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Strength retention of silicon nitride after long-term oil immersion exposure

H. T. Lin · T. P. Kirkland · A. A. Wereszczak ·
M. J. Andrews

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Abstract Two commercial grade silicon nitride ceramics (Honeywell GS44 and Kyocera SN235) were exposed to an oil ash to evaluate the long-term corrosion/oxidation resistance in a simulated diesel engine environment. The exposure condition was at 850 °C for 1000 h in air. Subsequently, the exposed specimens were tested in flexure for strength degradation at room temperature and 850 °C at stressing rates of 30 MPa/s and 0.003 MPa/s in air, respectively. A similar set of specimens not exposed to the oil ash was also tested in flexure for purpose of comparison. Little change in strength was measured after 1000 h exposure in the oil ash environment. Also, the values of Weibull modulus obtained for all of the exposed silicon nitride materials were similar to those with the unexposed specimens whose strength were obtained under the same conditions. However, both exposed and unexposed GS44 specimens exhibited a low fatigue exponent, suggesting a susceptibility to slow crack growth at test temperature. In addition, detailed SEM/EDAX analyses indicated that no oil ash elements (e.g., Zn, Ca, P, Na, and S) were detected beneath a thin layer in the surface; thus, there were no changes in the chemistry of the secondary phase(s) within the bulk. These elements were detected only in a region about 1–3 μm below the exposed surface, but no apparent changes in microstructure observed. Results of mechanical properties and microstructural characterizations indicated that these candidate silicon nitride materials exhibited excellent corrosion/oxidation resistance in the simulated diesel engine environment and, based on their excellent mechanical strengths, would be ideal candidates for diesel engine exhaust valve applications.

Introduction

Advanced silicon nitride ceramics with reinforcing elongated grain microstructure continue to be of interest for use as exhaust valves in advanced diesel engines. Compared to conventional stainless steels used to fabricate current valves, silicon nitride is lighter, harder, and can withstand higher operating conditions. Implementation of silicon nitride valves in advanced diesel engines potentially can result in better efficiency, lower exhaust NOx and CO emission, and improved reliability and longer lifetime [1–4]. A study was carried out by Rodgers et al. [3] to quantify this difference through the examination of a 2.8-l overhead valve V-6 engine. A 20% increase in engine speed, a 30% reduction in the maximum valve forces, and a 30% reduction in valve train friction could be realized with a change to silicon nitride valves, and this would manifest itself into as much as a 5% increase in fuel economy.

An extensive testing program was carried out to select candidate silicon nitride ceramics for valve components and, for the generation of probabilistic strength and fatigue database on several commercially available silicon nitride ceramics [5]. Based on the

H. T. Lin (✉) · T. P. Kirkland · A. A. Wereszczak
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6068, USA
e-mail: linh@ornl.gov

M. J. Andrews
Caterpillar Inc., Technology Center, Peoria, IL 61656, USA

mechanical results and extensive microstructural analysis, both Honeywell GS44 and Kyocera SN235 were then selected for long-term corrosion testing in a simulated diesel engine environment. The final section of a candidate silicon nitride material for exhaust valve manufacturing will be determined by the assessment of the long-term stability of microstructure and chemistry, and thus mechanical reliability in application environments. An oil immersion test was instrumented to evaluate the corrosion mechanisms of silicon nitride ceramics in heavy diesel engines [6]. This test allows one to elucidate the effects of engine lubricants and their combustion products on the corrosion resistance of silicon nitride ceramics. It is anticipated that the silicon nitride ceramics investigated could exhibit different corrosion mechanisms and mechanical performance as compared to the response of advanced candidate metallic alloys.

The present study involved the generation of probabilistic strength and fatigue databases on two candidate silicon nitride ceramics after 1000 h exposure to a simulated diesel engine environment (oil immersion test). The characteristic strength, fatigue performance, and microstructural stability are compared and discussed.

Experimental procedures

The silicon nitride ceramics tested in this study are GS44 (Honeywell Ceramic Components, Torrance, CA) and SN235 (Kyocera Industrial Ceramics, Vancouver, WA). GS44 was manufactured via cold-isostatic-pressing and gas pressure sintering (GPS) with sintering additives of MgO, Y_2O_3, and Al_2O_3, while the Kyocera SN235 was fabricated via GPS with Y_2O_3 and Al_2O_3 additives. Bend bar specimens with dimensions 3 mm × 4 mm × 50 mm of each material were machined and transversely ground with respect to the length of each bar from purchased billets per ASTM C1161 [7]. All specimens were longitudinally chamfered.

The silicon nitride test bars were place in platinum crucibles and covered with commercially available diesel engine oil. Crucibles were then heated in a furnace at 600 °C for approximately 30 min in air to ash the oil. After completion of oil-ash conversion, the specimens were covered with 1–2 mm thick oil ash powder, and were then heat-treated at 850 °C for 1000 h in ambient air. In this test environment the ash, a corrodent, could attack the silicon nitride ceramics during the long-term heat treatment. This oil immersion test simulates the most harsh corrosion/oxidation environment that the silicon nitride components would be subjected to during engine operation. The chemical analysis of oil ash using the energy dispersive spectroscopy showed the compositions of 20.4% Ca, 3.8% Mg, 6.1% Zn, 5.2% Na, 5.3% S, 8.4% P, and 50.7% O.

Flexure testing on exposed specimens was conducted in ambient air in four-point-bending using 20/40 mm, α-SiC, semi-articulating fixtures at two conditions: 20 °C and 30 MPa/s; and 850 °C and 0.003 MPa/s. The first test condition was chosen to evaluate the effect of long-term oil immersion on the inert characteristic strength at room temperature, while the second test condition was chosen to measure the slow crack growth (SCG) susceptibility at 850 °C after exposure. Note that dynamic fatigue tests at 850°C for as-machined GS44 and SN235 specimens were also carried out at a stressing rate of 30 MPa/s and 0.003 MPa/s to evaluate the temperature effect on the inert characteristic strength and SCG susceptibility. The results obtained for as-machined specimens at 850 °C will be used as a baseline for comparison. In addition, dynamic fatigue tests for oil ash exposed specimens were only carried out at 850 °C and 0.003 MPa/s due to the limited number of specimens available. Comparison of strength data obtained at 850 °C and 0.003 MPa/s for both as-machined and exposed specimens could provide an indication of the effect of long-term oil ash exposure on the SCG susceptibility.

Pneumatic actuators were programmed to produce the desired loading (and corresponding stressing rate) via a personal computer. The load was continuously measured as a function of time, and flexure strength was calculated using ASTM C1161 standard [7]. The accumulated strength data was then further analyzed. The strengths for each test set were fit to a two-parameter Weibull distribution using the program CERAMIC [8], which uses maximum likelihood estimation advocated in ASTM C1239 [9]. The reported results are uncensored because fractography analysis was not conducted to identify strength-limiting flaws.

After long-term exposure in the oil ash environment the surface morphology of both SN235 and GS44 were characterized using optical and scanning electron microscopy (SEM). X-ray analysis was also carried out to evaluate the phases formed from corrosion/oxidation reactions. Following the dynamic fatigue test, SEM analysis was carried out on fracture surfaces and polished cross-sections of selected bend bars to characterize the extent of corrosion/oxidation reaction as well as any degradation mechanisms. Note that the exposed specimens were embedded with epoxy to protect the oxide scale formed during cutting and metallographic preparation.

Results and discussion

Characterization of exposed materials

The surface morphologies of both GS44 and SN235 silicon nitride after 1000 h oil ash exposure were evaluated using optical microscopy and SEM. SEM examinations showed that there was a significant amount of white ash, which loosely adhered to the bend bar surfaces. Remnants of oxide scales, from reaction with the oil ash powder during the 1000 h heat treatment, were still bonded to the silicon nitride substrates, and observed on the surfaces (Figs. 1a and 2a). Observation of these surfaces showed that the original machining features, i.e., grinding ridges and roughness, were still apparent in most of the surface areas where the oxide scale and ash were absent (Figs. 1a and 2a). At higher magnification, there a noticeable thin layer of SiO_2 has formed. This was confirmed by EDAX and X-ray diffraction analysis, and resulted from the 1000 h exposure at 850 °C in air (Figs. 1b and 2b). X-ray analysis of the-exposed bend bars showed the presence of calcium zinc phosphate ($Ca_{19}Zn(PO_4)_{14}$), β-silicon nitride, and cristobalite. The formation of calcium zinc phosphate (oxide scales shown in Fig. 1a) resulted from the oxidation and reaction of oil ash elements, i.e., Zn, Ca, P, Na, and S, which were commonly present in the form of additives [6]. The formation of cristobalite was due to the oxidation of silicon nitride grains.

SEM examination of polished cross sections of as-exposed SN235 and GS44 silicon nitride revealed little changes in the subsurface microstructure below 1–3 µm depth (Fig. 3). Element mapping on the polished surface of each ceramic showed that the elements of Zn, Ca, P, Na, and S present in the engine oil were detected only in the top 1–3 µm region. Note that introduction of Ca and/or Na (known as glass modifiers) could significantly decrease the softening temperature and viscosity of any amorphous intergranular phase(s), possibly resulting in substantial degradation in mechanical performance at elevated temperatures. This is particularly true when the silicon nitride specimens were heat-treated at or near the softening temperatures of the intergranular phase(s). The very limited penetration by the oil ash elements suggests that the silicon nitride grains and the secondary phases of GS44 and SN235 are very stable at 850°C under the simulated diesel engine environment during the 1000 h time interval used in the present study.

Uncensored weibull strength distributions

The results for both the characteristic strength and the Weibull modulus obtained for GS44 and SN235 silicon nitride prior to (as-machined) and after 1000 h oil immersion are listed in Table 1 and displayed graphically in Figs. 4 and 5. The results of the mechanical tests at room temperature indicated that both GS44 and SN235 silicon nitride exhibited little or no degradation in both inert characteristic strength and Weibull modulus after 1000 h exposure to a simulated diesel engine environment. At 850 °C the as-machined GS44

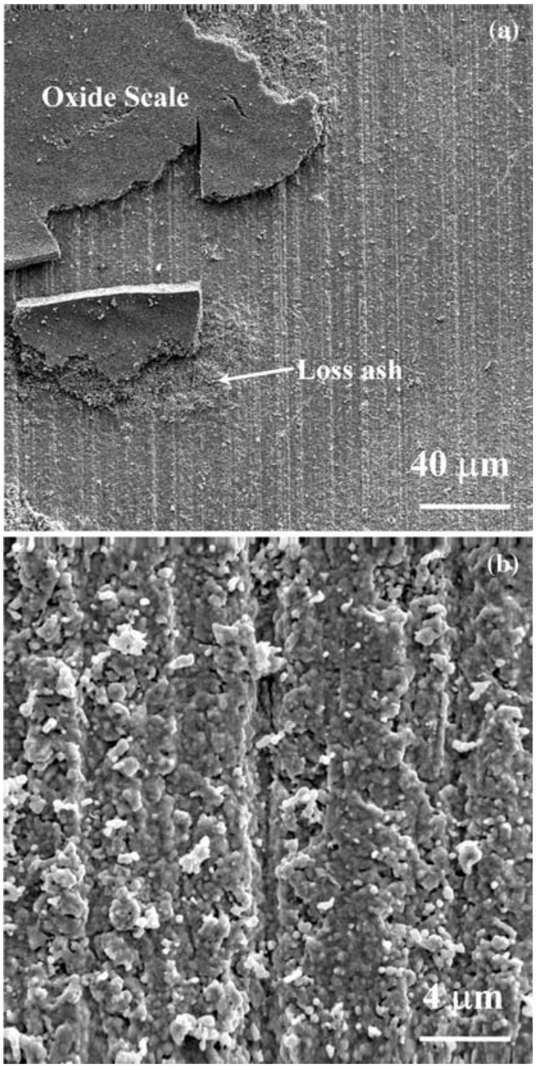

Fig. 1 SEM surface features of Kyocera SN235 after 1000 h oil immersion test. (**a**) Photo shows the oxide scale (calcium zinc phosphate) and machining marks. (**b**) Photo reveals the micro nodule feature due to oxidation reaction

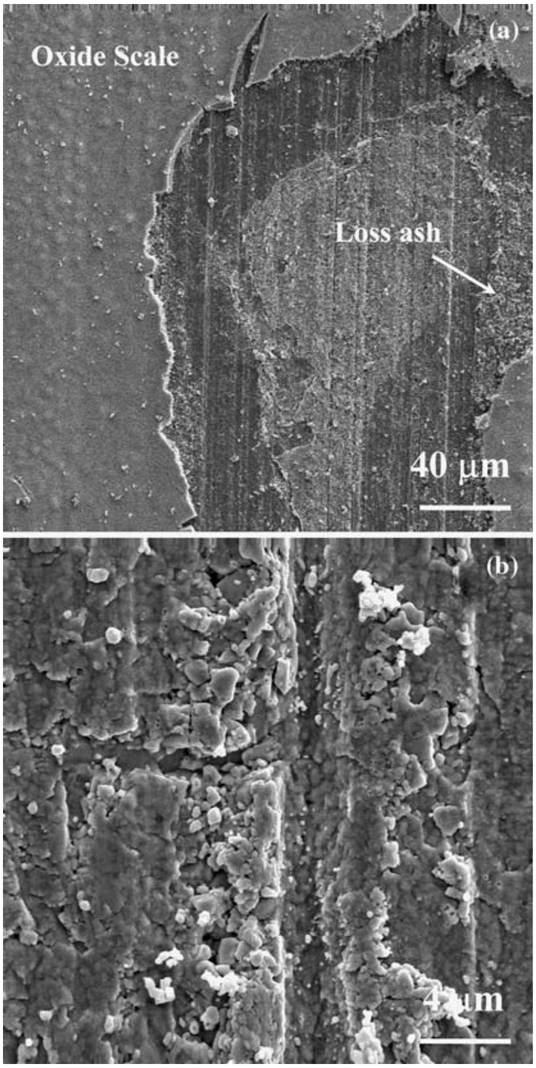

Fig. 2 SEM surface features of Honeywell GS44 after 1000 h oil immersion test. (**a**) Photo shows oxide scale (calcium zinc phosphate) and machining marks. (**b**) Photo reveals the micro nodule feature due to oxidation reaction

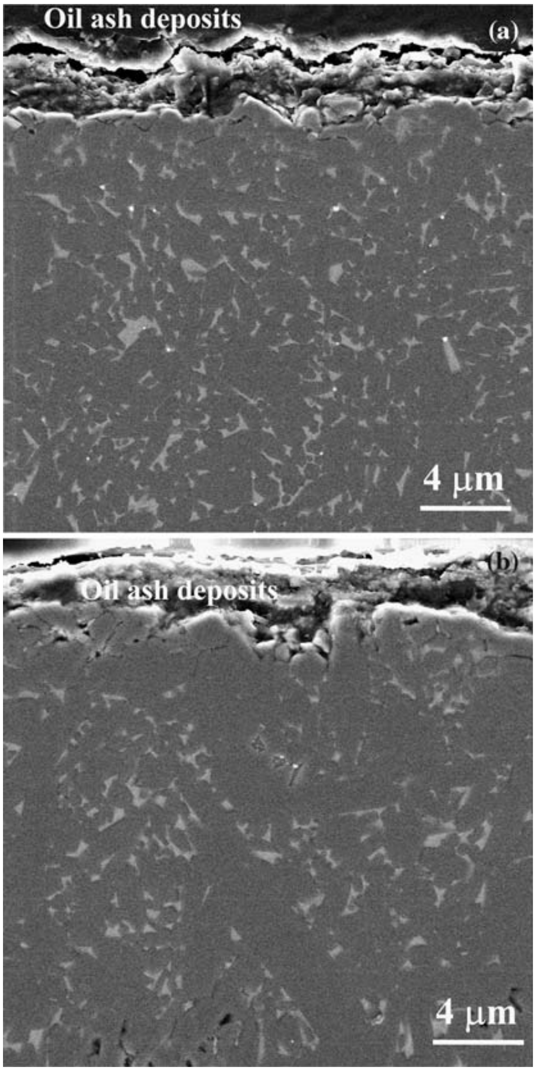

Fig. 3 Polished cross sections of (**a**) Kyocera SN235 and (**b**) Honeywell GS44 after 1000 h oil immersion test

specimens tested at 30 and 0.003 MPa/s stressing rate exhibited a low fatigue exponent, N, of 28, indicating high susceptibility to SCG. A previous study [5] attributed the low fatigue exponent of GS44 to the softening of the secondary phase at temperature, resulting in the initiation of SCG and/or creep processes.

The as-machined SN235 specimens tested at 850 °C exhibited a high fatigue exponent of 164, indicating little or no susceptibility to SCG. In addition, the strength and the Weibull modulus obtained at 850 °C and 0.003 MPa/s for the exposed bend bars were comparable to those obtained for the as-machined materials tested under the same test condition. The observed similarities in high temperature mechanical performance suggested that there was little change in the SN235 ceramics arising from the 1000 h exposure to oil ash environment, consistent with the SEM observations and element mapping results.

Examinations of the fracture surfaces for specimens tested at 850 °C (Fig. 6) showed no change in surface feature for the SN235 specimens Limited formation of a glassy phase and the presence of pores were observed in the 2–3 μm subsurface region of GS44, similar to the observations of Fig. 3b. The softening point of the secondary phase in GS44 is between 800 °C and 850 °C [5], while the softening point of SN235 is between 1150 °C and 1200 °C (H. T. Lin, unpublished results). It is expected that the long-term oil immersion test at 850 °C in air had a more profound effect on the mechanical performance of GS44 than SN235. It is hypothesized that the oil ash elements could readily

Table 1 Summary of uncensored Weibull strength distributions for GS44 and SN235 silicon nitride specimens, transversely machined per ASTM C1161, in as-machined and after 1000 h oil immersion test condition.

Material	# of specimens tested	Stressing rate (MPa/s)	Temperature (°C)	Uncensored weibull modulus	± 95% Uncensored weibull modulus	Uncensored characteriststic strength (MPa)	±95% Uncensored characteristic strength (MPa)
GS44	15	30	20	28.9	17.5, 43.0	793	775, 811
GS44*	10	30	20	39.20	21.8, 63.5	786	771, 800
GS44	15	30	850	20.2	14.6, 26.8	747	733, 761
GS44	15	0.003	850	25.8	16.6, 37.0	545	532, 556
GS44*	10	0.003	850	23.04	13.3, 35.8	488	472, 503
SN235	15	30	20	23.8	15.4, 33.9	901	879, 923
SN235*	10	30	20	18.64	10.24, 29.97	894	858, 929
SN235	15	30	850	26.7	18.0, 36.7	777	760, 793
SN235	14	0.003	850	18.5	11.8, 26.8	744	720, 767
SN235*	10	0.003	850	13.04	6.92, 21.52	827	777, 877

*Specimens exposed to an oil ash environment at 850 °C for 1000 h in air

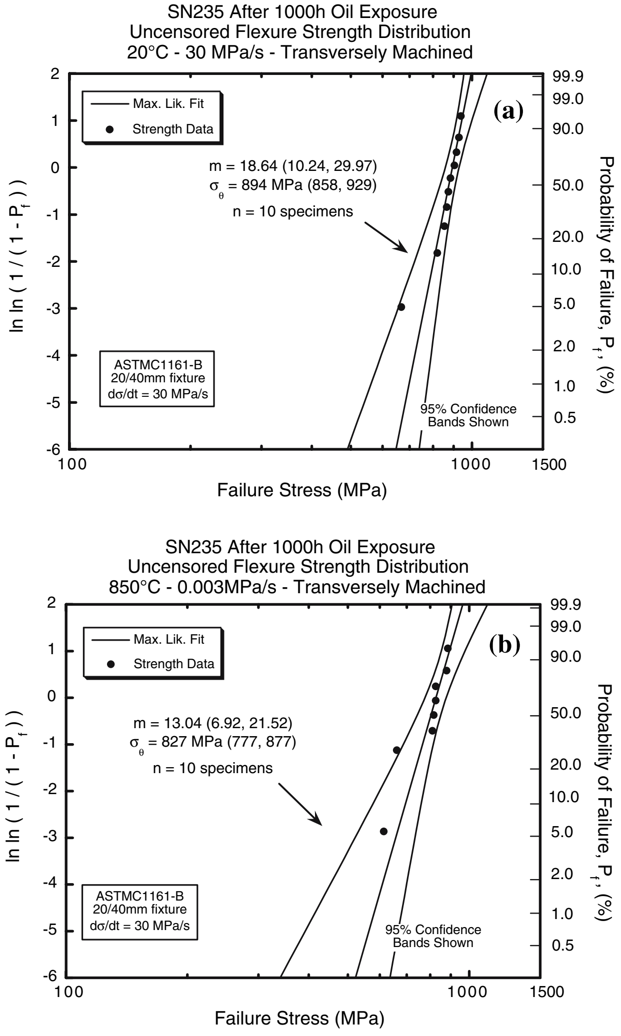

Fig. 4 Uncensored flexural strength distribution of exposed Kyocera SN235 tested at (**a**) 20°C and 30 MPa/s and (**b**) 850 °C and 0.003 MPa/s

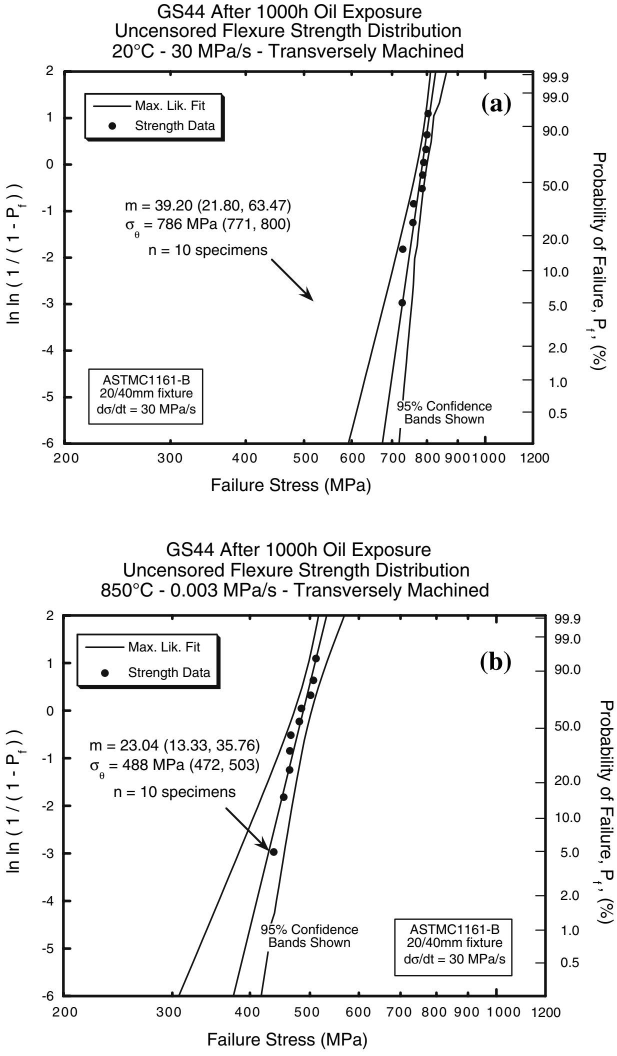

Fig. 5 Uncensored flexural strength distribution of exposed Honeywell GS44 tested at (**a**) 20 °C and 30 MPa/s and (**b**) 850 °C and 0.003 MPa/s

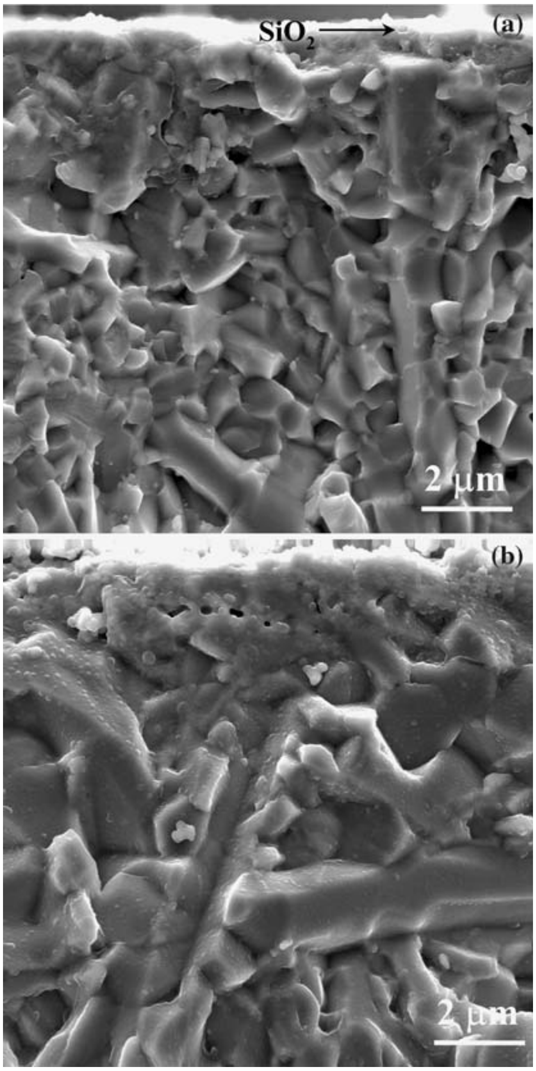

Fig. 6 Fracture surfaces of exposed (**a**) Kyocera SN235 and (**b**) Honeywell GS44 samples after flexural testing at 850 °C and 0.003 MPa/s

penetrate into the bulk of the GS44 along the viscous glassy phase at the grain boundaries further lowering the viscosity and degrading the high temperature mechanical properties. However, SEM/EDAX analysis showed little change in both the microstructure and chemistry of the exposed GS44 specimens, thus no degradation in mechanical performance arising from oil ash exposure, as seen in Table 1. It is possible that silica formation on the surfaces due to the oxidation of silicon nitride grains could inhibit the ingression of oil ash elements into the bulk and secondary phase. In addition, the calcium zinc phosphate that formed on the exposed surface is porous and not well bonded to the silicon nitride substrates. No significant reaction was observed between the calcium zinc phosphate and silicon nitride substrates within the 1000 h exposure time. However, a much longer exposure time up to 10,000 h (~500–600 k miles heavy-duty diesel engine lifetime) is needed to ensure the long-term stability of silicon nitride in a diesel engine environment.

The mechanical test results showed that the SN235 exhibited no mechanical strength degradation or susceptibility to SCG after 1000 h oil ash exposure. The SEM examinations also revealed little reaction or penetration of oil ash elements into the bulk and secondary phase of SN235, suggesting of excellent corrosion resistance to a diesel engine environment. The excellent resistance to SCG and diesel engine environment led the end user (Caterpillar) to select Kyocera SN235 as the final candidate for exhaust valve component applications. Metallic alloys, which are also candidates for valve components, showed the depths of corrosion ranging from 4 to 18 μm after only 48 h oil immersion tests at 750 °C (M. Andrews, Caterpillar Inc., private communication). The results of this study demonstrate that silicon nitride ceramics exhibit superior corrosion resistance to current candidate metallic alloys. A diesel engine test with SN235 silicon nitride ceramic valves will be carried out in the future to validate the probabilistic design, mechanical performance, and corrosion resistance.

Summary

Flexural tests were carried out on both Kyocera SN235 and Honeywell GS44 bend bars after 1000 h exposure to an oil ash environment at room temperature and 850 °C at stressing rates of 30 MPa/s and 0.003 MPa/s in air. Little change in strength was measured after 1000 h exposure to the mentioned oil ash environment. The Weibull modulus values obtained for all of the exposed silicon nitride materials were similar to those with as-machined surfaces tested under the same conditions. In addition, the detailed SEM/EDAX analyses showed that no oil ash elements were detected in the bulk, especially along the grain boundaries, which resulted in no changes in the chemistry of the secondary phase(s). Furthermore, no corrosion of silicon nitride grains was observed, and the oil ash elements were only present in a region about 1–3 μm below the exposed surface. The results of this study show that these candidate silicon nitride materials exhibit excellent corrosion/oxidation resistance to the simulated diesel engine environment. The silicon nitrides studied had superior corrosion resistance compared to the metallic alloys currently used for the diesel engine exhaust valves.

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