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Alumina Silica Brick Corrosion by Different Aluminium Alloys

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Abstract

In the last few years two major trends can be observed in the secondary aluminium industry.
On the one hand the producing companies were obliged to reduce their production costs of standard Al-alloys by increased use of external low quality aluminium scraps.
On the other hand the production-boost of high-alloyed Al-alloys typically used in the automotive industry and the aircraft industry but also in military and space applications provides new operation situations.
The aim of this work is to investigate the infiltration and corrosion mechanism of refractories exposed to melts during the melting process of aluminium alloys by means of chemical and mineralogical characterization of provided used brick samples as well as of samples from laboratory corrosion tests.

Introduction

The new market-requirements in the secondary aluminium industry, namely price-reduction but high quality of the different Al-alloys have induced a significant complexity- increase of the process- and productions conditions at the customer. Today yield increase and reduction of the production cost through the increment of aluminium scrap from standard 30% to currently 95% are the new customer goals. To melt this type of aluminium scrap economically in compliance with the regulations of environmental protection the existing melting furnaces have been modernized and new multi chamber melting furnaces with powerful combustion systems have been built. These new production facilities raise the melting temperatures and metal output which results in severely increased load on the refractory lining.

Based on the experience acquired through post-mortem studies carried out on used bricks from aluminium melting furnaces [2,3] together with practical knowledge from laboratory-trials,[1, 5] appropriate refractory product selection for these applications can be made.

Several standard testing methods are used in the laboratory such as the aluminium cup- test and full immersion in order to reflect, as well as possible, the production conditions at the customer. All these tests together with microscopic analysis enable a interpretation of the corrosion mechanisms of the tested refractory specimens
.
In addition for a correct interpretation of the corrosion mechanisms on refractory materials by molten aluminium alloys during operation of melting furnaces at the customer it is necessary to take into account the combination of a lot of further factors.

Experimental Procedure

For testing of unused refractory samples, namely brick and monolithic samples, standards and a new laboratory methods are used at RHI´s Technology Center Leoben.

Full Immersion Test

During this test, refractories samples with a dimension of 25x25x51 cm³ are totally immersed in a 3,5 kg high alloyed aluminium melt at a temperature range of 850°C to 890°C for 96 hours in a silicon carbide crucible (see figures 1 and 2)

This test contemplate only the infiltration and corrosion reactions of refractory specimens under the molten metal line of the Al-alloy bath but do not take into account the reactions in the transition zone, between Al-metal bath surface + alkalis and refractories. After the test with 5% Mg- metal, the spinel formation is the most known corrosion reaction of a high alumina brick.

The full immersion test device allows the addition of Mg- metal during the run phase in order to increase the corrosion conditions, without oxidation and/or generation of corundum phases.

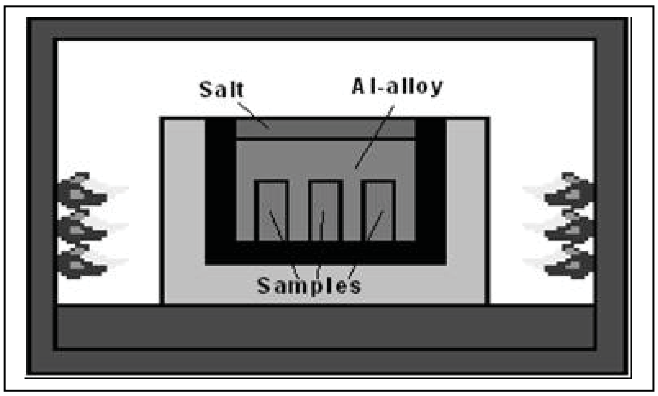


Fig.1. Full immersion test set up

Fig.2. Bauxite brick sample cross section after testing at 850°C/ 96h. No visible infiltration & cracks

Cup Test

The cup test is another used standard test, namely the aluminum cup infiltration test at 950°C, 72h with following parameters:
Cup dimensions 80 x80 mm square and min. 64mm height with a hole 54 mm diameter and 45 mm depth.
A cylinder of the testing Al-alloy (diameter 49.5 mm and 30 mm height) is placed inside the cup hole and covered with the salt mix (45% Na-Cl+45% KCl+10%NaF). Then the cup is closed with a lid to avoid oxidation.
The filled cup is then placed in the furnace at 950°C, for 72 h and after cooling down cut to measure the infiltration depth.

The salt mix proportions and composition can be changed according to customer requirements.

The aluminium cup test is performed to provide an initial impression of the brick behaviour, in contact with a specific Al-alloy. The cup test shows normally unsatisfactory results, in high- alumina refractory bricks without clear infiltration and corrosion differences between the tested specimens after the measurement of the cup. (see figures 3 and 4)

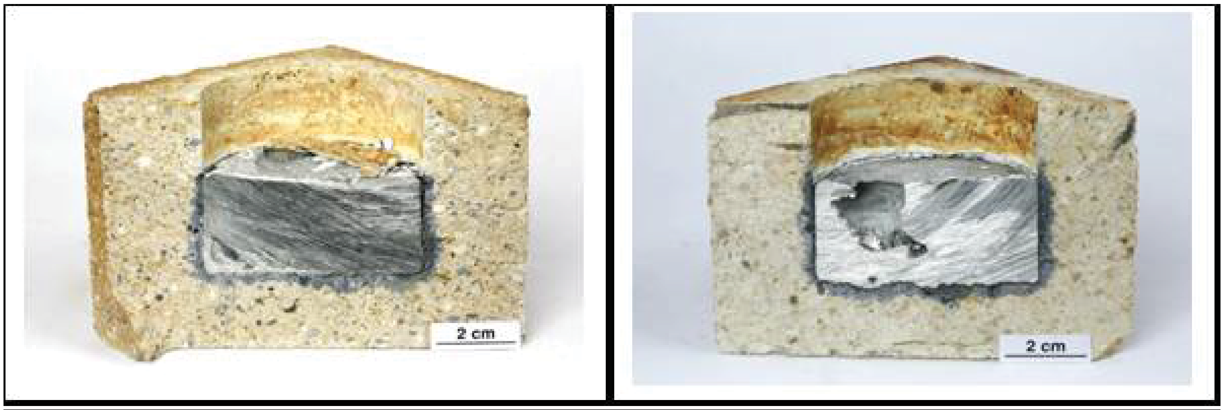


Fig.3. and Fig.4. Bauxite bricks after testing aluminium alkali- cup infiltration test 950°c/ 72 h with Al-alloy AZ8GU and a salt mix. (45% Na-Cl+45% KCL+10%NaF), Visible reaction-zone in both bauxite- brick cups with a infiltration value between 1,0 to 1,5 mm.

For identification of the corrosion mechanisms usually both tests complement one another and are carried out for evaluation.
However, these testing methods are time consuming and shows limitations, regarding their ability to reproduce comparable results of the corrosion mechanisms in service life time as well as direct comparison of the used materials.

To improve the corrosion-statements obtained from cup test and from full-immersion test, new dynamic testing methods *"Finger immersion method"* similar to the used method for testing refractories against in glass-melts will be performed.

<u>Finger immersion method</u>

The new finger Al- immersion test cis carried out in a silicon- carbide-crucible -(90%-SiC) with wall thickness 50 mm inner diameter 170 mm, depth 220 mm, total height 250 mm and a capacity of approx. 8 Kg. melted Al-alloy. This test allows to compare at the same time 5 different specimens under two different chemical- and physical-conditions.[2] (see figure 5 &6)

Every finger with the dimensions 200 x 30 x30 mm^3 is exposed to t the corrosion of upstream dissolved alkalis salts (45% NaCl+ 45% KCl+10% NaF) of the transition zone as well as below the metal line where the Al-alloy bath is enriched in Mg- Zn-among other metals.

The alkalis salts with a quantity of 400 g. /10 h. have a double function, on the one hand to cover the Al-alloy bath and on the other hand impede the corundum formation in the transition zone like as in operation. [5]

In order to see the two typical corrosion zones a aluminum immersion finger test at 850°C/ 48 h with the Al-alloy (see table1) and the salt mix (45% NaCl + 45% KCl+ 10% NaF) has been carried out.

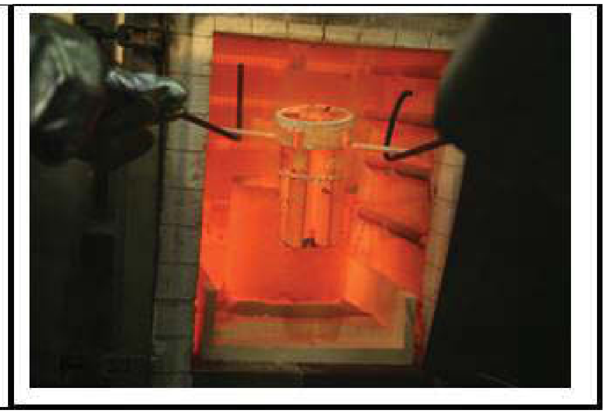


Fig.5. Silicon carbide crucible during the alkali salt input. Fig 6. Retainer with 5 fingers after 48 h. end of test

Analytical Procedures

Chemical Analysis and Mineralogical Investigation

Investigated materials are bauxite bricks with chemical ceramic bonding systems. The chemical analyses are carried out using X-ray fluorescence analysis (Bruker S8 TIGER), after dissolution of the sample in $Li_2B_4O_7$ (according to DIN 51001) as well as on the original sample. Additionally, mineralogical investigations are performed on polished sections using a reflected light microscope, X-ray diffraction (Bruker D8 ADVANCE), and a scanning electron microscope (JEOL JSM-6460) combined with an energy- and wave-length dispersive X-ray analyser.

Macroscopic Evaluation

A representative bauxite brick- sample of the finger immersion test was chosen for macroscopic evaluation of the infiltration behaviours after the cut cross sections but also microscopic investigations the same sections were carried out by X- Ray diffraction and SEM. (see figures 7 and 8)

Fig.7. Bauxite brick finger after Al-immersion test

Fig.8. Bauxite brick finger Macroscopic detail.

To obtain the real conditions during corrosion testing, initially a complete chemical characterization is carried out on used Al-alloys samples (see Table 1)

Table 1 Chemical composition of the Al-alloy (wt%).

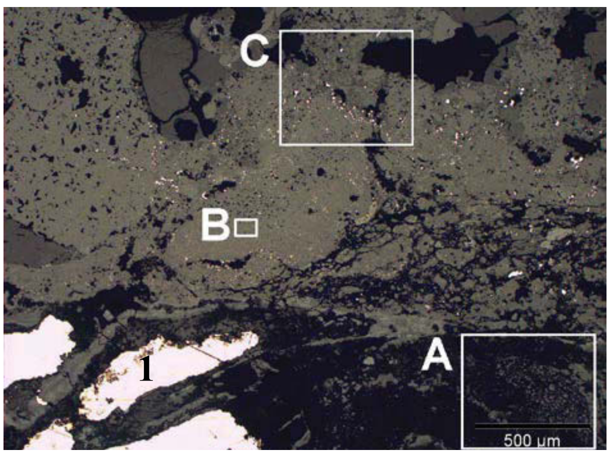
Si	Fe	Cu	Mn	Mg	Cr	Zn	Zr+tTi	Al
0,4	**0,5**	**1,2-1,9**	**0,5**	**4,5-5,5**	**0,05-0,25**	**7,2-8,4**	**0,25**	**rest**

<u>Microstructural Investigation</u>

The results of a microstructural investigation performed after testing a bauxite brick are shown in Figure 9. The brick microstructure at the immediate finger hot face shows a loosening and disaggregating of the bauxite- matrix directly in contact with the Al-alloys and. See figure 10 SEM photo and table 2 EDX analysis of the metal phase 1.

Table 2: EDX analysis of metals (1) by (wt%).

Fig	Spot	Na	Mg	Al	P	Ca	Ti	V	Cr	Cu	Zn
10	1			92,4					0,3	1,4	5,7



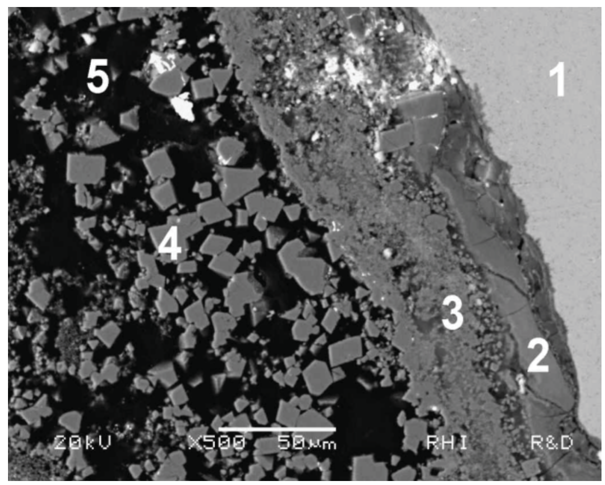
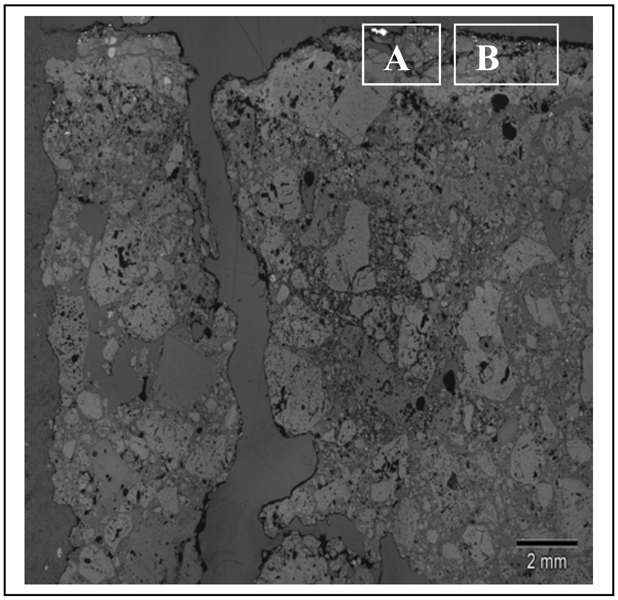


Figure 9. (left side) shows the hot face of the finger in contact with Al-alloys (1).
Figure. 10 (right side): in detail (area A) shows the reaction zone between 1 = Al-Zn alloy with 2 = corundum causing the formation of MA spinel, 3 and 4; Point 5 = resin.

A reaction zone was clearly visible in the Figures 9 and 10. Below the reaction zone an infiltrated and corroded brick microstructure was observed (see Figure 10). In the infiltrated brick microstructure, corrosion of the bauxite main component corundum had taken place. As observed in used brick samples from post mortem studies the main reaction product was MA-Spinel.

The alkali salts represented by a Na+ K chlorine phases promote the Mg & Al-metal transport but also the infiltration and reaction between the Al-alloy and the matrix inherent components [3] Due to these diffusion phenomena, the mineral corundum but also mullite as main component of bauxite reacted to form secondary MA Spinel precipitations (see figure 10 points 3 & 4).



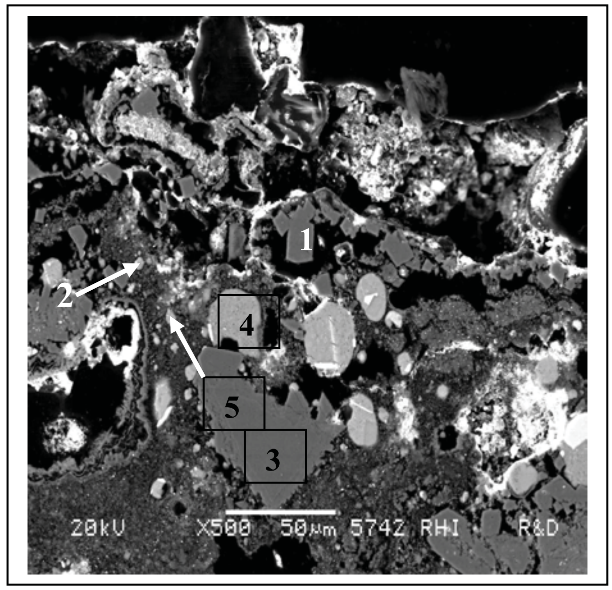
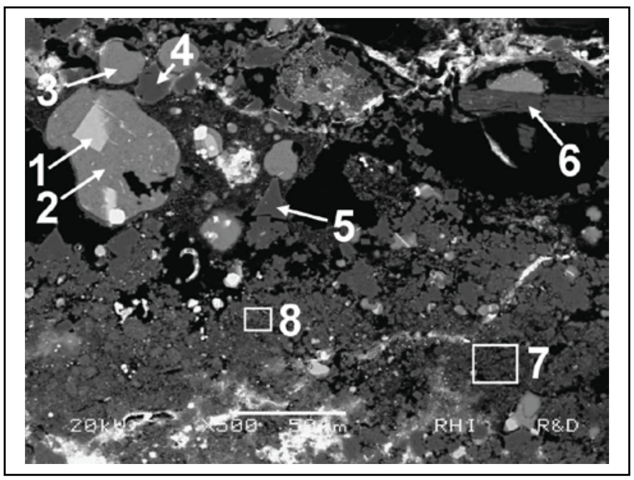


Figure 11. (left side) shows a crack on the hot face and of the finger after the immersion test.
Figure 12. (right side): in detail (area A) from Fig.11 Point 1& 2 = MA-Spinel; 3 = Alumina; 4= Al-Si- Zn metal; 5 = MA Spinel mix phase with K and Cl.



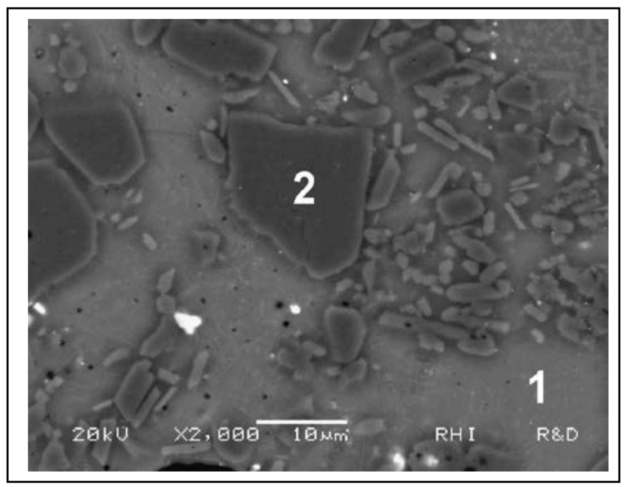


Figure 13. (left side) shows in detail (area B) of Fig 11.
Figure 14: (right side): in detail (area 8) 1 = Alkali-Al-Mg-phosphate-rich phase surrounding alumina = 2.

Table 3: EDX analysis by (wt%) of fig.13.

Fig.	Area or spot	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	Fe_2O_3
		%	%	%	%	%	%	%	%	%	%
13	4		28,6	71,4							
	5		29,6	70,4							
	6	2,5	1,7	79,3			10,9	3,9	1,8		
	7		67,6	12,1	14,5		2,3	1,2	0,7	1,6	
	8	1,7	24,0	43,58	8,3	14,32	2,3	0,6		1,2	3,9

Figure 13. spots 4 & 5 = MA-spinel; 1, 2 & 3 = Al-Si – metal; 6 = Alumina with K –and Na-chloride; 7 = MA- Spinel mix phase with K-chloride.

Discussion

Different refractory materials were tested for comparison to post mortem studies in order to evaluate wear and identify corrosion mechanism. Every sample was investigated at bath level (melt - salt - refractory interface) as well as below bath level (fully Al-melt-immersed refractory).
However corrosion phenomena coupled with the production activities at customer are very difficult to be reflected also by dynamic finger immersion laboratory tests.
For a correct interpretation of the typical main corrosions mechanisms of the secondary aluminium metallurgy in the most important furnaces zones, the combination of further influencing factors have to be considered, like:

Mayor factors of influence in the corrosion of refractory materials at the customer

- Characterisation of the leading Al-scraps namely: home scrap, inhouse scraps, external scraps [1]
- Composition & contaminations of the applied Al scraps in the Al-Alloys production.
- Percentage of the leading Al-scraps in melting process.
- Form and nature of the leading Al-scraps: bales, ingots, briquettes, chips, etc.
- Manner of feeding the Al-scraps in new lined aluminium melting furnaces.
- Al-alloy composition and amount of Mg-or other light metals.
- Al-alloy temperature (depending of the burner type heating up to 1200°C but also hot- -spots-temperatures >1200°C during Mg-metal alloying or in areas exposed to radiation of the flame.)
- Deepness of the Al-alloy bath, flow and circulation (bigger furnaces)
- Alkali bearing salt contents and its composition (increasing alkalis salts for melt homogenisation)
- Full immersion of the refractory products (refractories corrosion under bath or metal line)
- Partial immersion of the refractory products (refractories corrosion in the transition zone-gas-+ alkalis+ metal-bath)
- Furnace atmosphere + local atmospheric changes.
- Refractory main components, chemistry, grain size distribution and bonding system/s.
- Addition of non-wetting agents. pros and cons to this agents. [5]
- Shape of the tested or used bricks and position in the furnace, etc.

Conclusions

The combination of different test methods enable the best possible understanding of chemothermal brick wear on a pilot scale. The new finger test is a dynamic testing method which combines the advantages of the aluminium immersion test and the aluminium cup tests with an extension of the corrosion surface of the tested specimens but also an increase of the amount of melted Al-alloys.

The microscopical SEM investigation shows in case of direct contact between the Al-alloys, alkali –salts and the brick finger a loosening and disaggregating the microstructure of the refractory bauxite.

The precursor alkali- chloride- containing phases which serve as transport media of metals but also during the infiltration lead to the formation of MA- spinel and are additionally responsible for the mullitic- and corundum matrix corrosion in the brick texture.

The chemical bonding (phosphate phase) is fully transformed to $(Na,K,Mg)x(Si,Al)y(PO_4)Cl$. [6]
The ceramic bonding system is corroded in a second step: fine grained matrix corundum, but also coarse-grained mullite is corroded and transformed to nepheline, or sodalite.

These facts have shown an approach to the customer production process with a better understanding of the corrosion mechanisms of the refractory material used in the secondary aluminium industry.

Based on these research results and specific operation process knowledge from the customer, new brick developments were performed for appropriate lining solutions in different positions of the aluminium melting furnaces.

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