

FRACTURE AND STRENGTH OF Si_3N_4 CORRODED IN AN AQUEOUS SOLUTION OF SODIUM CHLORIDE

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Abstract

The work studies the corrosion of silicon nitride in 3% aqueous solutions of NaCl at temperatures range from 150 to 290°C. The corrosion of silicon nitride was controlled by the attack of Si_3N_4 matrix grains, while yttrium oxynitride grain boundary phase was corrosion resistant. Corrosion of Si_3N_4 in reference media - distilled water - at 290°C was characterised by formation of the passive layer, which hindered further dissolution of silicon nitride matrix. The corrosion significantly decreased the fracture strength of silicon nitride by creating corrosion related defects at the surface.

Keywords: *silicon nitride, sodium chloride, corrosion, fracture strength*

INTRODUCTION

The corrosion tests of ceramics are usually conducted in extremely harsh environments such as hot gases [1], molten salts, metals or slags [2], acidic and basic solutions [3,4] or supercritical water [5] due to their high corrosion resistance. However, the danger of corrosion of structural ceramics under more moderate conditions (< 300°C) in aqueous environments is often underestimated. Present paper is focused on the evaluation of corrosion resistance of silicon nitride against corrosion in an aqueous solution of sodium chloride. The investigation is mainly motivated by potential application of these materials for parts of car exhaust pipes, which must be resistant against salt corrosion due to winter road maintenance. Salt is known to accelerate corrosion in mixture with acids-containing exhaust gases, creating highly aggressive environment. Work quantifies the corrosion at various temperatures with respect to distilled water as the reference corroding medium. The influence of corrosion on fracture strength of studied ceramic material is evaluated.

EXPERIMENTAL

Si_3N_4 specimens were prepared from the powder SN-E10 (UBE Industries, Ltd., Japan) with 5 wt.% of Y_2O_3 sintering additive by hot pressing at 1750°C and pressure 30 MPa. Rectangular bars $3 \times 4 \times 50 \text{ mm}^3$ were polished, edges chamfered, ultrasonically cleaned in acetone for 15 min, rinsed with distilled water and dried for 3 h at 110°C before corrosion tests. Tests were carried out in stainless steel pressure reactors with inner PTFE lining preventing direct contact of corrosion medium with steel. A water solution of sodium chloride (p.a. purity, concentration $0.5 \text{ mol}\cdot\text{l}^{-1}$, i.e. 3 wt.%) in de-ionized water was used as the corrosion medium. Distilled water was used as the reference corrosion medium. The tests were carried out at temperatures 150, 200 and 290°C for up to 288 h. The tests were

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carried out in three reactors in parallel, i.e. 6 bars were corroded under the same conditions. The samples were rinsed with distilled water and dried after the test. One bar was used for investigation of corroded surfaces by scanning electron microscopy. Other five bars were used for the examination of strength after corrosion. The tests were carried out in four point bending with the inner and outer spans of 40 mm and 20 mm, respectively and at cross head speed of 0.5 mm/min. The fracture surfaces were examined in SEM after flexure tests.

RESULTS

SEM micrographs of corroded surfaces after 12 days of the test in an aqueous solution of NaCl and distilled water are shown in Fig.1. The surfaces of the corroded materials are covered with a layer of precipitates, which the X-ray diffraction identified as the mixture of at least three crystalline phases including cristoballite, silicon dioxide and yttrium silicon oxide nitride. The most striking feature is different morphology of precipitates formed in distilled water and in NaCl solution. While in the distilled water layer consisted of rounded particles of SiO_2 with the diameter of about 1–2 μm , angular crystals aggregated into larger globular precipitates with diameters of around 10 μm in sodium chloride solution. Figure 2 summarises the changes in fracture strength caused by a corrosive attack of corroding media. Temperature is a crucial factor for corrosion degradation of strength in silicon nitride for both used corroding media.

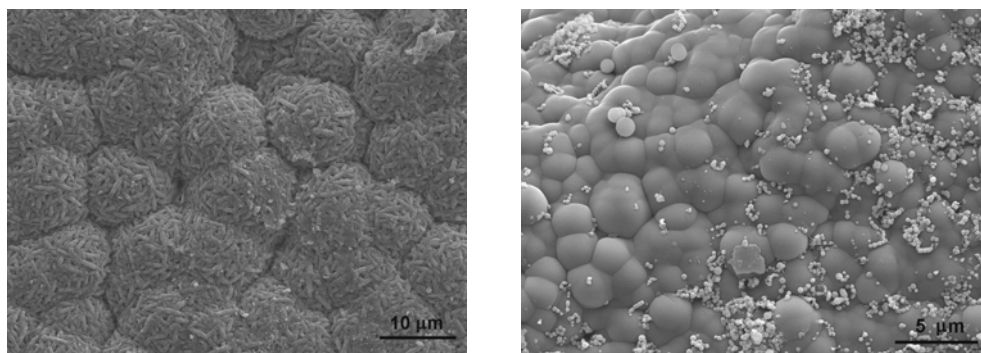


Fig.1. Corroded surfaces of silicon nitride tested for 12 days at 290°C in: a) 3 mol.% NaCl aqueous solution, b) in distilled water.

The influences of corrosion on the strengths are negligible at 150°C. At 200°C, slight decreases of the strength values were observed in both corroding media. Strength decreased from 700 to 290 MPa for Si_3N_4 corroded 12 days in NaCl solution at 290°C. Distilled water as corroding medium has lower degradation influence on the strength causing the decrease of strength from 700 MPa to 370 MPa after 12 days of corrosion test at 290°C. The chosen testing time has a negligible influence on the resulting strength.

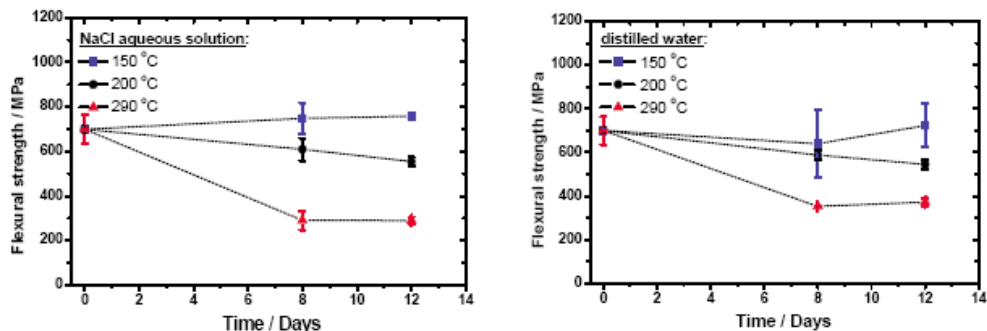


Fig.2. Change of the fracture strength after corrosion at various temperatures and time.

Figures 3 show the fracture surfaces of testing bars after the corrosion tests at different corrosion conditions. At 150°C, flaws degrading the strength have the same origin as in the case of uncorroded samples. Degradation of strength caused by the formation of SiO_2 layer and by the corrosion pits on the surface of samples appears at 200°C. Fracture of samples corroded at 290°C always originated at the surface. Corrosion damaged zones under the surface of the bars tested in distilled water were around one hundred micrometers. The corrosion damage zone for bars tested in aqueous solution of sodium chloride was larger than this one in distilled water - 200 μm . Damage zone in distilled water is compact layer consists of silica, in the case of sodium chloride damage zone is porous.

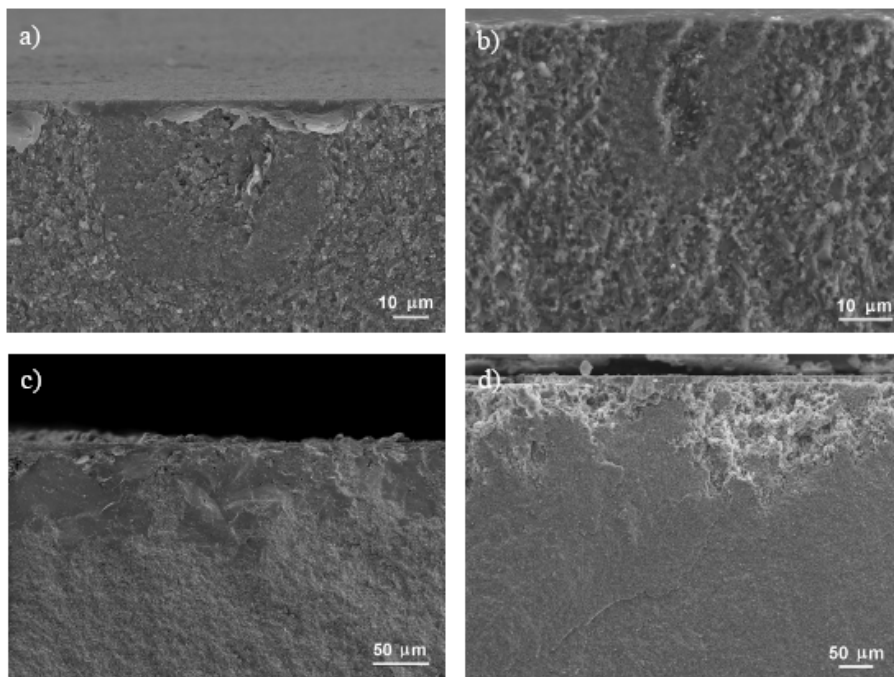


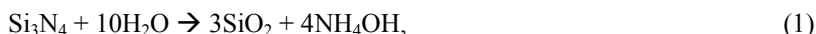
Fig.3. Fracture surfaces of Si_3N_4 after corrosion: a) in distilled water 12 days at 150°C; b) in NaCl 12 days, 150°C; c) in distilled water 12 days at 290°C; d) in NaCl 12 days at 290°C.

DISCUSSION

The different shape of corrosive layer for silicon nitride corroded in distilled water and in aqueous solution of sodium chloride is illustrated in Fig.1. The morphology of precipitates is influenced by the corroding media. However, X-ray analysis do not revealed the different structural phases presented in corrosion layer. This fact is connected to the detection limit of used analytic technique.

The porous corroded zone, Fig.3d, is caused by the dissolution of silicon nitride grains while the grain boundaries phases are intact or far less corroded. The investigations of Si₃N₄ ceramics [6] with Y₂O₃ and Al₂O₃ as sintering additives indicated that at 250°C, the dissolution rate of Si₃N₄ grains was even higher than that of the grain boundary phases, whereas at 180°C, no pronounced attack was found. This result is in agreement with the data observed in our investigation. It should be point out that the grain boundary phases consist of several phases Y₂Si₂O₇, Si₂N₂O and SiO₂, with different solubility in aqueous media.

The observed results suggest following corrosion mechanism. In both liquid media, silicon nitride corrodes by reaction of Si₃N₄ grains with water according to the reaction (1):



while the yttrium oxynitride grain boundary glass is corrosion resistant. The reaction is markedly accelerated by the increasing temperature. Leached silicon precipitates from the solution, and forms a different type of corroded layers regarding the corroding media.

CONCLUSIONS

The work studied the corrosion of silicon nitride in 3% aqueous NaCl solution and in distilled water at temperatures up to 290°C. Under these conditions, silicon nitride was less resistant in NaCl solution. Increase of the soaking time from 8 to 12 days did not influence the resulting residual strength. However, corrosion of studied silicon nitride significantly accelerated with the increasing temperature. The corrosive attack was controlled by the dissolution of Si₃N₄ matrix grains and diffusion through the layer of corrosion products. Dramatic change of fracture strength of Si₃N₄ at 290°C was observed due to the penetration of corroding media into the bulk of material and their reaction with the silicon nitride grains.

Acknowledgement

The financial support of this work by the grant APVV 0171-06, LPP 0203-07 and Centrum of Excellence NANOSMART is gratefully acknowledged.

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