Structure and mechanical properties of nanocomposite Ni-ZrO$_2$ films

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Abstract. The composite Ni-ZrO$_2$ films were produced by simultaneous reactive sputtering of two metal targets (Ni and ZrY). The phase ratio in the composites varies due to the change of the sputtering magnetron power. Depending on the partial pressure of oxygen one can obtain Ni-ZrO$_2$ composites ($P_{\text{Ar}} = 1.05$ Pa, $P_{\text{O}_2} = 0.01$ Pa) or NiO-ZrO$_2$ ($P_{\text{Ar}} = 1.05$ Pa, $P_{\text{O}_2} = 0.04$ Pa). The mechanical properties of the composites were studied using a nanoindentation system: the concentration dependences of hardness, Young’s modulus and fraction of the elastic component in the total deformation of the film were established. It is established that all mechanical parameters have a higher value in the NiO-ZrO$_2$ composites compare with the Ni-ZrO$_2$ system.

1. Introduction
Zirconium dioxide (ZrO$_2$) is one of the most widely used ceramic materials for thermoprotective barrier and hardening coatings formation. Improvement of the zirconia properties is possible if structure of the material is transferred to a nanostructured state. It is assumed that a decrease of the grain size and an increase of the density of intergrain boundaries, respectively, allows to reduce the thermal conductivity of the dioxide coating, thereby improve its performance characteristics [1]. Another option to improve the mechanical properties and adhesion strength of zirconia-based coatings can be the creation of nanostructured composites metal-zirconia. The possibility of obtaining of the nanostructured composite material based on nickel and zirconium dioxide by magnetron sputtering of metal targets was investigated in the present work.

2. Results of the study
Samples of nanostructured composite Ni-ZrO$_2$ films with different ratio of metal and dielectric phases were obtained by high-frequency magnetron reactive sputtering. The formation of the composites was carried out by two magnetrons sputtering in the reactive atmosphere (Ar + O$_2$) two metal targets (Ni and Zr$_{92}$Y$_8$) simultaneously. The change of the metal concentration in the composites was made by change on the power of the magnetron sputtering the nickel target, while the power of the magnetron sputtering the alloy target (Zr$_{92}$Y$_8$) remained constant. The structure of the obtained films was studied using a D2 PHASER X-ray diffractometer from BRUKER. The chemical composition was determined by electron-probe X-ray spectral microanalysis on a X-ray scanning JXA-840 microanalyzer. Two series of deposition process with different oxygen partial pressure were carried out. All the obtained composites were 1–1.5 μm thick and were deposited on a glass substrates.
Figure 1 shows the X-ray diffraction patterns of NiO-ZrO$_2$ composites obtained with high oxygen pressure of 0.04 Pa. The argon operating pressure was 1.05 Pa.

The only peaks from the tetragonal zirconia as well as the halo from the glass substrate (in the angular interval 20–30 deg) are present on the X-ray diffraction pattern from the composite with low nickel concentration (15 at. %). With increasing of the nickel concentration (25 at. % Ni) the diffraction peaks disappear and the film becomes X-ray amorphous. Apparently, this is a consequence of a significant reduction of the zirconia grains size caused by the presence of nickel, which begins to form a separate phase and prevents the growth of the dioxide crystals. A further increase of the nickel concentration (the range of 37–73 at. % Ni) leads to the appearance of peaks corresponding to nickel oxide. It is characteristic that diffraction peaks from zirconium dioxide in samples with high nickel content are not observed but the halo in the angular interval from 30 to 35 deg is preserved. This indicates the presence of a fine-grained zirconia phase since the halo is in the angles range where the main diffraction peaks of the dioxide are located. The presence of the nickel oxide phase instead of expected pure nickel indicates that the concentration of the reactive gas during the composites deposition is excessive. In fact the composite NiO-ZrO$_2$ samples were obtained as a result of the first series of deposition.

The grains size of crystalline phases in the obtained samples were determined using a specialized licensed software package “DifracEva” and a Scherrer method. The average size of nickel oxide crystals was 8.5 nm which indicates the formation of nanstructured morphology in deposited samples.

Mechanical properties of the obtained composites were studied by using of the NanoHardnessTester nanoindentation system from CSM Instruments. The operation principle of the used technique is based on indenting of a geometrically certified indentor under the action of a specified profile of the normal force $P(t)$ and simultaneously recording the depth of its immersion into the material $h(t)$ [2]. This allows to determine several parameters characterizing the mechanical properties of the material. Figure 2 shows the dependences of hardness, Young’s modulus ($E$) and the elastic deformation component of NiO-ZrO$_2$ composites on the metal concentration. With increasing of the nickel concentration (actually nickel oxide) the measured parameters do not change monotonically. For the hardness and elastic component of deformation a maximum is observed in the region of 25 at. % Ni (figure 2). The maximum values of the measured characteristics correspond to a composite with a “transition” (X-ray amorphous) structure. Apparently, this is a consequence of the finely dispersed structure of this composite. Since the initial partial pressure of oxygen used in the first series of the composites deposition was excessive (the metal phase was oxidized) the second series of depositions was carried out at a lower oxygen pressure (0.01 Pa). The results of X-ray diffraction analysis of the obtained films are presented in figure 3.

Despite the significantly lower partial pressure of oxygen (0.01 Pa) the evolution of the composites structure with an increase of the metal concentration follows the same pattern as in the composites of...
the first series of sputtering. The only peaks belonging to the high-temperature tetragonal modification of zirconia are presented on the X-ray diffractogram obtained from the composite with low nickel concentration (15 at. %). Increase of the nickel concentration to 25 at. % leads to the disappearance of peaks but halo in the region of 25–35 deg was appeared. Moreover, this halo is also observed in diffractograms from composites with a higher nickel content. This may indicates the presence of the finely dispersed zirconia phase in all obtained samples. The diffraction peaks from crystalline nickel are observed on the diffractograms obtained from composites with a higher nickel content (25–74 at. %).

Thus, a decrease of the oxygen partial pressure during the sputtering of two metal targets leads to formation of composite Ni-ZrO₂ structure. The average size of nickel granules in these composites was 6 nm according to Scherrer method.

![Figure 2](image1.png)

**Figure 2.** Concentration dependences of mechanical parameters of NiO-ZrO₂ films obtained in the regime with high oxygen pressure (0.04 Pa).

![Figure 3](image2.png)

**Figure 3.** X-ray diffraction patterns of Ni-ZrO₂ films obtained in a regime with a low oxygen pressure (0.01 Pa). Ni concentration is shown in at. %.

A comparison of the mechanical properties of two studied type of composites indicates that the absolute values of Young’ modulus and the hardness of oxide-oxide composites (NiO-ZrO₂) are higher than those of the metal-oxide composites (Ni-ZrO₂). This difference is particularly evident when the hardness values of the composites are being compared.

The hardness does not exceed 11.4 GPa in the Ni-ZrO₂ composites while the minimum value in the NiO-ZrO₂ composites is 11.7 and the maximum value reaches 18.2 GPa. Despite the fact that the properties of pure phases (Ni and ZrO₂) differ substantially from each other the concentration dependences of the mechanical parameters in Ni-ZrO₂ composite are weakly expressed (figure 4). The measured values of the parameters of Ni₁₅(ZrO₂)₈₅ and Ni₇₄(ZrO₂)₂₆ composites are slightly differ from each other.

3. Conclusions

Simultaneous reactive sputtering of nickel and Zr₉₂Y₈ alloy by high-frequency magnetrons in mixed atmosphere (Ar + O₂) allows to obtain composite films. Depending on the partial oxygen pressure a composite consisting of two oxide phases (NiO-ZrO₂) or a metal-insulator composite (Ni-ZrO₂) can be formed. The change of the power of one magnetron which sputter the nickel target allows to vary a phase ratio in very wide region in the composites forming during deposition process. It has been found that the hardness, the Young’s modulus and the fraction of the elastic component in the total deformation have higher values in the NiO-ZrO₂ composites compare to the Ni-ZrO₂.
Figure 4. Concentration dependencies of mechanical parameters of Ni-ZrO$_2$ composites obtained in the regime with reduced oxygen pressure (0.01 Pa).

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References
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