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Dissolution of alumina ceramics in HCl aqueous solution

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Abstract

Dissolution of a cold isostatically pressed high purity alumina ceramics in aqueous HCl solutions was studied as a function of immersion time and acid concentration. 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 the 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 amounts of ions released in the corrosive solutions was carried out by means of atomic absorption spectrometry (AAS). The corrosion of alumina ceramics in the HCl aqueous solution is determined by the solubility of alumina and the solubility of grain-boundary impurities. Very low dissolution values of Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, Si^{4+} and Fe^{3+} ions after the corrosion test of alumina ceramics showed a very good corrosion resistance in the HCl aqueous solution.

Keywords: C. Corrosion; Alumina ceramics; Degree of dissolution

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 and high temperature bearings. Therefore 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.

The surface dissolution of these ceramic materials is basically good, but it may be influenced by many factors, such as the composition and microstructure of the ceramic material, the chemical character of the corrosive medium, the exposure time and the temperature. 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 α-Al_2O_3 grains and intergranular phases, such as silica compounds, and a glass phase. Dopants and impurities often segregate to grain boundaries and may cause the formation of an amorphous or crystalline phase and/or may change the local defect chemistry. 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].

2. Materials and methods

The material used in corrosion tests in HCl solution was a cold isostatically pressed (CIP)-Al_2O_3 with a purity of 99.8%. The samples were sintered in a gas furnace at 1650 °C. The Archimedes density of the CIP-Al_2O_3 was 3.91 g/cm^3. The chemical composition of investigated alumina ceramics, according to manufactures declaration is shown in Table 1. The CIP-Al_2O_3 specimens were supplied by Applied Ceramics, Inc., Fremont, CA, U.S.A. Al_2O_3 ceramics contains MgO as a

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Table 1
Chemical composition of the Al_2O_3 ceramics.

Sample	Alumina ceramics
MgO (wt.%)	0.066
Fe_2O_3 (wt.%)	0.015
SiO_2 (wt.%)	0.02
Na_2O (wt.%)	0.05
CaO (wt.%)	0.013
Al_2O_3 (wt.%)	Rest

sintering aid and the usual impurities, i.e. SiO_2, CaO, Na_2O and Fe_2O_3.

After sintering, specimens were cut into rectangular coupons with the size of 0.8 cm × 1.0 cm × 2.0 cm. Each surface of Al_2O_3 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 h. These specimens were then used for corrosion testing. In the HCl corrosion tests, the specimen and 5 ml of an HCl solution were put into a sealed polypropylene (PP) tube. Samples were completely immersed in the solution. The corrosive environments were HCl solutions, with concentrations of 2, 10 and 20 wt.%. In parallel with corrosion testing, a blind test was also performed. The corrosion tests were carried out at room temperature (25 °C) from 24 to 240 h. To avoid an enrichment of leached components at the surface of samples, the solution was occasionally stirred. 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 Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, Si^{4+} and Fe^{3+} 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 h of immersion.

3. Results and discussion

During corrosion testing, the mass of specimens remained unchanged (it was measured on an analytical balance with the degree of precision of 10^{-5} g). Mechanisms responsible for corrosion processes were observed by determining the amount of ions released in the corrosive solution.

Fig. 1 gives the amount of Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, Si^{4+} and Fe^{3+} ions eluted from the alumina ceramics in dependence on the exposure time in different mass concentrations of hydrochloric acid. All data presented in Fig. 1 are averages of five values; therefore error bars are plotted. On the basis of

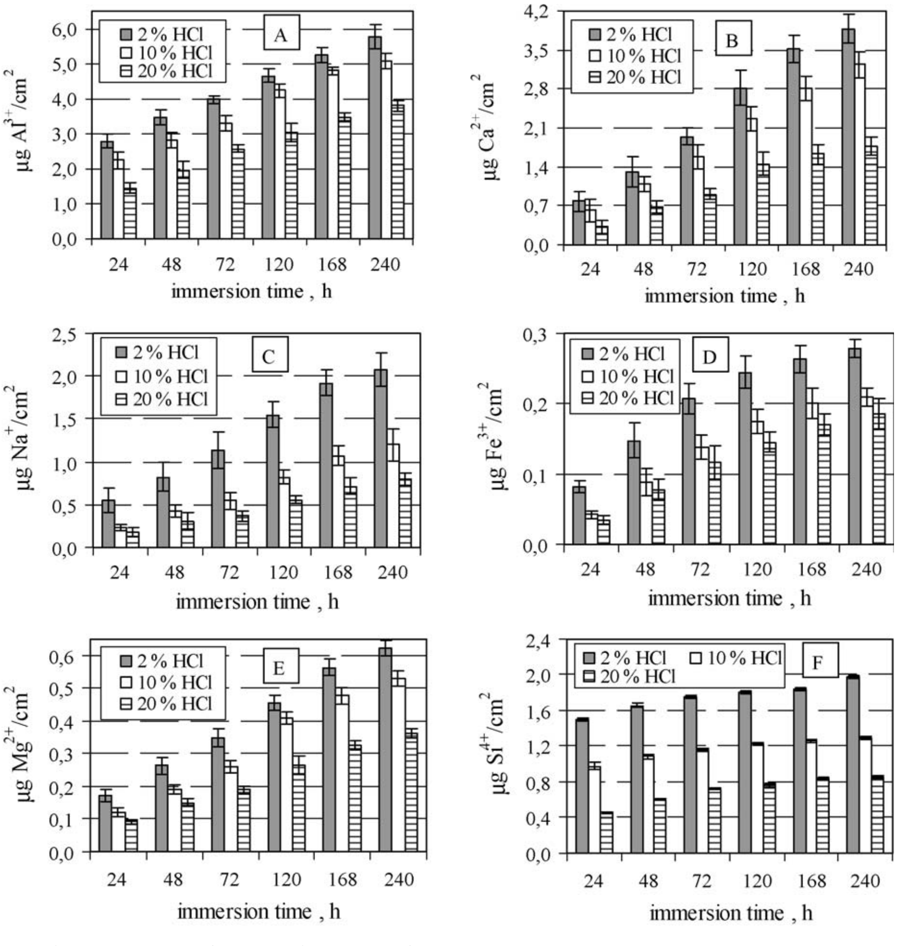

Fig. 1. The amount of Al^{3+} (A), Ca^{2+} (B), Na^{+} (C), Fe^{3+} (D), Mg^{2+} (E) and Si^{4+} ions (F) in the eluate as a function of immersion time from corrosion tests in 2% HCl, 10% HCl and 20% HCl (mean value and standard deviation).

the results given in Fig. 1, one can notice that the ions eluted during the exposure to the hydrochloric acid solutions of different mass concentrations are Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, Si^{4+} and Fe^{3+} ions. The Al^{3+} ions belong to the base material, the Ca^{2+}, Na^{+} Si^{4+} and Fe^{3+} ions belong to impurities, and the Mg^{2+} ions come from the MgO added as a sintering aid. In addition, one can notice that the amount of eluted Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+} Si^{4+} and Fe^{3+} ions depend on the concentration of the corrosive medium and on the exposure time. The largest amount of eluted ions was measured in hydrochloric acid of lowest mass concentration (2% HCl). The amount of eluted ions decreases with higher mass concentrations of hydrochloric acid (10% HCl and 20% HCl). The results also show that the highest elution rate of Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, Si^{4+} and Fe^{3+} ions occurs within the first 24 h.

In order to get an insight into the solubility of individual components of the specimens, the degree of dissolution for each chemical element was calculated from the amount of eluted Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, Si^{4+} and Fe^{3+} ions, using the following expression [10]:

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

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. The correlation between the degree of dissolution (χ_i) of each ion released from Al_2O_3 ceramics after immersion in different concentrations of the HCl solution and the immersion time is plotted in Fig. 2. All data presented in Fig. 2 are averages of five values; therefore error bars are plotted.

Fig. 3A–C shows the relationship between the degree of dissolution of each group of ions and the time of immersion in 2, 10 and 20 wt.% of HCl aqueous solution, respectively.

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-Al_2O_3 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-Al_2O_3 grains and intergranular phases, such as silica compounds, and a glass phase.

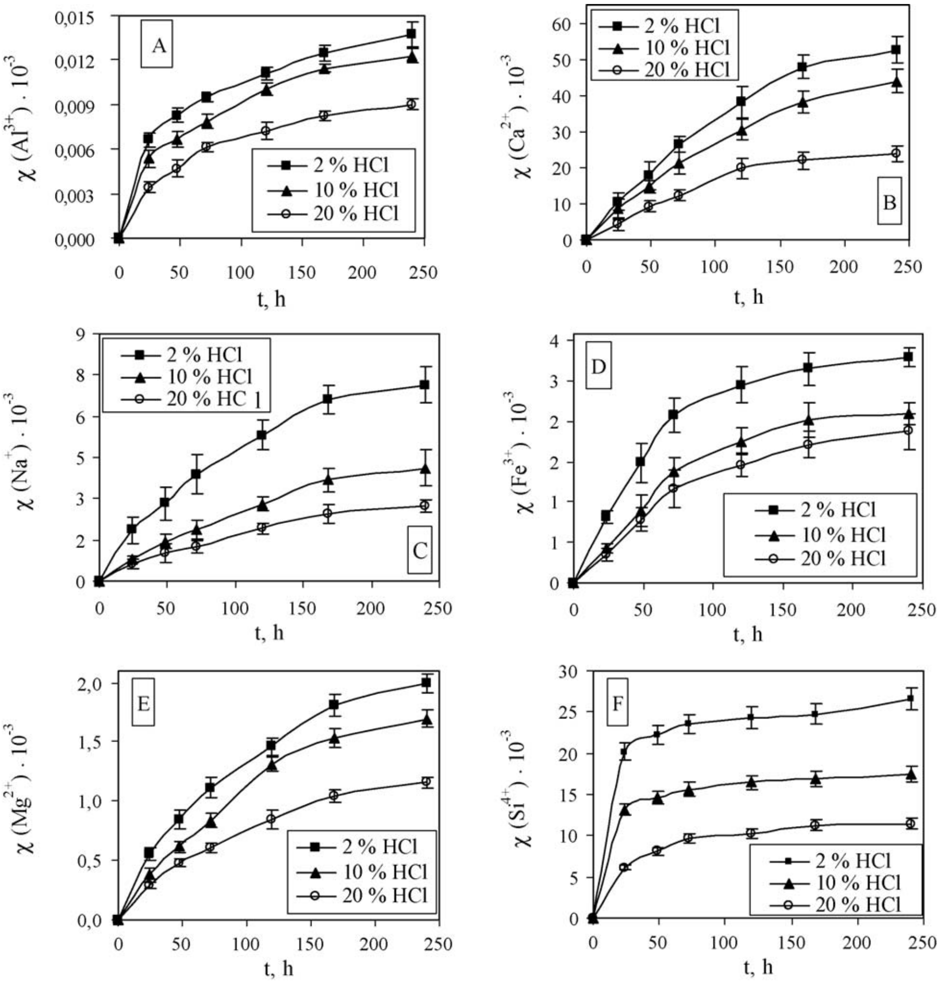

Fig. 2. Degree of dissolution (χ_i) of Al^{3+} (A), Ca^{2+} (B), Na^{+} (C), Fe^{3+} (D), Mg^{2+} (E) and Si^{4+} ions (F) from Al_2O_3 ceramics in different concentrations of HCl solution versus the immersion time (mean value and standard deviation).

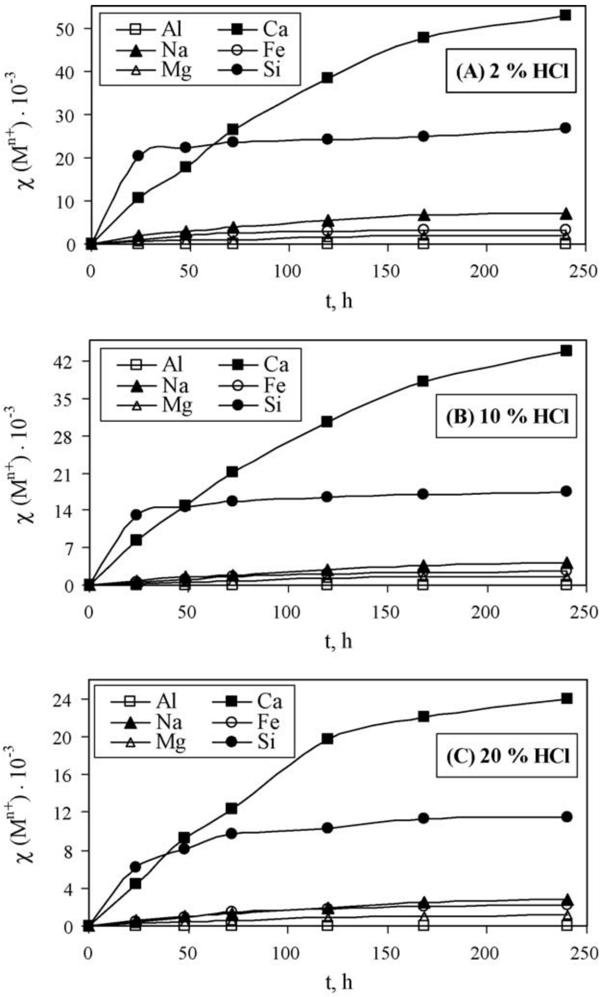

Fig. 3. Comparison of degree of dissolution (χ_i) of Al^{3+}, Ca^{2+}, Na^{+}, Fe^{3+}, Mg^{2+} and Si^{4+} ions versus immersion time in a 2% HCl (A), 10% HCl (B) and 20% HCl (C).

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 (Mg^{2+}, Ca^{2+}, Si^{4+}, Fe^{3+} and Na^{+}) and Al^{3+}. Table 2 presents the ionic radii of Mg^{2+}, Ca^{2+}, Si^{4+}, Fe^{3+}, Na^{+} and Al^{3+}. If the solubility limits of the cations in Al_2O_3 are exceeded, they segregate to the grain boundaries of ceramic materials. Enrichment of grain boundaries with cations whose charges and radii are different from aluminium, such as Si^{4+}, Na^{+}, Ca^{2+} and Mg^{2+}, causes the aluminium oxide lattice strain. With an increase in the content of impurities, the binding energy decreases [6–8]. By comparing the charge and ionic radius of impurities and Al^{3+}, it is clear that Ca^{2+} possesses the smallest solubility. Only Fe^{3+} carries the same charge as Al^{3+}, but the ionic radii of Fe^{3+} is 18% larger than the ionic radii of Al^{3+}. In the light of these data, Fe^{3+} as well as Ca^{2+} are expected mostly at the grain boundaries. On the basis of literature data, the 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 the grain-boundary phase [5,11,12]. Since the total amount of MgO, CaO, Na_2O, SiO_2 and Fe_2O_3 in the alumina ceramics is very low (only 0.164%), this is not sufficient for the formation of a new phase on grain boundaries [5,11]. Therefore, dopant (MgO) and impurities (CaO, Na_2O, SiO_2 and Fe_2O_3) segregate to grain boundaries and change the local defect chemistry. Since the highest degree of dissolution was measured for elements segregated at the grain boundaries it can be concluded that grain boundaries will be attacked first in the corrosion process [13–16].

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

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

Aluminium, which belongs to α-Al_2O_3 grains, has the lowest degree of dissolution, subsequently followed by Mg. 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. Si and Ca are common impurities in alumina, and are known to cause abnormal grain growth during sintering.

4. Conclusion

The corrosion of alumina ceramics in HCl solutions is determined by the solubility of grain-boundary impurities (Ca, Si, Na, Fe) and additive (Mg), while the dissolution of aluminium from alumina grains is negligible. These results indicate that the impurities and additives played an important role in the corrosion process of alumina ceramics.

Independent 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 h, 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. All obtained results indicate that the investigated alumina ceramics showed a very good corrosion resistance in the HCl aqueous solution.

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