

DEGREE OF DISSOLUTION OF ALUMINA CERAMICS IN HCl AQUEOUS SOLUTION

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ABSTRACT

Two main types of chemical resistance of ceramics are acid resistance and alkali resistance. Although ceramics are generally more stable in corrosive environments than common metallic materials, it is important to investigate the chemical resistance under highly corrosive conditions, such as a strong acid and a long period of exposure. Because of that, the corrosion behaviour of a cold isostatically pressed (CIP) high purity alumina ceramics in aqueous HCl solutions at the mass concentrations of 2, 10 and 20 wt. % has been studied. From the amounts of Al^{3+} , Mg^{2+} , Ca^{2+} , Na^+ , Si^{4+} and Fe^{3+} ions released in the corrosive solution, a degree of dissolution χ_i for each component was calculated according to equation $\chi_i = A/B$, where A and B are respectively the amount of the element released in the corrosive solution and the amount of the element in the untreated material. The determination of the amount of ions released in the corrosive solutions was carried out by means of atomic absorption spectrometry (AAS).

Keywords: alumina ceramics, degree of dissolution, corrosion

1. INTRODUCTION

Aluminium oxide, Al_2O_3 , more often referred to as alumina, is an exceptionally important ceramic material, which has many technological applications [1,2]. It has several special properties like high hardness, chemical inertness, wear resistance and a high melting point. Because of their excellent properties, alumina ceramics are widely used for many refractory materials, grinding media, cutting tools, high temperature bearings, a wide variety of mechanical parts, and critical components in chemical process environments where materials are subjected to aggressive chemical attack, increasingly higher temperatures, and pressures.

In the presented work, the degree of dissolution of high purity alumina was investigated at room temperature for 10 days in HCl solutions of different concentrations. All investigations showed that the corrosion resistance of alumina ceramics is influenced by the purity of the material due to the segregation of impurities to the grain boundaries during the sintering process. It is well known that alumina ceramics consist of $\alpha-Al_2O_3$ grains and intergranular phases, such as silica compounds, and a glass phase. If the ceramic has very high impurity content, a crystalline or amorphous grain boundary phase is formed and intergranular attack in aqueous acidic solutions can be expected [3-5]. Several researches have reported the selective dissolution of the grain-boundary phase [6-9]. The corrosion of alumina ceramics in HCl solutions is determined by the solubility of grain-boundary impurities and additives such as Ca, Si, Na, Fe and Mg, while the dissolution of aluminium from alumina grains is negligible.

2. MATERIALS AND METHODS

The material used in corrosion tests in HCl solution was a cold isostatically pressed (CIP)-Al₂O₃ with a purity of 99.8 % purity. The 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 ceramics contains MgO as a sintering aid and the usual impurities, i.e. SiO₂, CaO, Na₂O and Fe₂O₃. The specimens were rectangular coupons; with the size of 0.8 cm × 1.0 cm × 2.0 cm. The Archimedes density of the CIP-Al₂O₃ was 3.91 g/cm³.

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 corrosion tests, samples were thoroughly cleaned with alcohol and dried in a sterilizer (Instrumentaria, Zagreb, Croatia) at 150 ± 5 °C for 4 hours. In the HCl corrosion tests, the specimen and 5 ml of a 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, and dried in a warm heated oven at 150 °C. For each experimental condition, five tests were performed simultaneously.

The amounts of Al³⁺, Mg²⁺, Ca²⁺, Na⁺, Si⁴⁺ and Fe³⁺ ions dissolved in the corrosive solutions were determined by means of the atomic absorption spectrophotometry (AAS, AA-6800, Shimadzu). All data were averages of five values. The measurements were conducted after 24, 48, 72, 120, 168 and 240 hours of immersion.

3. RESULTS AND DISCUSSION

From the amounts of Al³⁺, Mg²⁺, Ca²⁺, Na⁺, Si⁴⁺ and Fe³⁺ ions released in the corrosive solution, a degree of dissolution χ_i for each component was calculated according to the following equation:

$$\chi_i = \frac{A}{B}$$

where A and B are respectively the amount of the element released in the corrosive solution (measured by AAS) and the amount of the element present in the untreated material. Figures 1, 2 and 3 show the relationship between the degree of dissolution of each group of ions and the time of immersion in different concentrations of HCl aqueous solutions. These results show that leached elements were Ca, Si, Na, Fe, Mg and Al. Regardless of the HCl concentrations, calcium has the highest degree of dissolution, followed in a descending order by silicon, sodium, iron, magnesium and aluminium. The degree of dissolution of aluminium is insignificant. The obtained results indicate that the corrosion of alumina ceramics mainly can be ascribed to the dissolution of Mg, Si, Ca, Na and Fe, while the dissolution of aluminium from α -Al₂O₃ is negligible. These results can be explained with the structure of alumina ceramics. Generally, properties of materials depend on their structure. It is known that alumina ceramics generally consist of α -Al₂O₃ grains and intergranular phases, such as silica compounds, and a glass phase.

The distribution of the impurities is specified by the solubility of cations in the alumina lattice. The solubility depends on the differences in the charge and the ionic radius of additives or impurities (Mg²⁺, Ca²⁺, Si⁴⁺ and Na⁺) and Al³⁺. Table 2 presents the ionic radius of Mg²⁺, Ca²⁺, Si⁴⁺, Na⁺ and Al³⁺. If the solubility limits of the cations in Al₂O₃ are exceeded, they segregate to the grain boundaries of ceramic materials [6-8]. By comparing the charge and ionic radius of impurities and Al³⁺, it is clear that Ca²⁺ possesses the smallest solubility. Only Fe³⁺ carries the same charge as Al³⁺, but the ionic radius of Fe³⁺ is 18 % larger than the ionic radius of Al³⁺. In the light of these data, Fe as well as Ca²⁺ are expected mostly at the grain boundaries.

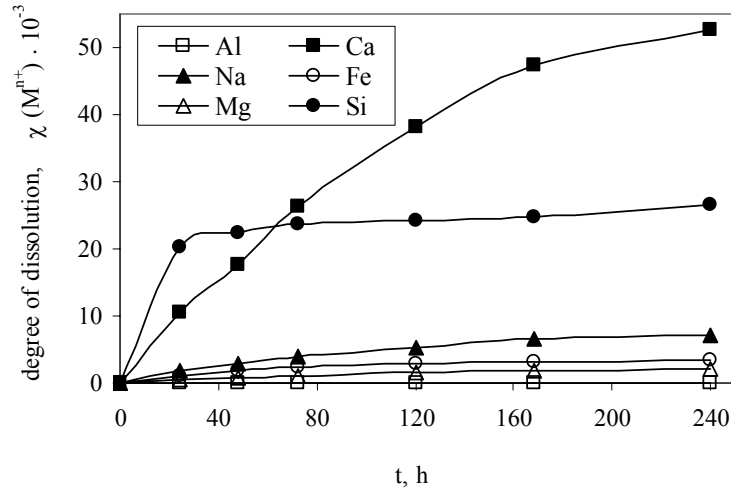


Figure 1. Degree of dissolution (χ_i) versus immersion time in a 2 % hydrochloric acid.

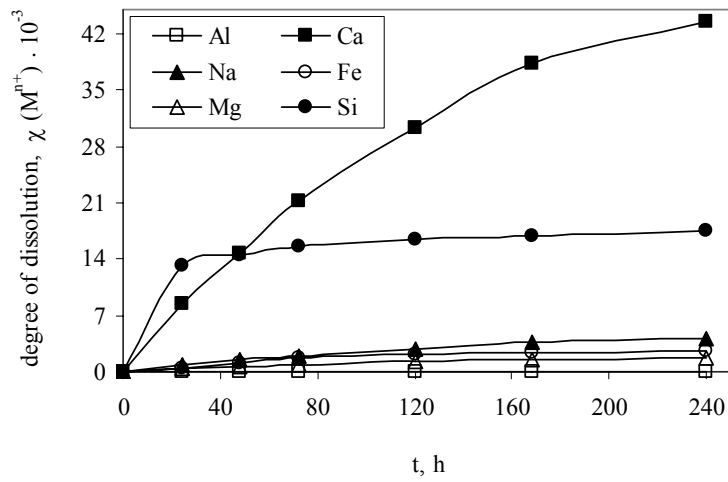


Figure 2. Degree of dissolution (χ_i) versus immersion time in a 10 % hydrochloric acid.

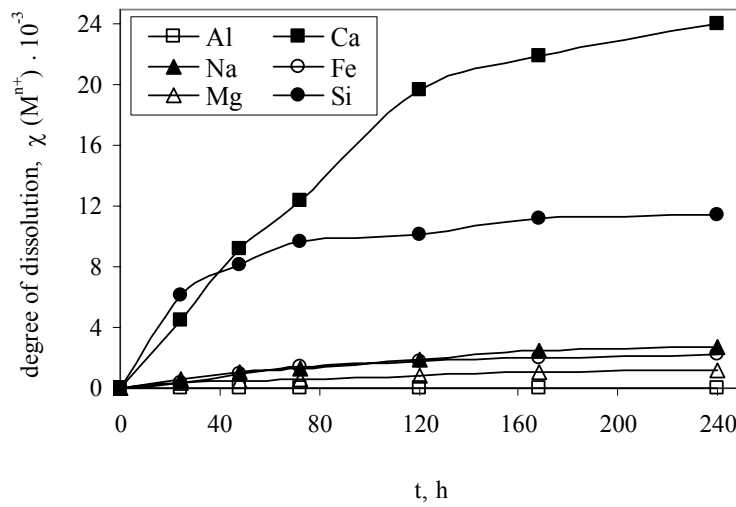


Figure 3. Degree of dissolution (χ_i) versus immersion time in a 20 % hydrochloric acid.

Table 2. 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

Aluminium, which belongs to α - Al_2O_3 grains, has the lowest degree of dissolution, subsequently followed by Mg. A relatively small dissolution degree of Mg; in comparison with the dissolution degrees of Ca and Si; can be attributed to the formation of Mg spinel, $MgAl_2O_4$, in alumina ceramics. MgO is one of the major dopants used to reduce the grain-boundary mobility during sintering. During cooling from the sintering temperature, the solubility of Mg in alumina is expected to decrease, which leads to the diffusion of Mg from the alumina grains to grain boundaries, and it can result in the second phase formation of $MgAl_2O_4$. Beside the spinel, a part of Mg can be soluted in α - Al_2O_3 grains or segregated at grain boundaries or surface. Spinel is more stable than silica compounds and glass. Na_2O and MgO can form $Na_2O \cdot 11Al_2O_3$ (β - Al_2O_3). SiO_2 causes the formation of silicate-rich glassy phase on the grain boundaries. This phase is easily attacked by mineral acids. Si and Ca are common impurities in alumina, and are known to cause abnormal grain growth during sintering.

4. CONCLUSION

These results indicate that the impurities and additives played an important role in the corrosion process of alumina ceramics. Independently of the HCl concentration, the degree of dissolution in a descending order is as follows: $Ca > Si > Na > Fe > Mg > Al$. The degree of dissolution of Al, Mg, Ca, Na, Si and Fe ions increased with the corrosion time. The degree of dissolution is highest in the first 24 hours, and after that, it decreases with the exposure time. In general, the corrosion susceptibility (the degree of dissolution) of the Al_2O_3 ceramics increases with increasing the corrosion time.

Acknowledgments

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