# STUDY ON HOT ALUMINUM RESISTANCE OF Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> CASTABLES WITH DIFFERENT Al<sub>2</sub>O<sub>3</sub> CONTENTS

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#### ABSTRACT

The working linings of melting and holding furnaces in aluminum industry are usually damaged by the attack of hot Al and its alloy. In order to improve the service performance of lining, hot aluminum resistance of Al2O3-SiO2 castables with different Al<sub>2</sub>O<sub>3</sub> contents was investigated by the crucible method and the immersion method. The microstructure of the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> castables corroded by hot aluminum was also analyzed by means of SEM and EDAX. The results show that: (1) with the increase of the Al<sub>2</sub>O<sub>3</sub> content, the hot aluminum resistance of the castables is enhanced; (2) the castable heat treated at  $1100 \,^{\circ}{\rm C}$ shows worse hot aluminum resistance compared with those heat treated at 110  $\mathbb{C}$ , 800  $\mathbb{C}$  or 1400  $\mathbb{C}$ ; (3) after the hot aluminum penetrates into the interior of castables, Al and even Mg react with SiO<sub>2</sub> in quartz and mullite, reducing SiO<sub>2</sub> into Si, while Al and Mg are oxidized into Al2O3 and MgO; MgO further reacts with Al<sub>2</sub>O<sub>3</sub> to produce spinel resulting in structural damage of the specimen; for the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> castable with a higher Al<sub>2</sub>O<sub>3</sub> content, a dense spinel rich layer is formed which prevents hot aluminum from penetrating further.

**Key Words:** Hot Al resistance, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> castable, Al<sub>2</sub>O<sub>3</sub> content, Microstructure after hot Al attack, Heat treatment temperatures

#### INTRODUCTION

As shown in Fig. 1<sup>[1]</sup>, the aluminum industry in China develops fast, it also shows the same trend for the aluminum processing. The production of large size aluminum alloy slab ingots as well as the further processing aluminum strips and foils puts forward higher requirements on accurate control of aluminum alloy composition. As the key equipment of aluminum alloy processing, the large size aluminum smelter and holding furnace play an important role in controlling the alloy composition, and their inner linings are extremely important for the acceptable service life. The temperature of the hot aluminum in a smelter is about 700-900 °C. However, Al, Mg, Si, and Zn in the melt show high activities, and the hot aluminum has low viscosity (0.104 Pas at 750 °C), so the refractories are vulnerable to hot aluminum corrosion and the hot aluminum is easy to be polluted as well. The literatures involved in these fields are not quite common [2-5].



Fig. 1: Production of primary aluminum of China and its percentage over the wolrd  $\ensuremath{^{[1]}}$ 

Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based refractories are widely used as the inner linings of aluminum smelters. The research of the hot aluminum corrosion on Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based refractories with different Al<sub>2</sub>O<sub>3</sub> contents seems very important enhancing the service performance and controlling the melt composition. In this work, the corrosion behavior of aluminum alloy 7075 on Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based refractories with different Al<sub>2</sub>O<sub>3</sub> contents heat treated at different temperatures was investigated.

# EXPERIMENTAL

#### **Starting Materials**

The main starting materials used in the experiments includes white fused alumina, brown fused alumina, high grade bauxite, low grade bauxite, chamotte, and fused silica. Their chemical composition and bulk density are shown in Table 1.

Tab. 1: Chemical composition and bulk density of starting materials

Starting materials	Chemical composition (w)/%				Bulk
	A1-O-	SiO.	CaO	R.O	density/
	Al <sub>2</sub> O <sub>3</sub>	5102	CaO	$R_2O$	(g·cm <sup>-3</sup> )
High grade bauxite	87.30			0.16	3.22
Low grade bauxite	62.99				2.50
White fused alumina	99.63	0.04		0.22	
Brown fused alumina	95.28				3.79
Chamotte	43.03				2.56
Fused silica		99.9			2.20
Alumina cement	69.52		29.42		

#### **Specimen Preparation**

The aggregates for Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based castables have different grain sizes: 8-5, 5-3, 3-1, and 1-0 mm. The mass ratio of aggregates to fines was (65-70): (30-35). Four formulations were designed to obtain castables with different Al<sub>2</sub>O<sub>3</sub> contents: 80%-85%, 65%-70%, 40%-45% and 25%-30% shown in Table 2, which were named as A80, A65, A40, and A25.

Tab. 2:	Formu	lations	of the	castables

Specimens	A80	A65	A40	A25
High grade bauxite clinker	٠			
Brown fused alumina	٠			
Low grade bauxite		•		
Chamotte			•	
Fused silica				•
White fused alumina				•
Alumina cement	٠	•	•	•
Silica micropowder	٠	•	•	•
Alumina micropowder	٠	•		•
Additive	•	•	•	٠

The batched mixes were dry-mixed for 2 min, added with water, wet-mixed with water for 4 min and shaped into crucible specimens (outer size:  $\varphi 100/90 \times 100$  mm, inner size:  $\varphi 50/44 \times 60$  mm) and strip specimens ( $70 \times 40 \times 40$  mm) by vibration casting. The specimens were cured within the moulds for 24 h and dried at 110 °C for 24 h. Then the dried specimens were heat treated at 800, 1100, and 1400 °C for 3 h respectively.

#### Hot Aluminum Corrosion Test

Aluminum alloy  $7075^{\#}$  was adopted in this experiment and its composition was Si 0.042%, Fe 0.11%, Cu 1.62%, Mn 0.01%, Mg 2.52%, Cr 0.17%, Zn 5.58%, and Ti 0.028% by mass.

The hot aluminum corrosion was tested by two methods. (1) The crucible method: 90 g alloy  $7075^{\#}$  was charged into the

crucible, then the crucible was put into a muffle furnace and fired at 850 °C for 72 h. (2) The hot aluminum immersion method: alloy 7075<sup>#</sup> bar was put into a silicon carbide sagger and then the sagger was heated in a chamber electric furnace at 850 °C; meanwhile strip specimens with size of  $70 \times 40 \times 40$  mm were heated at 850 °C for at least 1 h in a muffle furnace; the hot strip specimen was taken out and put into the heated and preserved (for 30 min) hot aluminum and kept standing for at 72 h with an dipping depth of 40 mm. After cooling down, the specimens were taken out and cut in half longitudinally and symmetrically.

The cross section of the corroded specimen was observed, and the corrosion area was calculated. The microstructure of the corroded specimens was characterized by SEM and EDAX.

## **RESULTS AND DISCUSSIONS**

# Effect of $Al_2O_3$ Content on Hot Aluminum Corrosion Resistance

The cross section photos of the specimens with different  $Al_2O_3$  contents after the crucible test are shown in Fig. 2. It is observed that specimens A40 and A25 are seriously corroded and penetrated; specimen A65 shows just a little corrosion and penetration at the bottom while specimen A80 has almost no corrosion and penetration at all. This result shows that the hot aluminum corrosion resistance of the castables is improved with the rising  $Al_2O_3$  content.



Fig. 2: Section photos of specimens with different  $Al_2O_3$  contents after crucible test

The corrosion area of the specimens with different  $Al_2O_3$  contents after the crucible corrosion test is calculated and given in Fig. 3. As can be seen, specimen A25 has slightly better corrosion resistance to hot aluminum than A40.



Fig. 3: Corrosion area of specimens with different  $Al_2O_3$  content after crucible test

The section photos of specimens with different  $Al_2O_3$  contents after immersion corrosion are shown in Fig. 4. Specimen A40 has collapsed to a mixed lump; A25 is better than A40 but is also seriously corroded. A65 is slightly corroded and A80 is not corroded at all. Therefore, the corrosion resistance results obtained by the two testing methods are consistent.



Fig. 4: Section photos of specimens with different  $Al_2O_3$  contents after immersion corrosion in hot aluminum

Specimens A25 and A40 contain fused silica and chamotte in their formulations, so they have more free  $SiO_2$  and  $3Al_2O_3 2SiO_2$ . When they meet hot aluminum in high temperature, Al reacts with  $SiO_2$  and  $3Al_2O_3 2SiO_2$  as follows and get worse resistance to Al hot metal.

$$\begin{split} 3SiO_2 + 4Al(l) &= 2Al_2O_3 + 3Si(s) \\ 3(3Al_2O_3\ 2SiO_2) + 8Al(l) &= 13Al_2O_3 + 6Si(s) \end{split}$$

The microstructure of specimen A25 after crucible test is shown in Fig. 5.

As observed from Fig. 5(a), the corroded specimen can be divided into an aluminum residual layer, a reaction layer, a penetration layer, and an original layer. The EDAX results show that the residual aluminum layer is composed of Al 45.35%, Si 42.22%, and Zn 8.65% by mass. Compared with alloy 7075#, Mg disappears, Si content increases greatly, and Zn content remains.

The EDAX result (shown in Fig. 6) of Fig. 5(b) indicates that a spinel rich area exists in the reaction layer. When hot aluminum penetrates into the castable, Mg and Al in the melt react with SiO<sub>2</sub> in the castable forming MgO and Al<sub>2</sub>O<sub>3</sub>, while SiO<sub>2</sub> is reduced into Si. Subsequently, MgO reacts with Al<sub>2</sub>O<sub>3</sub> in the castable or the formed Al<sub>2</sub>O<sub>3</sub>, forming spinel.

Fig. 5(c) shows the corrosion state of the quartz particles in the reaction layer. Although the quartz particles show their shapes remained,  $SiO_2$  has reacted with Al forming  $Al_2O_3$  and is replaced by the formed  $Al_2O_3$ .

In Fig. 5(d), the quartz particles in the penetration layer are being partly corroded by the hot aluminum and the margins of the particles are not clear.

In Fig. 5(e), Al and Si phases link together in the penetration matrix

Fig. 5(f) is the microstructure of the original layer. The quartz particles show clear and the original shapes.



Fig. 5: SEM photographs of specimen A25 after crucible corrosion test



Fig. 6: EDAX of microzone R in Fig. 5(b)

The microstructure of specimen A40 after crucible corrosion test is shown in Fig. 7. Similar with A25, a spinel rich area exists in the boundary between the reaction layer and the aluminum residual layer. There are large amounts of Al and formed Si in the reaction layer.

As shown in Fig. 7(a), the chamotte particles are relatively complete in the reaction layer.

The chamotte particles in the reaction layer were enlarged in Fig. 7(b). Quartz and mullite get penetrated by hot aluminum: SiO<sub>2</sub> in quartz and mullite reacts with Al, forming Si and Al<sub>2</sub>O<sub>3</sub>.

As observed in Fig. 7(c), three layers form after the chamotte particles are corroded: the outer layer is composed of the formed Al<sub>2</sub>O<sub>3</sub>, glass phase and metal Si (Fig. 7(d)); the middle layer is basically chamotte with loose structure (Fig. 7(e)); the inner layer is the original chamotte.



reaction layer



(c) Chamotte particles in penetration layer

(d) Outer layer of chamotte particles in penetration layer



(e) Middle layer of chamotte particles in penetration layer

Fig. 7: SEM photographs of specimen A40 after crucible corrosion test

The microstructure images of specimen A80 after crucible corrosion test are shown in Fig. 8. Since it has low SiO<sub>2</sub> content, the corrosion is slight: a spinel rich area is observed 0.5 mm away from the surface. However, the spinel rich area is dense so it can impede the penetration of hot aluminum into the interior of the castable.



Fig. 8: SEM photographs of specimen A80 after crucible corrosion test

#### Effect of Heat Treating Temperature on Corrosion **Resistance to Hot Aluminum**

Cross section photos of specimens A80 treated at different temperatures are shown in Fig. 9. The test specimens treated at 110 °C and 800 °C respectively have no obvious difference for the hot Al corrosion. The specimen treated at 1100 °C has loose structure as the hydration products of cement decompose and the it is not sintered, resulting in a poor corrosion resistance to hot Al. The specimen treated at 1400  $^{\circ}$ C shows better corrosion resistance because it relatively dense by sintering.



Fig. 9: Section photos of specimen A80 treated at different temperatures after corrosion by immersion in hot aluminum

As discussed above, the corrosion of hot aluminum to high alumina castable is expressed as follows: the hot aluminum wets the castable surface first and then penetrates along the pores to the interior of the castable; the active components Al and Mg in the melt react with quartz and mullite in the castable forming Al<sub>2</sub>O<sub>3</sub> or spinel which damages the structure of the specimen. The active Mg reacts firstly with quartz and mullite forming MgO which reacts with Al<sub>2</sub>O<sub>3</sub> further to form a spinel rich area near the surface. The spinel rich area restrains the further penetration to high alumina Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based castables.

#### CONCLUSIONS

(1) As the Al<sub>2</sub>O<sub>3</sub> content increases, the corrosion resistance to hot aluminum of Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based castables is improved remarkably. The castables with fused quartz and mullite show poor resistance to hot aluminum. When the Al<sub>2</sub>O<sub>3</sub> content increases to 80%, the castables show much better corrosion resistance to hot aluminum.

(2) The Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based castables with 80% Al<sub>2</sub>O<sub>3</sub> content heat treated at temperatures below 800 °C have no obviously difference of corrosion resistance to hot aluminum. While castable specimen treated at 1100 °C indicates poor corrosion resistance. However, when the treatment temperature rises to 1400 °C, the castable specimen is relatively dense by sintering, obtaining better corrosion resistance than that at 1100 °C.

(3) When the aluminum melt penetrates into the interior of the specimen, Al and Mg in the melt react with quartz and mullite in the castables, leading SiO<sub>2</sub> into Si, and Al and Mg oxidized into  $Al_2O_3$  and MgO. MgO further reacts with  $Al_2O_3$  forming spinel thus damaging the structure of the specimen.

(4) For Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> based castables with high alumina content, the spinel rich layer is relative dense, preventing the further penetration of the hot aluminum.

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