



CORROSION BEHAVIOUR OF ALUMINA CERAMICS IN AQUEOUS HCl SOLUTION

KOROZIJA ALUMINIJ OKSIDNE KERAMIKE U OTOPINAMA HCl

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Abstract: Two main types of chemical resistance of ceramics are: acid and alkali resistance. Although ceramics are generally more stable in corrosive environments than are common metallic materials, it is important to be investigate the chemical resistance under highly corrosive conditions for example: strong acid and long period of time expose. Because of that the corrosion behaviour of a cold isostatically pressed (CIP) high purity alumina ceramics in aqueous HCl solution at mass concentration of 2, 10 and 20 wt. % have been studied. The rate of corrosion was monitored by determination of mass concentration of Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ Si^{4+} and Fe^{3+} ions eluted in different concentration of HCl by means of atomic absorption spectrometry (AAS). Increasing the concentration from 2 to 20 wt. % it was notified that the corrosion susceptibility in HCl solutions for the CIP alumina specimens at room temperature decreases.

Key words: alumina ceramics, acid corrosion, corrosion kinetics

Sažetak: Dvije glavne vrste kemijske postojanosti keramike su: postojanost u kiselinu i lužini. Premda se keramika općenito smatra stabilnija u korozivnim uvjetima nego uobičajeni metalni materijali, važno je ispitati kemijsku postojanost u jako korozivnim uvjetima kao što je jaka kiselina i dulji vremenski period izlaganja djelovanju agresivnog medija. Zbog toga je u ovom radu ispitano korozijsko ponašanje visoko čiste aluminij oksidne keramike oblikovane hladnim izostatičkim prešanjem u otopinama HCl masene koncentracije od 2, 10 i 20 %. Praćena je brzina korozije mjerenjem masene koncentracije eluiranih iona Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ Si^{4+} i Fe^{3+} u različitim koncentracijama HCl uporabom atomske apsorpcijske spektrofotometrije (AAS). Uočeno je da povećanjem koncentracije HCl se smanjuje sklonost koroziji aluminij oksidne keramike pri sobnoj temperaturi.

Ključne riječi: aluminij oksidna keramika, korozija u kiselinu, brzina korozije

1. INTRODUCTION

Aluminium oxide, Al_2O_3 often more referred to as alumina, is an exceptionally important ceramic material, which has many technological applications. It has several special properties like high hardness, chemical inertness, wear resistance and melting point. Alumina ceramics can maintain up to 90% of their strength even at 1100 °C. Alumina is used in many refractory materials, grinding media, cutting tools, high temperature bearings, and a wide variety of mechanical parts. Alumina has different phases, of which α -alumina is a stable phase. Besides the thermodynamically stable α - Al_2O_3 or corundum there are many metastable structures of alumina, like γ - Al_2O_3 , which is widely used as a catalyst. Corundum or α -alumina is described by a hexagonal unit cell (Figure 1)[1, 2].

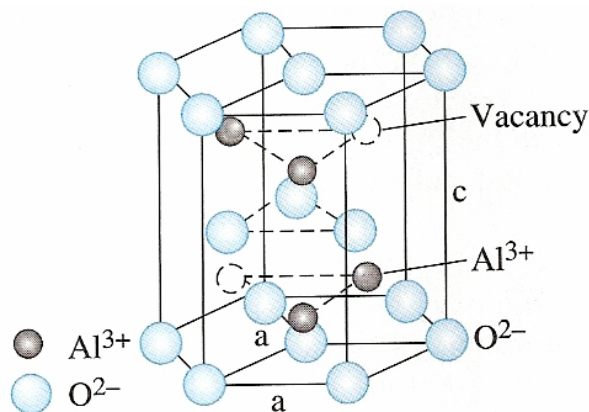


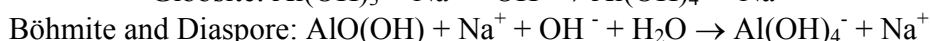
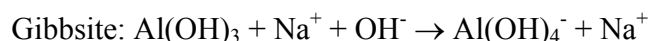
Figure 1. Corundum structure of alpha-alumina (α - Al_2O_3) [3].

Aluminium oxide, also known as alumina, is the main component of bauxite, the principal ore of aluminium. The largest manufacturers in the world of alumina are Alcoa, Alcan and Rusal. Companies which specialise in the production of speciality aluminium oxides and aluminium hydroxides include Alcan and Almatis. The bauxite ore is made up of impure Al_2O_3 , Fe_2O_3 , and SiO_2 .

The process of producing pure alumina from bauxite (the Bayer Process) has changed very little since the first plant was opened in 1893. The Bayer process can be considered in three stages [4]:

1.1. Extraction

The aluminium-bearing minerals in bauxite - Gibbsite, Böhmite and Diaspore - are selectively extracted from the insoluble components (mostly oxides) by dissolving them in a solution of sodium hydroxide (caustic soda):



After the extraction stage the insoluble bauxite residue must be separated from the Aluminium-containing liquor by a process known as settling. The liquor is purified as much as possible through filters before being transferred to the precipitators. The insoluble mud from the first

settling stage is thickened and washed to recover the caustic soda, which is then recycled back into the main process. The Fe₂O₃ does not dissolve in the base. The SiO₂ dissolves as silicate Si(OH)₆²⁻. Upon filtering, Fe₂O₃ is removed. When the Bayer liquor is cooled, Al(OH)₃ precipitates. The silicate remains in solution.

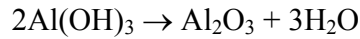
1.2. Precipitation

Crystalline aluminium trihydroxide (Gibbsite), conveniently named "hydrate", is then precipitated from the digestion liquor:



1.3. Calcination

"Hydrate", is calcined to form alumina for the aluminium smelting process. In the calcination process water is driven off to form alumina:



The formed Al₂O₃ is alumina with typical physical properties shown in table 1.

Table 1. Typical physical properties of Alumina

Property	
Melting point (°C)	2015±15
Refractive index	1.765
Molecular wt (g.mol ⁻¹)	101.96
ΔG _f ^o Free Energy of Formation (kJ.mol ⁻¹)	-1582.4
Density (g/cm ³)	3.986

2. MATERIALS AND METHODS

The material used in the corrosion tests in HCl solution was a cold isostatically pressed (CIP)-Al₂O₃ with 99.8 % purity. Chemical composition of investigated alumina ceramics is shown in Table 2. The CIP-Al₂O₃ specimens was supplied by Applied Ceramics, Inc., Fremont, California, U.S.A. Al₂O₃ ceramic contains MgO as sintering aid and the usual impurities SiO₂, CaO, Na₂O and Fe₂O₃. The specimens were rectangular coupons; size was 0.8 cm × 1.0 cm × 2.0 cm. The Archimed density of the CIP-Al₂O₃ was 3.91 g/cm³, thus the CIP-Al₂O₃ ceramic specimen attained 98.09 % of its theoretical density.

Table 2. Chemical composition of the Al₂O₃ ceramics.

sample	wt. %					
	MgO	Fe ₂ O ₃	SiO ₂	Na ₂ O	CaO	Al ₂ O ₃
alumina ceramics	0.066	0.015	0.02	0.05	0.013	rest

Each surface of Al₂O₃ specimens was polished to 1.5 μm. After polishing and before the corrosion tests, samples were thoroughly cleaned with alcohol and dried in the sterilizer

(Instrumentaria, Zagreb, Croatia) at 150 ± 5 °C for 4 hours. In the HCl corrosion tests, the specimen and a 5 ml of HCl solution were put into a sealed polypropylene (PP) tube. The corrosive environments were HCl solutions, with concentrations of 2, 10 and 20 %. The static corrosion tests were carried out at room temperature (25 °C) from 24 to 240 h. After the planned exposure time, the specimens were removed from the tubes, rinsed with boiling distilled water, dried in warm heated oven at 150 °C. For each experimental condition, five tests were performed, simultaneously.

The determination of the amount of Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+} ions eluted in the corrosive solutions was carried out with the atomic absorption spectrophotometry (AAS, AA-6800, Shimadzu). All data were an average of five values. The measurements were conducted after 24, 48, 72, 60, 84 and 240 hours of immersion.

3. RESULTS AND DISCUSSION

The correlation between the amount of eluted ions of Al_2O_3 ceramics after immersion in different concentrations of HCl solution and the immersion time is plotted in Figure 2. These results show that eluates after corrosion process contain ions of Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+} . These results indicate that the impurities played an important role in the corrosion process of alumina ceramics. The rates of corrosion of Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+} ions increased with corrosion time.

The corrosion kinetics of high purity Al_2O_3 ceramics after immersion in different concentrations of HCl solution at room temperature are shown in Figure 3. Figure 2 and 3 show that the corrosion rate is the highest in the first 24 hours, and after that, it is decreased with the exposure time. For this reason, curve, which present the amount of eluted ions vs. time (which is a measure of corrosion rate), have a parabolic shape. Figure 3 also shows that the corrosion rate changes with the HCl concentration. The highest corrosion rate is noted at the lowest concentration (2 wt. % of HCl). In general, the corrosion susceptibility (total amount of eluted ions) of the Al_2O_3 ceramics increased by increasing the corrosion time.

Corrosion kinetics in HCl solution follows parabolic rate relations. The Al_2O_3 corrosion kinetic relations in different concentration of HCl solution at room temperature can be expressed as the simplest form of the parabolic law, which is often used in the corrosion data processing [5]:

$$\left(\sum \mu\text{gM}^{n+} / \text{cm}^2 \right)^2 = K_p \cdot t$$

Where:

- K_p is the parabolic corrosion rate constant in $\mu\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$,
- t, s is time of immersion in seconds,
- $\sum \mu\text{gM}^{n+} / \text{cm}^2$ is the sum of the amount of eluted ions (Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+}) per square centimetre in $\mu\text{g cm}^{-2}$.

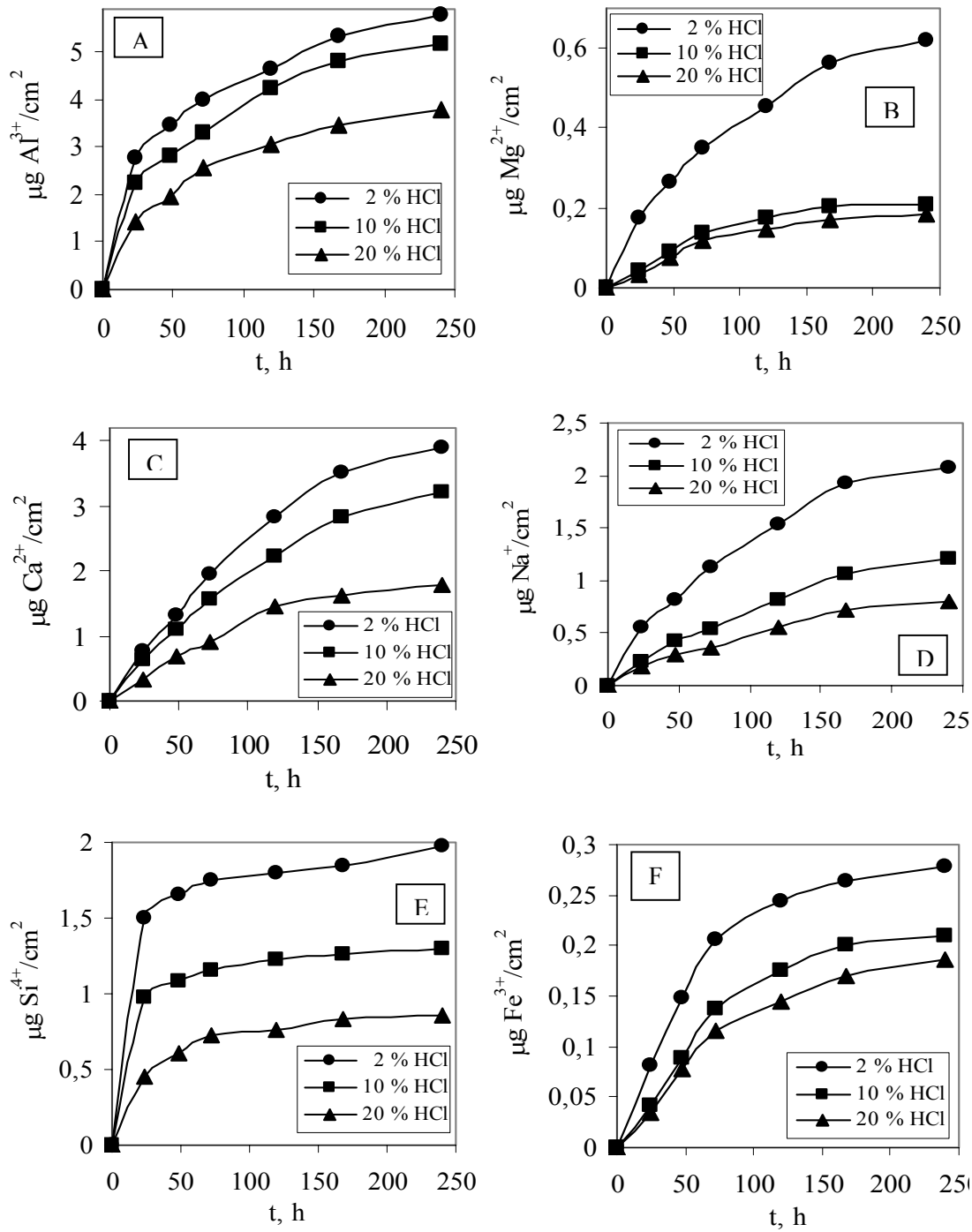


Figure 2. The amount of eluted ions of Al³⁺ (A), Mg²⁺ (B), Ca²⁺ (C), Na⁺ (D), (E) Si⁴⁺ and Fe³⁺ ions (F) from Al₂O₃ ceramics in different concentrations of HCl solution.

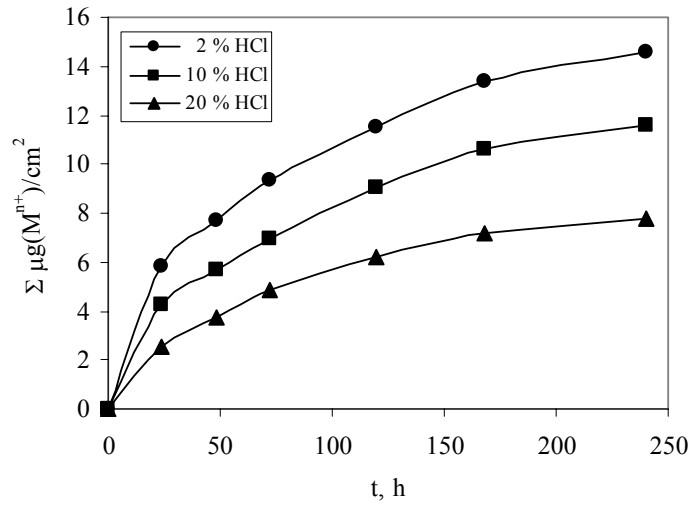


Figure 3. Total amount of eluted ions (Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+}) from Al_2O_3 ceramics in different concentration of HCl solution.

The plot (Figure 4) of the square of the total amount of eluted ions vs. the corrosion time can be fitted by straight line (correlation coefficient $R^2 = 0.98$ for 2 wt. % HCl, $R^2 = 0.98$ for 10 wt. % HCl and $R^2 = 0.97$ for 20 wt. % HCl), from which the values of the parabolic corrosion rate constants can be evaluated from the slopes. The corresponding values of the parabolic corrosion rate constants are given in Table 3.

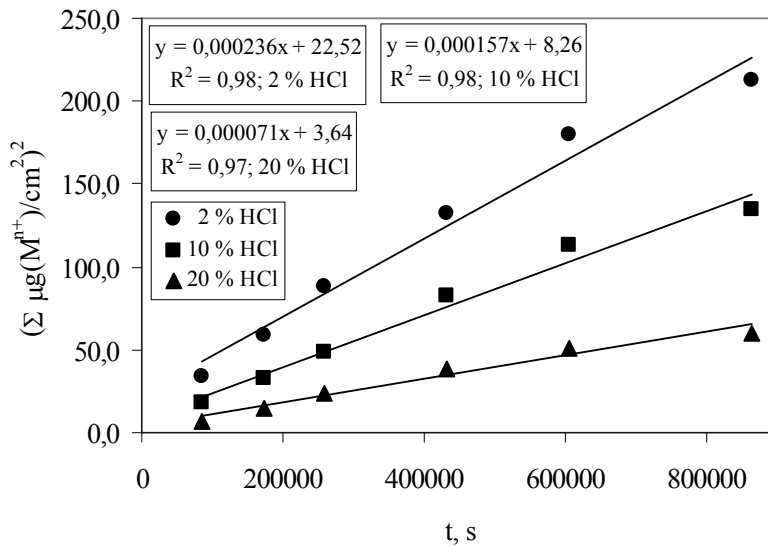


Figure 4. The square of the total amount of eluted ions vs. the corrosion time for different concentration of HCl solution.

Table 3. The parabolic (K_p) corrosion rate constant for Al_2O_3 ceramics after immersion in different concentration of HCl solution.

Concentration of HCl solution, wt. %	K_p , $\mu\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$	R^2
2	$23.6 \cdot 10^{-5}$	0.98
10	$15.7 \cdot 10^{-5}$	0.98
20	$7.1 \cdot 10^{-5}$	0.97

On the basis of literature data segregation of Si^{4+} , Na^+ , Ca^{2+} and Mg^{2+} to the grain boundaries will take place, but their concentrations at the grain boundaries are not sufficient for the formation of grain boundary phase [6, 7]. The distribution of the impurities is specified by the solubility of cations in alumina lattice. The solubility depends on the differences in the charge and ionic radius of impurities (Mg^{2+} , Ca^{2+} , Si^{4+} and Na^+) and Al^{3+} . Table 4 presents the ionic radius of Mg^{2+} , Ca^{2+} , Si^{4+} , Na^+ and Al^{3+} . By comparing the charge and ionic radius of impurities and Al^{3+} it is clear that Ca^{2+} possesses the smallest solubility. If the solubility limits of the cations in Al_2O_3 exceeded, they segregate to the grain boundaries of the ceramic materials [6-8].

Table 4. Ionic radius of Mg^{2+} , Ca^{2+} , Si^{4+} , Na^+ , Fe^{3+} and Al^{3+}

Ionic radius,	Al^{3+}	Mg^{2+}	Ca^{2+}	Na^+	Si^{4+}	Fe^{3+}
pm	57	79	106	98	26	67

The corrosion of alumina ceramics in HCl solutions is determined by solubility of alumina and solubility of grain-boundary impurities. Obtained results (Figure 2) indicate that the corrosion of alumina ceramics was mainly attributed to the dissolution of MgO , SiO_2 , CaO , Na_2O and Fe_2O_3 grain-boundary impurities. The dissolution of Al_2O_3 in bulk material is negligible. It means that the mechanism of corrosion is intergranular corrosion by preferential attack at the grain boundaries.

4. CONCLUSION

The corrosion susceptibility in HCl solutions for Al_2O_3 ceramics at room temperature decreases with increasing the concentration from 2 to 20 wt. %. Obtained results indicate that the strongest corrosive attack occurs in the first stage. After the first 24 h the amount of eluted of Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+} ions is considerably lower. According to the determined mass concentration of eluted ions which belong to the grain boundaries (Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+}) and Al^{3+} , which belongs to the grain, it means that the corrosion of alumina ceramics is mainly attributed to the dissolution of MgO , SiO_2 , CaO , Na_2O and Fe_2O_3 grain-boundary impurities.

Acknowledgments

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