has an Al-Zn matrix and second phases of Al_6(Fe, Mn) and Al_{12}(Fe, Mn)$_3$Si in the cast state. In this case, this process can be favorable for the manufacture of alloys that can be applied in the automotive sector.

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References

[1] Bojun X. Optimization of Recycling Process of Die Cast Aluminum A380 Machining Chips [thesis]. Ontario, Canada: University of Windsor; 2015

[2] Van der Harst E, Potting J, Kroeze C. Comparison of different methods to include recycling in LCAs of aluminium cans and disposable polystyrene cups. Waste Management. 2018;**48**:565-583. DOI: 10.1016/j.wasman.2015.09.027

[3] Stotz PM, Niero M, Bey N, Paraskevas D. Environmental screening of novel technologies to increase material circularity: A case study on aluminium cans. Resources Conservation Recycling. 2017;**127**: 96-106. DOI: 10.1016/j.resconrec.2017.07.013

[4] Capuzzi S, Timelli G. Preparation and melting of scrap in aluminum recycling: A review. Metals. 2018; **8**(249):2-24. DOI: 10.3390/met8040249

[5] David E, Kopac J. Use of separation and impurity removal methods to improve aluminium waste recycling process. Materials Today: Proceedings. 2015;**2**(10):5071-5079. DOI: 10.1016/j.matpr.2015.10.098

[6] Gray AR. United States Patent: 3871965; 2010

[7] Briolle E. United States Patent: 5232300; 1993

[8] Hiraki T, Miki T, Nakajima K, Matsubae K, Nakamura S, Nagasaka T. Thermodynamic analysis for the refining ability of salt flux for aluminum recycling. Materials. 2014;**7**(8): 5543-5553. DOI: 10.3390/ma7085543

[9] Kamat GR, Gupta CK. Open aluminothermic reduction of columbium (Nb) pentoxide and purification of the reduced metal. Metallurgical and Transactions. 1971; **2**(10):2817-2823. DOI: 10.1007/bf02813257

[10] Lin N, Han Y, Zhou J, Zhang K, Xu T, Qiuan Y. A low temperature molten salt process for aluminothermic reduction of silicon oxides to crystalline Si for Li-ion batteries. Energy and Environmental Science. 2015;**8**(11): 3187-3191. DOI: 10.1039/C5EE02487K

[11] Zhu HX, Abbaschian R. In-situ processing of NiAl-alumina composites by thermite reaction. Materials Science and Engineering: A. 2000;**282**(1):1-7. DOI: 10.1016/S0921-5093(99)00788-1

[12] Lima BB, Ramos AS, Nunes CA, Conte RA. Ni-65wt%Nb alloy by aluminothermic reduction process. International Journal of Refractory Metals and Hard Materials. 2000;**8**(6): 267-271. DOI: 10.1016/S0263-4368(00)00021-4

[13] Zhang L, Lv X, Torgerson AT, Long M. Removal of impurity elements from molten aluminum: A review. Mineral Processing and Extractive Metallurgy Review. 2011;**32**(3):150-228. DOI: 10.1080/08827508.2010.483396

[14] Muñiz R, Flores A, Torres J, Luna S, Rodríguez N. A kinetic study of the strontium extraction by metallothermic reduction using submerged SrO powders injection. Materials Letters. 2008;**62**(4–5):637-640. DOI: 10.1016/j.matlet.2007.06.024

[15] Hashiguchi T, Sueyoshi H. Removal of magnesium from molten aluminum scrap by compound-separation method with Shirasu. Materials Transactions. 2010;**51**(5):838-843. DOI: 10.2320/matertrans.mh200914

[16] Liu Y, Luo L, Han C, Ou L, Wang J. Effect of Fe, Si and cooling rate on the formation of Fe- and Mn-rich intermetallics in Al–5Mg–0.8Mn Alloy.

Journal of Materials Science & Technology. 2016;**32**(4):305-312. DOI: 10.1016/j.jmst.2015.10.010

[17] Kamat R, Ng-Yelim J, Saimoto S. Morphology and precipitation of α-Al (Fe, Mn)Si phase in hot rolled AA3004. Journal of Materials Research. 1995; **86**(1):49-53. DOI: 10.1515/ijmr-1995-860110

[18] Anyalebechi PN, Rouns T, Sanders RE. Microstructural analysis of second phase developed during casting and preheating of 3XXX aluminum alloys. In: Hirano K, Oikawa H, Ikeda K, editors. Proceedings of RASELM 91, Conference on Science and Engineering of Light Metals. Tokyo, Japan: Institute of Light Metals; 1991. p. 923