ELEMENTS OF REFRACTORY CORROSION IN SECONDARY ALUMINIUM MELTING FURNACES

ELEMENTI KOROZIJE VATROSTALNOG OZIDA PRILIKOM PRETAPANJA SEKUNDARNOG ALUMINIJUMA

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ABSTRACT

The mechanisms of refractory corrosion in secondary aluminium melting furnaces are discussed. There are three main, internally effected types of corrosion: (i) chemical, (ii) structural and (iii) physical; as well as three externally effected types of corrosion induced by: (i) thermal stress, (ii) mechanical stress and (iii) electrical power.

Chemical corrosion occurs by redox process which destroy oxides of the refractory wall into elemental metal which forms impurity to the molten mass. Heterogeneous structure of refractory sur/interface can cause corrosion of the refractory wall, too. Physical corrosion occurs with penetration of molten mass, dissolution of solid and precipitation of new products.

Thermal shock resistance dictates refractory performance on corrosion. Thermal stress of the refractory leads to the crack nucleation and/or propagation resulting in loss of strength. Also, the mechanical stress, e.i. the action of rotation in tilting rotary furnace, can be a reason of refractory wall corrosion. Similarly, higher specific electrical power of induction furnace can accelerate the corrosion.

The practical ways of avoiding corrosion of refractory wall are presented. In that sense, the influence of additives as well as protective coatings on corrosion resistance of aluminosilicate refractories is discussed.

Key words: refractory corrosion, secondary alluminium, melting furnaces

IZVOD

Razmatrani su mehanizmi korozije koji se javljaju u vatrostalnom ozidu prilikom topljenja aluminijuma. Postoje tri nezavine vrste korozije: hemijska (i), strukturna (ii) i fizička (iii), koje su posledica unutrašnjih uticaja, kao i vrste korozije izazvane spoljnim

delovanjem, kao što su: korozija izazvana temperaturskim naprezanjem (i), mehaničkim naprezanjem (ii) ili električnom energijom (iii).

Do hemijske korizije dolazi tokom redukcionih procesa u toku kojih dolazi do razaranja oksida koji su deo vatrostalnog ozida do elementarnog metalnog oblika, čije formiranje dovodi do onečišćavanja tečnog metala. Heterogena struktura vatrostalnog ozida, i granice faza tečan metal/vatrostalni ozid takođe može dovesti do korozije. Fizička korozija se javlja prilikom penetracije rastopa, razaranja vatrostalnog ozida i kada dolazi do pojave novih produkata kao posledice razaranje ozida.

Otpornost vatrostalnog ozida na termošok utiče i na njegovu koroziju. Temperaturska naprezanja u ozidu dovode do pojave i rasta prkotina, što dovodi do smanjenja čvrstoće ozida. Takođe, i mehaničko delovanje, kao što je okretanje rotacione peći, može dovesti do korozije vatrostalnog ozida. Na sličan način, i povećanje specifične električne snage u indukcionim pećima može ubrzati koroziju vatrostalnog ozida.

U radu su predstavljene praktične mogućnosti izbegavanja pojave korozije vatrostalnog ozida. U tom smislu razmatrani su i uticaji aditiva kao i zaštitnih premaza na otpornost alumosilikatnih ozida prema koroziji.

Ključne reči: korozija vatrostalnog materijala, sekundarni aluminijum, peći za topljenje

1. INTRODUCTION

Cost and price of the secondary aluminium and aluminium alloys greatly depends on the losses of the refractory during production. Choosing the appropriate refractory material for engineering applications involving extreme thermal, mechanical and chemical environments could be based on the different principals: heat transfer, fracture mechanics, thermal and mechanical properties, chemical, corrosion, thermodynamic and others.

In this paper, only corrosion aspect involving different mechanisms are presented. So, the mechanisms of refractory corrosion in secondary aluminium melting furnaces are classified as three main internally effected types: (i) chemical, (ii) structural and (iii) physical; as well as three externally effected types, induced by: (i) thermal stress, (ii) mechanical stres and/or (iii) electrical power.

Aluminosilicate refractories have been widely employed in the aluminium industry. Their common application is for lining of the furnaces used for holding and melting aluminium alloys. These materials exibit good mechanical properties at the service temperature and good thermal shock resistance, they are also inexpensive and widely aviable. Such trefractories, however, degrade via the reaction with molten aluminium alloys due to the strong reducing effect of aluminium.

The conversion of aluminosilicate refractories, also referred to as corrosion, can cause several problems, such as a sharp decrease in the mechanical properties of the refractory, contamination of molten bath, aluminium loss, and

enormous heat loss due to undesirable higher thermal conductivities of corroded refractory.

2. CRITERIA FOR REFRACTORY SELECTION

The main criteria used for the characterization of refractory bricks are: (1) refractoriness, (2) chemical composition, (3) bulk density and specific gravity, (4) porosity and water absorption, (5) linear expansion, (6) consistence of volume, (7) accuracy of shape, dimensional tolerance, (8) mechanical strength and resistance to abrasion, (9) gas permeability, (10) specific heat and thermal conductivity, (11) insulating property, (12) electrical resistivity, (13) spalling resistance, (14) refractoriness under load, (15) resistance to slags, (16) resistance to oxidation and reduction and (17) resistance to hydration.

No refractory brick combines all these properties in the best possible way. In service, refractory bricks are first of all subjected to thermal stress. In addition, mechanical and chemical attacks occur quite often. The relative operation stress, which the refractory material will have to withstand, determines the extent of wear and thus the service life. Table 1. gives the decisive operational factors, in order to make a proper choice of suitable refractory materials prior to their application.

Whereas the selection of proper refractory is comparatively easy in the case of thermal stress only, considerable difficulties arise as soon as mechanical stress and chemical stress accompany thermal stress.

Additionally, in secondary aluminium melting furnaces we have the mixed scrap of all kinds, with specific interaction to refractories and slags. Note that melting furnaces in the secondary aluminium industry melt mixed and contaminated scrap, often containing ferrous inserts, oil, paint and other organic and inorganic contaminants. As illustration, the Table 2. [5] describes the types of scrap (where possible, the ISRI international classification) and gradings versus percentage metal recovery for different secondary aluminium melting furnaces.

Table 1. Suitability of refractory materials for selection [1]

Operation effect on refractory materials during application	Properties of refractory bricks to be considered optionally
THERMAL STRESS caused by:	
- Types of Furnace	Refractoriness
- Size of Furnace	Refractoriness under Load
- Temperature	Load Bearing Capacity

- Distribution of Temperature in Furnace	Consistence in Volume
- Supply of Temperature per Time Unit	Thermal Expansion
- Decline of Heat in Brickwork	Spalling Resistance
- Stored Heat, Transition of Heat	Thermal Conductivity
- Intermittent or Continuous Operation	Specific Heat
- Point of Application of Refractory Material:	Bulk Density
Heated on all sides or one side only	
Pressure of load or tension	
MECHANICAL STRESS caused by:	
- Furnace Construction, Fixed or Tilting	Cold Crushing Strength
- Physical Properties of the Charge	Resistance to Abrasion
- Travel of the Charge inside Furnace	Texture and Embedding of Grain
- Speed of Combustion Gases	Total Porosity
- Proportion and Composition of Flue Dust	
- External Mechanical Influences	
(e.g., manner of charging and discharging, vibration, deformation of furnace)	
CHEMICAL STRESS caused by:	Chemical Composition
- Furnace Atmosphere	Distribution of Different Size Pores
- Products of Combustion	
- Combustion Residues	Gas Permeability
- Chemical Composition of Charge	Resistance against Slags, Fluxes, Gases and Vapours
- Chemical Composition of Reaction Products	
- Possible Influence by Air, Humidity and Stream	

Table 2. Gradings vs percentage metal recovery for different secondary aluminium melting furnaces [5]

GRADE OF SCRAP	ISRI	NOTES	REVERB WET HEARTH	REVERB DRY HEARTH	REVERB COMB. WET&DRY	REVERB PUMP MULITWELL	ROTARY FIXED AXIS	ROTARY TILTING	CRUCIBLE
CAST	TENSE	A	1:90	2:89	1:90	1:92	1:92	1:92	1:92
WROUGHT	TAINT/TABOR	A	1:90	2:89	1:90	1:92	1:92	1:92	1:92
MIXED C&W		A	1:87	2:89	1:87	1:92	1:92	1:92	1:92
LOW Fe SCRAP	IRONY/TENSE	B	1:85	1:85	1:85	1:85+	3:85	2:85	4:-
HIGH Fe SCRAP	IRONY/TENSE	C	4:-	1:30-80	1:30-80	1:30-80	4:-	3:30-80	4:-
NEW SCRAP	TOUGH	D	1:92	2:90	1:92	1:93+	1:93+	1:93+	1:93+
PROFILES			1:92	2:90	1:92	1:93+	1:93+	1:93+	1:93+
PAINTED			1:90	2:88	1:90	1:92+	1:92+	1:92+	1:92+
OILY SWARF	TELIC	E	4:-	4:-	4:-	1:90+	1:90+	1:90+	1:90+
LITHO	TABLET		4:-	4:-	4:-	1:90+	1:90+	1:90+	1:90+
UNTREATED UBC	TACLRED	F	3:60	4:-	3:60	1:95+	1:90+	1:90+	1:90+
DROSSES			4:-	4:-	4:-	4:-	1:30-70	1:30-70	4:-
SHREDDED	TWITCH		3:80	3:78	3:80	1:92+	1:92+	1:92+	1:92+
REMELT INGOT	THROB		1:95+	1:95+	1:95+	1:98+	1:98+	1:98+	1:98+

Gradings	NOTES
1 = Excellent 2 = Good 3 = Adequate 4 = Unsuitable	A= Scrap free from Iron Max 2% B= Scrap with some iron at low levels, Average 5%, Max 10% C= Scrap with Iron above 10%, can be up to 75%. Including Transmissions (N.B. Recovery with this grade of scrap is proportional to Iron Content) D= Single Allow, New Production E= Assumes swarf has been dried and Iron removed F= Assumes shredded and de-lacquered through a kiln

3. INTERNALLY EFFECTED CORROSION

These fundamental types of corrosion occur on molten aluminium / solid refractory interfaces. On micro scale, various processes may cause resistance to overall reaction occurs at liquid-solid interface. For an element of single pore between two grains of polycrystalline refractory surface, Figure 1., one can visualize: (i) *Liquid metal film resistance.* Reactants diffuse from the main body of the liquid metal to the exterior surface of solid refractory specimen. (ii) *Pore diffusion resistance.* Reactants move through the pore into the refractory. Most of the reaction takes place within the pore. (iii) *Surface phenomena resistance.* At some point in their wandering reactant molecules become associated with the surface of refractory. They react to give products which are then released to the liquid phase within pore. (iv) *Pore diffusion resistance for products.* Products then diffuse out of the pore. (v) *Liquid metal film resistance for products.* Products then move from the mouth of pore into the main liquid stream. (vi) *Resistance to heat flow.* For reactions accompanied by heat release or absorption the flow of heat into or out of the reaction zone may not be so fast enough to keep the liquid metal/solid refractory specimen isothermal. If this happens the specimen will cool or heat, strongly affecting the rate. Thus the heat transfer resistance across the liquid film or within the refractory could influence the rate of reaction.
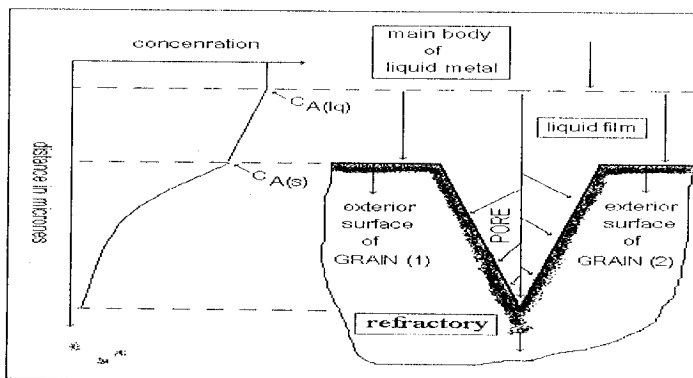

Figure 1 - Phenomena around an element of single pore between two grains at refractory surface

Note, in this simple description, the micro scale phenomena are consideration.

3.1. Chemical corrosion

Chemical reactions at liquid metal/polycrystalline refractory interface are complex. To explain the action of polycrystalline surface it is thought that reactant molecules of liquid metal are somehow changed, energized, or affected to form intermediates in the regions close to the surface. In one theory the intermediate is viewed as an association of a reactant molecule with a region of the surface, in other words the molecules are somehow attached to the surface. In another theory molecules are thought to move down into the liquid metal close to the surface and be under the influence of surface forces. In this view the molecules are still but are nevertheless modified. In still a third theory it is thought that an active complex, a free radical, is formed at the solid surface. This free radical then moves back into the main liquid stream, triggering a chain of reactions with fresh molecules before being finally destroyed. In the contrast with two theories, which consider the reaction to occur in the vicinity of the surface, this theory views the surface simply as a generator of free radicals, with the reaction occurring in the main body of liquid metal.

On the other hand, in order to obtain knowledge of the reactivity, it is very important to respect the changes of the standard free energy for the formation of oxides against temperature, Table 3. From these thermodynamic data, when metal (Al) is placed in contact with oxide refractory, we are able to predict whether the metal can decompose the refractory to form its oxide.

Table 3. Values of free enthalpies of formation for various oxides
   $(- G^o{}_T = RT \cdot lnpO_2)$

Oxide	at 660 °C kJ	At 850 °C kJ	At 1000 °C kJ
CaO	-1070	-1040	-1010
MgO	-1020	-976	-942
BaO	-942	-900	-871
Al_2O_3	-921	-879	-850
TiO_2	-741	-699	-678
SiO_2	-699	-670	-640
FeO	-410	-385	-364

The degradation of aluminosilicates by aluminum attack has well been known. When alloying elements such as magnesium and zinc are present in molten aluminium, this deterioration is more pronounced. Brondyke [1] reported that liquid aluminium reduces silica and its bearing constituents of aluminosilicate refractories (e.g., mulite), see Figure 2.

The silica and silicates in refractory are reduced to element Si and metallic Al becomes aluminium oxide. Al acts as a strong reducing agent. The rate of attack depends on silica content of refractory, transport of several elements, free enthalpies of oxide formation and temperature. Table 3. shows the values of free enthalpies of formation at various temperatures for oxides dominating in refractories. All oxides listed above Al_2O_3 cannnot be reduced by Al as their values of free enthalpy are lower than for Al_2O_3, whereas the oxides below Al_2O_3 can be reduced by Al.

The process of chemical corrosion involves coming into contact of reactants for starting of reaction, and moving away of the products formed for reaction to continue. For the first step, physical texture, microstructure and composition plays important role. For the second step, characteristics of the melt and reaction products determine the rate.
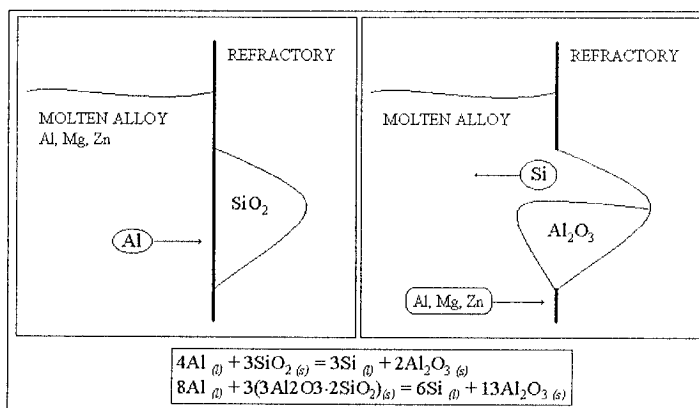

$$4Al_{(l)} + 3SiO_{2\,(s)} = 3Si_{(l)} + 2Al_2O_{3\,(s)}$$
$$8Al_{(l)} + 3(3Al2O3 \cdot 2SiO_2)_{(s)} = 6Si_{(l)} + 13Al_2O_{3\,(s)}$$

Figure 2 - Schematic diagram of molten aluminium alloy attack on a silica containing refractory

The refractory wall is made of granular materials and contains grains, variety of pore shapes and sizes, mineralogical species corresponding to overall composition. When refractory comes in contact with melt, there may be reaction between two. If refractory is not homogeneous, various simultaneous reactions occur and forms low melting products. These products in turn react with the melt.

3.2. Structural influenced corrosion

Refractory properties depend on composition, structure and phase distribution. Phase distribution depends on manufacturing technique, raw materials used, phase equilibrium relation, kinetics of phase changes, sintering and grain growth.

The refractory wall contains well sintered large and small grains withsome pores at interfaces. Pores may be open or closed type. Open pores directly affect properties such as permeability, vacuum tightness and surface available for

catalytic reactions and chemical attack, whereas closed pores have little effect on those properties. The mechanism of penetration of molten mass is favorable in the capillary when large amounts of pores are greater than 0.05 µm.

For aluminium industries, the used refractories contain mainly Al_2O_3 and SiO_2, some impurities like Cao, MgO, Na_2O and K_2O which reduce the melting temperature depending upon their contents. Together with main oxides impurities form compounds, of which some have a rather low melting point. These compounds lead to premature sintering and as a result thermal stresses extended on refractories below the normal sintering temperature.

The aluminium melts at a temperature of $660°C$, but aluminium enriched with 11.7% of silicon melts at a lower temperature of $577°C$. Hence melt in direct contact with wall has much lower viscosity and penetrate deeper into wall where reaction with refractories continues and ultimately destroys the wall.

Refractory materials may have two sizes of porosity: large and small. The larger pores are always more difficult to get rid of, for two basic reasons. Firstly, simple kinetics dictates a longer time to fill a larger void by diffusion. Secondly, a large pore can be thermodynamically stable depending on the value of the dihedral angle and pore size(grain size ratio). For a given angle and pore size there is a critical grain size above which the pore is unstable (and cannot sintered).

According to Zhao and Harmer experimental evidence, the large pores do not readily disappear even when thermodynamics is permitting, verifying that kinetics, rather than thermodynamics, is determining factor in the pore size range.

3.3. Physical corrosion

When refractory wall comes into contact with any molten metal/slag, some of following phenomena may occur:

a)   penetration of molten material into the open capillary like pores of the body,

b)   dissolution of the refractory in the molten mass,

c)   precipitation of new solid.

Generally, the rate of dissolution in such system is controlled by mass transport (δ/D) in the liquid and/or heterogeneous phase boundary reaction ($1/k$). In simplified version, which ignores the motion of liquid near the interface, one can write:

$$j = \Delta C/[(1/k) + ((\delta/D)]$$

where: j - the flux density of dissolving species relatively to the phase boundary, D – the binary diffusion coefficient in the solution for exchange of solute and solvent, $\Delta C = (C^i_L - C^\infty_L)$ – the difference between the concentration

of the interface (i) and the bulk (∞), δ - the effective boundary layer thickness and k – the first order rate constant for the heterogeneous reaction at the interface.

Corrosion of oxides often occurs not by dissolution or evaporation of the oxide, but by the penetration of the solid by some or all the species from the fluid/molten Al. The liquid phase may be puled into the open porosity of the solid by capillary forces, and species from the fluid will diffuse down the grain boundaries and into the bulk of the solid /refractory wall. Such processes can cause deterioration of the solid by:

1) completely encasing a volume of the solid by the fluid phase,

2) causing either an expansion or contraction of the solid with the associated development of stresses and, ultimately, fracture, or

3) introduction of a species into the solid which causes the various properties to change adversary.

After the penetration of melt in the open porosity and subsequent reactions with the refractory mass, two types of situation may occur according to the viscosity of the local melt:

Case I. Melt that penetrates a pore will react with pore wall and the local melt composition might have a much higher viscosity. Then absorption rate will be smallest. The product will adhere to the pore wall and the thickness will increase with time, eventually reducing the absorption rate to zero. The result may vary with varying pore sizes since narrow passages may clogged easily.

Case II. If due to incongruent dissolution, the product formed have viscosity lower than that of the bulk then adsorption rate will be higher. Pores my be enlarged and since no precipitation may form, a somewhat faster absorption may occur.

According to Bikerman, the rate of penetration Q (g/s), of an uniform liquid with viscosity η, surface tension γ, sp. density ρ, into a number of uniform capillaries with a total cross section of S (cm^2), radius r(cm), after a penetration of t(s), is:

$$Q = S\rho[(\gamma r)(8\eta t)]^{1/2}$$

Slag attack, as applied to refractories, is normally by fusion occurring between the refractory and another chemical (usually an oxide) which acts as a flux, i.e. produces a reaction product having a lower melting range than the refractory itself.

In certain case of slag-refractory combinations if active flux does not wet the refractory surface then no reaction occurs between them. In many cases, the flux is drawn deeply into the pores of the refractory by capillary action and this has the effect of increasing the availability of active flux at the commencement of fluxing reaction.

4. EXTERNALLY EFFECTED CORROSION

For a sake of clarity, external thermal, mechanical and electric power acting on refractory are presented in form of Table 4, similarly to []. Althought, these are the primary stresses acting on refractories, fundamentally, the mechanisms of corrosion caused by these acting are the same as in internally effected corrosion situation.

Table 4. The primary stresses acting on refractories

THERMAL

METAL BATH	HEATING, EXOTHERMIC REACTIONS	DISCONINUOUS OPERATION	LADLE TILTING
INFILTRATION	TEMPERATURE LEVEL	THERMAL SHOCK	THERMAL FATIGUE

MECHANICAL

LADLE TILTING	MOVEMENT OF MOLTEN METAL	CHARGING	BRICKLAYING
MECHANICAL FATIGUE	EROSION	ABRASION, IMPACT, SHOCK	BRICKWORK, STRESSES

ELECTRICAL POWER

- CORELESS INDUCTION FURNACES -	- CHANNEL INDUCTION FURNACES -
COMPLEX CIKLIC MOVEMENT OF MOLTEN METAL IN CRUCIBLE	MOVEMENT OF MOLTEN METAL THROUGH THE CHANNEL
HEAT GENERATION IN MOLTEN METAL NEAR REFRACTORY WALL OF CRUSIBLE	HEAT GENERATION IN MOLTEN METAL NEAR REFRACTORY WALL OF CHANNEL

5. ADDITIVES AND PROTECTIVE COATINGS

Generally, there are two main practical ways of avoiding corrosion of refractory: (a) addition of additives in refractory material during its fabrication and (b) protective coatings on refractory wall.

It is generally believed that aluminosilicate refractories having less silica content, or higher $Al_2O_3SiO_2$ ratios, normally exibit a superior resistance to aluminium attack, however, this has not always been experienced in practice, indicating that other factors are also involved in the corrosion. Low contents of alkaline oxides (Na_2O and K_2O) were generally found beneficial since these oxides usually form low melting compounds with poor corrosion resistance.

Moreover, it has been patented [6] that specific additives, called nonwetting agents, can lower the wettability of aluminosilicate refractories by molten alumunium, and therefore, they enhance corrosion resistance. Materials such as aluminium borate, barium sulfate ($BaSO_4$), and calcium fluoride (CaF_2), or a combination of these have been used as nonwetting agents. These additives are proprietary of the refractory companies, and only the enhanced properties of the refractories containing them have been presented in the literature.

Little information has been published concerning the mechanism involved in the improvemennt of the corrosion resistance of refractories. Recently, the authors have suggested that in the aluminosilicate refractory castables containing $BaSO_4$, the formation of hexacelsian ($BaAl_2Si_2O_8$) could be one of the possible reasons for improved corrosion resistance. Hexacelsian forms on the firing of raw materials (refractory casables) containing $BaSO_4$ at $1000°C$.

Protective coatings are used for making the refractories impervious to the molten mass by filling the open porosity. It also makes the surface homogeneous and thus minimizes the abrasion and slag erosion. A satisfactory coating should have a low shrinkage and adhere well to lining so that no peeling or checking is observable on heating to the working temperature. The manufacturers' recommendation should be taken, because a coating that may work well with one type of refractory may not work at all with another, even though of very similar properties.

Coatings can be applied to the lining with a brush or with a sprey gun. Particular care should be taken that the lining surface is clear and free from dust before the coating is applied.

It has been observed that the coating has a limited durability. The refractory must be periodically re-impregnated.

Experience under industrial condition shows that, in some cases, the alkaline protection increases the life of refractories which have relatively short life. It may be assumed that this improvement is compesated by an increased slag formation, by the necessity for renewing the coatings, and perhaps by a risk of metal contamination.

6. CONCLUSION

As a consequence, several attempts have been focused to improve the resistance of these refractories to aluminium attack and penetration.

Durability of refractory used in secondary aluminium melting furnacescan can be increased by improving the stability of bonding mateials and oxides towards the liquid Al or its alloys to be processed. Application of thin and uniform alkaline coating on lining surface after few melting may heal up the cracks and pores. Using the furnace atmosphere with oxigen or with vacuum or using some types of layers etc. the outside oxide formation can be minimized.

By careful heating and not charging of liquid Al and/or Al scraps in cold furnace, the wall life can be increased.

Favorable refractory properties for melting aluminium and its alloys should be:

- high content of aluminium(III)-oxide in refractory
- low porosity and high density
- elimination or reduction of all conditions which increase the rate of diffusion

REFERENCES

[1] G. Gelsdore and K. Kreuels, Infiltration of aluminium into unshaped refractory, Interceram, 30(1981) 319

[2] B. Clavud and V. Jost, Refractiries used in melting furnace for aluminium alloys, Interceram, 30(1981) 306

[3] H.J.Heine, Refractories for metalcasting, Foundry M&T, Parts: I – IV, (1985)

[4] K.J. Brondyke, Effects of molten aluminium on alumina-silica refractories, J.Am.Ceram.Soc., 36(1953)171-174

[5] www.ttcfurnaces.com

[6] M. Allahevrdi, S. Afshar and C. Allaire, Additivers and corrosion resistance of aluminosilicate refractories in molten Al-5Mg, JOM, 50(1998)30-34

[7] J.Zhao and M.P.Harmer, Effect of pore distibution on microstructure decelopment: II part, J.Am.Ceram.Soc., 71(1988) 530

[8] F.T.Felice, Aluminium resistance refractory compositions, US patent 4,522,926(11 June 1985)

[9] A.D. Porterfield, Aluminium resistance refractory compositions, US patent 4,806,509(21 Feb 1989)

[10] Z.V.Popovic, J.Nonia, K.T.Raic, T.D.Volkov, The types of corrosion of refractory in coreless induction furnaces, Foundryman, 84 (1991)327-330.

[11] T.D.Volkov-Husovic, R.M.Jancic, Z.V.Popovic, K.T.Raic, Comparison of critical DT values with R parameter of thermally shocked alumina refractories, Interceram, 46 (1997)12-15.

[12] T.D.Volkov-Husovic, R. M.Jancic, Z. V.Popovic, K. T. Raic, Selection of calculation methods for temperature distribution in 99 mass%Al_2O_3 refractories, Interceram, 47(1998)230-235

[13] Z. V.Popovic, T. D. Volkov-Husovic, K.T.Raic, Thermodynamical aspects of refractory using during the melting of aluminium and aluminium based alloys, International Symposium Light Metals and Composite Materials, Proceedings, 1999, Belgrade, p.21-23

[14] K.T.Raic, Unsteady or starting phenomena at liquid metal/ceramic interfaces, P. Vincenzini Ed., Techna srl, Faenza, Italy, 2002 (10th CIMTEC, World Ceramics Congress, Florence, 2002)

[15] Z.V. Popovic and K.T. Raic, Energetics of Metallurgical Furnaces – collection of solved examples, Belgrade University, Zavod za graficku tehniku TMF-a Beograd, 1986., 183 str. (in serb)

[16] Z.V. Popovic and K.T. Raic, Metallurgical Furnaces and Project Design - collection of solved examples, Belgrade University, Zavod za graficku tehniku TMF-a Beograd, 1988., 298 str. (in serb)