Determination of phase composition of titanium dioxide nanoceramics

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The problems of investigation of the structure, phase composition and characteristics of interface regions of oxidic ceramics are connected with the presence of a complicated hierarchy at nano-, meso- and macrolevels, as well as with the existence of interface regions. In the present work, the phase composition and its distribution in nanostructured TiO_2 ceramics compacted by impulse pressing [1] with subsequent annealing in a resistance furnace (RF) or by microwave (MW) heating [2] have been analyzed by the AFM, XRD, XPS methods, and the method of thermal phonon kinetics at He temperatures [1].

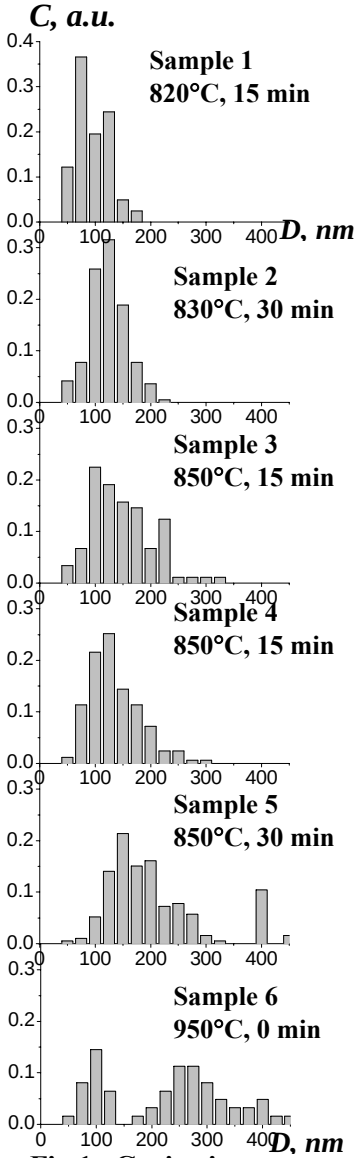

Fig.1 . Grain size histograms of RF-ceramics

The XRD analysis of the samples studied has allowed the fraction of the rutile and anatase phases in ceramics, and the average size of crystallites to be determined. It should be noted that the average size of crystallites increases and the fraction of the anatase phase rapidly decreases, as the ceramic density grows. The ceramics obtained by microwave heating contain, as compared to RF ceramics, a greater proportion of residual anatase and are characterized by elevated microhardness.

The AFM measurements of the fracture surface of ceramics were performed in semi-contact mode using a scanning probe microscope P47-MDT (NT-MTD, Russia).

The AFM analysis has made it possible to detect the scale levels of crystallites, grains and aggregates in TiO_2 nanoceramics. According to the AFM-images the destruction of the sample in all the cases involves an intercrystalline mechanism. It have been found that the grain size depends on the baking temperature and the power of microwave heating.

In ceramics obtained by backing in the resistance furnace the grain size increases with temperature and the backing time (Fig.1), and aggregates of grains with size up to 1.5 μm are observed. For sample 1 two groups of grains may be separated out in the fracture image in topography regime: grains of about 50 nm and less, and 100 nm and higher in size (Fig.2a). The appearance of a second characteristic scale level in the range of greater magnitudes (samples 3,5,6) testifies that the secondary grain recrystallization has begun.

To define the chemical composition, the regime of phase contrast has been used, because, as was demonstrated earlier [3], the influence of modulus of elasticity on the phase shift was dominant for hard materials and the influence of adhesion on phase shift was negligible compared to elastic modulus. Therefore, the relative variation of stiffness of surface in scan region can be identified from the phase contrast images.

AFM measurements in PC regime have revealed the existence of two phases on the fracture surface (Fig.2b) displayed as bright and dark areas. Bearing in mind the XRD data, these phases can be considered as the titanium dioxide modifications: anatase and rutile. The difference in the areas brightness allows one to identify the dark grains as anatase, and the bright ones as rutile.which has greater hardness. It should be noted that for all samples with large amount of anatase, obtained by furnace backing, the boundary formation is not completed. The grain boundaries are rounded, the contact between them is not continuous, and nanopores are observed in triple interfaces. Significant difference in stiffness between the grains and their boundaries allowed the real grain structures to appear in the phase contrast image. Both regions (anatase grains and boundaries) indicated the presence of materials with low stigffness (elastic modulus) bat the dark grey regions exhibited relatively lower stiffness than the medium grey regions. As the grain boundaries were less than the grains, they were represented as dark grey scale values in phase contrast images.

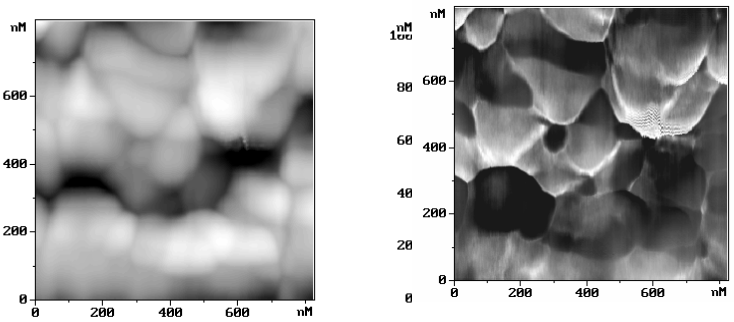

Fig.2. AFM topography (a) and phase contrast (b) image of RF-ceramics (820°C, τ=15 min). (Write grains - rutile, dark grains – anatase in PC image.) Sample 1

On microwave heating up to 800 C in low-power regimes, two phases are observed on the fracture surface. They have been found to exist as separate grains whose size depends on the power of microwave heating. It has been shown, in particular, that the rutile grains (50-70 nm) form at the boundaries of coarse anatase grains (200-300 nm) that may unite in aggregates up to 1 μm in size (Fig.3). With increasing the power applied a transition from the metastable state (anatase) into the stable phase (rutile) is observed, which is accompanied by an increase in the rutile amount and the grain size growth. In this case the number of phases obtained from the AFM data coincides with the XRD data. In particular, for sample 7 the phase distribution follows the lognormal law, amounting to 85% anatase and 15% rutile (AFM) as compared to 84:16 for XRD data. In Fig.4b the function of roughness distribution in presented for the same sample as in Fig.4a. The fact that this function has three characteristic peaks indicates that this parameter depends not only on the chemical composition but also on the characteristic fracture topography of different phases.

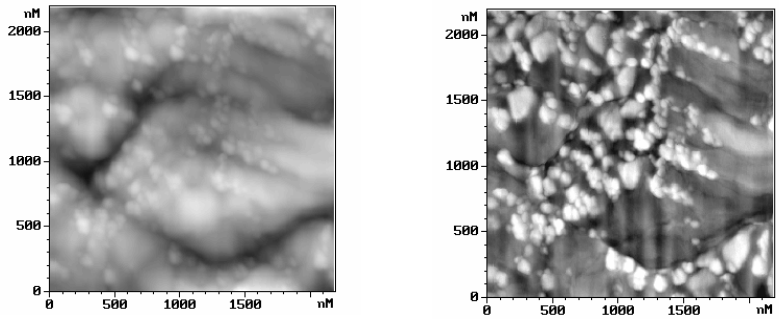

Fig.3. AFM topography (a) and phase contrast (b) image of MW-ceramics (600°C, τ=0). (Write grains - rutile, dark grains – anatase in PC image.). Sample 7

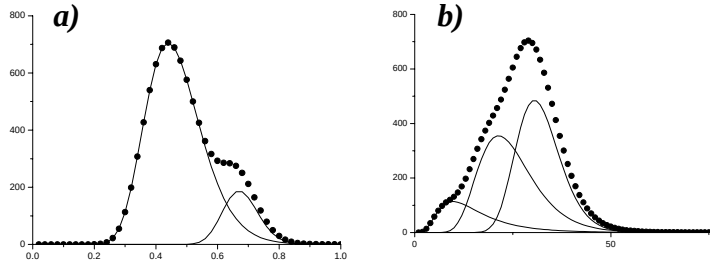

Fig.4 Phase ratio according to AFM-data in PC-region (a) and roughness distribution(b) for sample 7.

The phonon diffusion coefficients for TiO_2 samples obtained by both baking methods are found to be determined by the interface region properties. For the RF samples the ceramic grain interlayer is rather thick and porous, while for the MW samples it is more stiff and thin, which may be explained in the model of interface regions between the ceramic grains, since the phonon scattering in these regions is governed by the acoustic matching of media.
According to the XPS analysis of the nanoceramic spall surfaces, the composition of the interface regions, apart from TiO_2, includes also Ti_2O_3,TiO and graphite-like carbon whose fractions depend on the baking conditions (Table).

Chemical composition of interface regions in mol.% according XPS data

Samples	TiO	Ti_2O_3	TiO_2	graphite-like carbon	carbide
RF-baking (820°C, τ= 15 min)	2.3	4.5	12.7	80.5	–
RF-baking (850°C, τ= 15 min)	3	11.6	30.5	54.5	-
MW-baking (850 °C, τ=0)	5.8	5.2	34.2	46.8	7.9

The Ti_2O_3 and TiO formation as the result of high-temperature dissociation of TiO_2 during baking leads to the changes in the structure and properties of the interface regions. The quantitative ratio between elements depends on the regime of ceramic preparation. For samples 1 and 4 the increase in backing temperature only by 30° results in doubled amount of Ti_2O_3. Because of low density of Ti_2O_3 this can lead to a more loose structure of interface regions. In particular, the increase in Ti_2O_3 content in RF-samples results in a decrease of phonon permeability of the intercrystallite boundaries due to the lower Ti_2O_3 density. For MW-samples the Ti_2O_3 fraction is small, which may be explained by $Ti_2O_3 \rightarrow TiO$ reduction. At the same time, the TiC_{1-x} formation in the interface region leads to the stiffness increase and boundary stabilization. The interface phase content being small, it cannot be detected by XRD. In AFM phase contrast images MW-samples of there are interface regions which have a higher stiffness than the original matrix (Fig.5). The AFM, XPS and phonon experiments have yielded the same value of 7-10 nm for the thickness of this region.

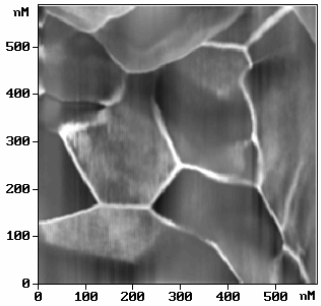

Fig.5 Phase contrast images MW-sample 850°C, τ= 15min

Summary

The phase contrast images in semi-contact mode atomic force microscopy together with XPS, XRD and method of thermal phonon kinetics allow one to estimate inhomogeneity in micromechanical properties of the nanoceramics spalls and to identify the anatase and rutile phases and to follow the evolution of the formation of the structure, phase composition and the state of interface regions.

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2. Bykov Y., Eremeev A., Egorov S. et al.//Nanostructured Materials, **8** (1999) 115-118.
3. R.G.Winkler, J.P.Spatz, S.Seiko, M Möller et al. //Phys. Rev. B, **54** (1996) 8908-8912