High-Temperature TEM investigation of the phase composition and structure of the Zr-Y-O / Si-Al-N multilayer coatings

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Abstract. Deposition of nanostructured multi-layered coatings on the basis of Zr-Y-O was implemented by the pulse magnetron methods. Structural-phase statesand morphology of the nanostructured coatings were investigated by SEM and the high-temperature TEM method. Thehigh-temperature TEM revealed the presence of reversible phase transition of the tetragonal phase to the monoclinic phase, which can ensure stress relaxation and closure of surface cracks.

1. Introduction

Ceramics on the basis of Zr holds the leading place among fire-resistant constructional materials as it retains high mechanical properties up to 0.8…0.9 of the melting temperature of 3173 K. That is why ZrO_2coatingsare mainly used as thermal barrier coatings in hot turbine sections and other engine units.

It is known that ZrO_2 has three stable crystal structures depending on temperature: the monoclinicphase from the temperature of 1170 ºC, the tetragonal phase within 1170 ºC…2370 ºC and the cubic phase from the temperature of 2370 ºC. Mechanical properties of zirconium dioxide ceramics are known to be the function of phase composition and structure. Tetragonal zirconium dioxide possesses high strength and toughness. Various methods and technologies were improved for production and stabilization of the tetragonal phase of the zirconium dioxide material [1-2]. The most common method is the production of tetragonal zirconia by adding to it some stabilizing compounds. Analysis of published data shows that the yttrium oxide Y_2O_3 is commonly used as a stabilizing agent, which contributes to transformation of the tetragonal phase to monoclinic one at cooling.

A special attention is paid to reversible martensitic transformations in metal alloys (the so-called transformational conversion) due to the potential of their practical use in many fields of science, technology, medicine and industry. These alloys belong to the group of the so-called 'smart' functional materials, as they allow controllingtheir behavior [3-4]. These are transformation-hardening materials which are widely used in engineering practice as structural materials. The majority of such ceramic materials are developed on the basis of zirconium dioxide that is partially stabilized in the tetragonal phase [5-7]. The tetragonal phase is capable of a monoclinic martensitic phase transition. The phase transition is accompanied by development of the shear and volume strain, stress relaxation, and closure of surface cracks. The hardening effect can result in ceramic materials with the strength properties (fracture toughness and strength) comparable to that of structure materials.

Experiments of the direct observation mechanisms of martensitic transformations are rare. In [8] 'in-situ' by TEM was observed martensitic transition from the tetragonal ZrO_2 (*t*) to a monoclinic (*m*) phases. In this experiment, defect-free tetragonal ZrO_2 single crystals 0.2 µmin size were investigated. Phase transition of the tetragonal phase to monoclinic was initiated by some heterogeneity in individual particles, when the amplitude of the stress exceeds a critical value. Then the motion of interphase boundaries observed between the tetragonal and martensitic phases 'in-situ' [9].

The paper deals with investigation of change in grain structure, grain and interphase boundaries, structure and phase composition during heating mode 'in-situ' in the microscope column and followed by thermos elastic phase transition in the multi-layer coating based on Si-Al-N / Zr-Y-O in ZrO_2 layer.

2. Experimental

Deposition of the coatings was carried out in the KVANT-03MI [10] unit equipped with a magnetron with a mosaic zirconium-yttrium target. The magnetron was powered from a pulse source at the frequency of 50 kHz. The samples were placed in the chamber on the rotating table. The sample temperature during the deposition was 573 K.

The structural-phase state of the surface layers of the copper substrate was investigated by transmission electron microscopy (TEM) using the JEM-2100 microscope (Jeol Ltd., Japan). Foils were prepared by the 'cross-section' method using the ION SLISER-EM-09100IS installation (Jeol Ltd., Japan). The elemental composition of the coatings was determined by energy dispersive X-ray (MRSA) using the INCA-Energy microanalyzer (EDX) (Oxford Instruments) with the built-in SEM LEO EVO-50XVP.

3. Results

Figure 1 shows a cross-section of the Zr-Y-O / Si-Al-N coating obtained by TEM. SEM investigation using the mapping method of cross section of multilayer coatings shown that the layers of the multilayer coating actually consist of elements Zr, Y, O, Si, Al, N (Figure 1b, the red rectangle shows research area).

a   b
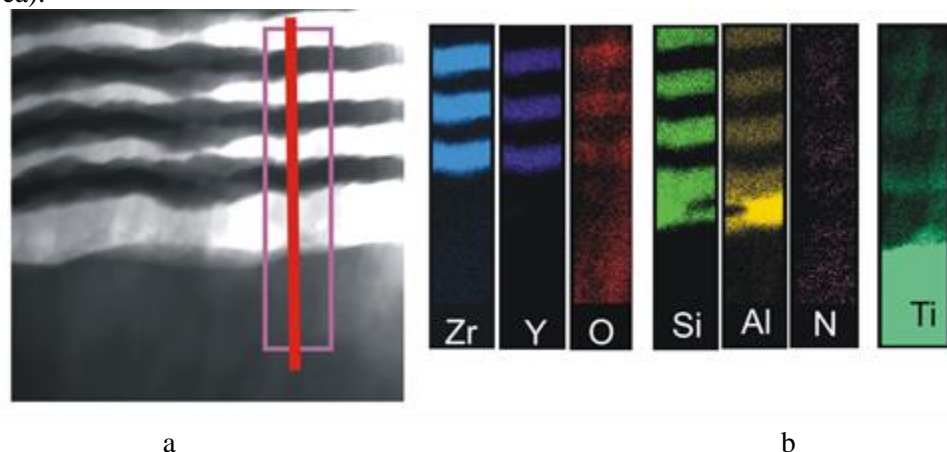
Figure 1. The results of microprobe analysis in mapping mode. It is seen present elements in characteristic radiation in the multi-layer coating.

We can see that the boundary between the layers of Si-Al-N and Zr-Y-O is sharp enough. The coating consists of layers having a different contrast: light and dark (Figure 1a). As shown previously [11], the layer on the basis of Zr-Y-O has a dark contrast and two modifications of the ZrO_2 phase: the tetragonal and monoclinic ones. The layer on the basis of the Si_3N_4 phase has a light contrast.

The grain structure of the coating layer on the basis of Zr-Y-O is columnar (Figure 2a). The longitudinal size of the grains of the ZrO_2 phase coincides with the axis of growth of the coating. The height of the column is determined by the layer thickness, and the average cross dimension of the

grains is less than about 80 nm. The height of the columns depends on the deposition time of the layer and may be adjusted depending on the application. In this particular case, the column height of the coating layer is about 1000 nm (Figure 1a).
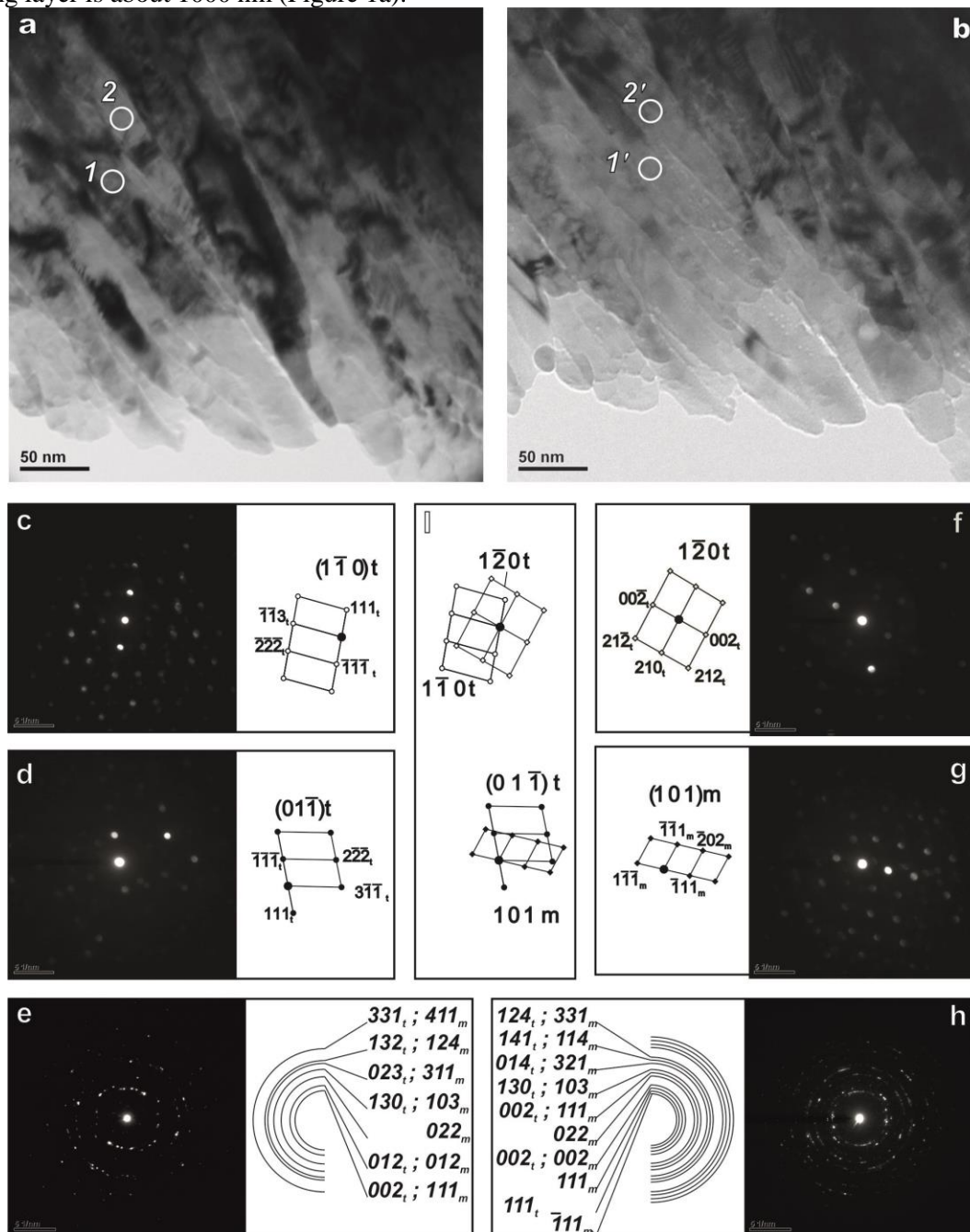
Figure 2. TEM image of coating layer on the basis of Zr-Y-O: bright-field image of the coating structure in the initial state (a) and after heating up to 900 ^{o}C (b); micro diffraction patterns for the initial state (c, d, e) and their indexing schemes; microdiffraction patterns and their indexing schemes for coatings, heated to 900 ^{o}C (f, g, h); schemes of misorientations of crystalline lattices of phases in the initial state and at $T = 900$ ^{o}C at sites 1 and 1' and 2 and 2'.

Figure 2a and Figure 2b show the bright field image and microdiffraction patterns obtained in the nanodiffraction mode from sites 1 and 1' (sites marked by circles in bright field image) and their

indexing scheme for the initial state and at a temperature 900 $^{\circ}$C (Figure 2c, f). In the initial state at RT we observes reflexes belonging to the plane of the reciprocal lattice (1$\bar{1}$0) of the ZrO$_2$tetragonal phase, then at 900 $^{\circ}$C we see plane (1$\bar{2}$0) the same modification.

In this case, the heating led to a reorientation of the crystal lattice of the columnar grains of tetragonal ZrO$_2$. The angle of reorientation of grains is 18 degrees (Figure 2I). Figure 2 (f, g, h) shows diffraction patterns and indexing scheme obtained from the second site, marked on the bright-field image. It is evident that in the initial state at the micro diffraction pattern there are reflexes belonging to the plane (01$\bar{1}$) tetragonal phase ZrO$_2$. At heating foil up to 900 $^{\circ}$C a tetragonal phase transfer to monoclinic one under the thermal stress. This phase transition is a martensitic.

Figure 2g shows micro electron diffraction with reflexes belonging to the plane 101 of the reciprocal lattice of the ZrO$_2$ monoclinic phase. These data are confirmed by the data obtained at interpretation of ring diffraction patterns. Figure 2e and Figure 2h shows microdiffraction patterns obtained in initial state and at a temperature of 900 $^{\circ}$C. They can be identified as belonging to the tetragonal and the monoclinic phases ZrO$_2$. As shown in [12], microscopic mechanism of formation of a martensitic phase consists in the movement of dislocations of transformation along interphase boundary causing local reorganization of a lattice from high-temperature in a low-temperature phase. At the reverse martensitic transformation dislocations move in the opposite direction.

The reversible movement of phase boundaries between the low-temperature and high-temperature phases m-ZrO$_2$ $\leftrightarrow$ t-ZrO$_2$ was found at research of a coating on the basis of Zr-Y-O is in the basis of the mechanism of transformation hardening [12].

Locally occurring martensitic transformation $t \rightarrow m$ in ZrO$_2$ contribute to closing the edges of the cracks formed during thermal cycling or other loads, thanks to what intensity of concentrators of tension near defects decreases. As a result the existing or again formed microcracks become stable at preservation of level of external loading [9]. It is promoted by martensitic phase transformations which are followed not only development of shifts, but also essential change of volume of material [11]. The transition from the tetragonal to the monoclinic phase is accompanied by an increase in phase by 4 % [12].

4. Conclusion
By SEM and TEM it has been established that coatings on the basis of Zr-Y-O produced by the magnetron sputtering methods have a nanograin column structure where the columns are spread through the entire coating thickness.

In the initial state layers on the basis of Zr-Y-O are two-phase and consist generally of the tetragonal phase ZrO$_2$ with a small amount of monoclinic one.

At heating layer in a column of TEM in the 'in-situ' mode we can observe: 1) turns of grains of the main phase together with change in the angle of disorientation crystallographic planes, 2) martensitic transition of the tetragonal phase to the monoclinic 3) modification of grain boundaries – their total length increases, the form of grains changes, in initial column grains there are cross boundaries, i.e. there is a process of fragmentation of grains.

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