ELSEVIER

Ceramics International 30 (2004) 267–271

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Protection of silicon nitride ceramics against corrosion in acidic aqueous solutions by enforced internal passivation

B. Seipel, K.G. Nickel*

Eberhard-Karls-University Tuebingen, Institute for Geosciences, Applied Mineralogy, Wilhelmstr. 56, 72074 Tuebingen, Germany

Received 3 March 2003; received in revised form 30 March 2003; accepted 12 May 2003

Abstract

Silicon nitride ceramics with Y_2O_3 and Al_2O_3 as sintering additives were corroded in 1 N sulphuric acid at 90 °C. Any classical corrosion rate model cannot describe the overall kinetics of the corrosion process successfully. At longer corrosions times a kinetic break occurs, after which slow linear corrosion kinetics prevail. The passivation is due to the formation of a defective silica sublayer in the corrosion zone. We show that it is possible to enforce this passivation long before it would occur naturally by a simple hot drying (150 °C) procedure after a critical time. As consequence the total mass loss decreases by a factor of 2–3.

Keywords: B. Grain boundary; C. Corrosion; D. Si_3N_4; E. Structural applications

1. Introduction

Silicon nitride based materials are candidates for applications in chemical plants and energy systems, in which hot fluids are encountered. Pure Si_3N_4 has an excellent resistance against many acids, at least at temperatures up to 100° C [1,2]. In sintered silicon nitride ceramics additives are present and change the corrosion behaviour. The most common additives are Y_2O_3 and Al_2O_3, which we have used in our studies. The corrosion process in acids is then dominated by grain-boundary attack and depends accordingly on the composition and the degree of crystallization of the grain boundary phase [3]. Significantly, corrosion was reported for hydrofluoric acid [3], nitric acid [4] and sulphuric acid [5–8].

Corrosion of those ceramics in aqueous solutions is usually accompanied by a mass loss to the corrosive medium. Previously we reported that the mass loss can be attributed to the dissolution of the glassy Y–Al–Si–O grain boundary phase in Y_2O_3/Al_2O_3-containing Si_3N_4 ceramics corroded in diluted sulphuric acid [6]. For some cases the process was shown to involve the preferential leaching of Al and Y and yielded a duplex corrosion zone with silica free outer and a silica containing inner corrosion layer (Fig. 1). These sub-layers were also confirmed by others [7].

The grain boundary attack occurs primarily at triple junctions while the thin interface grain-boundary layers are still intact [8]. TEM investigations indicated that the composition of these interface grain-boundary phases have a higher nitrogen contents than the triple junctions [9]. The incorporation of nitrogen improves the corrosion resistance in acids by orders of magnitude [10]. We therefore assume that a minute amount of grain boundary phase persists at the interfaces and stabilises the skeleton of Si_3N_4 grain within the ‘‘silica-free’’ corrosion zone.

The formation of the inner corrosion layer caused a strong reduction of the corrosion velocity and hence pointed to the possibility to retard the corrosion. In this work we show the first results on the controlling parameters for the internal passivation of silicon nitride ceramics.

2. Experimental set-up

We used a Si_3N_4 ceramic with app. 6 wt.% Y_2O_3 and 4 wt.% Al_2O_3 from the Fraunhofer-Institut of Ceramic Technologies and Sintered Materials (IKTS Dresden). XRD investigations did not give any evidence for crystalline phases within the grain boundaries.

---

* Corresponding author. Fax: +49-7071-293060.
E-mail address: klaus.nickel@uni-tuebingen.de (K.G. Nickel).

0272-8842/03/$30.00 © 2003 Elsevier Ltd and Techna S.r.l. All rights reserved.
doi:10.1016/S0272-8842(03)00098-1

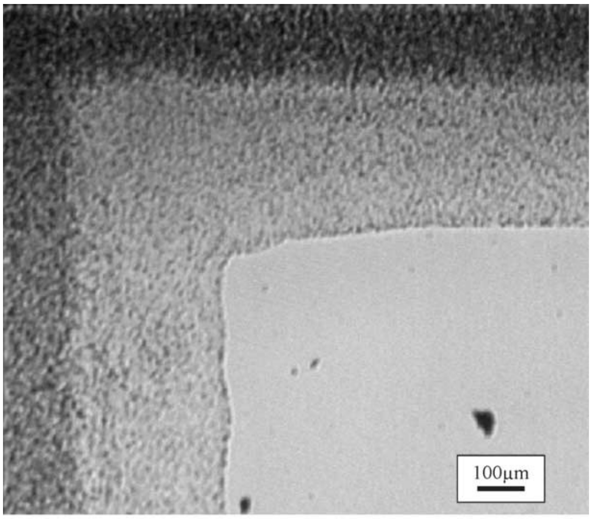

Fig. 1. Optical micrograph of a duplex corrosion zone in a silicon nitride ceramic after 48 h in 1 N H_2SO_4. Grey levels mark clearly outer and inner corrosion layer and the uncorroded material.

The samples were cut and ground in rectangular 3.5/3/45 mm beams. The samples were tested in 1 N sulphuric acid in a steady-state-apparatus to avoid any possibility of a change in the corrosion medium during the experiment. The apparatus was described elsewhere [6]. All experiments were conducted at a temperature of 90 °C.

The standard preparation procedure after corrosion experiments was to wash the samples in acetone for 10 min, rinse with deionised water, place them into a cabinet dryer for ⩾2 h at 150 °C and weigh them on a microbalance (Sartorius; $d = 0.01$ mg) after a 2 h cooling period.

To test the influence of the drying step on the corrosion behaviour we performed experiments in three different ways:

(1) Continuous corrosion (CC): every experiment is performed on a fresh, untreated sample and continuously corroded for the time of the experiment. This is the most common test procedure in corrosion science.

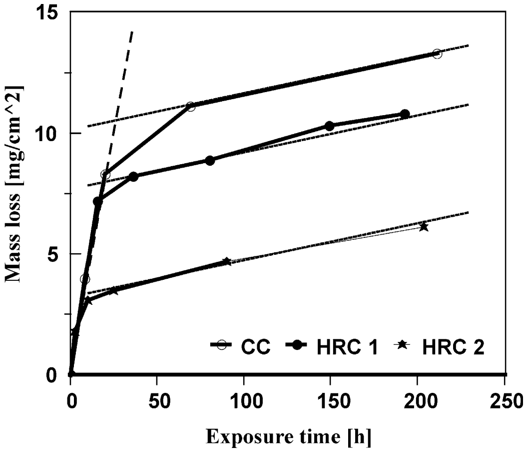

Fig. 2. Continuous (CC) and hot-dried re-corrosion (HRC) experiments with different times of treatment. The lines indicate the two linear corrosion rates.

(2) Hot dried re-corrosion (HRC): After the corrosion treatment and the standard preparation procedure with the 150 °C drying step the sample is re-introduced into the corrosion medium. This procedure is repeated until the final time is reached.

(3) Cold dried re-corrosion (CRC): The procedure differs from (2) only in the drying step. Here we dried the samples at room temperature for ⩾12 h.

The surfaces and the cross sections of the corroded materials were analysed by light microscope and micro Raman spectroscopy (LABRAM, Dilor) using a wavelength of 632 nm.

3. Results

In a first set of experiments we compared CC and HRC 1 experiments. The mass losses are shown in Table 1. The first break in the HRC 1 experiment was after 16 h. The treatment of CC and HRC 1 are identical up to the first break and therefore it is no surprise that the HRC 1 experiments are exactly in line with the set of CC experiments up to 20 h (Fig. 2).

Table 1
Mass losses for the tested materials

CC		HRC 1		HRC 2		CRC	
Time (h)	Mass loss (mg/cm^2)	Time (h)	Mass loss (mg/cm^2)	Time (h)	Mass loss (mg/cm^2)	Time (h)	Mass loss (mg/cm^2)
8.25	4.0	16	7.2	3	1.8	4.5	2.1
20.00	8.3	36.25	8.2	10	3.1	6.75	2.7
69.00	11.1	80.5	8.9	25	3.5	10.25	4.0
211.00	13.3	149.25	10.3	90.5	4.7	34.25	8.5
		192.75	10.8	203.5	6.1		

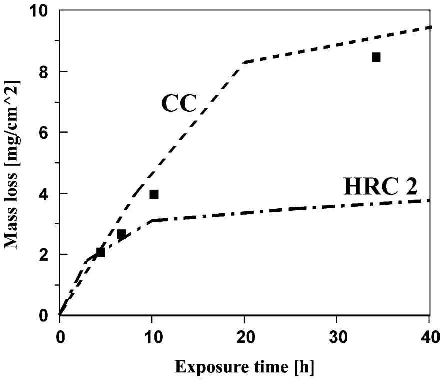

Fig. 3. Cold-dried re-corrosion experiments (CRC, squares) in comparison to CC and HRC.

In Fig. 2 several features are shown: (a) the initial stage of the corrosion process is a linear process with high mass losses, (b) CC experiments for times exceeding 20 h deviated strongly from the linear correlation with time, (c) HRC 1 experiments do not follow the original linear correlation after re-introduction and (d) they are linearly correlated to the exposure time, but with a much lower rate constant.

In a second set of experiments the time of the first removal of the corrosion specimen was decreased (Table 1). Fig. 2 shows also the mass change of HRC 2, which was treated after 3, 10, 25, 90.5 and 200 h. It can be clearly seen that the slope of the mass-loss curve breaks away from the original correlation, but it does so only after the second removal of the sample from the corrosion process at 10 h. As a consequence the mass losses for longer exposure times were reduced to below 50%. All mass loss curves in Fig. 2 appear to be linear and parallel after the break from the first linear correlation.

In the third set of experiments we conducted cold dried re-corrosion (CRC) treatments. The mass changes of the samples after exposure times up to 34.25 h are given in Table 1 and shown in Fig. 3. The CRC sample behaves similar to the CC experiments.

Raman spectroscopy line scans with a 10μm spacing across the corrosion zones of a CRC and a HRC sample are shown in Fig. 4. The Raman intensities plotted cannot be compared directly, because the measuring time at a given spot was 3 s for the CRC sample and only 0.5 s for the HRC sample. This was necessary, because the luminescence in the HRC sample would have exceeded the detector limit at longer times. Therefore the increase of luminescence at the edge of the CRC sample is by far lower than the peak for the HRC sample. The luminescence maximum of the HRC sample is at the inner part of the corrosion zone.

4. Discussion

In the corrosion of the silicon nitride ceramic by diluted H_2SO_4 a loss of material was observed. The mass losses show a linear behaviour in the initial stage of the corrosion process. This is indicative of a dissolution

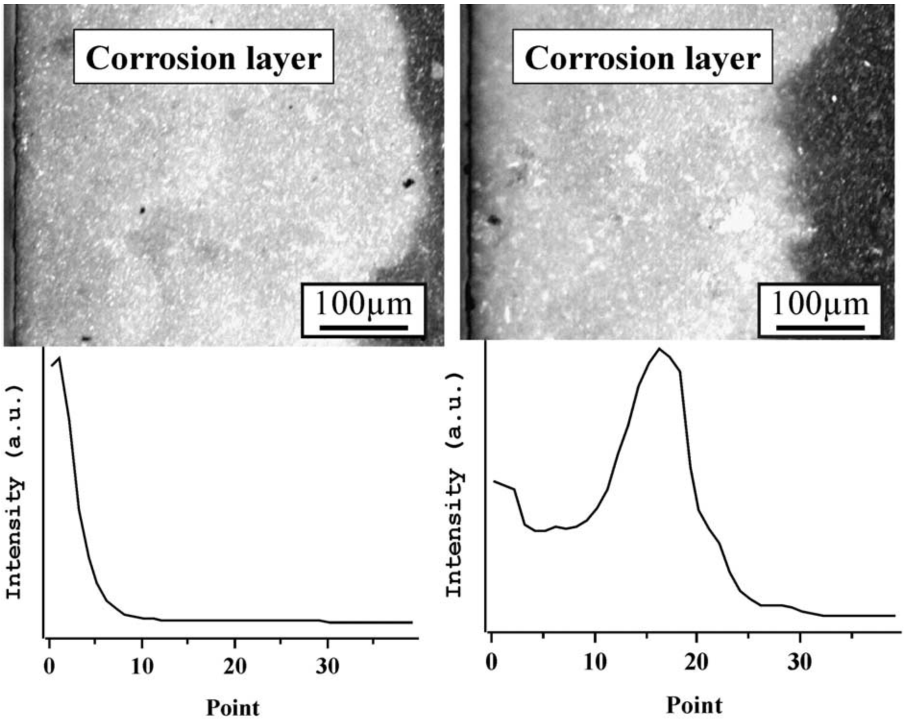

Fig. 4. Relative intensity of the luminescence detected by Raman spectroscopy: Left: cold dried re-corroded; Right: hot dried re-corroded. The maximum at the edge of the CRC sample is far less then the peak of HRC, because integration times are 6 times longer.

process without protective layer. At longer exposure times the corrosion rate decreases.

The corrosion is an attack on a glassy grain boundary phase. Hence for the interpretation of this phenomenon classical glass corrosion experiences have to be considered [10]. The leaching of the network modifiers and the formation of a hydrated glassy network dominate the dissolution of SiO_2-containing glass under acidic conditions

$$\equiv n(\mathrm{Si{-}O}) - \mathrm{M}^{n+} + \mathrm{nH}^{+} \rightarrow n\mathrm{SiOH} + \mathrm{M}^{n+}_{(\mathrm{aqu.})} \qquad (1)$$

$$\equiv n(\mathrm{Si{-}O}) - \mathrm{M}^{n+} + n\mathrm{H_2O} \rightarrow n\mathrm{SiOH} + \mathrm{M}^{n+}_{(\mathrm{aqu.})} + n\mathrm{OH}^{-} \qquad (2)$$

In long time corrosion the dissolution of the hydrated glassy phase

$$\equiv \mathrm{Si{-}O{-}SiO}_{3-n}(\mathrm{OH})_n \ + \mathrm{H}^{+}(\mathrm{aq.})$$

$$\rightarrow \ \mathrm{Si{-};\,OH} \ + \mathrm{SiO}_{3-n}(\mathrm{OH})_{n+1}(\mathrm{aq.}) \qquad (3)$$

becomes the rate-controlling step in the further corrosion process. The kinetics of the combined hydration-leaching-dissolution process is usually modelled in the form [11,12]

$$\frac{\Delta m}{A} = k_{\mathrm{lin}}t + k_{\mathrm{para}}\sqrt{t} \qquad (4)$$

where k_{lin} and k_{para} represents the linear and parabolic rate constants, Δm the weight change, A the surface area of the sample and t the corrosion time.

However, detailed kinetic investigations on Si_3N_4 materials with various amounts of sintering additives revealed that for those the passivation mechanism can not described by Eq. (4) [7], because the slowing down of the corrosion is stronger then predicted.

This is true for our experimental data as well. In Fig. 5 we have plotted the experimental data of the CC-samples along with fits according to Eq. (4), varying the fit from a purely parabolic one (k_{lin} $=0$) to fits with increasing linear contribution. It is evident that it is impossible to describe the behaviour correctly with the classic glass-corrosion Eq. (4).

The reason was thought to involve a condensation reaction in the corrosion layer

$$2 \equiv \mathrm{Si{-}O{-}H} \ \rightarrow \ \mathrm{Si{-}O{-}Si} \equiv + \mathrm{H_2O} \qquad (5)$$

which turns soluble silicic acid into hydrated silica [8], which acts as a protective barrier.

In a previous paper [6] we confirmed the role of silica by Raman spectra of corrosion layers, which were dominated by high luminescence, which could be attributed to defect structures of SiO_2. From Fig. 4 it is obvious that the change in the corrosion kinetics in the presented experiments is likewise due to the presence or absence of this layer of defective silica.

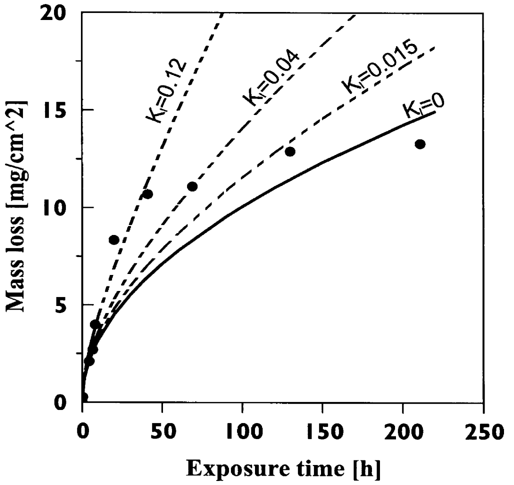

Fig. 5. Experimental data from CC-experiments (dots) with approximations according to Eq. (4). $K_{\mathrm{l}} = K_{\mathrm{lin}} = 0$ is equivalent to a pure parabolic rate law. There is no possible agreement between the classic model and the data.

In the results of this work we showed that the formation of such a protective silica layer could be enforced by a hot drying post-treatment procedure. The important parameter for this behaviour seems to be the drying temperature, because the samples dried at room temperature did not form such a layer, which was confirmed by Raman spectroscopy. It is assumed that the drying process at 150 °C supports a condensation reaction analogue to (5) in the grain boundaries. Recent investigations confirmed that the dehydration of sianol groups into siloxane bonds belonging to three-membered silicate rings, takes place at temperatures above 150 °C [13].

The linear and parallel character of the mass loss curves in Fig. 2 indicates that a reaction-controlled process prevails, probably the dissolution of the previously formed silica. The fact that there is an outer corrosion zone practically without silica (Fig. 1) is evidence for the dissolution. The linear kinetic has a consequence for the modelling: the barrier formation is a true break in the corrosion kinetics, and therefore no classic continuous equation is able to predict the process completely.

The change in corrosion rate can be forced to occur earlier then the natural break during continuous corrosion, but from the data in Fig. 3 it can be seen that it requires a minimum advance of the corrosion. A pre-corrosion treatment for less then 10 h was insufficient to make an enforced protective layer. Currently we do not know, which is the limiting parameter (minimum corrosion depths, concentration gradient in the solution in the corrosion zone, critical thickness of the layer) for this threshold.

Thus clearly detailed studies are needed to transform this mechanism into a reliable treatment for industrial practice. However, the possibility for a simple low-cost method to lower the corrosion levels of Si_3N_4 materials attacked by sulphuric acid is evident.

5. Conclusion

Sintered silicon nitride ceramics with a glassy Y–Al–silicate grain boundary phase are attacked by diluted sulphuric acid. At 90 °C the corrosion process follows initially classical glass corrosion kinetics with a combined hydration–leaching–dissolution mechanism. At longer exposure times/corrosion depths a kinetic break occurs. The new kinetic is linear with a much lower rate constant than the initial process.

The formation of a defective silica layer within the corrosion zone is responsible for the break. The layer, which is formed during continuous corrosion at a certain corrosion progress can be artificially enforced by a drying procedure. It was shown that a hot (150 °C) treatment was necessary; it did not work on room temperature drying.

The layer formation marks a true kinetic break in the corrosion kinetics. Therefore no classic corrosion rate model can describe the overall kinetics.

With an enforced layer the overall corrosion mass loss can be lowered significantly. The method is simple and low-cost.

To be able to enforce the layer formation a critical corrosion progress before drying is necessary. Currently, we are investigating the limiting parameter for the threshold value.

Acknowledgements

The authors thank the Fraunhofer-Institut of Ceramic Technologies and Sintered Materials (IKTS Dresden), namely Dr. Matthias Herrmann and Jochen Schilm, for preparing the material. We greatfully acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG) under contract number Ni299/7.

References

[1] L. Lewis, Corrosion Resistance of Technical Ceramics, Her Majesty's Stationery Office, London, 1984.

[2] T. Sato, et al., Corrosion of silicon nitride ceramics in aqueous hydrogen chloride solutions, J. Am. Ceram. Soc. 71 (12) (1988) 1074–1079.

[3] T. Sato, et al., Corrosion of silicon nitride ceramics in aqueous HF solutions, J. Mat. Sci. 23 (1988) 3440–3446.

[4] K. Kanbara, et al., Corrosion of silicon nitride ceramics by nitric acid, Mater. Res. Soc. Symp. 287 (1993) 533–538.

[5] A. Okada, et al., Corrosion behaviour of silicon nitride ceramics in aqueous solutions (Part 2)—weight loss and bending strength tested in boiling sulfuric acid, J. Ceram. Soc. Jpn. Int. Ed. 100 (1992) 80–84.

[6] B. Seipel, K.G. Nickel, Corrosion of silicon nitride in aqueous acidic solutions: penetration monitoring, J. Eur. Ceram. Soc. 23 (2003) 595–602.

[7] J. Schilm, M. Herrmann, G. Micheal, Kinetic study of the corrosion of silicon nitride materials in acids, J. Eur. Ceram. Soc. 23 (2003) 577–584.

[8] M. Herrmann, et al., Corrosion of silicon nitride materials in acidic and basic solutions and under hydrothermal conditions, J. Eur. Ceram. Soc. 23 (2003) 585–594.

[9] Y. Bando, M. Mitomo, K.J. Kurashima, An inhomogeneous grain boundary composition in silicon nitride, Mater. Synth. Process. 6 (1998) 359.

[10] H. Scholze, Glas—Natur, Struktur und Eigenschaften, Springer Verlag, 1988.

[11] R.W. Douglas, T.M.M. El-Shamy, Reactions of glasses with aqueous solutions, J. Am. Ceram. Soc. 50 (1967) 1–8.

[12] D.E. Clark, C.G. Pantano, Corrosion of Glass, Books for Industry and the Glass Industry, New York, 1979.

[13] A.S. D'Souza, C.G. Pantano, Hydroxylation and dehydroxylation behavior of silica glass surfaces, J. Am. Ceram. Soc. 85 (6) (2002) 1499–1504.