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Peculiarities of Nanostructured Silicon Carbide Films and Coatings Obtained by Novel Technique

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Abstract—A new method has been developed for obtaining various versions of nanostructured SiC films and coatings, whose structure can be altered in a controlled way for different applications. The films and coatings obtained can be useful in metallurgy, nuclear power industry, microelectronics, and high-temperature furnaces.

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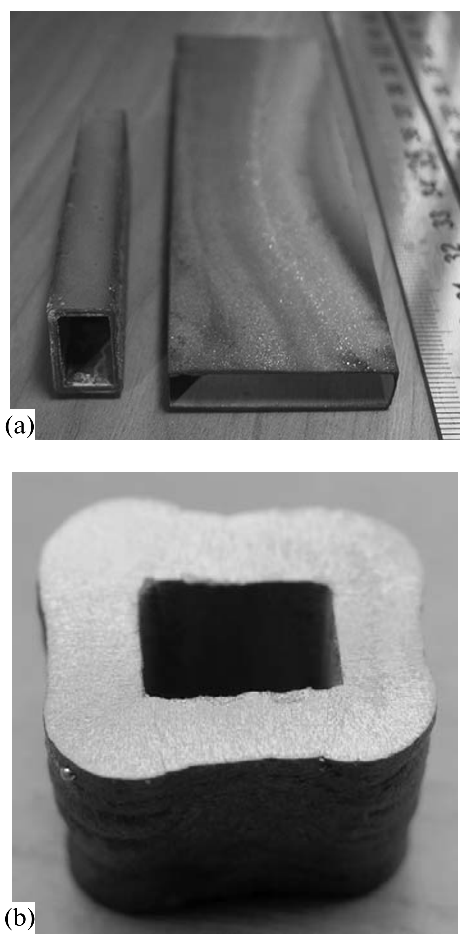
SiC structural ceramics features a unique set of properties and therefore its production and examination is a hot topic for scientists and technologists process engineers both in Russia and abroad. Alongside with the development of SiC-based ceramic materials, parallel efforts focus on the production of SiC coatings with chemical inertness, radiation resistance, homogeneity, wear resistance, and strong adhesion to a number of materials at high temperatures [1–6].

SiC coatings and films are applied in many engineering problems, including production of crucibles and other parts for melting metals, such as silver, gold, copper, aluminum, etc.; structural elements in aircraft and spacecraft; structural elements of nuclear reactors; SiC-based or graphite-based heaters capable of operating satisfactorily up to 1600°C in oxidizing media; chemical apparatus; and electronic devices.

SiC films and coatings can be obtained by various methods: magnetron sputtering [7], laser processing [8], plasma chemical vapor deposition [9], low pressure chemical vapor deposition with various precursors [5], and many others.

We have designed a new procedure for obtaining high-performance SiC coatings and films, based on interaction of silicon melt (or vapor) with carbon formed as a result of disintegration of hydrocarbon molecules. The approach developed makes it possible to obtain coatings of various thickness (from few tenths of a micron to several centimeters) on articles of various geometrical shape: cylinders, polyhedra, plates, rods, etc. Our examination of the structure and properties of SiC coatings on various bases, as determined by their production conditions, has shown that in some cases the new method can yield nanostructured layers significantly exceeding micro- and macrocrystalline coatings in a number of parameters.

Since SiC coatings can be deposited onto removable bases (for example, graphite) of various configurations, one can obtain macroscopic articles of complex form (shaped SiC) from nanostructured SiC. As an example, Fig. 1 shows SiC-based hollow articles obtained in this way.



(a) (b)

Fig. 1. Shaped SiC with a wall thickness of (a) 1–2 and (b) 6–9 mm, obtained by deposition onto a removable base.

The coating composition can be varied in a controlled way, from high-purity and stoichiometric to that containing necessary alloying elements with required concentrations.

Depending on the feed rate, pressure, and temperature of silicon vapor and of gaseous carbon in the interaction zone, one can vary in a wide range the grain size in SiC coatings (from microcrystalline to nanoscaled), their porosity, and atomic structure of grain boundaries, thus controlling the composition of SiC polytypes and its morphology.

In this context, depending on the application conditions, one can controllably obtain either pore-free coatings consisting of nanocrystals with a homogeneous grain size distribution or coatings of SiC nanoparticles agglomerated into clusters with controllable nanopore content.

As an example, Fig. 2a shows a coating consisting of SiC nanocrystals with a typical size of 70 nm, whose crystal structure corresponds to regular hexagon (6H polytype). One can obtain in the same way SiC coatings with other structure (from cubic to a large variety of polytypes).

Figure 3 demonstrates the X-ray diffraction spectrum of a coating with a moissanite 3C polytype structure (sp. gr. F-43m, a = 4.358 Å, and V = 82.77 Å^3). The X-ray powder diffraction spectra were measured on a Siemens D-500 diffractometer in the Bragg–Brentano scheme using CuK_α radiation (λ = 1.5418 Å) with a curved secondary graphite monochromator. The spectrum was scanned with a step of 0.05° and an exposure period of 2 s. The PDF-2 database of reference diffraction spectra was used to identify the phases.

The spectrum lines exhibit no marked broadening as compared to the instrumental one; in particular, the Cu$K_{\alpha 1}$/$K_{\alpha 2}$ doublet lines are well-resolved, a for the indicative of crystallinity and high structural quality of the grains. The presence of weak reflections (marked by arrows in the diffraction pattern) suggests the existence of twin boundaries with stacking faults in the cubic structure.

In is noteworthy that the SiC films obtained by the aforementioned technique exhibit a high photoluminescence (PL) in a number of cases. Figure 4 shows a PL spectrum of one of the specimen excited a 325-nm UV laser. The high spectral intensity and relatively narrow spectral distribution of fluorescence at room temperature are indicative of good film quality. The position of the PL band maximum indicates that, under the given conditions, the film has a hexagonal polytype structure. this is most likely the 4H-SiC polytype.

This fact suggests also that the boundaries between nanograins are not nonradiative recombination centers, which they generally are for polycrystals with microsized grains. Consequently, the grain boundaries in nanostructured coatings (SiC films in our case) exhibit a high degree of interatomic bond coherence.

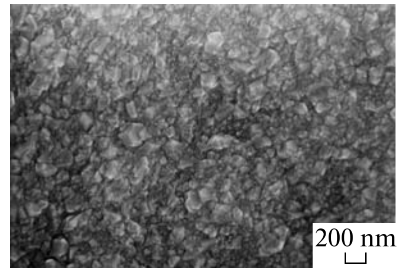


Fig. 2. SiC-nanocrystalline coating.

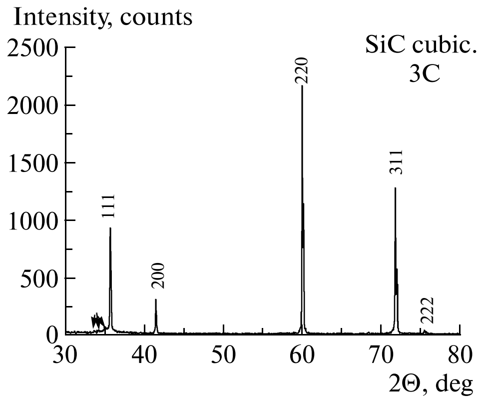


Fig. 3. Diffraction spectrum of SiC coating with a SiC-polytype structure.

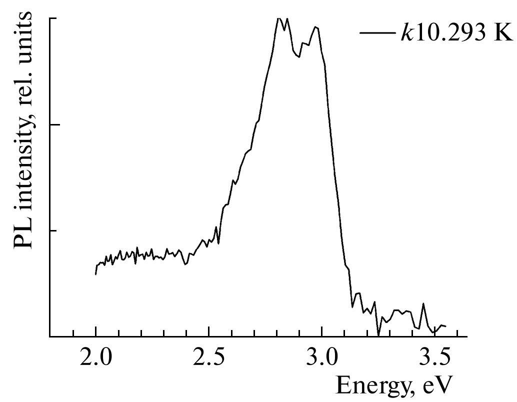


Fig. 4. SiC-film photoluminescence.

As an example of high chemical strength and resistance to thermal stress, Figure 5 shows an electric heater made of SiC-based ceramics with a protective coating of nanostructured SiC. Such heaters are rated for the use in aggressive environments at temperatures above 1500°C and can withstand repeated rapid (few seconds) heating and cooling. For comparison, we showed note that silite heaters based on conventional SiC ceramics are rated for very low heating and cool-

Fig. 5. SiC-based ceramic heater with a SiC nanocrystalline anti-corrosion coating.

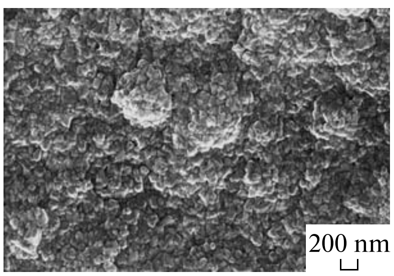


Fig. 6. SiC coating composed of nanoparticles agglomerated into clusters (two-level structure).

ing rates (as slow as 150 K/h; in other words, it takes 10 h to heat to 1500°C).

A morphologically opposite case is illustrated in Fig. 6, which shows a two-level structure consisting of SiC nanoparticles with sizes from 10 to 80 nm, agglomerated into clusters up to several tens of microns; this structure has important advantages in a number of specific applications. For example, for materials rated for use under high radiation, the presence of nanocavities, which ensure quick emerge and annihilation of radiation defects is of great advantage. Thus, the radiation strength of a structural element made of this material (for nuclear reactors, these are elements of heat shields, piping, coolant pumps, units for moving graphite moderators, etc.) may be increased by several orders of magnitude.

Usually, the time of defect emergence to the particle surface is determined by the expression $\tau = R^2/D$, where R is the particle radius and D is the diffusion coefficient. With characteristic nanoparticle radii of 20 nm and typical self-diffusion coefficients on the order of 10^{-12} cm^2 s^{-1}, the annihilation time of radiation defects is only few seconds. For radiation flows from 10^{12}–10^{14} cm^{-2} s^{-1} in operating reactors and SiC radiation absorption coefficient of about 1 cm^{-1}, it takes from 10 to 1000 s between absorption events in an individual nanoparticle; this time exceeds the annihilation time of radiation defects. Thus, SiC materials with such a structure exhibit stable performance in reactor cores.

ACKNOWLEDGMENTS

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