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Improved Oxide-Based Interfacial Coatings for the Next-Generation of CMC's

N.I. Baklanova[1, a], B.N. Zaitsev[2,b] and A.T. Titov[3,c]

[1]Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk 630128

Russian Federation

[2]State Scientific Center "Vector", Novosibirsk region 630559 Russian Federation
[3]General Institute of Geology, Geophysics and Mineralogy SB RAS, Novosibirsk 630090
Russian Federation

[a]baklanova@solid.nsc.ru, [b]zaitsev@vector.nsc.ru, [c]titov@uiggm.nsc.ru mail

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Abstract. CMC's reinforced by SiC-based fibers achieve high toughness and damage tolerance through the disposal of weak fiber coating which can deflect cracks and promote debonding at the fiber/matrix region. Refractory oxide-based systems are considered as the most promising ones for this purpose. Sols of zirconia, including stabilized zirconia were used as simple and readily processable precursors for obtaining interfacial coatings on SiC tow and cloth. The morphology, composition, topography, roughness, tensile properties of as-prepared and exposed to air at 1000°C coated fibers were evaluated by SEM/EDS, XPS, XRD, AFM, micro Raman analysis. The peculiarities of the behavior of oxide-coated fibers are governed by the properties of initial sols, procedure for coating fabrication, chemical and nanostructural factors. The peculiarities of the behavior of the stabilized zirconia interphase with accurate phase control will be discussed. A monitoring of the $t \rightarrow m$ phase transformation within ZrO_2 interfacial coating on SiC fiber using micro Raman makes it possible quantitatively to evaluate an ability of ZrO_2 as oxidation resistance and readily deformable weak interfacial coating for the next-generation CMC's.

Introduction

Ceramic matrix composites (CMC's), reinforced by ceramic fibers, namely, SiC/SiC is a promising alternative to monolithic ceramics due to combination of high-temperature capability, toughness and damage-tolerance. The incorporation of the reinforcing fibers into the ceramic matrix prevents catastrophic crack growth by such mechanisms as fiber debonding, sliding, and crack bridging [1]. In order to achieve these properties, the fiber/matrix interface must be sufficiently weak to deflect cracks and allow subsequent fiber sliding. In relation to mechanical properties, the influence and the control of the interface structure and properties is of critical significance for the development of CMC's. The best from mechanical point of view interphase materials, such as carbon and BN exhibit an environmental instability at operating temperatures. Therefore, there is a strong interest to study alternative interphases which would be more oxidation-resistant than carbon and BN coatings. Among alternative interphases the refractory oxide-based systems, in particular, ZrO_2 are considered as promising ones [2].

Zirconia is unique ceramic material due to thermal, chemical stability, high melting point and high fracture toughness. The last is related to the fact that in the stress field of propagating macrocrack the tetragonal→monoclinic ($t \rightarrow m$) martensitic transformation induced by large tensile stress ahead of the crack tip can occur, with the energy from external stress being absorbed during the phase transformation [3]. As this phase transformation is accompanied by a large volume increase and shear, further growth of crack is suppressed. The recognition that a ZrO_2 can exhibit improved strength and high toughness has stimulated intensive efforts to use it as an interphase material for CMC's [4, 5].

It is well-known a sensibility of the material toughness to its microstructure. Especially it is true for the ZrO_2-based materials whose toughness is related to the $t \rightarrow m$ transformation. This is why thorough investigation of microstructure, including morphology, topography and roughness of ZrO_2-based interfacial coatings on ceramic fibers must be fulfilled before evaluation of them as constituents for CMC's. The aim of this work is to develop an approach to obtain the interfacial ZrO_2 coatings with controlled phase composition on SiC-based fibers and to examine the peculiarities of their microstructure.

Experimental

Materials and Coating Preparation. Hi-Nicalon™ (Nippon Carbon Co., Japan) and Tyranno-SA™ (Ube Co., Japan) fiber tow and cloths were used as substrate materials. Prior to coating, both types of fiber were desized and then thermally treated in air at 500°C.

The preparation of coated ceramic fibers was similar to that described in [4]. The same alcohol sol was used for preparation of multi-component rare earth oxide stabilized zirconia coatings on both types of ceramic fibers. To obtain tetragonal zirconia coatings sols with different (3-6% mol.) content of rare earth elements were synthesized. At least two components were incorporated in conventional zirconia-yttria oxide system. Samples were named after the rare earth oxides content, i.e. $6Re\text{-}ZrO_2$ means 6 % (mol.) Re_2O_3 (where Re are rare earth elements) and 94% (mol) ZrO_2. The coating stage involved firstly the immersion of the ceramic fiber tow or cloth into sol, drying on air at ambient temperature and then slow heating in argon flow at atmospheric pressure till 1000°C. To increase of thickness of interfacial coating the dipping-annealing procedure was repeated several times. The desized Hi-Nicalon™ and Tyranno-SA™ fibers, as well as the coated and exposed to air at for 30 hrs fibers were under investigation.

Specimen Characterization. The morphology and composition of the initial and coated ceramic fibers before and after exposition to air at 1000°C were examined by scanning electron microscope (SEM: LEO 1430VP). Elemental composition of coating was carried out using energy dispersive spectroscopy (EDS, Oxford).The topography and surface roughness of fibers was examined by atomic force microscope (AFM) SolverP47Bio (NT-MDT, Russia) using contact and intermittent contact modes. Silicon cantilevers NSG11 (NT-MDT) were used. A roughness and other statistical parameters of selected areas were obtained using software of device. The AFM images were flattened before analysis using 2nd order surface subtraction.

Micro Raman spectra of the Y-PSZ coated Nicalon™ fibers were recorded using a Triplemate, SPEX spectrometer equipped with CCD spectrometric detector cooled by liquid nitrogen and microscope attachment for back scattering geometry in the 40-1700 cm^{-1} region. The 488 nm radiation from an argon laser was used for spectral excitation. All measurements were carried out using a laser power of 5 mW. The laser beam was focused with an optical objective on spot with diameter of 2µm.

Mechanical tensile tests of the initial and coated fibers were conducted at room temperature using FM-4 (Hungary) testing machine. The 10 mm gauge length was used and crosshead speed was set at constant rate of 1.3 mm/min. The diameter was measured in the middle of filament using laser interferometry. The average diameter was 6.86 ± 0.09 for Tyranno-SA™ and 15.67 ± 0.36 µm for Hi-Nicalon™ fibers.

Oxidation tests of coated fibers were carried out in air at 1000°C in muffle. A total time of exposition was 30 h.

Results and Discussion

AFM and SEM/EDS Characterization.

Hi-Nicalon™ Fibers. SEM images of the Re-doped ZrO_2 coating (one dipping-annealing cycle) on Hi-Nicalon™ fiber are represented in Fig. 1 a, b. The coating is rather smooth and uniform along length and diameter, with the thickness of coating being about 150-200 nm. Separate well-developed crystals can be seen on the surface. One can note that no any large crystals were observed in the non-stabilized ZrO_2 coatings [6]. Earlier it was shown [7] that the stabilization of ZrO_2 sols by rare earth elements results in the formation of strong coagulation of sol particles. The study of the rheological behavior of non- and stabilized ZrO_2 sols with different content of rare earth elements showed that the initial viscosity (at small strain rate) is sharply increased with increasing of the stabilizer level from 0 to 9% (mol). One can suggest that the formation of large crystals is related to rheological properties of the sol precursors. The EDS analysis showed that all elements of coating are rather uniformly distributed through the surface of filament.

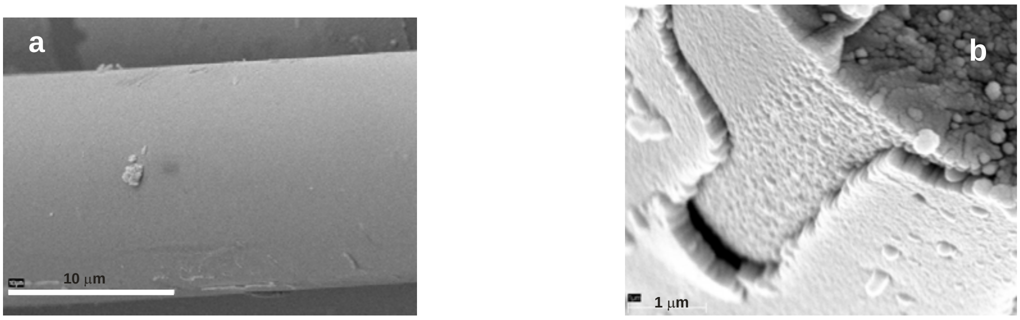

Fig.1 a, b. SEM images of the $ReZrO_2$-coated Hi-Nicalon™ fibers

Topographic study of the surface relief of the desized Hi-Nicalon™ fibers showed the surface is rather smooth and composed from particles of elongated shape. Separate aggregates of large size are present and they can be originated from sizing agent. The AFM image of the $ReZrO_2$-coated Hi-Nicalon™ fiber is represented in Fig. 3. One can see that the grains of coating have oblate ellipsoid forms with an aspect ratio of about 3. Lateral sizes are 120-150 nm. Grains have preferred orientation along axe of filament. SEM analysis data confirm this observation.

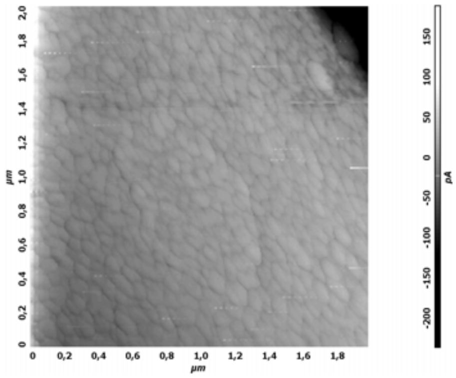

Fig. 3. AFM image of the $ReZrO_2$-coated Hi-Nicalon™ fiber.

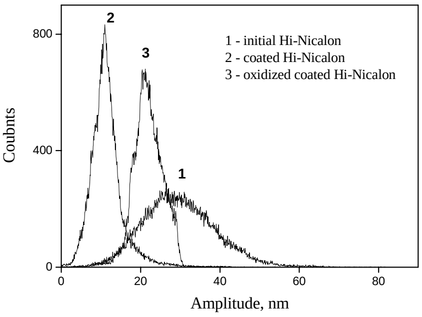

Fig. 4. Histogram of the height distribution of Hi-Nicalon™ fiber.

One can see from Fig. 4 that the height distribution calculated for $3.1 \times 3.1\ \mu m^2$ area of the initial fiber is diffuse one, with the average height magnitude being 31.2 nm. After application of coating a distribution narrows, with the average height being diminished till to 12 nm (for the same size of tested area). Exposition to air results in increase of height till to 22 nm and slight increase of the distribution width. SEM data confirm these results. Actually, one can see (Fig.5) that after oxidation topography of relief is changed not so drastically. The roughness parameters for the Re-ZrO_2 coated Hi-Nicalon™ fiber after exposition to air at 1000°C are approximately of the same order of magnitude as for fibers before exposition, e.g. R_a (roughness determined as a standard deviation of height value within the scanned area) is about 3-4 nm. Thus, application of sol-gel derived $ReZrO_2$ coating resulted in an improving of topography of surface of Hi-Nicalon™ fiber.

Fig. 5 a, b. The $ReZrO_2$-coated Hi-Nicalon™ fiber after oxidation at 1000C: a – SEM image, b - AFM image.

It should be noted that the features of the $t \rightarrow m$ transformed zones are detected on some places of the surface of coated Hi-Nicalon™ fibers, such as edges of large pores and rumpled relief as one of the most important characteristics of martensitic transformation is clearly seen (Fig. 5 b). This figure shows that some *m* laths formed in *t* grains are parallel to each other. One can note that this is a rare occurrence for *t*-ZrO_2 coated Hi-Nicalon fiber™.

Tyranno-SA™ fibers. The same sol was applied both to Hi-Nicalon and Tyranno-SA fibers. The surface of both initial and coated Tyranno-SA fiber is rather rough and generally nodular in nature (Fig.6 b). Rather large nodules are present on the surface of separate coated monofilaments. This inhomogeneity appears to be as a consequence of pronounced inhomogeneity of the surface of the initial Tyranno type fibers. The coating is composed from prismatic crystals, with the lateral sizes being 100-200 nm (Fig. 6 a). One can see that the coating is a textured one. The SEM analysis data allow us to detect some microstructure features of coating. It consists of the oblate ellipsoid form grains elongated perpendicularly to axe of filament. Besides, on the surface of some filaments separate large well-developed crystals grains were observed. These non-uniformaties can be as a route of stresses in the coating.

Another characteristic feature of morphology of the *t*-ZrO_2-coated Tyranno-SA™ fiber is an appearance of a rather elongated area of coating with rumpled relief and crack near edge of the cross-section of filaments (Fig. 6 c). The relief is typical stack of self-accommodating martensitic variant pairs. It could be proposed that the stresses which were applied to the tetragonal particles of coatings during crack propagation induced the phase transformation from tetragonal to monoclinic ZrO_2 modification, with an energy has being absorbed for the transformation.

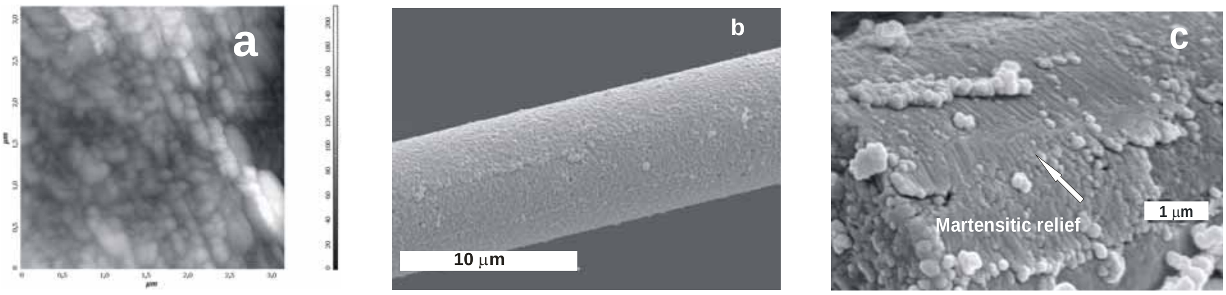

Fig. 6 a-c. The $ReZrO_2$-coated Tyranno-SA™ fiber: a – AFM image; b, c - SEM images.

It is known [3] that the $t \rightarrow m$ phase transformation is accompanied by a large volume increase and shear, and one can see the large shear strain induced by transformation. The formation of elongated areas (autocatalytic transformed bands) can be related to the fact that residual stresses not accommodated by the transformation-induced plasticity may be used to trigger the transformation of neighboring grains [8].

Quantitative analysis of AFM images of the initial, ReZrO_2-coated and exposed to air at 1000°C Tyranno-SA™ fibers allows us to calculate some characteristics of the fiber relief. A roughness is increased approximately by a factor of 2 after applying of the Re-ZrO_2 coating on fiber and it is 14.5 nm. After exposition to air at 1000°C, the roughness of the coated fiber is also increased approximately by a factor of 2, with it being about 27.5 nm. One can see from Fig. 7 that the height distribution calculated for 3.1×3.1 μm^2 area of the initial Tyranno fiber is diffuse one, with the average height magnitude being 31.2 nm. After application of coating not only the average height magnitude is increased but the distribution is broadening. The tendency is enhanced after exposition to air of the coated Tyranno-SA™ fiber.

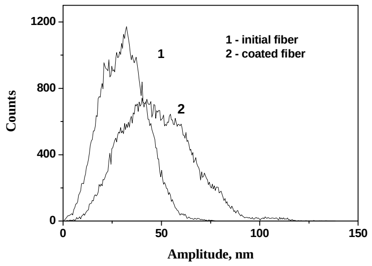

Fig. 7. Histogram of the height distribution of the initial and coated Tyranno-SA™ fiber.

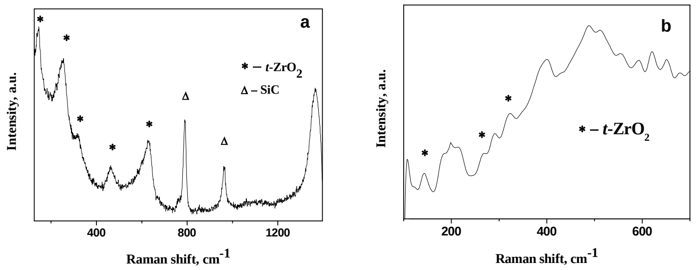

Fig. 8 a, b. Micro Raman spectra of the ReZrO_2-coated Tyranno-SA™ fiber before (a) and after oxidation (b).

Micro Raman spectra taken from the ReZrO_2-coated Tyranno-SA™ fibers detected the presence of peaks belonging to tetragonal ZrO_2 modification together with peaks of SiC and carbon phases of fiber itself (Fig. 8 a). New features which can be ascribed to monoclinic modification were detected in micro Raman of coated fibers after exposition to air at 1000°C (Fig. 8 b).

The quantitative phase analysis in the interfacial tetragonal zirconia coatings was done using an accurate calibration curve directly determined from the Raman spectra of standard mixtures with known monoclinic and tetragonal phase ratios in accordance with procedure described in [9]. It was found that the interfacial stabilized zirconia coatings underwent the $t\rightarrow m$ transformation, with the extent of this transformation being different for various areas of the same filament and for various filaments. In first turn, it can be caused by micro heterogeneity of the coating, including the grains sizes, reactivity towards water vapor, a variation in composition along filament, defects, the stress level within grains.

The tensile strength of the initial and coated Tyranno-SA™ fibers was measured by single filament method at room temperature. The tensile strength data were analyzed on the basis of the two-parameter Weibull statistics. The ReZrO_2-coated fibers showed an average tensile strength of 2.43 ± 0.02 GPa indicating a slight strength degradation (vs. 2.51 GPa for the initial fiber) during coating procedure. Weibull modulus was 2.55. It is known that the distribution of fiber strengths is responsible for the “graceful” mode failure of CMC’s. Therefore, strong fibers with low Weibull modulus are preferential ones.

Summing up results, one can note that the microstructural features of ReZrO_2 interfacial coatings on SiC fibers including the morphology, topography, roughness, the extent of the $t\rightarrow m$ transformation are greatly distinct for both types SiC fibers in despite of the fact that the coatings were obtained using the same sol. The microstructural features of thin interfacial coatings are governed in great extent by properties of SiC fiber itself.

Conclusions

Sol-gel approach was proposed to produce the stabilized zirconia interfacial coatings with predictable and exactly controllable phase composition on SiC -based fibers type Hi-Nicalon™ and Tyranno-SA™. The approach allows us to produce uniform along length and diameter of filaments non-bridging coatings which are composed of tetragonal zirconia modification. In despite of the fact that the coatings on different types of SiC-based fibers were obtained using the same sol the microstructural features of coatings are distinct. The application of coating on Hi-Nicalon™ fiber results in the improvement of topography of surface. All statistic parameters obtained by AFM analysis, including roughness and the average heights are decreased. They are only slightly increased after exposition of coated Hi-Nicalon™ fibers to air at 1000°C. On the contrary, after application of the stabilized zirconia interfacial coating on Tyranno-SA fiber and especially after oxidation at high temperatures a roughness of surface is increased in great extent. It was demonstrated that the tetragonal zirconia interfacial coating is readily deformable due to mechanism of martensitic transformation.

The results on roughness of coated fibers can be significant in its consequences for evaluation of the mechanical behavior of CMC's, e.g. $SiC/ZrO_2/SiC_f$. Among mechanisms contributing to increase the work of fracture and resistance to crack propagation debonding and sliding of fibers relative to the matrix are strongly dependent on properties of interfacial coatings, especially on the fiber surface roughness parameters. Therefore the obtained results could be used as design parameters for optimization of CMC's composites in future.

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References

1. A. G. Evans, D.B. Marshall “Mechanical Behavior of Ceramic Matrix Composites” in “Fiber Reinforced Ceramic Composites” Ed. K.S. Mazdiyani, General Atomics, San Diego, California, 1990, p.1-39.
2. W.J. Lee, E. Lara-Curzio, and K.L. More. Multilayered Oxide Interphase Concept for Ceramic-Matrix Composites. *J.Am.Ceram.Soc*., 1998, 81(3), p.717-720.
3. R.H.J. Hannink, P.M. Kelly, B.C. Muddle. Transformation Toughening in Zirconia-Containing Ceramics. *J.Am.Ceram.Soc*., 2000, 83(3), p.461-487.
4. H. Li, J. Lee, M.R. Libera, W.Y. Lee, A. Kebbede, M.J. Lance, H. Wang, and G.N. Morsher. Morphological evolution and weak interface development within chemical-vapor-deposited zirconia coating deposited on Hi-Nicalon™ fiber. *J.Am.Ceram.Soc*., 2002, 85(6), p.1561-68.
5. N.I. Baklanova, A.T. Titov, A.I. Boronin, and S.V. Kosheev. “The yttria-stabilized zirconia interfacial coating on Nicalon™ fiber”. *J.Eur.Ceram.Soc.*, 2006, 26(9), p.1725-1736.
6. N.I. Baklanova, T.M. Zima, and A.T. Titov. “The Behavior of the oxide-coated Nicalon fibers exposed to air at 1000°C”. *J.Eur.Ceram.Soc.*, 2005, 25(11), p.1943-1952.
7. T.M. Zima, N.I. Baklanova, E.I. Belyaeva, and N.Z. Lyakhov. “The peculiarities of the formation of ZrO_2 and Y_2O_3-ZrO_2 coatings on silicon carbide fibers”. Inorg.Materials, 2006, 42(6), (in Russian).
8. S. Deville, H.El Attaoui, J.Chevalier. “Atomic force microscopy of transformation toughening in ceria-stabilized zirconia”. J.Eur.Ceram.Soc., 2005, 25(13), p.3089-3096.
9. N.I. Baklanova, B.A. Kolesov, T.M. Zima. “Raman study of yttria stabilized zirconia interfacial coatings on Nicalon™ fiber”. *J.Eur.Ceram.Soc.*, 2006 (accepted).