BEHAVIOR OF REFRACTORY MATERIALS FOR Al-Li ALLOY

M.Toyoshima, S.Kurino, K.Ohara and O.Wakasaki
Alithium Ltd.
2-2-2, Ogosohigashi, Yokkaichi, 510, Japan

Abstract

The aim for our investigation is to find refractory materials suitable for the container, the tools and assemblies for molten aluminium-lithium alloys. In this study, a composite of alumina-silicon nitride was applied to a 4ton scale vacuum induction furnace and corrosion resistance, contamination of molten metal and life of the refractory were investigated experimentally. In order to evaluate the corrosion-resistant properties , the specimens of tested refractory material were checked by visual observation and X-ray diffraction, and chemical pick up into molten alloys were measured by emission spectroscopy analysis. The results obtained showed that the alumina-silicon nitride refractory material had better corrosion-resistant properties.

Introduction

Lithium metal added in aluminium alloys yields the unique merit to increase the elastic modulus and to reduce the density of alloys. The addition of 3 mass% lithium to aluminium can increase the elastic modulus and reduce the density of aluminium alloy in 10% concurrently. When lithium metal is used, careful melting and casting are needed because of high activity. A wide variety of refractory materials is used to line the metal contact zones of aluminium melting furnaces. In general, however, it is believed that conventional refractory materials are difficult to be used as a lining for extremely-corrosive molten Al-Li alloy. It is object of the present investigation to find refractory materials suitable for the container, the tools and assemblies for the molten Al-Li alloys.

In earlier study, the behavior of various type of refractory materials (about 50 types of oxide and non-oxide refractory materials) for molten Al-Li alloy was examined for corrosion resistance and contamination of molten metal by impurities from refractory materials by using an electric furnace and a small size induction furnace under the inert (argon) atmosphere. The results obtained showed that a high purity alumina-magnesia, and a composite of alumina-silicon nitride and graphite-alumina had better corrosion-resistant properties and protective properties from contamination[1-3] . In second stage, these materials were applied to a 200kg and/or 4ton scale vacuum induction furnace[4-7].

In this paper, a composite of alumina-silicon nitride was applied to the 4ton scale vacuum induction furnace and corrosion resistance, contamination of molten metal and life of the refractory material were investigated experimentally. In addition, process requirements for melting atmosphere, temperature measuring, degassing, homogenization during lithium-addition and deslagging were investigated.

Experimental procedure

Properties and lining profile of the refractory materials

The properties of the refractory materials are listed in Table I , and the lining profile of the refractory materials of the 4ton scale vacuum induction furnace is illustrated in Figure 1 . After the back-up material was added and rammed on bottom of the furnace , the pre-sintered crucible was placed concentrically within the induction coil. Lastly, the back-up refractory material was rammed around the pre-sintered crucible. These refractory materials were dried by charging commercial pure aluminium material into the crucible and raising the temperature slowly by

Table I Typical properties of the refractories

	Crucible	Back-up
Chemical composition		
Al_2O_3 (mass%)	85.7	88.1
Si_3N_4	10	-
TiO_2	2	1.4
CaO	1.5	-
SiO_2	0.6	8.7
Fe_2O_3	0.1	0.2
B_2O_3	-	1
Physical properties		
Bulk density(kg/m^3)	3.08×10^3	
Apparent porosity(%)	13	
Modulus of rupture(MPa)	8.8	
Crushing strength(MPa)	50	
Thermal expansion at 1273K(%)	0.7	

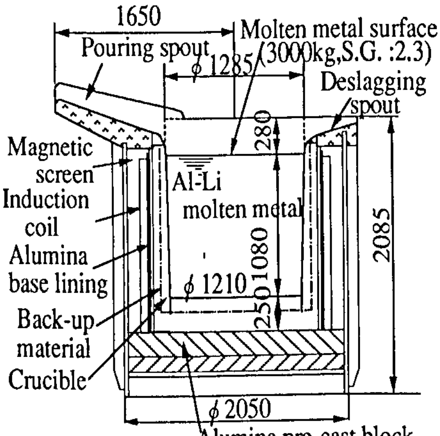

Figure 1 Lining profile of refractories.

controlling power input to the induction coil.

Furnace and melting process

The specifications and schematic illustration of the 4ton scale vacuum induction furnace are shown in Table II and Figure 2 respectively. This furnace is equipped with sampling tool, Ar-gas lancing pipe, thermocouple, deslagging tool and lithium addition unit, which enables melting,

Table II Specification of 4ton scale vacuum induction furnace

Furnace type	HFV-LNP3000		
Crucible		Vacuum chamber	
Capacity	3000kg	O.D. of vacuum chamber	ϕ 3100mm
Inside diameter	ϕ 1240mm	Height of vacuum chamber	4180mm
Height of molten bath	1080mm	Vacuum data	
Electrical data		Operating pressure	4~13Pa
Connected load	1400kW/3000V	Nominal pumping capacity	
Frequency	500Hz	Rotary pump	$0.1m^3 \cdot s^{-1}$
Cooling water	650l/min	Mechanicai booster pump	$5.6m^3 \cdot s^{-1}$

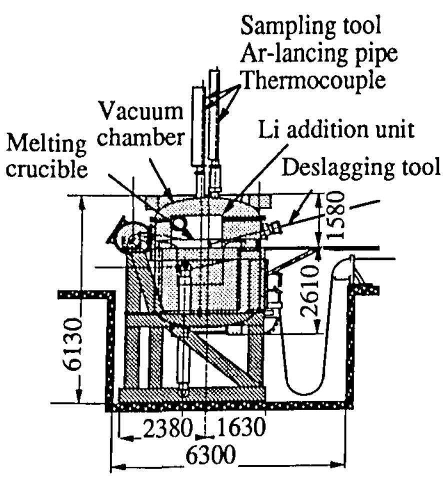

Figure 2 Schematic illustration of vacuum induction melting furanace.

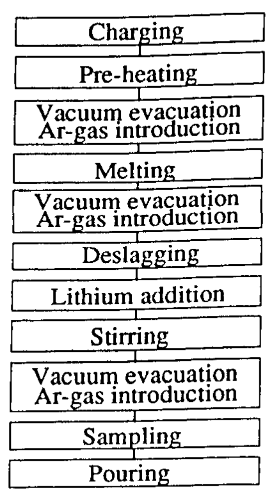

Figure 3 Melting process.

treatment, temperature measurement, sampling and alloying of Al-Li under controlled inert gas atmosphere. Melting process flow is shown in Figure 3 . Commercial pure aluminium (>99.9mass%) and high purity alloy additions were prepared as melting alloys. Lithium was added in form of high purity Li metal rod. The melting practice of the 4ton scale vacuum

Table III Melting practice of 4ton scale vacuum induction furnace

Melting alloy	Number of melting	Melting charge No.
Pure Aluminium	3	417,418,428
Al-Cu-Li(Li:0.1～0.6)	6	419～424
2090	3	425～427
2091	5	429～433
8090	4	434～437

induction furnace and typical cycle for Al-Li alloy melts are shown in Table III and Figure 4 respectively. The furnace was charged with dried raw materials (about 3000kg) except for Li metal and Mg metal, which was evacuated to a vacuum of 4 ~7 Pa ; subsequently, argon gas was introduced into the furnace up to a slight positive pressure. Thereafter, all melting operations such as melting, vacuum degassing, deslagging, Li addition, Ar-gas lancing, vacuum degassing, temperature measuring, sampling and recharging were carried out within the argon atmosphere to prevent contamination of the furnace atmosphere. The furnace atmosphere was maintained at oxygen levels of below 10 mass ppm and dew point of 243~253K throughout all operations. The specimens of the refractory material were taken after 21 melts in order to investigate the damage

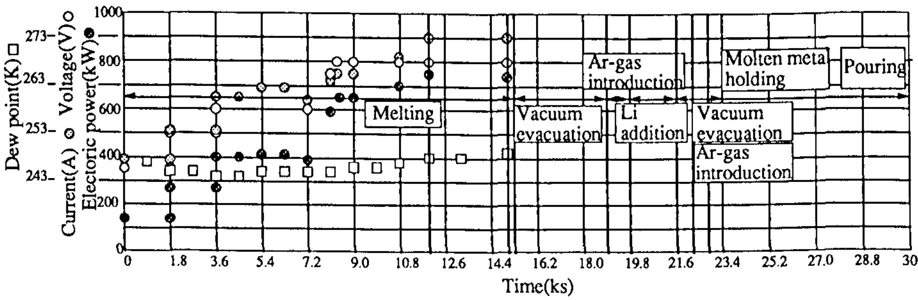

Figure 4 Typical cycle for Al-Li alloy melts.

of corrosion. The samples of molten alloys were taken right before each pouring into ingots in order to investigate the contamination of molten metal from the refractory material.

Results

Appearance of the refractory material after use

Figure 5 shows a states of inside surface of the crucible and molten metal penetration into the crack of the refractory. Serious corrosion was observed on the side wall near the slag line after the melting charge No.426, but it was not observed at the other melting charges. The occurrence of corrosion damage is considered to be caused by contact of the added Li rods with the refractory

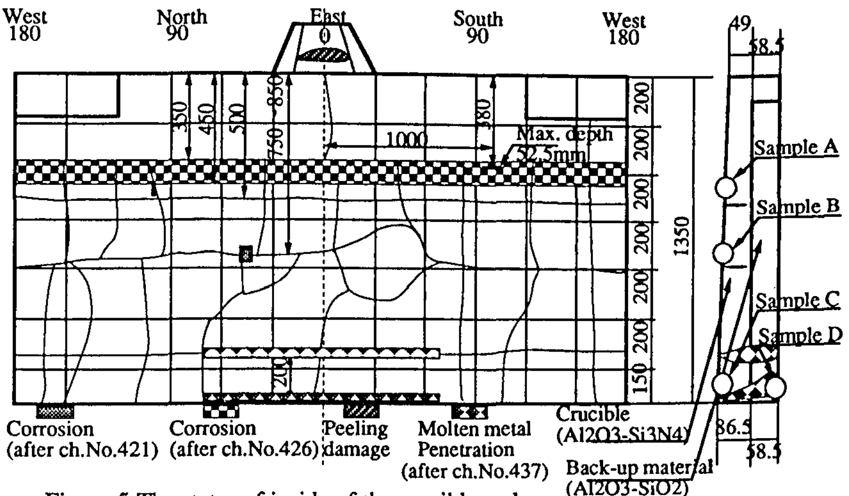

Figure 5 The states of inside of the crucible and molten metal penetration into the crack of the refractory.

material. Therefor, the corrosion on the slag line is able to prevent by mechanical stirring of molten metal at addition of the Li rods. The portion which suffered severe corrosion damage were repaired with a high pure alumina cement. On the other hot face, serious corrosion was not observed. While a vertical and circumferential cracks were observed on the hot face, the maximum width of them was less than 1mm consequently. Serious molten metal penetration was observed in the circumferential cracks at near the bottom of the crucible after the melting charge No.437. The molten metal penetration was reached to the base lining. The occurrence of these cracks is considered to be caused by the lack of mechanical strength of the refractory material and the thermal shock between the melting operations. It is necessary to select a suitable conditions to melting cycle and lining method, binder content, size and form for the refractory material.

X-ray diffraction

The specimens were cut from portion depicted in Figure 5. The results of X-ray diffraction

Table IV Results of X-ray diffraction analysis on the refractories after use 21 times

Mineral components	distannce from the hot face (mm) Sample A 0~3	Sample A 3~10	Sample B 0~3	Sample C 0~3	Sample D Bach-up
α-Al_2O_3	++++	++++	++++	++++	++++
α-Si_3N_4	++	++	++	++	−
γ-$LiAlO_2$	+	−	++	++	−
α-$LiAlO_2$	+	−	+	+	−
Al	++	−	−	++	+
γ-Al_2O_3	−	−	−	−	+

conducted on the refractory materials after 21 melts are listed in Table IV . As shown in Table IV, in addition to the original mineral components of the refractory material γ -$LiAlO_2$, α -$LiAlO_2$ and metallic Al were identified in each specimens in the range of 0 to 3mm in the hot surface layer by X-ray diffraction analysis. On the other hand, reactant was not found in the range of 3 to 10mm from the hot face. Accordingly, corrosion is considered to have occurred near the hot face. In the portions which suffered molten metal penetration, metallic Al and γ -Al_2O_3 component were identified. The presence of these components indicated that a large amount of molten metal penetrated and these portions were heated at excessively high temperature by induction heating of penetrated molten metals.

Quality of molten metal

Figure 6 shown the chemical composition as determined by a emission spectroscopy analysis of

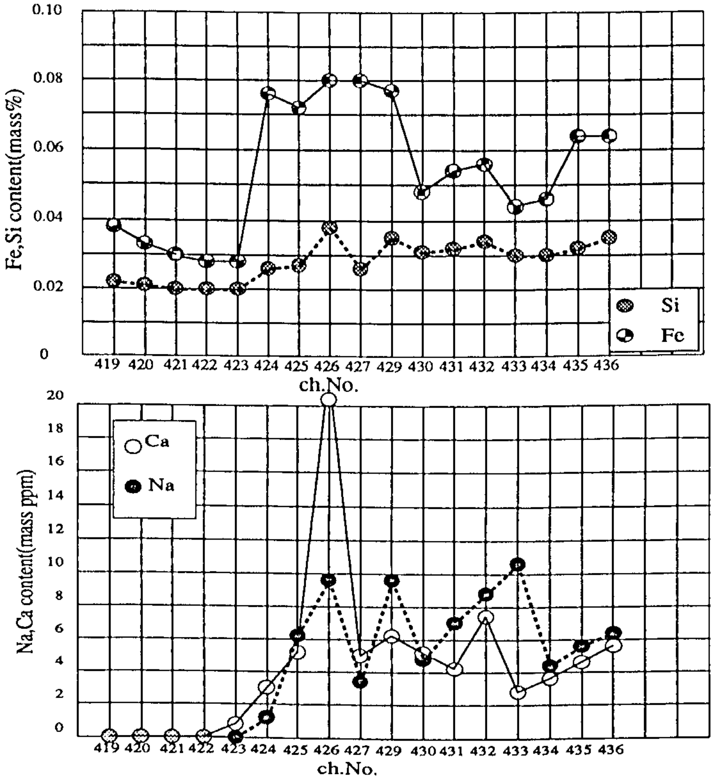

Figure 6 Contamination of Fe, Si, Na and Ca from the refractory by the emission spectroscopy analysis.

each melting alloy right before pouring into ingots. The contamination by Si, Na and Ca from the refractory material was observed in the melting charge of standard Al-Li alloys. Si concentration from the raw aluminium ingot was calculated approximately 0.02~0.03mass% , hence, the contaminated value of Si was estimated approximately 0.004~0.010mass%, with the exception of melting charge No.426 in which severe corrosion damage was caused. Na and Ca concentration from the Li metal and the raw aluminium ingot were calculated to be approximately 3~5mass ppm respectively, hence, the contaminated values of each element were estimated approximately 3~5mass ppm, with the exception of melting charge No.426 in which severe corrosion damage was caused. No contamination by Fe from the refractory material was observed in all of the melting because the Fe concentration from the raw aluminium ingot was calculated approximately 0.03~0.08mass%. From these results it was concluded that Fe, Si, Na and Ca from the refractory material were not a serious problem.

Conclusion

The composite of alumina-silicon nitride was applied to the 4ton scale vacuum induction furnace and corrosion resistance and contamination of molten metal were investigated experimentally. The following results were obtained.

(1)While a reacted layer caused by Al-Li molten metal contact was observed near the hot face, the reacted layer and corrosion of refractory material occurred only 3mm or less from the hot face. Thus, this refractory material resulted in improved corrosion resistance to molten Al-Li alloys.

(2)The severe corrosion was observed on the side wall near the slag line, though it is able to prevent by the mechanical stirring of molten metal at addition of the Li rods.

(3)The serious molten metal penetration was observed in the circumferential cracks at near the bottom of the crucible. Therefor, it is necessary to select a suitable conditions to the melting cycle and to improve the properties of refractory material.

(4)The contamination by Fe, Si, Na and Ca from the refractory material was considered a negligible value except when severe corrosion at near the slag line was caused. This refractory material resulted in improvement against contamination.

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