Bulletin of Electrochemistry 2(6) November-December 1986, 619-620

ELECTROMETALLURGY AND THERMICS

REMOVAL OF MAGNESIUM FROM ALUMINIUM SCRAP AND ALUMINIUM-MAGNESIUM ALLOYS

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ABSTRACT

Most of the commercial grade aluminium and aluminium alloys containing varying percentages of magnesium (0.5 - 5.0%) are cheap raw materials for superpure aluminium by electrorefining. Since the presence of magnesium will consume the electrolyte of the refining bath and because of the possibility of magnesium depositing in the pure aluminium cathode, prior removal of magnesium is a necessity. Removal of magnesium by air-oxidation, chlorination, chemical treatment and electrolysis have been reported. A suitable fluoride based flux has been formulated and the results of the efficiency of magnesium removal has been discussed and compared with the other results.

Key words : Magnesium removal, flux treatment, aluminium refining

INTRODUCTION

Aluminium is normally alloyed with small percentages of magnesium to impart strength, castability and in making permanant mould alloys. Scrap generated during the production of varied products such as sheet, rod and cans, contain 0.5 to 5% magnesium. In developed countries where aluminium alloys are extensively used, the annual availability of scrap is tending to a steep rise. These scraps are cheap starting materials for secondary aluminium as well as for the production of superpure aluminium. Scrap utilisation or recycling is an attribute, since it reduces production energies, decreases disposal problems and lowers demand of dwindling natural resources. Removal of magnesium from such scrap and alloys is a prerequisite since the magnesium present in the alloy will not only foul the electrolyte, but also cause contamination of the product.

METHODS FOR REMOVAL OF MAGNESIUM

Oxidation method

Removal of magnesium by air oxidation in view of its affinity for oxygen, resulting in the formation of magnesium oxide is perhaps the simplest. But even with very high temperatures of the order of 900° - 1000°C and prolonged treatment, the elimination is not satisfactory and hence is not widely practised.

Use of other solid oxides as a source of oxygen has been tried with success. it is claimed [1] that by treatment with silica, 90% of the magnesium content is extracted within 1 hour at about 600-650°C. But this method is effective for materials containing 1 to 1.4% magnesium only.

Chlorination methods

The principle underlying in this is to chlorinate selectively the magnesium in preference to aluminium, taking advantage of the free energy of formation. Magnesium chloride being lighter than molten aluminium, floats on the melt and removed as a dross. Chlorine gas [2] either alone or mixed with nitrogen or argon is bubbled into molten aluminium and the magnesium chloride formed is removed. This suffers from the pollution caused by the gaseous emission. To overcome this in "Conalco process" [3] a gaseous chlorine compound like freon (12%) in admixture with nitrogen (3%) is heated with molten aluminium, while the melt is covered with a thin layer of halide flux. The freon is decomposed to chlorine, fluorine and carbon which react with magnesium to form a dross.

Electrolytic method

Magnesium has been electrolytically removed in an experimental three-layer set up [4]. Molten aluminium-magnesium alloy containing 1.5% magnesium has been used as the bottom anode, separated by a molten electrolyte of alkali, alkaline earth chlorides containing 10% $MgCl_2$, and a top layer of pure molten magnesium acting as the cathode. Magnesium level has been brought down to 0.005 wt%.

Chemical treatment

Chemical or flux treatment is generally employed for melt refining of metals. The principle underlying in this is to melt the metal under a cover of a suitable flux, an ingredient of which will remove the metallic impurity or oxide as a dross. Chloride or fluoride based fluxes are often used for the treatment of light metals. A look into the Ellingham diagram of chloride and fluoride series of metals shows that at the tempeature of operation (750-750°C) formation of fluorides is more favoured than chlorides. Since magnesium fluoride is more stable, attempts were directed to remove the magnesium as a fluoride using cryolite based flux [5]. Magnesium is removed by the following reactions.

$$3\ Mg + 2\ AlF_3 \longrightarrow 3\ MgF_2 + 2\ Al$$
$$3\ Mg + 6\ NaF \longrightarrow 3\ MgF_2 + 6\ Na$$
$$6\ Na + 2\ ALF_3 \longrightarrow 6\ NaF + 2\ Al$$

A flux having 20-55 wt% NaCl, 10-15 wt% KCl, and 30-70 wt% cryolite has been used. Aluminium fluoride is the effective demagging agent, and NaCl and KCl aid in lowering the liquidus temperature and increasing the fluidity of the bath. Nearly twice the theoretical quantity of cryolite is required. By treatment with the above fluxes, 80-90% of the magnesium content is eliminated.

In the present studies, replacement of cryolite by aluminium fluoride has been carried out.

EXPERIMENTAL

Aluminium-magnesium alloys of various compositions-2,5 and 10 wt% magnesium were prepared by melting the metals in a graphite crucible using a resistor furnace. 500 g of the alloy with an equal quantity of flux was melted in a graphite crucible, kept externally heated by a resistor furnace. Sodium chloride - potassium chloride mixtures containing

15, 20 and 30 wt% aluminium fluoride were used as flux. The molten mass was stirred periodically with a graphite rod and the temperature was maintained at 750° - 800°C. Samples of the metal were withdrawn at regular intervals by a graphite spoon and the magnesium content analysed using Atomic Absorption Spectrophotometer (AAS). Effect of treatment time, composition of the alloy and flux composition on magnesium removal was studied and the results are presented in Table I.

Table I Performance data on magnesium removal

Weight of alloy taken: 500 g Weight of flux added: 500 g

Magnesium content in the starting material (Wt%)	Treatment time (minutes)	Magnesium content in the treated materials (Wt%)		
		Flux 1	Flux 2	Flux 3
10	30	6.1	5.6	4.9
	60	5.2	4.3	3.6
	90	4.6	3.4	2.9
	120	4.5	3.0	2.5
	150	4.4	2.9	2.2
	180	4.4	2.9	2.0
5	30	2.0	1.20	0.50
	60	1.1	0.50	0.20
	90	0.6	0.20	0.03
	120	0.4	0.10	0.02
	150	0.3	0.06	0.02
	180	0.3	0.05	0.01
2	30	0.51	0.20	0.10
	60	0.20	0.07	0.03
	90	0.08	0.04	0.02
	120	0.04	0.03	0.02
	150	0.03	0.02	0.01
	180	0.03	0.02	0.01

Composition of the flux (Wt%) used:
Flux 1: NaCl 60 KCl 25 AlF_3 15
Flux 2: NaCl 60 KCl 20 AlF_3 20
Flux 3: NaCl 50 KCl 20 AlF_3 30

RESULTS AND DISCUSSION

Effect of initial magnesium content

It could be seen from Table I that the demagging efficiency decreases with increase in the initial concentration of magnesium in the starting material. With alloys containing about 10 wt% magnesium, a maximum of 80% removal of magnesium only is effected even after three hours of continuous treatment with flux containing 1-3 times of AlF_3 than the theoretical requirement for reaction. On the other hand, with 5 and 2 wt% magnesium containing materials, the efficiency of removal of magnesium is more than 99% in less than 1 hour.

Effect of time

The demagging efficiency with time, in 10 and 2% alloys for the three flux compositions are presented in Figure 1. The efficiency of removal is the maximum at the initial stages and slows down subsequently with a tendency towards a steady state. In the case of low magnesium alloys, the steady state is attained, when the magnesium removal is almost complete, but in magnesium rich alloys, the steady state is reached even at a lower level of elimination (80%) with prolonged treatment, and high AlF_3 flux.

Effect of flux

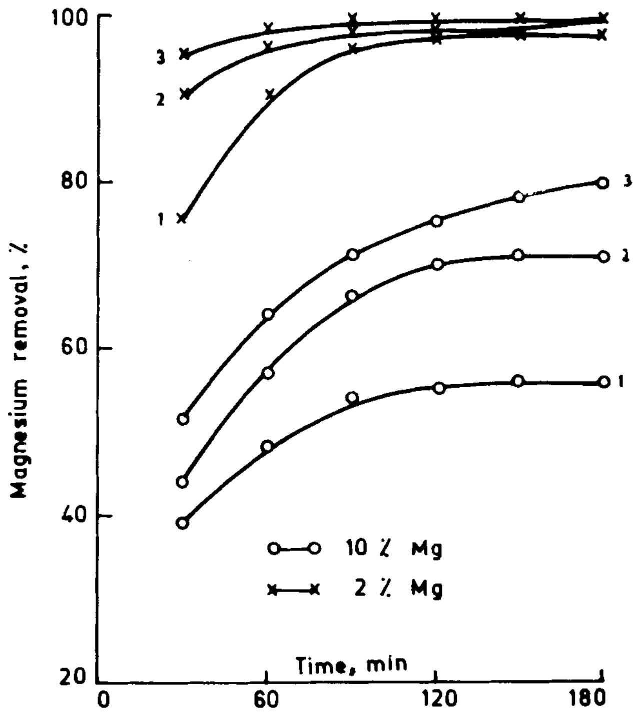

Fig. 1 Magnesium removai efficiency vs time
1. 15% AlF_3 flux
2. 20% AlF_3 flux
3. 30% AlF_3 flux

Since aluminium fluoride is the effective reactant in the flux, its concentration is a factor to be reckoned. As the aluminium fluoride concentration increases, elimination efficiency also increases as expected. However, the rate of increase of elimination is not proportional to the aluminium fluoride content especially in the case of magnesium rich alloys. This may probably be due to the higher output of the formed magnesium fluoride retarding the reaction.

CONCLUSION

(i) Aluminium fluoride flux used in the present study is a better demagging agent than cryolite, since more than 90% removal is realised.
(ii) Flux treatment may not be suitable for magnesium-rich alloys.
(iii) For alloys containing more than 5% magnesium, increase in aluminium fluoride in the flux or duration of treatment, is not effective. For such extreme cases, a two stage treatment will be more beneficial than a single stage treatment.

Acknowledgement: The authors are thankful to Sri P.S. Desikan, Head, Electropyrometallurgy Division, for his interest and encouragement and to other colleagues for their cooperation.

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