Proceedings of
2003 ASME Turbo Expo: Power for Land, Sea & Air
June16-19, Atlanta, Georgia, USA

GT2003-38919

DYNAMIC FATIGUE OF CVD-MULLITE COATED SN88 SILICON NITRIDE

H.-T. Lin, M. K. Ferber, T. P. Kirkland, and S. M. Zemskova[1]

Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6068

ABSTRACT

Studies of dynamic fatigue were carried out on CVD-mullite coated and uncoated of SN88 silicon nitride at 850°C and at 30 MPa/s and 0.003 MPa/s in air. The objective of the studies was to evaluate the effect of thin CVD-mullite coatings on the mechanical reliability and lifetime performance of SN88 subjected to mechanical loading conditions. Mechanical results showed that the CVD-mullite coated SN88 samples exhibited similar strength degradation and lifetime performance to those uncoated samples under similar test conditions. SEM examinations of both coated and uncoated samples after mechanical testing also showed similar development of damage zone (i.e., pores and cracking were generated in SN88 surface region) due to oxidation reaction. Results of mechanical testing and SEM examinations indicated that the CVD-mullite coating could not environmentally protect SN88 to ensure a long-term mechanical performance and lifetime in gas turbine environments.

INTRODUCTION

Silicon nitride ceramics with in-situ reinforcing elongated grain microstructure are leading candidates for use as high-temperature structural components in advanced gas turbines due to their superior thermomechanical properties [1-5]. Recent ceramic gas turbine programs, funded by US Department of Energy (DOE), at both Solar Turbines and Rolls Royce Allison [6,7] have carried out many field tests to increase the experience base concerning the behavior of ceramic components in industrial gas turbine environments. For instance, Solar Turbines was awarded the Ceramic Stationary Gas Turbine (CSGT) Development contract from the DOE in 1992 [6,8].

The goals of this program were to improve turbine engine performance (fuel efficiency and output power) and reduce CO and NOx exhaust emissions. The approach involved retrofitting an existing Solar Centaur 50S gas turbine (4.14 MW) with silicon nitride nozzles, silicon nitride blades, and a SiC fiber-reinforced SiC ceramic matrix composite combustor liner.

In September 1998, a 100-h nozzle engine test was planned in which the engine would be subjected to cold and hot engine restarts and shutdown cycles that progressively increased in severity. The nozzles were fabricated from a commercially available SN88 silicon nitride ceramic, manufactured by NGK Insulators, Ltd, Nagoya, Japan. The first engine test was successfully carried out including one-hour full load and 10-h total run time. Subsequently, the second engine test was initiated for a 100-h endurance test. However, the second test did not reach completion, since borescope inspections, which were conducted after routine shutdown cycles, revealed severe cracking after 68 h of engine testing including 15 start/stop cycles. The planned 100-h engine test with SN88 silicon nitride nozzles was, therefore, terminated.

The cracking, which was observed on the airfoil surface of SN88 silicon nitride nozzles, initiated at the region near airfoil/platform transition region, as shown in Fig. 1. Finite-element-analysis of temperature distribution at steady state (~ 1120°C) during engine operation indicated that the temperature in the airfoil/platform transition region ranged from 800 to 900°C [9]. Therefore, the failure of SN88 silicon nitride nozzles, which resulted from crack generation in the

[1] Now with Caterpillar, Inc., Peoria, IL 46206-0402

airfoil/platform transition region, would lead one to surmise that the SN88 silicon nitride might exhibit a mechanical instability at intermediate temperatures in an oxidizing environment. Recently studies carried out by Haynes et al. have shown that thin CVD mullite coatings (~ 2 µm) can effectively suppress the rapid oxidation of SiC/SiC CFCC with CVD SiC seal coats in high-temperature, high-pressure steam environments [10]. Thus, it is hypothesized that the dense CVD-mullite coatings could also provide effective protection from oxidation and subsequent phase change of SN88 silicon nitride components during engine operation. The long-term mechanical reliability and lifetime performance of SN88 silicon nitride can then be retained.

This paper describes the results of the dynamic fatigue study on the CVD-mullite coated and uncoated SN88 silicon nitride ceramic carried out at 850°C in air. Both optical and scanning electron microscopy were used to elucidate the changes in the microstructures arising from the oxidation process. The stability of the secondary phases was evaluated using x-ray diffraction.

EXPERIMENTAL PROCEDURE

The SN88 silicon nitride material evaluated in the present study was gas-pressure-sintered using rare-earth sintering additives (NGK Insulators Ltd., Nagoya, Japan). The predominant secondary crystalline phase present after densification is $Yb_4Si_2O_7N_2$, designated as the J-phase, as identified by X-ray diffraction. Bend bar specimens with dimensions 3 mm x 4 mm x 50 mm were machined from purchased billets. The bend bars were longitudinally machined per ASTM C1161 [11]. Some of the SN88 bend bars from the same billet were coated with CVD mullite in the laboratory-scale horizontal CVD reactor at ORNL. Two bend bar specimens were coated per CVD run. Deposition conditions were as follows: deposition temperature - 1000°C, gas flow rates (sccm) – Ar-150, H_2-300, CO_2-50, $SiCl_4$-8.5. Standard deposition time was 2h, and the final coating thickness was 2-2.5µm. The experimental details of coating procedures can be found elsewhere [10].

Dynamic fatigue testing was conducted in four-point-bending using 20/40mm, α-SiC, semi-articulating fixtures at test conditions of 20°C and 30 MPa/s; 850°C and 30 MPa/s; and 850°C and 0.003 MPa/s in ambient air per ASTM C1465 [12]. The first two test conditions were chosen to compare the inert characteristic strength dependence on temperature, while the last two conditions were chosen to measure dynamic fatigue susceptibility at 850°C. Note that 15 and 6 test specimens for uncoated and coated samples were employed for each test condition, respectively. The test frame's pneumatic actuators were programmed to produce the desired loading (and corresponding stressing) rates via a personal computer through sintered α-SiC push rods. Load was continuously measured as a function of time, and flexure strength was calculated using the total thickness of coated bend bars via the ASTM C1161. Upon the failure of the last sample in the furnace chamber the sensors interrupt the furnace power supply circuit to allow the bend bars to cool rapidly to minimize damage and oxidation of the fracture surface of the last test bend bar.

Fractography and SEM analysis were performed on selected samples to provide insight into the dominant failure controlling process as a function of test temperature and stressing rate. X-ray diffraction analysis was also carried out to compare the dominant secondary phase(s) present before and after dynamic fatigue tests at elevated temperatures in air. Polished cross sections for selected samples, which included fracture surface edges, were also prepared to elucidate the change in microstructure as a function of test condition.

RESULTS AND DISCUSSION

Figure 2 summarizes the dynamic fatigue response of SN88 silicon nitride with and without CVD mullite coating at 850°C and at stressing rates of 30 MPa/s and 0.003 MPa/s. Note that the strength result of SN88 tested at 20°C and 30 MPa/s, illustrated by the shaded horizontal bar line, was included as a reference. Results showed that the fracture strength obtained for CVD-mullite coated SN88 was similar to that obtained for the uncoated SN88 tested at 850°C and 30 MPa/s, which was also similar to that obtained at room temperature. The results suggested that the mechanical strength of SN88 silicon nitride was not altered by the presence of a thin CVD mullite coating. Also, the characteristic strength of SN88 was not influenced by the test temperature range employed.

On the other hand, the flexural strength of both coated and uncoated SN88 silicon nitride was very sensitive to stressing rates at 850°C. For instance, both type samples tested at 30 MPa/s exhibited a comparable strength to those obtained at room temperature (738-759 MPa vs. 825 MPa), while samples tested at 0.003 MPa/s exhibited a substantial decrease in strength (~ 42-44 %, from 825 MPa to 464-483 MPa). In addition, SN88 silicon nitride exhibited a low fatigue exponent of 16-22, suggestive of a high susceptibility to slow crack growth (SCG) at test temperature. Therefore, the results obtained at 850°C and 0.003 MPa/s suggested that the dense CVD mullite coating could not effectively protect SN88 silicon nitride under a dynamic fatigue loading condition. Note that the observed strength degradation for both coated and uncoated SN88 silicon nitride at 850°C and 0.003 MPa/s was contradictory to the data reported previously, which showed SN88 exhibiting excellent SCG and creep resistance at temperatures between 1038 and 1350°C [13].

Since the coated and uncoated SN88 exhibited a significant SCG susceptibility at 850°C under the dynamic fatigue loading condition, studies of stress rupture were subsequently carried out to understand how the applied CVD-mullite coating as well as the stress levels would influence the lifetime of SN88 at 850°C. Figure 3 shows the lifetime versus applied stress data at 850°C. Results showed that the lifetimes of coated SN88 were similar to those obtained for the uncoated SN88 under the stress range applied, which suggested that the lifetime performance of SN88 was not enhanced by the application of CVD mullite coating. Also, both the coated and uncoated SN88 exhibited a strong stress-dependent lifetime behavior at stress levels as low as 200 MPa. In addition, the SN88 exhibited a low stress exponent of ~10-15, similar to the low fatigue exponent (16-22), again indicative of a strong susceptibility to SCG at 850°C.

Analysis of optical fractography for uncoated SN88 samples tested at 0.003 MPa/s over the temperature range employed or under stress rupture tests at 850°C revealed a light-colored layer on all surfaces of the bend bars (as shown in Fig. 4a), indicating the presence of an environmentally-affected zone (EAZ). The light-colored layer was only observed on the tensile surface region of coated samples (as shown in Fig. 4b) where dominant cracks initiated. In addition, the depth of the EAZ developed in both coated and uncoated SN88 samples after stress rupture tests increased with an increase in lifetime. Note that a similar light-colored EAZ was also observed in the crack region of the SN88 nozzle that failed after the 68 h engine test [14]. SEM examinations of the fracture surfaces of coated and uncoated samples tested at 0.003 MPa/s at 850°C indicated a change in the secondary phase microstructure, i.e., presence of pores, inside the EAZ (Fig. 5). The change in secondary phase microstructure was not observed in material outside the EAZ. Therefore, these SEM observations suggested that the EAZ developed in SN88 silicon nitride was a thermally-activated, time-dependent process.

The light-colored EAZ became more evident on polished cross sections of 0.003 MPa/s test samples for both coated and uncoated SN88. SEM observations showed a ~ 30 μm damage zone consisting of multiple cracks and pores in the secondary phase (Fig. 6). The formation of an EAZ was observed in all four surfaces of the uncoated SN88, suggesting that the development of the EAZ was not a stress-promoted phenomenon, but solely oxidation-related. Results of X-ray diffraction analysis for 0.003 MPa/s test samples indicated a change in the secondary phase from J-phase ($Yb_4Si_2O_7N_2$) to $Yb_2Si_2O_7$ plus Yb_2SiO_5. Similar phase transformation of secondary phase was also observed in SN88 nozzles, which failed during engine test [14]. The phase transformation from J-phase to $Yb_2Si_2O_7$ plusYb_2SiO_5 will introduce a high residual tensile stress in the EAZ due to a ~71% decrease in material volume [15,16]. The development of a high tensile stress would then lead to fracture of elongated Si_3N_4 grains and generation of intergranular cracks in the surface region of the bend bars. The formation of these through-surface flaws would result in a substantial decrease in mechanical strength and reliability. Similar mechanical instability at intermediate temperatures due to phase changes was previously reported for Si_3N_4 materials sintered with Y_2O_3 additive [17-19].

As for the coated SN88 samples, a dominant crack in the CVD-mullite coating induced at the earlier stage of mechanical testing would allow the oxygen to readily diffuse into the substrate and oxidize the surface. This would result in an undesirable phase change and the resultant mechanical degradation. Therefore, a more compliant coating system needs to be engineered to ensure that proper protection and thus long-term mechanical reliability of SN88 silicon nitride components under various mechanical loading conditions in gas turbine environments.

SUMMARY

The dynamic fatigue susceptibility of SN88 silicon nitride bend bars with and without a thin, dense CVD mullite was evaluated at 850°C at loading rates of 30 MPa/s and 0.003 MPa/s in air. Dynamic fatigue results showed that the CVD-mullite coated SN88 samples exhibited strength degradation similar to that of uncoated samples under identical test conditions. Also, the coated SN88 exhibited similar stress-dependent lifetime behavior to that of the uncoated samples under the stress range employed. SEM examinations revealed similar defects, i.e., pores and cracks were generated, due to oxidation reaction in both the coated and uncoated samples. Results, therefore, indicated that the CVD mullite coating could not effectively protect SN88 in an oxidizing environment under mechanical loading conditions. Both mechanical testing and SEM examinations suggested that cracking in CVD mullite could initiate in the earlier test stages, and, thus allow oxygen to readily diffuse to the silicon nitride and oxidize its surface. This would result in the undesirable phase change and the resultant degradation in mechanical reliability. Consequently, a more compliant EBC system needs to be engineered to ensure that proper protection of SN88 silicon nitride components occurs under various mechanical loading conditions in gas turbine environments.

REFERENCES

[1] Anson, D., Ramesh, K. S., and DeCorso, M., "Application of Ceramics To Industrial Gas Turbines"; Volume 1 Technology Background; Volume 2 Economics, Market Analysis, and R&D Plan DOE/CE/40878-1&2; Battelle Columbus March 1991.

[2] Helms, H. E., Johnson, R. A., and Groseclose, L. E., "AGT 100-Advanced Gas Turbine Technology Development Project," pp. 137-55 in Proceedings of the Twenty-Third Automotive Technology Development Contractors' Coordination Meeting, P-165, Society of Automotive Engineers, Warrendale, PA, March 1986.

[3] van Roode, M., “Ceramic Retrofit Program,” pp. 77-93 in Proceedings of the Joint Contractors Meeting: FE/EE Advanced Turbine Systems Conference FE Fuel Cells and Coal-Fired Heat Engines Conference, DOE/METC-93/6132, August 1993.
[4] Carruthers D., and Lindberg, L., "Critical Issues for Ceramics for Gas Turbines," pp. 1258-1272 in Third International Symposium on Ceramic Components and Materials for Engines, edited by V. J. Tennery, American Ceramic Society, Westerville, Ohio, 1988.
[5] Haley, P. J., Holtman, R. L., Groseclose, L. E., Hilpisch, S. J., and Bell III, A. H. "Advanced Turbine Technology Applications Project (ATTAP)", pp. 19-29 in Proceedings of the Twenty-Ninth Automotive Technology Development Contractors' Coordination Meeting, Society of Automotive Engineers, Warrendale, Penn., June 1992.
[6] Parthasarathy, V., van Roode, M., Price, J., Gates, S., Waslo, S., and Hoffman, P., "Review of Solar's Ceramic Stationary Gas Turbine Development Program, Proceedings of the 6th International Symposium on Ceramic Materials and Components for Engines, Arita, Japan, October 19-23, 1997. pp. 259-264, 1997.
[7] R. Wenglarz, S. Calcuttawala, and J. E. Pope, “Ceramics Vane Demonstration in an Industrial Turbine,” ASME paper 97-GT-155, presented at the International Gas Turbine and Aeroengine Congress and Exposition, Orlando, FL, June 2-5 (1997).
[8] W. D. Brentnall, M. van Roode, P. F. Norton, S. Gates, J. R. Price, O. Jimenez, and N. Miriyala, “Ceramic Gas Turbine Development at Solar Turbines Incorporated,” pp. 155-192, in Ceramic Gas Turbine Design and Test Experience. Edited by M. van Roode, M. K. Ferber, and D. W. Richerson. American Society of Mechanical Engineers, New York, NY (2002).
[9] Private communication with van Roode M. at Solar Turbines, San Diego, CA.
[10] Haynes, J. A., Lance, M. J., Cooley, K. M., Ferber, M. K., Lowden., R. A., and Stinton, D. P., “CVD Mullite Coatings in High-Temperature, High-Pressure Air-H_2O,” *J. Am. Cera. Soc*., 83 [3] 657-59 (2000).
[11] “Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperatures,” ASTM C1161, Annual Book of ASTM Standards, Vol. 15.01, American Society for Testing and Materials, West Conshohocken, PA, 1999.
[12] “Standard Test Method for Determination of Slow Crack Growth Parameters of Advanced Ceramics by Constant Stress-Rate Flexural Testing at Elevated Temperatures,” ASTM C1465, Annual Book of ASTM Standards, Vol. 15.01, American Society for Testing and Materials, West Conshohocken, PA, 1999.
[13] Wereszczak, A. A. and Kirkland, T. P. “Creep Performance of Candidate SiC and Si_3N_4 Materials for Land-based, Gas Turbine Engine Components,” ASME Paper 96-GT-385 presented at the International Gas Turbine and Aeroengine Congress and Exposition, Birmingham, UK, June 10-13, 1996.
[14] Lin, H. T., Ferber, M. K., and van Roode, M., "Mechanical Reliability of Si_3N_4 Nozzles After Exposure in an Industrial Gas Turbine," pp. 97-102 in the Proc. of the 7th International Symposium on Ceramic Materials and Components for Engines," eds. J. G. Heinrich and F. Aldinger, Wiley-Vch, New York (2001).
[15] Wills, R. R., Stewart, R. W., Cunningham, J. A. and Wimmer, J. M., “The Silicon Lanthanide Oxynitrides,” *J. Mater. Sci.*, 11 (1976) 749-759.
[16] Powder Diffraction File, PDF Card # 37-0458 ($Yb_2Si_2O_7$) and #40-0386 (Yb_2SiO_5) International Centre for Diffraction Data, Newtown Square, PA 19073-3273, USA..
[17] Lang, F. F., Singhal, S. C., and Kuznicki, R. C., “Phase Relationship and Stability Studies in the Si_3N_4-SiO_2-Y_2O_3 Pseudoternary System,” *J. Am. Ceram. So*c. Vol. 60, No. 5-6, 249-252, 1997.
[18] Quackenbush, C. L. and Smith, J. T., “Phase Effects on Si_3N_4 Containing Y_2O_3 or CeO_2: II, Oxidation,” *J. Am. Ceram. So*c. Vol. 59, No. 5, 533-537, 1980.
[19] Govila, R. T., “Fracture and intermediate Temperature Instability in Yttria-Doped Hot-Pressed Silicon Nitrides,” *Am. Ceram. Soc. Bull*., 65, 1287-92 (1986).

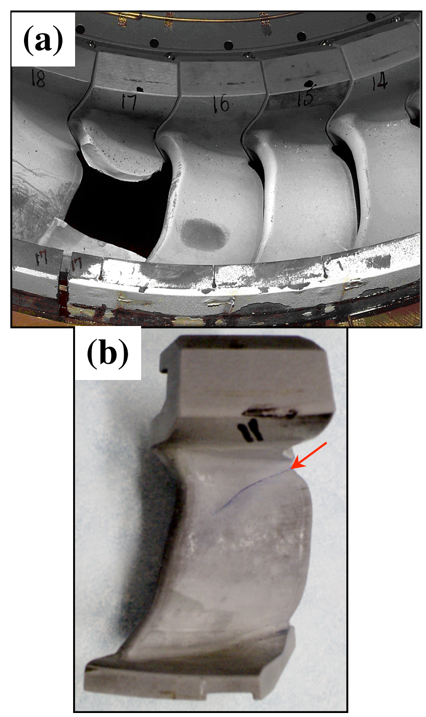

Figure 1. Photos of (a) SN88 silicon nitride nozzle sections after 68 h engine test and (b) nozzle show crack initiated at the air foil/platform transition region.

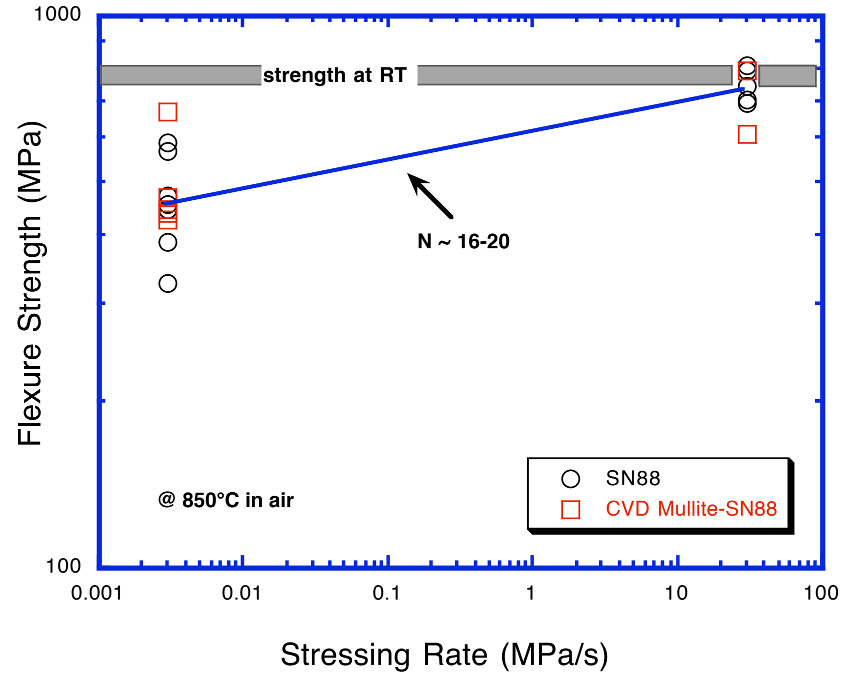

Figure 2: Flexure strength versus stressing rate curves of CVD-mullite coated and uncoated SN88 silicon nitride tested at 850°C in air.

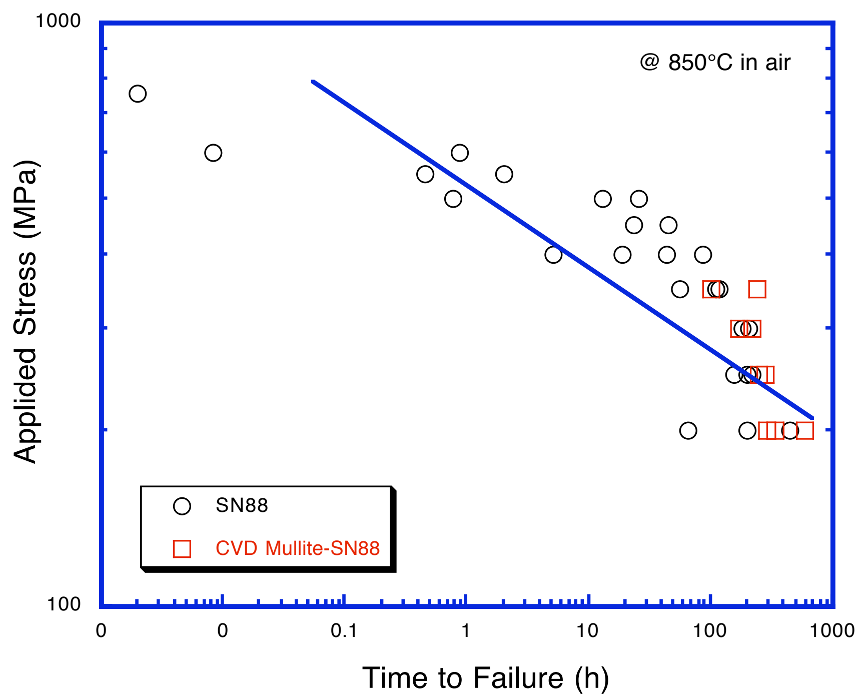

Figure 3. Applied stress versus time-to-failure curves of CVD-mullite coated and uncoated SN88 silicon nitride tested at 850°C in air.

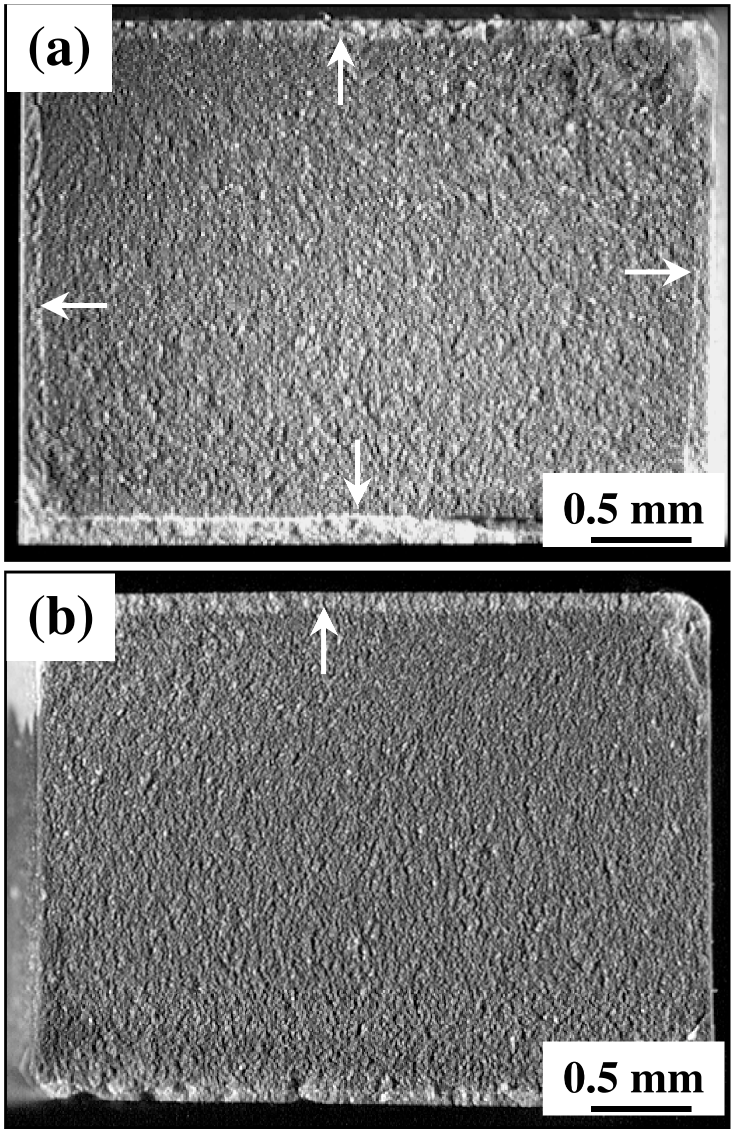

Figure 4. Optical fractography of (a) uncoated and (b) CVD-mullite coated SN88 tested at 850°C and 0.003 MPa/s in air.

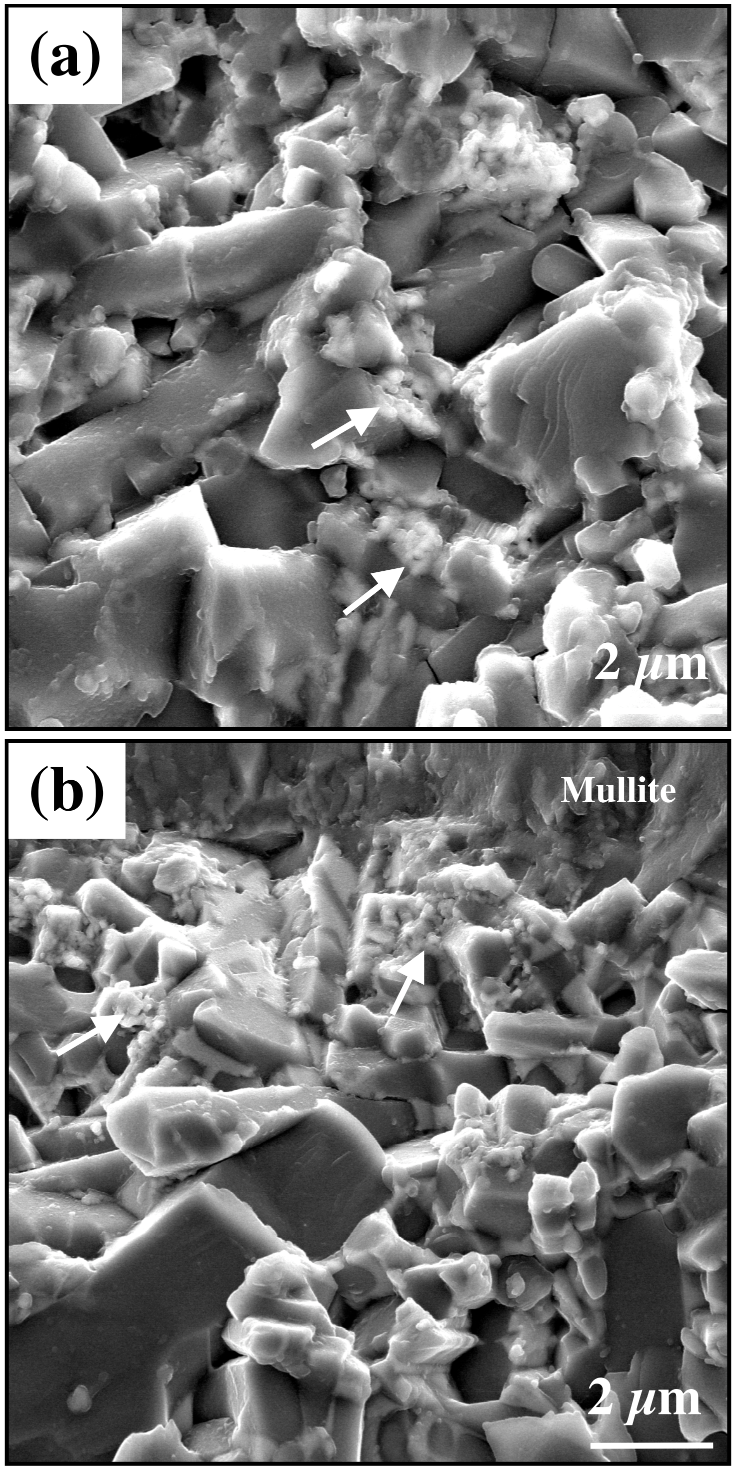

Figure 5. SEM of fracture surface for (a) uncoated and (b) CVD-mullite coated SN88 silicon nitride tested at 850°C and at 0.003 MPa/s. Arrows denote pores in secondary phase.

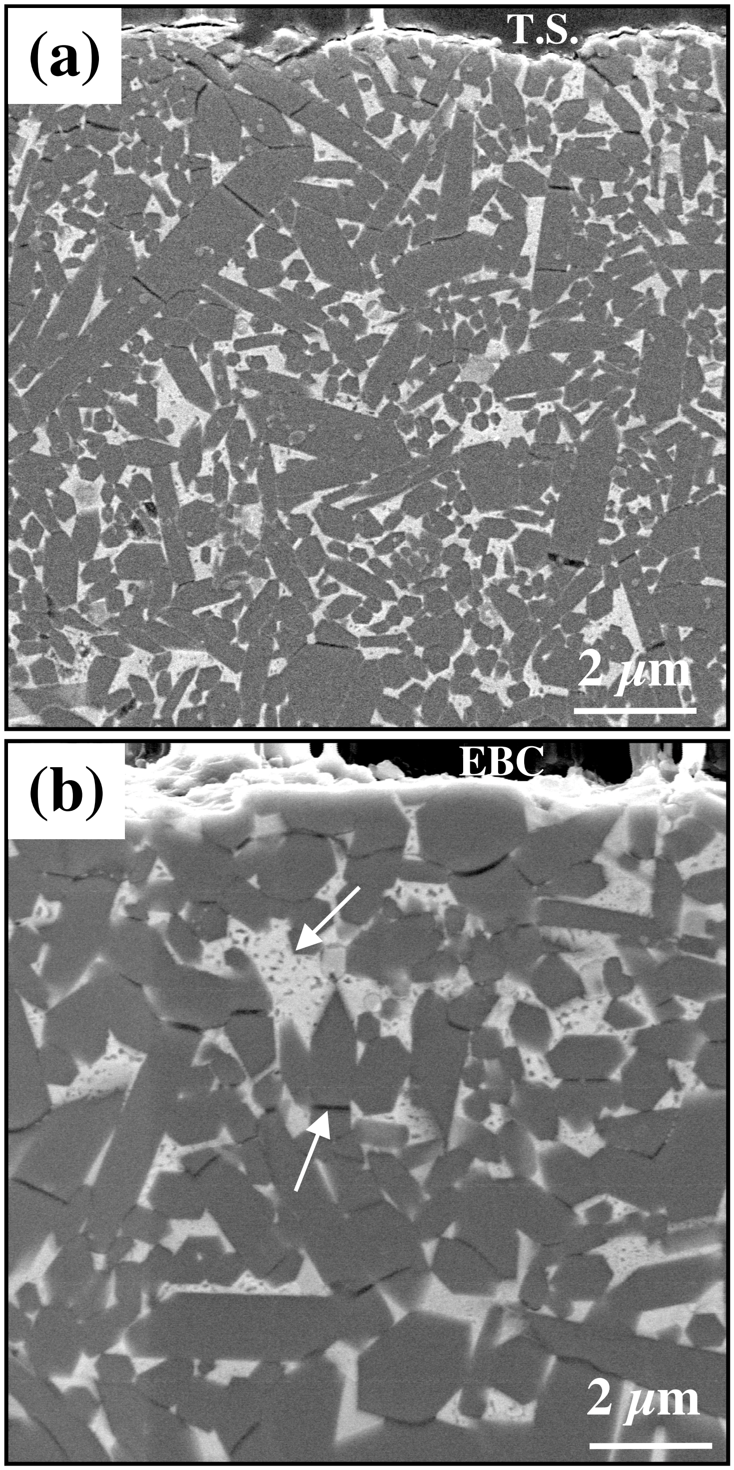

Figure 6. SEM micrographs of polished cross section of (a) uncoated and (b) CVD-mullite coated SN88 silicon nitride tested at 850°C at 0.003 MPa/s. Arrows denote pores in secondary phase and fracture of silicon nitride grains and grain boundaries. Also, T.S. and EBC denote the tensile surface and CVD-mullite region, respectively.