SCIENCE FOR CERAMIC PRODUCTION

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X-RAY PHOTOELECTRON SPECTROSCOPY OF A COMPLICATED CERAMIC OXIDE OF THE SYSTEM BeO – TiO₂ – C

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The methodological aspects of using x-ray photoelectron spectroscopy to study the chemical composition, charge state, and electronic parameters of the surface of a complex oxide ceramic containing sections with different electronic conductivity are discussed for ceramic in the system BeO – TiO₂ – C. Questions concerning surface preparation of a ceramic by means of Ar⁺ ion bombardment and mechanical cleaning with a diamond scraper in vacuum are examined.

Key words: BeO – TiO₂ – C ceramic, surface, x-ray photoelectron spectroscopy.

Oxide ceramics comprise a wide class of functional materials (refractory, durable, etc.) with a wide spectrum of practical applications. The complex chemical composition and macro- and microstructures, the presence of extended interfaces and intergrain interactions, as well as a number of other factors give rise to substantial difficulties which arise with the use of many conventional physical-chemical methods of constructing a detailed description the structure and properties of these materials. The study of the surface these materials, whose properties strongly influence the service characteristics of specific ceramic composite materials, is also problematic.

An effective method of studying the surface properties of ceramic materials is x-ray photoelectron spectroscopy (XPES).

In the present article a number of methodological aspects of using XPES to study the chemical composition, charge state, and electronic parameters of the surface of oxide ceramic containing sections with different electron conductivity are discussed for ceramics in the system BeO – TiO₂ – C. Questions concerning the surface preparation of the ceramic by means of Ar⁺ ion bombardment and mechanical cleaning with a diamond scraper in vacuum are examined.

We note that a ceramic based on beryllium oxide BO is applicable, for example, as a refractory in special metallurgy, construction materials in electronic technology, materials of fuel elements in nuclear reactors, neutron reflectors, neutron filters, and so on [1 – 5]. Attempts are being made to optimize further the functional characteristics of beryllium-oxide ceramic by modifying it with various additives (for example, titanium dioxide TiO₂ and carbon [6, 7]) which are capable of creating different surface microstructures on the boundaries of the crystallites of BeO ceramic [4].

EXPERIMENTAL PROCEDURE

The technology of [6] was used to prepare BeO – TiO₂ – C ceramic samples. Chemically pure beryllium oxide and ultrapure titanium dioxide were used as the initial reagents. A mix of BeO with 30% TiO₂ added was prepared. The BeO powder was calcined at 1470 K to impart to the powder stable physical-chemical properties. The TiO₂ powder was pre-heat-treated at 1070 K. The articles were formed by slip casting using an organic binder. The mix was prepared by wet mixing of the initial oxides in a ball mill for 4 h. The slip, based on a wax-paraffin binder, was prepared in a heated mill at 348 – 358 K. The amount of the organic binder in the slip was 10 – 13%. The organic binder was burned out of the article at 1470 K in 4 h. Sintering was performed in a preparatory furnace with graphite heaters in a carbon monoxide atmosphere (in graphite crucibles and graphite fill, where the CO pressure was varied in the range 1 × 10⁻² – 5 × 10⁻² mm Hg) at maximum temperature near

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X-ray phase analysis of the ceramic was performed on a STADI-P autodiffractometer, using a CuKα x-ray source, in the range of angles 2θ from 20 to 100° with step 0.02°.

The electronic microscopy of the surface of the ceramic with EDX analysis was performed on a JOEL JSM 6390LA+JED-2300 facility.

XPES measurements of the ceramic were performed on the ESCALAB MK II electronic spectrometer using non-monochromatic MgKα radiation hv = 1253.6 eV. The transmission energy of the analyzer was 20 eV and the scanning step 0.1 eV; the energy resolution of the spectrometer was evaluated according to the width of the Ag3d line at half-height 0.85 eV; calibration of the energy scale was performed according to the C1s line from the surface hydrocarbons (284.5 eV). During the measurements the vacuum was kept at the level 10−8 Pa. It is well known that the XPES method analyzes the surface layer of the sample to depth ~ 5 nm, so that to study the “volume” characteristics of ceramic it is important to choose a method for removing surface contaminants from the surface of the sintered sample. Two methods were used in this work: atomization of the surface layers by a beam of argon ions (E = 5 keV, I = 20 μA) and mechanical cleaning of the surface with a diamond scrubber in the vacuum chamber of an electron spectrometer.

RESULTS AND DISCUSSION

According to the XPA data the base of the experimental ceramic BeO – TiO2 – C consists of crystalline oxides BeO and TiO2; in addition, weak additional diffraction peaks (1–2% arb. units) belonging to unidentified phases are observed. The content of the phase TiO2 in the sample was about 19%, which corresponds to the formula BeO–0.08TiO2–C.

Figure 1 contains images of a ceramic surface which were obtained with a scanning electron microscope. It can be concluded that the ceramic BeO – TiO2 – C is a mechanical mixture of oxides, weakly chemically interacting with one another. The distribution of the TiO2 crystallites in BeO is inhomogeneous; inclusions of regions of grouped TiO2 microcrystals with average size 30–70 μm are encountered. Microanalysis of the lateral distribution of the elements over the surface of the ceramic does not show the presence of titanium carbides (or oxycarbides) in the form of free crystallites or layers on the surface of TiO2. A thin layer of carbon, probably in a free state, is present on the boundaries of TiO2 and BeO crystallites (Fig. 1b), but it is difficult to identify its chemical form precisely by the EDX method. To analyze the chemical state of carbon, titanium, and beryllium on the boundaries of the microcrystals of the ceramic requires a special surface-sensitive method, for which x-ray photoelectron spectroscopy was used.

Figure 2 displays panoramic XPES spectra of the surface of a BeO – TiO2 – C ceramic for four variants of its preparation: for the initial surface of the ceramic after sintering (a); surface after mechanical cleaning with a scrubber in vacuum (b); after ionic sputtering of the surface layers by a Ar+ beam (c); and, after repeated mechanical scrubbing in a vacuum (d).

The lines of carbon and oxygen from surface contaminants dominate the panoramic spectrum of the surface of the initial sample; peaks due to Ti, Be, silicon, nitrogen, and calcium are also present. The latter three elements are, together with C and O, constituents of the surface contaminants. The strong contamination of the surface of the initial samples makes it necessary to prepare the surface by special methods before measurements are performed. It is extremely difficult to obtain a chip of the beryllium ceramic in the vacuum chamber of the XPES spectrometer, so that alternative methods were used — mechanical cleaning in vacuum and ionic atomization of the surface layers. After the surface is mechanically cleaned with a scrubber in vacuum the silicon, nitrogen, and calcium bands in the panoramic spectrum practically vanish, the intensity of the carbon lines weakens, and the peaks from the electronic states of titanium and beryllium increase (see Fig. 2b).

Even though the band Be1s of the states in the XPES spectrum is relatively weak (because of the small photoionization cross section), the conversion of the intensities of the bands Be1s, Ti2p, O1s, and C1s into atomic concentrations shows that the BeO phase dominates on the surface of the ceramic. Quantitative XPES evaluations of the gross composition of the ceramic in units reduced to the beryllium content give the conventional formula BeO · 0.09TiO2 · xC, which