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+ and Si4+ 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 Al$_2$O$_3$ ceramics.

<table>
<thead>
<tr>
<th>sample</th>
<th>MgO</th>
<th>Fe$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Na$_2$O</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>alumina ceramics</td>
<td>0.066</td>
<td>0.015</td>
<td>0.02</td>
<td>0.05</td>
<td>0.013</td>
<td>rest</td>
</tr>
</tbody>
</table>

Each surface of Al$_2$O$_3$ 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 ºC for 4 hours. In the H$_2$SO$_4$ corrosion tests, the specimen and a 5 ml of H$_2$SO$_4$ solution were put into a sealed polypropylene (PP) tube. The corrosive environments were H$_2$SO$_4$ solutions, with concentrations of 2, 10 and 20 %. The static corrosion tests were carried out at room temperature (25 ºC) 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 ºC. 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$_2$O$_3$ ceramics after immersion in different concentrations of H$_2$SO$_4$ solution and the immersion time is plotted in Figure 1. 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$_2$O$_3$ ceramics after immersion in different concentrations of H$_2$SO$_4$ 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 H$_2$SO$_4$ concentration. The highest corrosion rate is noted at the lowest concentration (2 wt. % of H$_2$SO$_4$). In general, the corrosion susceptibility (total amount of eluted ions) of the Al$_2$O$_3$ ceramics increased by increasing the corrosion time. Corrosion kinetics in H$_2$SO$_4$ solution follows parabolic rate relations. The Al$_2$O$_3$ corrosion kinetic relations in different concentration of H$_2$SO$_4$ 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]:

$$\left(\sum \mu g M^{m+} / cm^2\right)^2 = K_p \cdot t$$

Where:
- $K_p$ is the parabolic corrosion rate constant in µg$^2$ cm$^{-4}$ s$^{-1}$,
- $t$ is time of immersion in seconds,
- $\sum \mu g M^{m+} / cm^2$ 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 µg 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. % H$_2$SO$_4$, $R^2 = 0.96$ for 10 wt. % H$_2$SO$_4$ and $R^2 = 0.98$ for 20 wt. % H$_2$SO$_4$), 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 $\text{Al}^{3+}$ (A), $\text{Mg}^{2+}$ (B), $\text{Ca}^{2+}$ (C), $\text{Na}^{+}$ (D), (E) $\text{Si}^{4+}$ and $\text{Fe}^{3+}$ ions (F) from $\text{Al}_2\text{O}_3$ ceramics in different concentrations of $\text{H}_2\text{SO}_4$ solution.
Figure 2. Total amount of eluted ions ($\text{Al}^{3+}$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Na}^{+}$, $\text{Si}^{4+}$ and $\text{Fe}^{3+}$) from Al$_2$O$_3$ ceramics in different concentration of H$_2$SO$_4$ solution.

Figure 3. The square of the total amount of eluted ions vs. the corrosion time for different concentration of H$_2$SO$_4$ solution.

Table 2. Values of the corrosion rate constants ($K_p$) for Al$_2$O$_3$ ceramics after immersion in different concentration of H$_2$SO$_4$ solution.

<table>
<thead>
<tr>
<th>Concentration of H$_2$SO$_4$ solution, wt. %</th>
<th>$K_p$, $\mu$g $^{2}$ cm$^{-4}$ s$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$19.9 \cdot 10^{-3}$</td>
<td>0.98</td>
</tr>
<tr>
<td>10</td>
<td>$10.9 \cdot 10^{-3}$</td>
<td>0.96</td>
</tr>
<tr>
<td>20</td>
<td>$2.3 \cdot 10^{-5}$</td>
<td>0.96</td>
</tr>
</tbody>
</table>
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$_2$O$_3$ 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$^{3+}$

<table>
<thead>
<tr>
<th>Ionic radius, pm</th>
<th>Al$^{3+}$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Na$^{+}$</th>
<th>Si$^{4+}$</th>
<th>Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>57</td>
<td>79</td>
<td>106</td>
<td>98</td>
<td>26</td>
<td>67</td>
</tr>
</tbody>
</table>

The corrosion of alumina ceramics in H$_2$SO$_4$ 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$_2$O and Fe$_2$O$_3$ grain-boundary impurities. The dissolution of Al$_2$O$_3$ 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$_2$SO$_4$ solutions for Al$_2$O$_3$ 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$_2$O and Fe$_2$O$_3$ grain-boundary impurities.

Acknowledgments

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5. References