

KINETIC STUDY OF THE CORROSION OF ALUMINA CERAMICS IN SULPHURIC ACID AQUEOUS SOLUTION

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Abstract:

The study of corrosion resistance of ceramics in acid and alkalis makes it possible to predict their service properties in these media. For this reason, the corrosion resistance of cold isostatically pressed (CIP) high-purity alumina ceramics (99.8 % Al₂O₃) was studied in different concentration of sulphuric acid (2 wt. %, 10 wt. % and 20 wt. %) at room temperature. Corrosion was monitored by determination of mass concentration of Al³⁺, Mg²⁺, Ca²⁺, Na⁺ Si⁴⁺ and Fe³⁺ ions eluted in different concentration of sulphuric acid by means of atomic absorption spectrophotometry (AAS). The corrosion rate constants for CIP-alumina specimens after immersion in H₂SO₄ solution using different concentration were determined.

Increasing the concentration from 2 to 20 wt. % it was notified that the corrosion susceptibility in H₂SO₄ solutions for the CIP alumina specimens at room temperature decreases.

Keywords: alumina ceramics, corrosion resistance, corrosion kinetics

1. INTRODUCTION

Alumina ceramics, which contains more than 80 % Al₂O₃, is the most important oxide ceramic material. It is characterised by high strength and hardness, high wear and corrosion resistance, high thermal conductivity, excellent insulation properties, high toughness and high-temperature strength. Alumina ceramics increasingly used in applications such as pump seals, wear plates for industrial components, sand blast nozzles, extrusion dies etc. Alumina is also being widely used as a bio-inert material in various orthopedic devices such as hip joint prosthesis, knee joint etc. [1].

The corrosion behaviour in various environments is a limiting factor for the lifetime of such ceramic components.

Many papers have been published on the corrosion of alumina ceramics under various conditions [2]. In the presented work, the corrosion behaviour of high purity alumina was investigated at room temperature for 10 days in H₂SO₄ solution of different concentrations. This study shows that the major cause of eluate chemistry in corroded alumina ceramics are the additives or the impurities, such as MgO, CaO, SiO₂ and Na₂O, which exist at grain boundaries.

2. MATERIALS AND METHODS

The material used in the corrosion tests in H₂SO₄ solution was a cold isostatically pressed (CIP)-Al₂O₃ with 99.8 % purity. Chemical composition of investigated alumina ceramics is shown in Table 1. The CIP-Al₂O₃ specimens were 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 1. 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 H₂SO₄ corrosion tests, the specimen and a 5 ml of H₂SO₄ solution were put into a sealed polypropylene (PP) tube. The corrosive environments were H₂SO₄ 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 Al³⁺, Mg²⁺, Ca²⁺, Na⁺, Si⁴⁺ and Fe³⁺ 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 Al₂O₃ ceramics after immersion in different concentrations of H₂SO₄ solution and the immersion time is plotted in Figure 1. These results show that eluates after corrosion process contain ions of Al³⁺, Mg²⁺, Ca²⁺, Na⁺, Si⁴⁺ and Fe³⁺. These results indicate that the impurities played an important role in the corrosion process of alumina ceramics. The rates of corrosion of Al³⁺, Mg²⁺, Ca²⁺, Na⁺, Si⁴⁺ and Fe³⁺ ions increased with corrosion time.

The corrosion kinetics of high purity Al₂O₃ ceramics after immersion in different concentrations of H₂SO₄ solution at room temperature are shown in Figure 2. Figure 1 and 2 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 2 also shows that the corrosion rate changes with the H₂SO₄ concentration. The highest corrosion rate is noted at the lowest concentration (2 wt. % of H₂SO₄). In general, the corrosion susceptibility (total amount of eluted ions) of the Al₂O₃ ceramics increased by increasing the corrosion time. Corrosion kinetics in H₂SO₄ solution follows parabolic rate relations. The Al₂O₃ corrosion kinetic relations in different concentration of H₂SO₄ solution at room temperature can be expressed as the simplest form of the parabolic law, which is often used in the corrosion data processing [2]:

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

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 (Al³⁺, Mg²⁺, Ca²⁺, Na⁺, Si⁴⁺ and Fe³⁺) per square centimetre in $\mu\text{g cm}^{-2}$.

The plot (Figure 3) 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. % H₂SO₄, $R^2 = 0.96$ for 10 wt. % H₂SO₄ and $R^2 = 0.98$ for 20 wt. % H₂SO₄), 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 2.

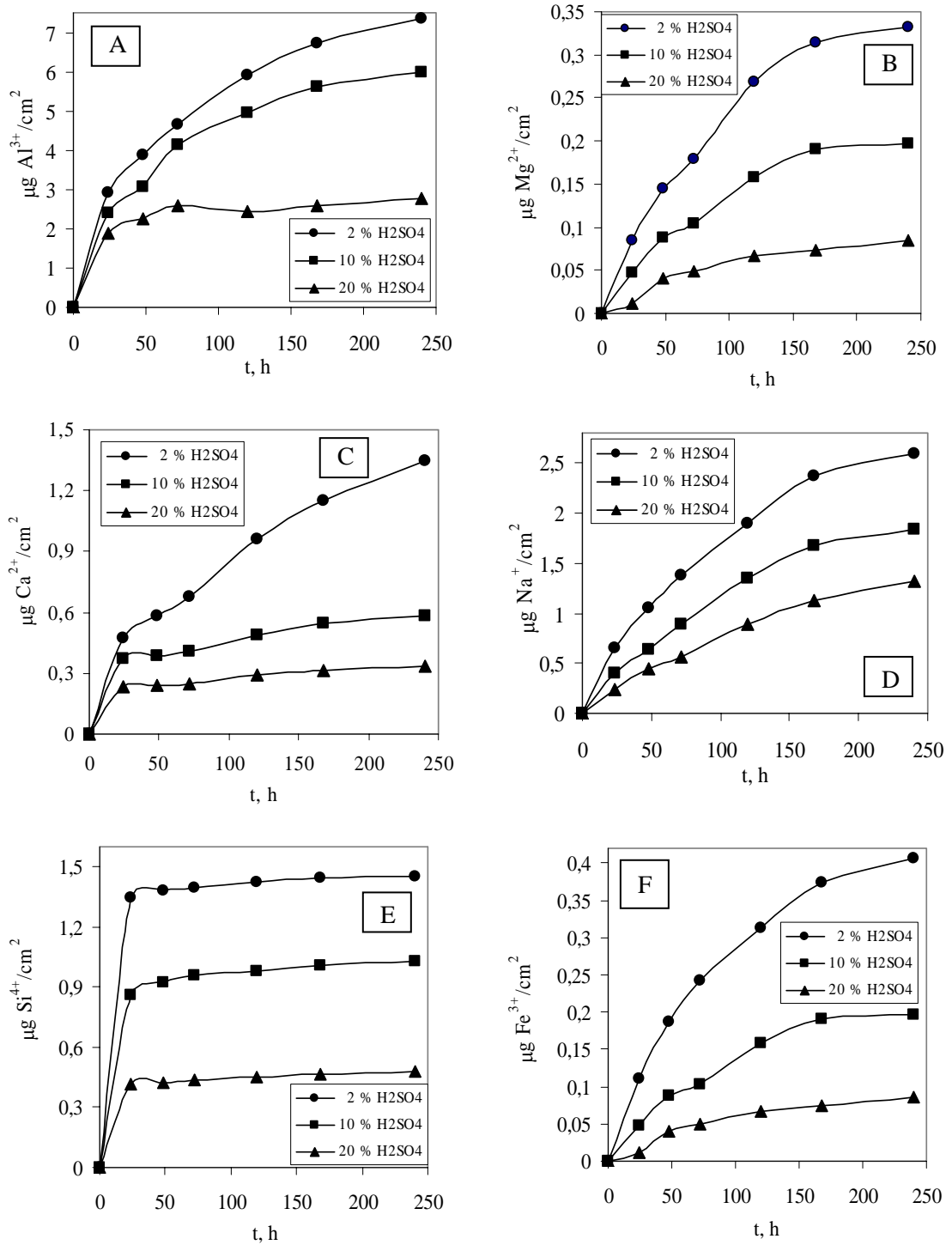


Figure 1. The amount of eluted ions of Al^{3+} (A), Mg^{2+} (B), Ca^{2+} (C), Na^+ (D), (E) Si^{4+} and Fe^{3+} ions (F) from Al_2O_3 ceramics in different concentrations of H_2SO_4 solution.

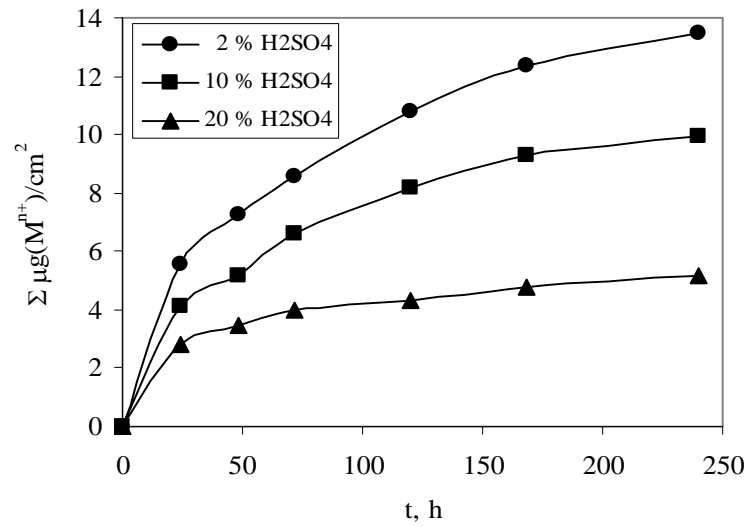


Figure 2. Total amount of eluted ions (Al^{3+} , Mg^{2+} , Ca^{2+} , Na^{+} , Si^{4+} and Fe^{3+}) from Al_2O_3 ceramics in different concentration of H_2SO_4 solution.

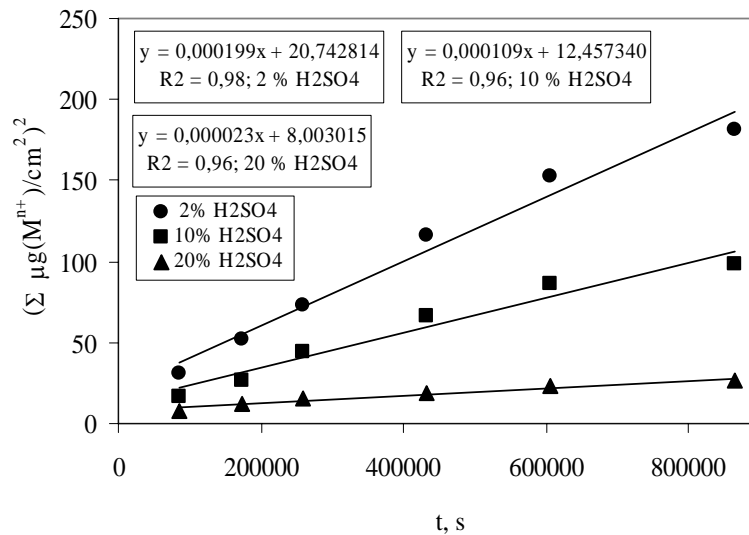


Figure 3. The square of the total amount of eluted ions vs. the corrosion time for different concentration of H_2SO_4 solution.

Table 2. Values of the corrosion rate constants (K_p) for Al_2O_3 ceramics after immersion in different concentration of H_2SO_4 solution.

Concentration of H_2SO_4 solution, wt. %	K_p , $\mu\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$	R^2
2	$19.9 \cdot 10^{-5}$	0.98
10	$10.9 \cdot 10^{-5}$	0.96
20	$2.3 \cdot 10^{-5}$	0.96

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 [3, 4]. 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 3 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 [3-5].

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

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

The corrosion of alumina ceramics in H_2SO_4 solutions is determined by solubility of alumina and solubility of grain-boundary impurities. Obtained results (Figure 1) 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 H_2SO_4 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.

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5. References

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