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Ceramics International 31 (2005) 277–280

CERAMICS INTERNATIONAL

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Effect of TiN on the corrosion behavior of Y-(α + β)-sialon/TiN materials in hot hydrochloric acidic solutions

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Received 3 October 2003; received in revised form 8 March 2004; accepted 3 May 2004
Available online 10 August 2004

Abstract

The corrosion behavior of Y-(α + β)-sialon/TiN materials in hot hydrochloric acidic solutions (80°C) was studied. The effect of TiN on the corrosion behavior of Y-(α + β)-sialon/TiN materials was investigated. The results revealed that the introduction of TiN accelerate the corrosion. With the increasing of TiN content, the α-sialon content on the final composition decreased and more yttrium remains on the grain boundary phase. Therefore, the corrosion was severed due to the formation of soluble YCl_3.

Keywords: B. Grain boundaries; C. Corrosion; Y-(α + β)-sialon/TiN

1. Introduction

Si_3N_4-based materials have been successfully applied in the chemical industry in several components, including bearings, ball valves, and other armatures. Therefore, silicon nitride-based materials often find application in environments, such as acidic or basic solutions at various temperatures [1,2]. Although, ceramics are generally more stable in corrosive environments than common metallic materials, their chemical resistance under these highly corrosive conditions deserves to be evaluated. Though the corrosive behavior of silicon nitride-based materials in aqueous media has been studied extensively [3–10], there is still a lack of understanding of the details of the corrosion mechanism in acids and the effect of secondary phase on the corrosion behavior need further investigation. The main purpose of this work is to investigate the corrosion of Y-(α + β)-sialon/TiN materials in hot hydrochloric acidic solutions and the effect of TiN on the corrosion behavior on the Y-(α + β)-sialon/TiN materials was discussed.

2. Experimental procedure

The starting materials were Si_3N_4, Al_2O_3, Y_2O_3, AlN, and TiN. Si_3N_4 was from UBE with grade SN-E10, and the others were local products of high purity (>99.2%). The samples were prepared according to the weight ratios of Si_3N_4:AlN:Y_2O_3:Al_2O_3 = 81.1:8.0:4.4:6.5, and the content of TiN is various from 0 to 10 wt.%. The powders were mixed in alcohol and milled in a plastic jar with sialon balls as milling media. After drying, the powder mixtures were sieved and uniaxially pressed at 20 MPa, and then cold isostatically pressed at 200 MPa. The isostatically pressed green compacts were placed in a graphite crucible and sintered at a temperature of 1780 °C for 2 h in 0.1 MPa N_2 atmosphere. The as-received samples were machined into 3 mm × 4 mm × 20 mm bars.

Corrosion tests were conducted in separated containers (glass tube sealed by rub lid), with 50 ml of 8 M HCl solutions. Containers were placed in a constant temperature bath at 80 °C. One sample type per container was specified to avoid cross-contamination. Aqueous dissolution of ceramics is typically controlled by chemical reactions or mass transfer at the solid–liquid interface and not by diffusion, so static condition is acceptable. HCl is hazardous and proper safety precautions must be followed. After the planned

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0272-8842/$30.00
doi:10.1016/j.ceramint.2004.05.015

exposure time, the specimens were removed from the tubes, rinsed in boiling deionizated water, dried and weighed. Then the weight loss $D_W = \Delta W/S$ (mg/cm^2) was calculated.

Density and porosity was measured and calculated by the Archimedes method. The amount of yttrium ion dissolved in the solution was measure and calculated by ICP–OES (coupled plasma optical emission spectrometers) method. X-ray diffractometry (XRD) was conducted to detect the final phase composition. The microstructure was examined by SEM.

3. Results and discussions

The samples with 0, 2, 5, 8, and 10 wt.% TiN content were called A0, A2, A5, A8, and A10, respectively. Fig. 1 shows the fracture surface morphology of the A10 sample before and after 100-h corrosion. It could be observed that the corrosion mainly occurred at the grain boundary. Fig. 2 shows specific mass loss of the materials as a function of TiN content. The mass loss is increased with the increasing of TiN, which indicated that the introduction of TiN accelerated the corrosion of the materials.

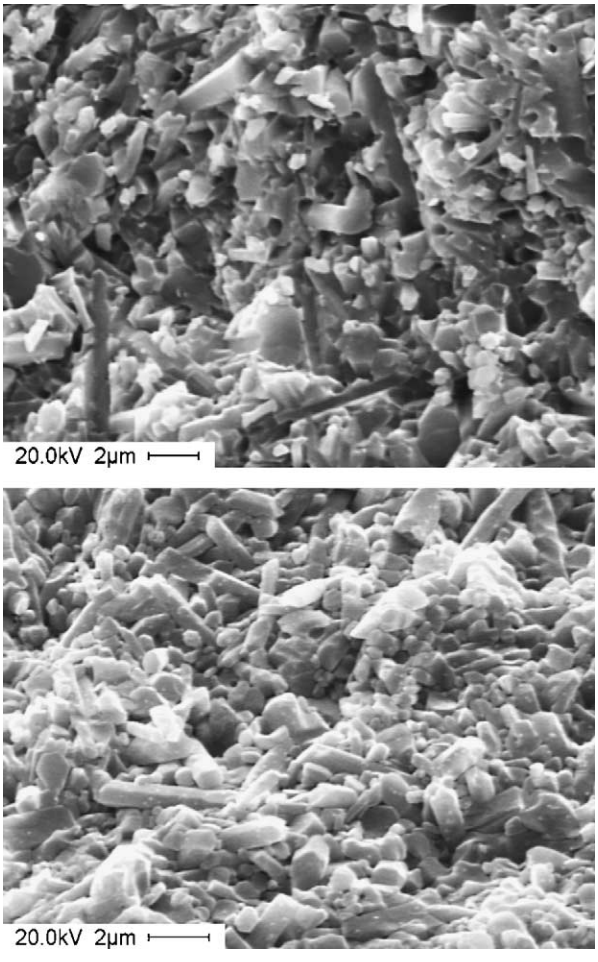

Fig. 1. The fracture surface morphology of the A10 sample: (a) before corrosion and (b) after corrosion.

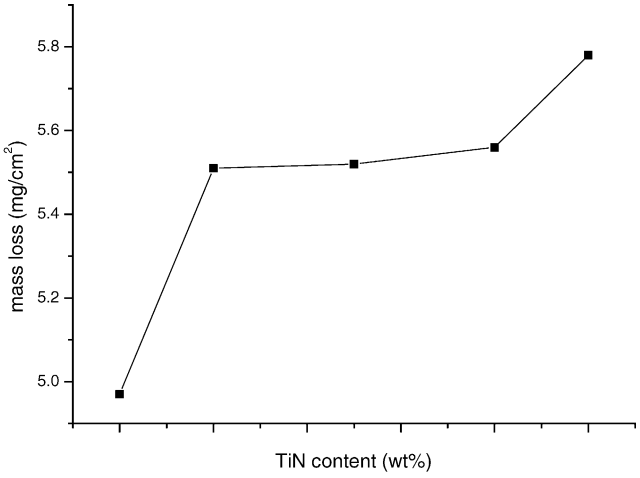

Fig. 2. Mass loss with various TiN content in hydrochloric acidic solutions at 80 °C (100 h).

Fig. 3 shows the results of density and open porosity of the samples as a function of TiN content. The density increased with the increasing TiN content because the theoretical density of TiN is higher than that of Si_3N_4. It is known that the open porosity is important for corrosion resistant, because the high open porosity increased the actual contact area. In present work, however, the open porosity varied in a very narrow range, therefore, the major factors which influence the corrosion should be TiN and its reaction with the matrix.

It is well known that the chemical stability of Si_3N_4-based ceramics in acid or basic environments is strongly affected by grain boundary phase, depending on its composition, amount, distribution and crystallinty, while Si_3N_4 matrix is usually less affected by the corrosion [3,8,9]. The addition of a secondary phase (TiN in this paper), influences the overall corrosion of the material due to two concurrent features: (i) the second phase has individual and specific corrosion characteristic and (ii) it changes the composition of the grain boundary phase [10].

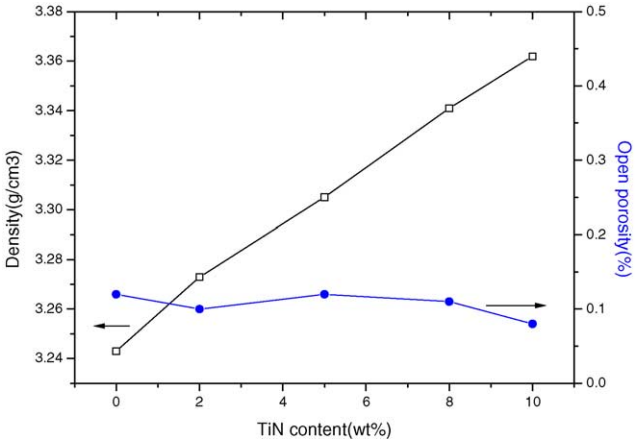

Fig. 3. Density and open porosity as functions of TiN content.

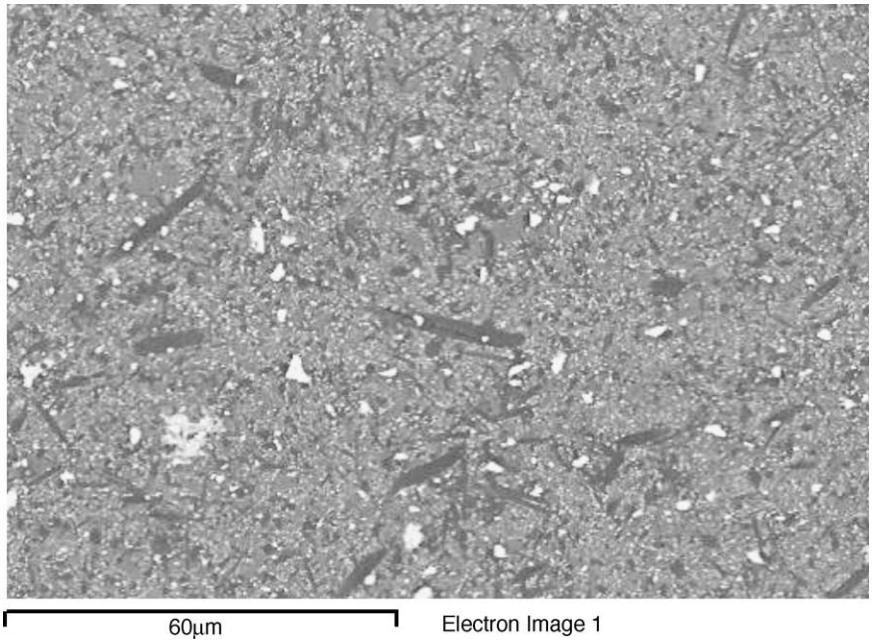

Fig. 4. Back scattered micrograph of the A10 sample (white areas are TiN particles).

The microstructure of the materials consists of elongate grained β-sialon grains and equiaxied α-sialon grains surrounded by a glassy grain boundary phase and of well dispersed secondary phase (TiN) particles (Fig. 4). The grain boundary phase is composed mainly of amorphous phases in the systems Al–Y–Si–O–N and Y–Ti–O. The Y_2O_3 introduced as sintering aids, enters in solid solution in α-sialon grains during the re-precipitation phenomena that occur in the liquid phase sintering process. Moreover, Y_2TiO_5 was identified in sample A10 among the re-crystallized grain boundary phases after annealing tests, indicating that during sintering of the TiN-containing mixture, TiO_2 present on the surfaces of TiN particles interacts with Y_2O_3 leading to the formation of yttrium titanate [11]; this phase is therefore, present in the amorphous state in the as pressuerless sintered material. The XRD results showed that the α content in the final composition decreased with the introduction of TiN, as shown in Fig. 5, which means the residual yttrium in the grain boundary phase increased. It is known that the yttrium is responsible for the degradation of the resistance in HCl solution due to the formation of soluble YCl_3 [12,13] Therefore, with the increasing of TiN, the corrosion rate increased.

Fig. 6 shows the amount of titanium and yttrium ions dissolved in the corrosion solution. It revealed that with the increasing of TiN content, titanium and yttrium ions increased, which indicated that more yttrium remained in the ground boundary phase due to the introduction of TiN during the sintering process and then dissolved in the acid solution during the corrosion process.

Fig. 7 shows the mass loss of sample A0 and A10 as a function of corrosion time. The results showed that the

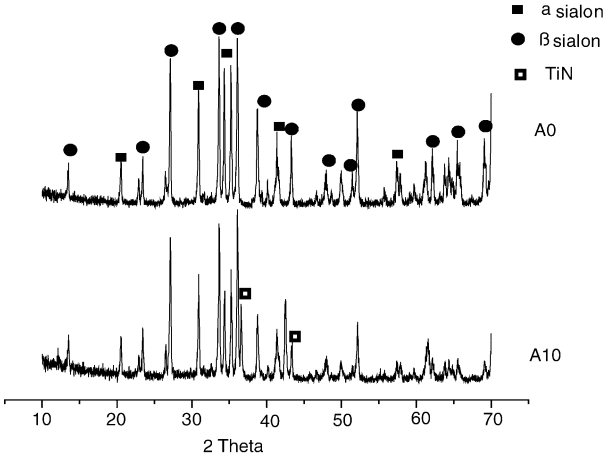

Fig. 5. XRD patterns of A0 and A10 samples.

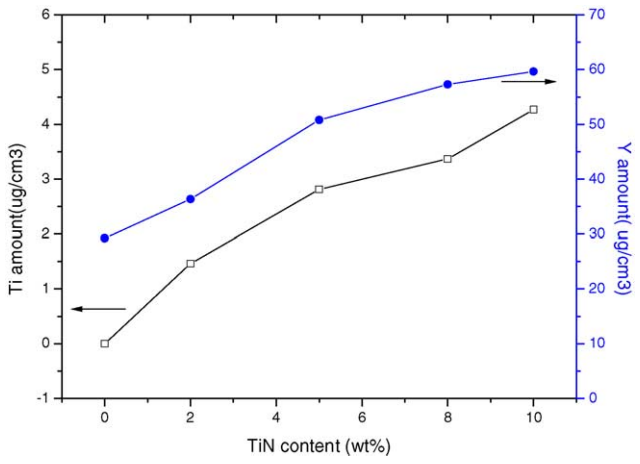

Fig. 6. Amount of Ti and Y dissolved in the corrosion solution.

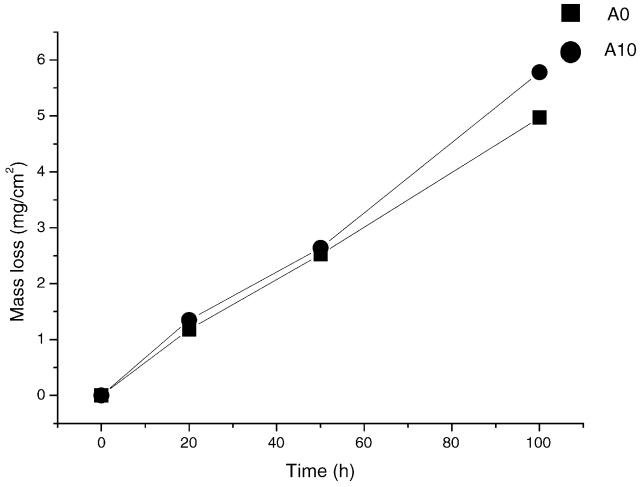

Fig. 7. Mass loss of A0 and A10 samples after different exposure time.

corrosion rate is nearly linear, which indicated that the progress of acidic attack is completely interfacial- and reaction-controlled.

4. Conclusions

The corrosion behavior of Y-(α + β)-sialon/TiN materials in hot hydrochloric acidic solutions (80 °C) was studied and a conclusion could be drawn that the introduction of TiN decreased the corrosion resistance due to changing the final composition, especially the residual yttrium in the grain boundary phase. The corrosion was interfacial- and reaction-controlled and, therefore, the corrosion rate was nearly linear in present experiment condition.

References

[1] V.A. Izhevskiy, L.A. Genova, J.C. Bressiani, F. Aldinger, Progress in SiAlON ceramics, J. Eur. Ceram. Soc. 20 (2000) 2275–2295.
[2] Salah-Ud Din, Saif Ullah, Corrosion of hot-pressed silicon nitride by potassium oxide and sulphur dioxide vapours, Mater. Lett. 31 (1997) 141–144.
[3] S.W. Sharkawy, A.M. El-Aslabi, Corrosion of silicon nitride ceramics in aqueous HCl and HF solutions at 27–80 °C, Corr. Sci. 40 (7) (1998) 1119–1129.
[4] B. Seipel, K.G. Nickel, Corrosion of silicon nitride in aqueous acidic solutions: penetration monitoring, J. Eur. Ceram. Soc. 23 (2003) 595–602.
[5] F. Monteverde, C. Mingazzini, M. Giorgi, A. Bellosi, Corrosion of silicon nitride in sulphuric acid aqueous solution, Corr. Sci. 43 (2001) 1851–1863.
[6] S. Shimada, T. Okuyama, H. Kiyono, J. Takahashi, Corrosion of HIPed beta-$Si_{6-z}Al_zO_zN_{8-z}$ z = 0, 1, 2, 3 ceramics by NaCl vapor, J. Eur. Ceram. Soc. 23 (2003) 1735–1741.
[7] K.R. Mikeska, S.J. Bennison, S.L. Grise, Corrosion of ceramics in aqueous hydrofluoric acid, J. Am. Ceram. Soc. 83 (5) (2000) 1160–1164.
[8] M. Herrmann, J. Schilm, G. Michael, J. Meinhardt, R. Flegler, Corrosion of silicon nitride materials in acidic and basic solutions and under hydrothermal conditions, J. Eur. Ceram. Soc. 23 (2003) 585–594.
[9] J. Schilm, M. Herrmann, G. Michael, Kinetic study of the corrosion of silicon nitride materials in acids, J. Eur. Ceram. Soc. 23 (2003) 577–584.
[10] V. Medri, M. Bracisiewicz, A. Ruffini, A. Bellosi, Corrosion of hot pressed Si_3N_4–TiN composite in sulphuric acid aqueous solution, Corr. Sci. 45 (2003) 2525–2539.
[11] S. Bellosi, A. Guicciardi, Tampieri, Development and characterization of electroconductive Si_3N_4–TiN composites, J. Eur. Ceram. Soc. 9 (1992) 83–94.
[12] Sato, T.Y. Tokunaga, Corrosion of silicon nitride ceramics in aqueous hydrogen chloride solutions, J. Am. Ceram. Soc. 71 (1988) 1074–1079.
[13] T. Sato, Corrosion of silicon nitride ceramics in aqueous HF solutions, J. Mater. Sci. 23 (1988) 3440–3446.