Review on Oxide Formation and Aluminum Recovery Mechanism during Secondary Smelting

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Abstract

The remelting, refining, and casting process of aluminum alloys often generate aluminum dross containing primarily oxides and nitrides of aluminum and entrapped metallic aluminum at the surface of the molten metal as a result of reactions within the furnace atmosphere at elevated temperatures. The handling of dross is an expensive but necessary activity during aluminum smelting. Furthermore, the amorphous Al_2O_3 oxide film formed on the pure molten aluminum surface due to the liquid metal randomly distributed atoms is impermeable to the diffusion of aluminum metal and oxygen. In amorphous materials, there is a low mobility of the charge carriers and an absence of preferred diffusion paths. This film can transform to crystalline Al_2O_3 by nucleation and grows with time and opportunity. This review discusses the mechanism of oxide formation and the aluminum metal recovery processes.

Keywords:

1. INTRODUCTION

Aluminum scrap recycling is a secondary production process. This metal and its alloys are 100% recyclable without property loss and can be melted and recast over and over again. Hence, aluminum is a renewable resource that has endless opportunities for generations to come.

The primary aluminum production generates more than 40 kg of Al dross per ton and about 200 kg of Al dross per ton in secondary aluminum smelting [1]. The energy required for the secondary smelting of aluminum is often estimated to be 5% of that required for primary aluminum production and yields similar quality aluminum of that obtained in the primary smelting operation [2–4]. The secondary smelting of aluminum leads to raw material saving, as the used product can be recycled instead of dumped in a landfill. Also, it helps to reduce pollutant emission to the atmosphere (~17%), with about 5- to 9-times-less solid waste and 35-times-less water consumption than the primary aluminum process [5]. Thus, recycling aluminum is beneficial and sustainable compared to primary aluminum production.

The continuous film on the liquid Al surface (known as dross) is a mixture of gases, nitrides, carbides, and other substances [6, 7]. The amount of dross formed/skimmed per cycle depends on factors such as type and quality of the input material (primary aluminum and aluminum scrap), operating conditions, type of technology, and the used melting furnace [8]. About 1% of aluminum is oxidized each minute that the uncooled dross remains exposed to the air during production [9]. Aluminum dross is divided into three types; namely, white dross (wet dross), black dross (dry dross), and salt cake. The dross obtained from primary melting operations is known as white dross and is often a compact material in large clotted lumps consisting mainly of aluminum oxide (with some oxides of other alloying elements such as magnesium and silicon) and ~15–70% recoverable metallic aluminum. The dross from secondary smelting operations is known as black dross; it is granular in sizes with high metal content in the coarse fraction and chiefly oxides and salt in the fines. Lazzaro et al. [10] gave the composition of black dross from a secondary smelting as a mixture of aluminum/alloy oxides and slag, with recoverable aluminum contents ranging from 12–18%. Salt cake is a nonmetallic by-product residue from secondary smelting operations with 3–5% of metallic aluminum [11]. In the past, salt slag was used for landfilling [12]. However, the possibility of treatment has led to the minimization of its use for that purpose. This practice is the present order in Europe, the US, and Canada. Both aluminum and salt are recovered during the salt slag treatment [13].

The dross formed during aluminum smelting operations constitutes a loss and a source of inclusion in cast products. Researchers have associated Al metal loss to the furnace atmosphere as well as variations in temperature and pressure during smelting [14–16]. Consequently, the reduction in dross formation is an attractive venture that can lead to cost reduction and improved yield.

2. ALUMINUM DROSS FORMATION

One or a combination of several activities causes dross formation. Such processes include melt surface oxidation, oxide skin crushing by bath movement, oxide particles sinking and floating, oxide particle conglomeration, metallic aluminum filling up interspace, dispersed aluminum oxidation, dross skimming, and the follow-up oxidation of solids during dross cooling [17]. Antrekowitsch [17] and Freti et al. [18] recommended that cascading molten aluminum during the transfer from one process stage (e.g., melting) to another (holding in the furnace) should be eliminated by counter-tilting the furnace. The method will enable the molten aluminum to flow under an existing oxide layer without mechanical cleaning in the melting furnace afterwards. However, their study focused on a typical smelter cast house operation whose analyses apply to re-melt and casting operations.

A significant increase in the oxidation rate can result in breakaway oxidation, which is characterized by the formation of an abnormally thick oxide layer. This observation was first identified in industrial melting furnaces. An early reference to this phenomenon by Thiele [19] shows that oxidation proceeds rapidly from the beginning with alloys containing 10 and 20% Mg, while those with a 5% Mg alloy showed the phenomenon of breakaway oxidation most clearly. Table 1 shows that oxidation occurred steadily for ~40 hours before the rate of weight change increased suddenly.

Table 1
Effect of Mg concentration on the percentage of formed dross [19]

Time, hr	Weight % of oxide formed during smelting			
	3% Mg	5% Mg	10% Mg	20% Mg
0	0	0	0	0
10	0.10	1.0	1.9	4.25
20	0.10	1.5	3.9	8.0
30	0.15	2.25	4.25	9.25
40	0.20	3.0	5.00	12.0
50	0.25	4.0	4.0	12.25
60	0.25	5.25	5.25	12.25

Cochran et al. [20] investigated the oxidation phenomenon of the Al-Mg alloy observed by Thiele [19]. The researcher measured the oxidation rates of relatively small samples continuously with precise measurement techniques and presented the results in a general oxidation curve (Fig. 1). The profile summarized all of the oxidation inhibition or accelerating effects and provides a clear explanation of the formation of breakaway oxidation.

It can be seen from Figure 1 that the time interval between A and B decreases if the temperature of the metal surface increases. If the Mg concentration in the melt increased, the melted surface is "seeded" with crystalline MgO or $MgAl_2O_4$, and the melting is carried out more slowly. An increase will occur if a Be or Na addition is in the melt or if the melt surface was doped with boron and rapid melting and homogenization of the solid charge occur just before reaching the melt temperature.
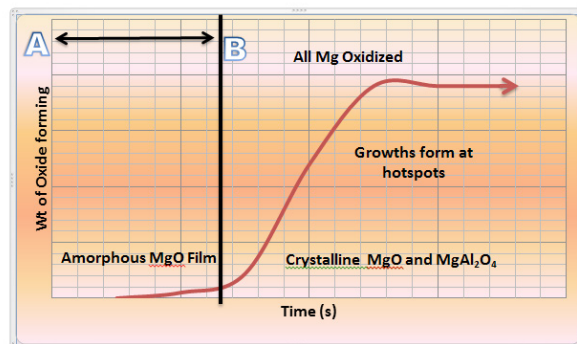

Fig. 1. General oxidation behavior of Al-Mg melts [19]

Impey et al. [21] also investigated the effect of Mg additions to molten aluminum and obtained a 15% yield reduction in aluminum metal due to metallic aluminum entrapment within the formed dross. Silva and Talbot [22] suggested that MgO rather than $MgAl_2O_4$ (spinel) is responsible for the onset of breakaway oxidation and that the process starts immediately (without an incubation period) if the melt is within the zone between the liquidus and solidus temperatures. At intermediate magnesium levels between 0.005 and 2 wt.%, a mixed oxide $MgOAl_2O_3$ (known as spinel) is formed [22]. The oxidation mechanism was considered to start with the formation of amorphous MgO, $MgAl_2O_4$, or Al_2O_3, which transforms to a crystalline MgO, or $MgAl_2O_4$, or γ-Al_2O_3 film. The oxide films change from magnesia to spinel and finally to alumina with the progressive depletion of magnesium at the oxide melt interface.

Stewart et al. [23] studied alloy composition, scrap thickness, and the effect of organic coatings on melt loss. The result of the study showed that increasing the melting time from 40 to 105 minutes increased dross formation to between 3 and 8% of the melt. The authors recommend the removal of all coatings, and that light-gauge and finely divided scrap should be submerged in a molten bath. In another study, Stewart and McCubbin [24] investigated the effect of sheet gauge thickness, magnesium content, and coating effects on melt loss in a 22-kg gas-fired furnace. The results showed that decreasing the gauge thickness had an extremely pronounced effect on melt loss, as it increased exponentially. As the metal sheet begins to heat and melt, a tightly adhering oxide film forms when the aluminum inside the film melts drains away due to gravity effect.

Moreover, the experimental results showed that, for heavy gauge sheet (greater than 15 mm), increasing levels of magnesium content had little effect on melt loss. However, on thinner gauge sheet (0.5 mm), increasing the magnesium

content from 0–2.5% Mg resulted in an increased melt loss of between 4 and 8%. This observation was attributed to the thicker oxide film on the aluminum-containing magnesium alloy [24].

Wenz [25] carried out a complementary study using a sophisticated pilot scale laboratory furnace. Table 2 shows the effect of gauge thickness on the quantity of the dross formed on melting aluminum. The 0.34 mm gauge thickness shows that increasing the melt rate reduces the percentage skim from 26% (with the lowest power input) to 21 % when the power input rate was increased to 117 kW. Furthermore, the effects of paints and lacquer coatings on melt loss were also investigated. In each case where coatings were present, melt losses to dross increased. The release of volatile compounds from the submerged scrap caused dross formation on the surface of the melt. The findings from their work provided much of the justification for the development of the Alcan UBC decoating process, which was based on the possibility of melt loss reduction from >15% to < 5% by removing the coatings before melting.

Table 2
Effect of heat input rate on melt loss [26]

Power, kW	Skim weight % of charge		
	gauge length, mm		
	25	2.5	0.34
33	3.0	–	26.0
45	4.0	5.0	25.5
60	3.0	6.0	24.0
65	2.5	5.5	23.0
90	30.0	5.0	22.5
117	3.0	3.5	21.0

Mechanism of aluminum oxide formation

The oxidation of liquid aluminum starts with amorphous alumina layer formation due to the randomly distributed atoms of the liquid metal. This phase will transform to the crystalline form by nucleation and growth at a higher temperature [18–19]. After an incubation time of 5–10 minutes at about 750°C, the amorphous film transforms to a crystalline form of γ-Al_2O_3 or η-Al_2O_3. The transformation occurs rapidly at the melt/oxide surface. However, once the crystalline alumina has formed, ion diffusion is hindered, resulting in a low oxidation rate. After an incubation period that can last several hours based on many factors such as temperature, alloy type and environment, the structure converts to α-Al_2O_3 crystal (corundum) [20].

The amorphous oxide film is impermeable to the diffusion of aluminum metal and oxygen because of the lower mobility of charge carriers in this material and the absence of preferred diffusion paths such as the grain boundaries. The amorphous film is typically very thin, with estimated thicknesses of between 20–45 Å (10^{-10} m) [26] and about 100 Å; however, this may be up to 2–3 nm [27] and form

a protective layer over the molten aluminum [20]. This film is unstable compared to the crystalline alumina [22]. During the oxidation process, cracks can form within the oxide layer and combine with the aluminum ions (with high mobility), leading to a much faster oxidation rate.

Cochran, Belitskus, and Kinosz [20] stated that the crystalline alumina grew laterally and vertically by the continuous oxidation of the metal and not by the recrystallization of the amorphous film, whereby oxygen must be supplied from the atmosphere. At temperatures at around 700°C, the lattice diffusion rate in refractory oxides such as Al_2O_3 is too slow to provide enough oxygen. Therefore, open pathways between the atmosphere environment and the melt are required to maintain the reaction between the aluminum and oxygen. Jeurgens, Sloof, Tichelaar, and Mittemeijer [28] demonstrated that, below a certain critical thickness, an amorphous film could be more thermodynamically stable than the crystalline form, owing to the relative free energy of the bulk material and the free energy of the material surface. In systems with large surface areas (i.e., a thin oxide film), the total free energy is dominated by the surface energy, which is lower in the amorphous form than in the crystalline form. In thicker films where the ratio of the surface area to the volume is low, the total free energy is dominated by the bulk energy of the material, which is higher in the amorphous form as compared to the crystalline form.

Wilson and McConnell [29] suggested that the transformation from γ-Al_2O_3 to α-Al_2O_3 is challenging to obtain in practice since the total conversion occurs on heating above 1200°C for more than one hour. However, α-Al_2O_3 crystallization has been reported by Impey et al. [30] to occur at 750°C after an incubation time of about five hours in an industrial grade 319 alloy (Al-6Si-3Cu alloy). Traces of α-Al_2O_3 were identified even at the early stages of melting. The transformation resulted in a 24% reduction in oxide volume, which causes film rupture and further exposes the liquid metal beneath to oxidation. The melt will react with oxygen to form alumina on the initially formed Al_2O_3 film [21]. Hence, the development and growth of oxide films on liquid Al alloys result from the local penetration of the film.

It has been proposed by Agema and Fray [31] that oxidation occurred through oxygen transportation in continuous pathways that penetrated the oxide film. The pathways in the oxide films at the surface of the melt could be cracks, pores, or zones of loose structure inherent in the films or formed by the volume change associated with the conversion of metal to oxide. Although Sleepy [32] had earlier proposed that oxidation caused aluminum ion diffusion through the oxide film, the difficulty of this model was the oxide was almost impermeable to both metal and oxygen diffusion. Another suggestion was that the arrival of the metal at the surface of the film was not by diffusion but by melt flow along the capillary channels, which is much faster [33].

Oxide films exhibit a variety of appearances, owing to the differences in the chemical compositions, thickness, strength, and interaction with the melts. The morphology of aluminum oxides has been categorized [32] into 'old oxides' (thick) and 'young oxides' (thin). Old oxides develop from

the thickening of the oxide that initially exists on the ingot's surface during the melting process and during the transport of the liquid from the furnace to a crucible. Old oxides form under longer exposure times to an oxidizing atmosphere. An earlier study by Thiele [19] on the thickening of the oxide film indicated that, after five seconds at 700°C, the measured oxide film thickness on the surface of a melt was 24 nm and increased to 900 nm after being held for one hour at the same temperature.

Dignam [34] used a high purity (99.996%) aluminum foil that was oxidized at temperatures from 454–530°C. The amorphous oxide can be present up to the incubation time and then decreases with increasing temperatures. After the incubation period, transmission electron microscopy and electron diffraction showed the presence of crystalline oxide particles, which were presumed to be γ-Al_2O_3 and observed to nucleate at the metal/oxide interface [35–38]. There have been issues raised as to whether the amorphous oxide transforms into a crystalline oxide or the crystalline oxide nucleates separately. It has been observed that the oxide film growth and the solid aluminum substrate observed an orientation relationship [35]. However, with a transmission electron microscope (TEM) and electron diffraction techniques, the oxide present was identified as γ-alumina. Impey, Stephenson, and Nicholls [21] observed α-alumina in oxide films formed on molten aluminum using TEM to study the morphology of oxide films at the initial stages of oxidation. Samples were taken from the melt using a copper-loop, and the sampled material was dissolved in a 3% bromine-methanol solution to dissolve the aluminum from the oxide. The α-Al_2O_3 crystals that nucleated first were observed to be from the γ-Al_2O_3 film. Moreover, Drouzy and Mascré [39] had earlier noted that, at longer times, α-alumina is observed to form. Thus, it is accepted that this α-alumina forms from the transformation of γ-alumina.

The furnace choice may also facilitate oxide growth, and air convection may bring inclusions such as ceramic particles from furnace linings and large dust particles onto the aluminum surface [33]. If these inclusions are sufficiently heavy, they break through the oxide into the melt. These inclusions attach to the oxide layers and may become incorporated into the melt as part of a bifilm defect [33].

3. ALUMINUM RECOVERY FROM DROSS DURING SECONDARY SMELTING

Recycling aluminum dross is a challenging task in secondary smelting processes due to the difficulty in separating the oxides from the metallic aluminum even at a high temperature. Several activities described by its life cycle assessment (LCA) influence aluminum product market cost. In 2010, aluminum LCA showed that ~50% of the total ingots produced in Spain were from the secondary aluminum industry and ~20% from imported secondary aluminum [40]. At elevated temperatures in a recovery furnace, the dross will melt, and the free metallic aluminum becomes susceptible to oxidation and tends to ignite or burn in the air, emitting toxic gases [41]. This aluminum burning has been reported to significantly decrease the amount of recovered aluminum [42, 43].

Aluminum dross contains metallic aluminum as well as nitrides, carbides, and sulfides of aluminum along with some other compounds. The typical chemical composition of raw aluminum dross and calcined dross is shown in Table 3 based on the study by Yoshimura et al. [44]. The analyzed dross was calcined at 1450°C for an hour, which resulted in the oxidation of phases such as aluminum nitride (AlN), Al, calcium fluoride (CaF_2), corundum, and spinel phases, with small amounts of beta β-Al_2O_3.

Table 3
Composition of raw and calcined dross [wt.%] [44]

Raw Dross		Calcined Dross	
composition	weight percentage	composition	weight percentage
$MgAl_2O_4$	48	Al_2O_3	84
AlN	28	MgO	11
α-Al_2O_3	7	SiO	2
$NO_2Al_{22}O_{34}$	6	CaO	1
$NaAl_{11}O_{17}$	6	Na_2O	0.7
CaF_2	3	K_2O_3	0.4
Al	2	Fe_2O_3	0.3
–	–	TiO_2	0.3

The chemical composition of aluminum dross particles before and after the purification procedure, which involved boiling the dross in water followed by stirring, cooling, milling, and vacuum filtration was analyzed as shown in Table 4. After purification, the main constituent in the final product is found to be aluminum oxide. The aluminum in the dross hydrolyzed to Al_2O_3 during the water treatment.

Table 4
Composition comparison of aluminum dross [45]

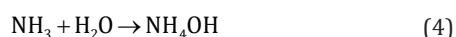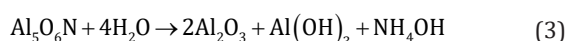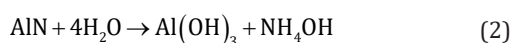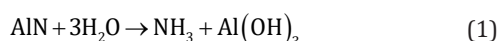| Oxide/element	As-received, wt.%	After purification, wt.%
Al_2O_3	78.24	94.74
SiO_2	1.46	1.56
Na_2O	6.28	0.03
CaO	0.47	0.13
TiO_2	0.13	0.03
MgO	0.97	0.03
K_2O	1.47	0.53
Zn	0.05	0.53
Cu	0.51	0.55
Al	1.16	1.24
Mn	0.03	0.03

The methods for aluminum recovery from aluminum dross [46–52] include reducing metal loss during cooling, physical separation of metal from the dross, and the remelting of the metallic fraction. Groteke [53–56] developed a method to stir hot dross for the easy separation of molten aluminum from the dross. This method combines agitation and chemical reactions, which can lead to a recovery of up to 90% of the Al in the dross. The agitation by the rabble stirrer promoted Al droplet coalescence.

Black dross (obtained from the secondary smelting of Al) can be managed by hydrometallurgical (the selective dissolution of metals from their waste) and pyro-metallurgical processes (the use of heat to separate metals). Pyrometallurgical processes involve high energy consumption that also requires some reducing agents and relatively high temperatures [57–59]. The hydrometallurgical leaching process is carried out either by alkaline or acid leaching. Pure aluminum sulfate, known as 'paper-makers' alum or filter alum ($Al_2(SO_4)_3 12H_2O$) used in water treatment, cellulosic insulation, dying, and fire-proofing fabrics was produced from aluminum black dross by the acid leaching process [60–63]. Other similar processes targeted at the recovery of pure aluminum hydroxide by the neutralization of sulfuric leach liquor and recovery of pure alumina by heat treatment of the produced aluminum hydroxide [64]. The alkali leaching process was based on Al and Al_2O_3 dissolution in a strong sodium hydroxide solution at atmospheric or high-pressure conditions. Aluminum is recovered as aluminum hydroxide by crystallization/precipitation. High-grades of metallurgical alumina will then be produced by calcination at a high temperature (1100°C) [2].

Miskufova et al. [65] examined the leaching propensity of Al from dross fines after mechanical pre-treatment in alkaline solution under atmospheric conditions. The result showed 98% of leachable Al from the dross was achieved by leaching with a 10% NaOH solution at 96°C for 120 minutes. Lucheva et al. [43] also investigated the possibility of alkaline leaching of black dross. The leach liquor consists of a 10% volume-to-volume ratio (v/v) – NaOH, with a molar ratio (alkaline module) Na_2O/Al_2O_3 equal to 2. The results yield ~42% of Al and other minor elements

Tsakiridis et al. [66] investigated the possibility of aluminum recovery from aluminum black dross by alkaline pressure leaching. The dross was crushed in a jaw crusher and ground in a ball mill to ~100 μm. Firstly, soluble salts were recovered by atmospheric pressure via water leaching, and aluminum was then recovered by pressure leaching at 200°C with sodium hydroxide. The result showed that ~57.5% of aluminum by weight was recovered using this technique.

The non-metallic byproduct residue from dross smelting operations known as "salt cake" contains 3–5% residual metallic aluminum. It is classified as toxic and hazardous waste [67], and this material is considered to be a highly flammable, irritating, and harmful but leachable substance [68, 69]. The gaseous emissions from the salt slag that result from contact with water are of great environmental concern [70–73]. Ammonia gas is produced by the hydrolysis of nitrides (pH increase) present in salt slag as described by Equations (1)–(4).

$$AlN + 3H_2O \rightarrow NH_3 + Al(OH)_3 \tag{1}$$

$$AlN + 4H_2O \rightarrow Al(OH)_3 + NH_4OH \tag{2}$$

$$Al_5O_6N + 4H_2O \rightarrow 2Al_2O_3 + Al(OH)_3 + NH_4OH \tag{3}$$

$$NH_3 + H_2O \rightarrow NH_4OH \tag{4}$$

Ammonia is easily soluble in water, simultaneously increasing its pH to 9 or higher. The odor of ammonia gas (NH_3) near a problematic landfill is evidence that the environment is alkaline. The high pH of the soil environment dissolves the alumina film on the unrecovered aluminum particle surface, and hydrogen is generated from the hydrolysis of metallic aluminum (Eqs. (5) and (6)) [66].

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 + heat \tag{5}$$

$$Hot\ H_2 + O_2(air) + combustible \rightarrow fire \tag{6}$$
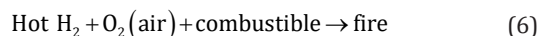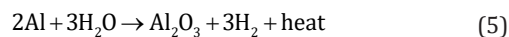
Methane is generated through the reaction of Al_4C_3 with water (Eq. (7)). The amount of methane evolved from the salt slag is a quantitative indicator of its aluminum carbide content.

$$Al_4C_3 + 6H_2O \rightarrow 3CH_4 + 2Al_2O_3 \tag{7}$$
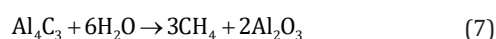
In the cases of increased pressures and temperatures within landfills [66], aluminum cyanide could be produced because of the presence of aluminum carbides (Eq. (8)). Aluminum cyanide hydrolysis could lead to HCN generation (Eq. (9)).

$$Al_4C_3 + 6N_2 + 9C \rightarrow 4Al(CN)_3 \tag{8}$$

$$4Al(CN)_3 + 6H_2O \rightarrow 2Al_2O_3 + 12HCN \tag{9}$$
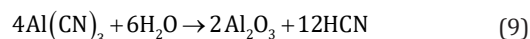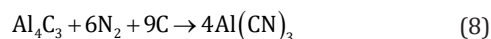
Finally, except for aluminum carbide and nitride, aluminum phosphide and sulfide can rapidly react with water, even with moisture of the air (Eqs. (10) and (11)).

$$AlP + 3H_2O \rightarrow Al(OH)_3 + PH_3 \tag{10}$$

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S \tag{11}$$
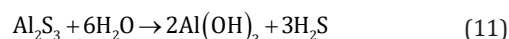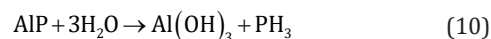
As a result, the improper disposal of aluminum slag at landfills can lead to the contamination of groundwater (e.g., F^-, Cl^-, NH_4^+, CN^-, high pH) and the ambient air (e.g., CH_4, H_2, NH_3) [74]. However, because of increasing local environmental and institutional barriers to the development of new landfills, the disposal of salt cake residue is anticipated to be rare and expensive [74, 75].

Nevertheless, aluminum can be recovered from this material (salt cake). This was accomplished by Tsakiridis et al. [66] via a rotary salt furnace process that involved a charge of scrap/dross and salt flux. The mechanism leading to the recovery has also been discussed in the literature [34, 66, 74]. The metal in contact with the air formed aluminum oxide at the outer surface of the melt. The "salt" shields the metal from the reactive atmosphere, which facilitates agglomeration and metal separation while enhancing metal recovery [34, 66]. The process also improves the heat transfer to the metal, inhibits oxidation, and takes up unwanted compounds such as oxides, nitrides, carbides, and others contained in the scrap or produced by reactions during the melting process. After melting, aluminum metal and salt slag were tapped from the furnace. The non-metallic components from the

raw mix were completely absorbed by the flux and formed the dross after tapping and cooling the salt slag or salt cake from the molten metal surface [76].

4. CONCLUSION

This review discussed the Al oxidation mechanism during melting and its recovery from dross. Techniques to separate Al metal from its dross such as stirring hot dross, crushing and screening cold dross, bubble flotation and leaching processes were discussed, including the oxide formation mechanism and the causes of aluminum metal loss into the dross. The amount of dross formed/skimmed cycle depends on factors such as the type and quality of the input material (primary aluminum and/or aluminum scrap), operating conditions, type of technology, and choice of heating furnace.

REFERENCES

[1] Hong J.-P., Wang J., Chen H.-Y., Sun B.-D., Li J.-J. & Chen Ch. (2010). Process of aluminium dross recycling and life cycle assessment for Al-Si alloys and brown fused alumina. *Transactions of Nonferrous Metals Society of China*, 20, 2155–2161.

[2] Das B.R., Dash B., Tripathy B.C., Bhattacharya I.N. & Das S.C. (2007). Production of η-alumina from waste aluminium dross. *Minerals Engineering*, 20, 252–258.

[3] Verdier J.-F., Butruille J.-R., Leroy M. & Valax D. (2009). Process for Recycling Aluminium Alloy Scrap Coming from the Aeronautical Industry. Patent No. 20090285716, US.

[4] Mukhopadhyay J.Y., Ramana V. & Singh U. (2005). Extraction of value added products from aluminium dross material to achieve zero waste. *TMS Light Metals*, 1209–1212.

[5] Drossel G., Friedrich S., Hupattz W., Kammer C., Lehnert W., Liesenberg O., Paul M. & Schemme K. (2003). *Aluminium Handbook: Forming, Casting, Surface Treatment, Recycling and Ecology*, Beuth Verlag GMbH, 636-640.

[6] Han Q. (2003). Dross formation during remelting of aluminium 5182 remelt secondary ingot (RSI). *Materials Science and Engineering*, 363(1–2), 9–14.

[7] Manfredi O., Wuth W. & Bohlinger I. (1997). Characterizing the physical and chemical properties of aluminium dross. *Journal of Material*, 49(11), 48–51.

[8] Blacha L., Burdzik R., Smalcerz A. & Matuła T. (2013). Effects of pressure on the kinetics of manganese evaporation from the OT4 alloy. *Archives of Metallurgy and Materials*, 58(1), 197–201.

[9] Taylor M.B. & Gagnon D. (1995). The Inert Gas Cooler (IGDC). In: *Light Metals*, ed. J. Evans. The Minerals, Metals & Materials Society, Warrendale PA, 819.

[10] Lazzaro G., Eltrudis M. & Pranovi F. (1994). Recycling of aluminium dross in electrolytic pots. *Resources, Conservation and Recycling*, 10, 153–159.

[11] Kulik G.J. & Daley J.C. (1990). Aluminium Dross Processing in the 90's. In: *Second International Symposium – Recycling of Metals and Engineered Materials*, J.H.L. van Linden, D.L. Stewart Jr & Y. Sahai (eds.), Warrendale PA, TMS, 427.

[12] Shinzato M.C. & Hypolito R. (2005). Solid waste from aluminium recycling process: characterization and reuse of its economically valuable constituents. *Waste Management*, 25(1), 37–46.

[13] Gil A. (2005). Management of the salt cake from secondary aluminium fusion processes. *Industrial & Engineering Chemistry Research,* 44(23), 8852–8857.

[14] Alfaro I. & Ballhord R. (1997). The applications of aluminium-oxide obtained from the recycling of aluminium. In: *Proceedings of the Third International Conference on Recycling of Metals*, ed. I. Alfaro, Barcelona, Spain, 405–419.

[15] Sridhar S. & Sohn H.Y. (2005).The Kinetics of Metallurgical Reactions. In: *Fundamentals of Metallurgy*, ed. S. Seetharaman, Cambridge, England: Woodhead Publishing, 270–349.

[16] Medved J., Mrvar P. & Voncina P. (2009). Oxidation Resistance of Cast Magnesium Alloys. *Oxidation Materials*, 71, 257–270.

[17] Antrekowitsch H. (2005). Treatment of Al-dross and recovery of metal. *Short Report of Department of Nonferrous Metallurgy*. Montan University Leoben.

[18] Freti S., Bornand J.D. & Buxmann K. (1982). Metallurgy of Dross Formation on Aluminium Melts. *Light Metals*, proceedings of *the Metallurgical Society conference,* Dallas, 1003-1016.

[19] Thiele W. (1962). Oxidation of Aluminium and Aluminium Alloys. *Aluminium,* 38, 780–786.

[20] Cochran C.N., Belitskus D.L. & Kinosz D.L. (1976). Oxidation of Aluminium – Magnesium Melts in Air, Oxygen, Flue gas, and Carbon Dioxide. *Light Metals*, 2, 203–227.

[21] Impey S., Stephenson D.J. & Nicholls J.R. (1990). A Study of the Effect of Magnesium Additions on the Oxide Growth Morphologies on Liquid Aluminium Alloys. In: *Proceedings of the International Conference on Microscopy of Oxidation*, Institute of Metals, Cambridge, UK, 238–244.

[22] Silva M.P. & Talbot D.E.J. (1988). Oxidation of Liquid Aluminium-Magnesium Alloys. In: *Light Metals*, ed. P.G. Campbell, TMS.

[23] Stewart A.L., McCubbin J.G. & Sulzer J. (1977). Melting Aluminium and Aluminium Alloys. *Light Metal Age*, 35(12), 13–15.

[24] Stewart L. & McCubbin J.G. (1977). Melting Aluminium and Aluminium Alloys. In: *Proceedings of the first international aluminium extrusion technology*, Aluminium Company of Canada Ltd, Ontario, Canada.

[25] Wenz D.A. (1979). Laboratory Investigation of Skim Formation, Cast Shop Technology. *Metallurgical Society AIME*, 2, 771–780.

[26] Kubaschewski O. & Hopkins B.E. (1953). *Oxidation of metals and alloys*. London: Butterworths Scientific Publications.

[27] Wilsdorf H.G.F. (1951). Structure of Amorphous Aluminium Oxide Films. *Nature*, 168(4275), 600–601.

[28] Jeurgens L.P.H., Sloof W.G., Tichelaar F.D. & Mittemeijer E.J. (2002). Structure and morphology of aluminium-oxide films formed by thermal oxidation of aluminium. *Thin Solid Films*, 418, 89–101.

[29] Wilson S.J. & McConnell J.D.C. (1980). A kinetic study of the system γ-AlOOH/Al$_2$O$_3$. *Journal of Solid State Chemistry*, 34(3), 315–322.

[30] Impey S., Stephenson D.J. & Nicholls J.R. (1988). Mechanism of Scale Growth on Liquid Aluminium. *Journal of Materials Science and Technology*, 4, 1126–1132.

[31] Agema K.S. & Fray D.J. (1989). *Preliminary Investigations on the Deformation Behaviour of an Oxide Scale on Molten Aluminium*. Department of Material Science and Metallurgy, University of Cambridge.

[32] Sleepy W.C. (1961). Oxidation of molten high purity aluminium in dry oxygen. *Journal of Electrochemical Society*, 108(12), 1097–1102.

[33] Campbell J. (2003). *Castings*, 2nd ed., Oxford – Boston: Butterworth Heinemann.

[34] Dignam M.J. (1962). Oxide Films on Aluminium Ionic conduction and structure. *Journal of the Electrochemical Society,* 109(3), 184–191.

[35] Doherty P.E. & Davis R.S. (1963). Direct observation of the oxidation of aluminium single-crystal surfaces. *Journal of Applied Physics*, 34(3), 619–628.

[36] Scamans G.M. & Butler E.P. (1975). In situ observations of crystalline oxide formation during aluminium and aluminium alloy oxidation. *Metallurgical Transactions A*, 6(11), 2055–2063.

[37] Dignam M.J., Fawcett W.R. & Böhni H. (1996). The Kinetics and Mechanism of Oxidation of Superpurity Aluminium in Dry Oxygen I. Apparatus Description and the Growth of Amorphous Oxide. *Journal of the Electrochemical Society*, 113(7), 656–662.

[38] Impey S.A. (1989). *The mechanism of dross formation on aluminium and aluminium-magnesium alloys*. Cranfield Institute of Technology.

[39] Drouzy M. & Mascré C. (1969). The oxidation of liquid non-ferrous metals in air or oxygen. *Metallurgical Reviews*, 14, 25–46.

[40] Galindo R., Padilla I., Rodríguez O., Sánchez-Hernández, López-Andrés S. & López-Delgado A. (2015). Characterization of Solid Wastes from Aluminium Tertiary Sector: The Current State of Spanish Industry. *Journal of Minerals and Materials Characterization and Engineering*, 3, 55–64.

[41] Wang S., Hu H., Chu Y.-I. & Cheng P. (2008). Dross Recovery of Aluminium Alloy 380. In: *Proceedings of the Cast Expo 2008*. Atlanta, Georgia, USA, 60090, 1–7.

[42] Hwang J.Y., Huang X. & Xu Z. (2006). Recovery of Metals from Aluminium Dross and Saltcake. *Journal of Minerals & Materials Characterization & Engineering*, 5(1), 47–62.

[43] Lucheva B., Tsonev T. & Petkov R. (2005). Non-Waste Aluminium Dross Recycling. *Journal of Chemical Technology and Metallurgy*, 40(4), 335–338.

[44] Yoshimura H.N., Abreu A.P., Molisani A.L., de Camargo A.C., Portela J.C.S. & Narita N.E. (2008). Evaluation of Aluminium Dross Waste as Raw Material for Refractories. *Ceramics International*, 34(3), 581–591.

[45] Kevorkijan V.M. (1999). The Quality of Aluminium Dross Particles and Cost-effective Reinforcement for Structural Aluminium-based Composites. *Composites Science and Technology*, 59(11), 1745–1751.

[46] Peterson R.D. (2002). Review of aluminium dross processing. In: *Light Metals*, ed. W. Schneider, TMS, Warrendale, PA, 1029–1037.

[47] Martin B. & Daniel G. (1995). The Inert Gas Cooler (IGDC). In: *Light Metals*, ed. J. Evans, The Minerals, Metals & Materials Society, Las Vegas, 819–822.

[48] Van Linden J.H.L. (1991). Aluminium Melt Treatment and Casting. *2nd Australian Asian Pacific Course and Conference, University of Melbourne Parkville*, Victoria, Australia, 121–129.

[49] Rezac K.H. (1991). Aluminium Melt Treatment and Casting. *2nd Australian Asian Pacific Course and Conference, University of Melbourne*, Parkville, Victoria, Australia, 111–117.

[50] Nijhof G.H., van Olst K. & Schokker E.A. (2000). New techniques for separation of non-ferrous metals from waste streams. In: *The Minerals, Metals and Materials Society*, Warrendale, PA, 865–870.

[51] Soto H. & Toguri J.M. (1986). Aluminum recovery from dross by flotation. *Conservation Recycling*, 9(1), 45–54.

[52] Bruckard W.J. & Woodcock J.T. (2004). Characterization of metal-containing waste products in relation to retreatment methods for metal recovery and recycling. In: *Green Processing 2004. 2nd International Conference on the Sustainable Processing of Minerals*, The Australasian Institute of Mining and Metallurgy, Melbourne, 217–224.

[53] Groteke D.E. (1998). An aluminium reclaimer for small foundry applications. *The Journal of Minerals, Metals and Materials Society*, 50(5), 46–47.

[54] Groteke E. (2000). Reducing melt losses in die casting operations. *Die Casting Engineer*, 44(4), 40.

[55] Groteke E. (2000). Dross Reclamation at aluminium melting furnace sites. In: *Fourth (4th) International Symposium on Recycling of Metals and Engineered Materials: roceedings of a symposium organized by the Recycling Committee of the Extraction & Processing Division and the Light Metals Division of TMS*, eds. D.L. Stewart Jr, J.C. Daley & R.L. Stephens, *October 22-25, Pittsburgh, Pennsylvania*, 1123–1134.

[56] Groteke E. (2000). Dross Reclamation at aluminium melting furnaces. In: *Transactions of the American Foundry Society and the proceedings of the one hundred fourth annual meeting*, Pittsburgh PA, 108, 579–584.

[57] Ünlü N. & Drouet M.G. (2002). Comparison of salt-free aluminium dross treatment processes. *Resources Conservation and Recycling*, 36(1), 61–72.

[58] Drouet M.G. (1994). Dross treatment in a rotary arc furnace with graphite electrode. *Journal of Metals*, 5, 26–27.

[59] Ridderbusch M., Jaroni B., Arnold A. & Friedrich B. (2009). From oxide residues of Al-slag treatment to SiAl-masteralloys via carbothermic reduction. 5th European Metallurgical Conference (EMC), Innsbruck, Austria, 173–188.

[60] Mukhopadhyay J.Y., Ramana V.U. & Singh U. (2005). Extraction of value added products from aluminium dross material to achieve zero waste. In: *Light Metals*, ed. A.T. Tabereaux, TMS The Minerals, Metals and Materials Society, Warrendale PA, 1209–1212.

[61] Amer A.M. (2002). Extracting aluminium from dross tailings. *Journal of Metals*, 54, 72–75.

[62] Huckabay D.A. & Skiathas A.D. (1981). Aluminium dross processing. Patent No. WO2014207072A1, US.

[63] Durward A. & Arthur D.S. (1982). Aluminium sulfate manufacture from aluminium dross tailings. Patent No. 4320098A, US.

[64] Dash B., Das B.R., Tripathy B.C., Bhattacharya I.N. & Das S.C. (2008). Acid dissolution of alumina from waste aluminium dross. *Hydrometallurgy*, 92, 48–53.

[65] Miskufova A., Petranikova M., Kovacs M., Havlik T., Orac D. & Briancin J. (2009). Leaching of aluminium dross in alkaline solution. *Emc 2009: European Metallurgical Conference*, Innsbruck, Austria, Global Growth of Nonferrous Metals Production: Proceedings, GDMB, Clausthal-Zellerfeld, 1339–1350.

[66] Tsakiridis P.E., Oustadakis P. & Agatzini-Leonardou S. (2003). Aluminium recovery during black dross hydrothermal treatment. *Journal of Environmental Chemical Engineering*, 1(1–2), 23–32.

[67] Schwarz H.G. (2004). Aluminium Production and Energy. In: *Encyclopedia of Energy*, ed. C.J. Cleveland, Elsevier, 81–95.

[68] Chemicals Decree 675/1993; amendments up to 555/2001 included, Section 3.

[69] European Waste Catalogue and Hazardous Waste List (2002). Environmental Protection Agency, Ireland.

[70] Xiao Y., Reuter M.A. & Boin U. (2005). Aluminium recycling and environmental issues of salt slag treatment. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 40, 1861–1875.

[71] Calder G.V. & Stark T.D. (2010). Aluminium reactions and problems in municipal solid waste landfills. *Practice Periodical of Hazardous Toxic and Radioactive Waste Management*, 14, 258–265.

[72] Lorber K.E. & Antrekowitsch H. (2010). Treatment and disposal of residues from aluminium dross recovery. *2nd International Conference on Hazardous and Industrial Waste Management*, Crete.

[73] Lorber K.E. (2002). Disposal of dross on landfill: A case study. In: *Proceedings of International Solid Waste Association (ISWA), World Environment Congress*, Istanbul, Turkey.

[74] Tsakiridis P.E. (2012). Aluminium salt slag characterization and utilization – A Review. *Journal of Hazardous Materials*, 217–218, 1–10.

[75] El-Katatny E.A. (2000). Recovery of high surface area alumina from aluminium dross tailings. *Journal of Chemical Technology & Biotechnology*, 75, 394–402.

[76] Zhang L. (2006). State of the art in aluminium recycling from aluminium dross. *Light Metals: Proceedings of Sessions*, TMS Annual Meeting, San Antonio, TX, 931–936.