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THERMAL RESISTANCE AND PHASE TRANSITIONS STUDIES FOR SOME COMPOSITE MATERIALS BASED ON Al_2O_3

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In this paper the studies of phase transitions in some material compositions based on Al_2O_3 caused by high-temperature processes are presented. These material compositions may be used to high-temperature resistant plasma sprayed coatings. The occurring phase transitions are studied by X-ray diffraction methods. Phase transitions and thermal resistance for studied oxide systems are different. In the coatings from the materials belonging to Al_2O_3–NiO and $Al_2O_3-ZrO_2$ systems complex phase transitions were observed. More resistant to the conditions of thermal fatigue are coatings containing aluminum titanate Al_2TiO_5 and mullite 3 Al_2O_3–2 SiO_2.

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1. Introduction

The presented studies are connected with the works on high-temperature resistant protective coatings especially of thermal barrier type (TBC), being products of advanced technology. This type of coatings is applied in different branches of industry and technology among others in gas turbines and Diesel engines [1–3]. The studied coatings are deposited mainly by plasma spraying process. This process (described in detail elsewhere) forms preferred conditions to phase transitions with forming (in some cases) of metastable and disordered phases due to short (range of ms) time of flight of the material particles by the high-temperature region of plasma arc (about 10^4 K) and subsequent high cooling rate (10^5-10^6 K/s) [4, 5]. In the result of plasma spraying alumina transforms most frequently into metastable forms of γ type, which undergo transition to thermodynamically stable corundum form after thermal treatment. In order to counteract these transitions or at least decrease its extent, some amounts of other oxides are added [4–6].

The aim of the performed works is of twofold character. First research side — to determine phase transitions and thermal stability for some recently studied material composites. Second practical side is to find the best coatings compositions of increased resistance to high-temperature oxidation, corrosion and thermal shocks conditions.

Some recent X-ray data showing phase transitions caused by the plasma spraying and coatings thermal treatment at the processes described below in the material composites listed in the next point are presented.

2. Experimental

The studied materials and coatings belong to the following systems:
Al_2O_3–NiO,
Al_2O_3–SiO_2,
Al_2O_3–TiO_2,
Al_2O_3–ZrO_2.
Thermal resistance is determined in two types of applied processes:

1) Annealing in furnace in the time range from 10 to 100 h with slow heating and cooling. This process is applied both to materials in the form of powders before spraying and coatings.

2) Processes with thermal shock conditions.

The latter concerns two main processes. The first one consists in coatings deposition by plasma spraying described in detail elsewhere [4, 5]. Conditions of this process, mentioned in preceding section, may induce phase transitions especially in studied materials. The second process concerns experiments with coatings as sprayed, performed on special arrangement with the use of robot and microprocessor with multiplied short time (10–120 s) cycles of heating by burner and cooling by air blow. These experiments described in detail earlier make conditions near to further coatings applications in turbines and engines and therefore may be treated as a first test of coating resistance before exploitation tests [4–6].

Phase transitions appeared in the coatings due to aforementioned processes are determined mainly by X-ray diffraction methods (XRD) with the use of Cu monochromatic radiation. Light microscopy (LM) and scanning electron microscopy (SEM) are used as complementary methods in order to reveal microstructure changes accompanying phase transitions.

3. Results and discussion

Experimental results for the studied groups of materials and coatings differ from each other in the dependence on the studied oxide systems. First, some new data for the coatings from Al_2O_3–NiO containing up to 20 weight % NiO will be presented.

These coatings show in the earlier works performed under research project supported by the Committee for Scientific Research high thermal resistance in particular up to 100 thermal shocks [4, 5]. The stability of the spinel-type crystalline phase $NiAl_2O_4$ has been observed. But after more than 100 thermal cycles a characteristic effect was noticed and demonstrated in Fig. 1. In the central part of the coating (on the trace of burner flame) a dark, degradation circle has been formed. Inside this circle the spinel phase decomposes and γ phase changes into stable α phase. As a result two separate phases occur and strong peaks of α-Al_2O_3 and three weak peaks of NiO are observed in Fig. 1a. Beyond this circle, in the outer part of the coating, the common peaks of the γ phase and the spinel phase (marked by X) remain unchanged (Fig. 1b).

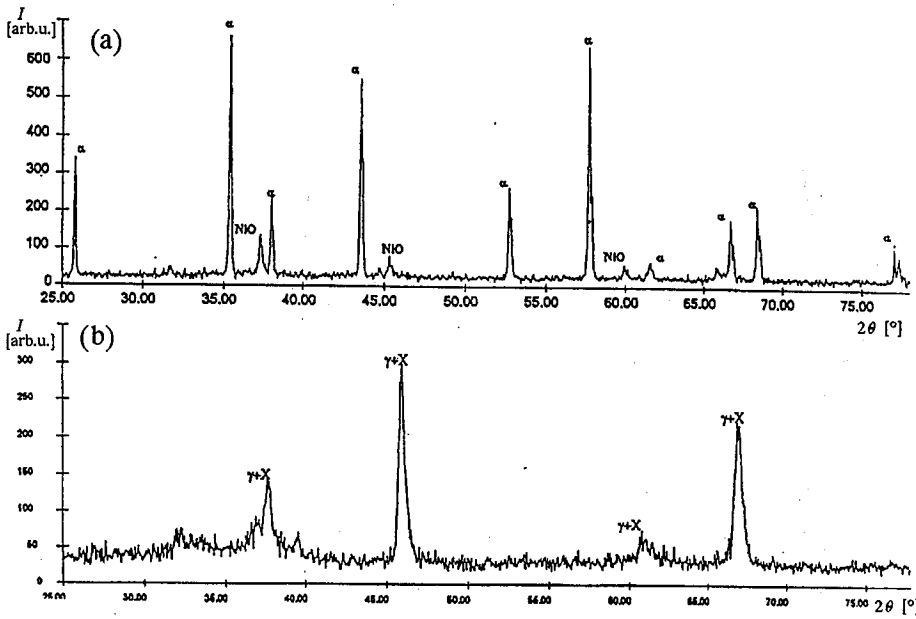

Fig. 1. Diffraction pattern of the Al_2O_3 + NiO coating after 150 thermal shock cycles, (a) within central part of the coating, (b) in the outer part. α — α-Al_2O_3, γ — γ-Al_2O_3, X — $NiAl_2O_4$.

Coatings from the materials belonging to Al_2O_3–TiO_2 system, especially those which contain aluminum titanate Al_2TiO_5 as a crystalline phase, show high resistance to even 150 thermal shocks. Macroscopically visible degradation changes are rather small and no phase composition changes of the similar type as in the case of materials with NiO have been observed. The results of recent experiments are consistent with those described earlier [5, 7]. It is worthwhile to remark that Al_2TiO_5 shows characteristic thermal expansion anisotropy causing very high thermal shock resistance which may be subjected to numerous applications [6, 8–10]. The problem of rather poor mechanical strength of aluminum titanate and the temperature range of its formation may be solved by the choice of suitable coating composition. Further works concerning this compound are planned in the near future.

Materials and coatings belonging to the oxide systems with SiO_2 and ZrO_2 have as yet been subjected only to annealing and thermal shocks with the use of furnace. Materials from the first system exist in the mullite (3 Al_2O_3–2 SiO_2) type of crystal lattice, which is stable to the conditions of performed experiments. Neither change to another phase nor decomposition to simple oxides have been observed. But another effect may be visible in the course of comparing diffraction patterns of powders and coatings before and after thermal treatment shown in Fig. 2. Some differences in several peak intensities may be observed. Two factors may cause these differences. First, it can be some kind of recrystallisation process with the changes in crystallite sizes and ordering due to thermal treatment. It can also be a polytypism with probable doubling of c axis, which may be possible in

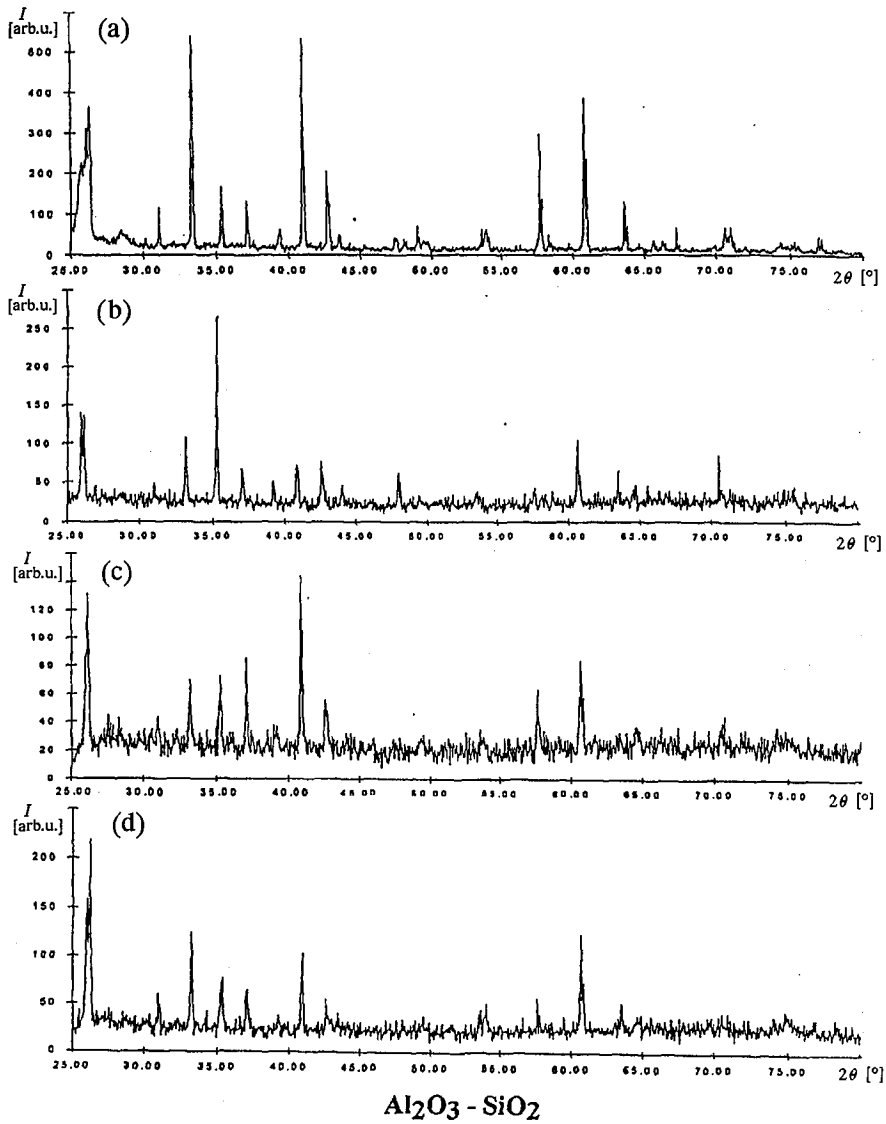

Fig. 2. Diffraction patterns of mullite with effects of probable polytypism: (a) powder before spraying, (b) coating as sprayed, (c) coating after 50 h annealing in 1200 K, (d) coating after cooling in liquid nitrogen.

mullite type of structure and may change the observed intensities. For a comparison the theoretical pattern of mullite performed on the basis of data from powder diffraction file is presented in Fig. 3. The peaks intensities distribution in the diffraction patterns shown in Fig. 2c and 2d are closely resembling those shown in Fig. 3. Specimens annealed during 50 h and cooled in liquid nitrogen appear thus to be nearer to the thermodynamic equilibrium than the other samples.

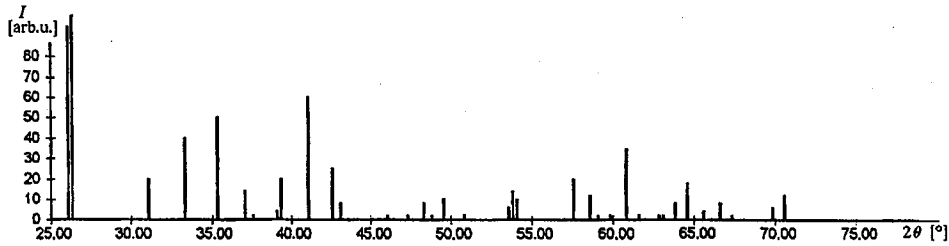

Fig. 3. Theoretical pattern of mullite according to powder diffraction file (PDF).

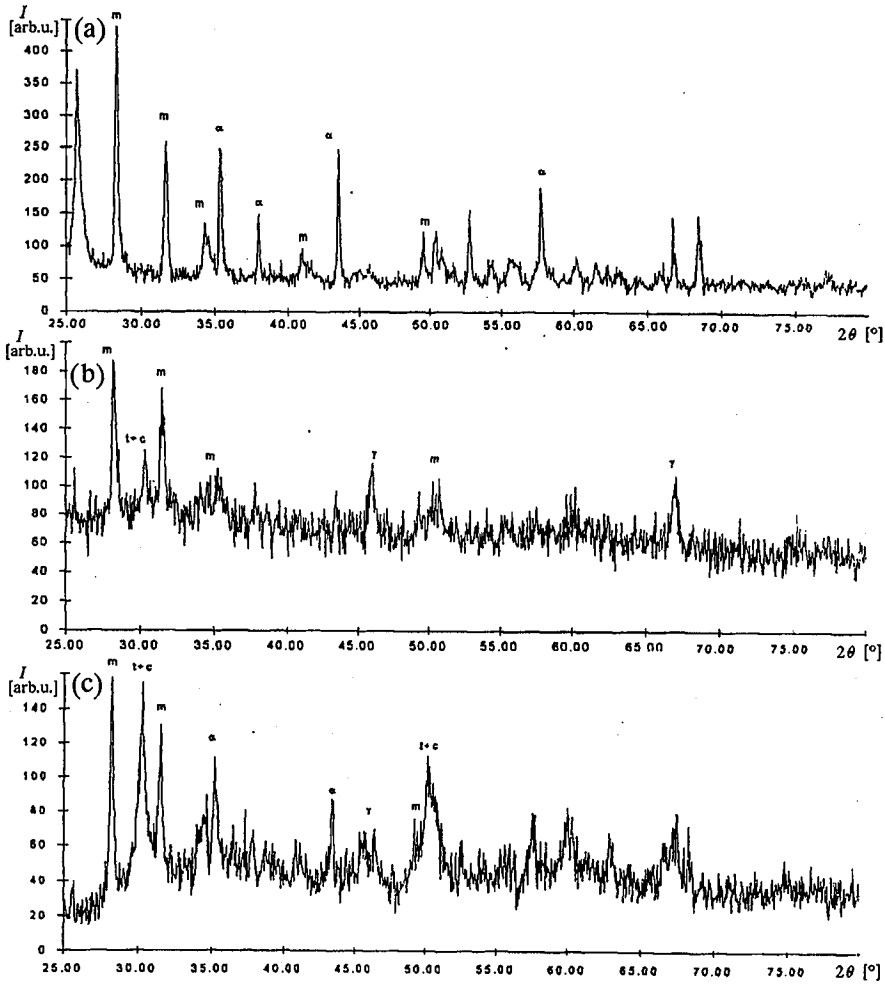

Fig. 4. Diffraction patterns of the materials belonging to Al_2O_3–ZrO_2 system: (A) powder before spraying, (B) coating as sprayed, (C) coating after 50 h annealing in 1200 K, c — cubic, t — tetragonal, m — monoclinic ZrO_2, α, γ-polymorphs of Al_2O_3.

Further works on this problem are still in progress. It is worthwhile to emphasize that mullite is widely applied in the high temperature region in the form of bulk material but not yet in the form of the coatings [11, 12].

The last oxide system to be described seems interesting by the possibility of connecting properties of the two main high-temperature ceramic oxides. The studied materials containing about 40 weight % of ZrO_2 exist however in the form of separate oxides. Therefore on the diffraction patterns before spraying two independent crystalline phases are present: ZrO_2 in the monoclinic form and Al_2O_3 in the stable α form (Fig. 4a). After plasma spraying an interesting effect has been observed. A new peak corresponding to higher symmetry zirconia polymorphs (tetragonal and cubic) stable at high temperatures and existing at room temperatures only in the presence of stabilising additions has appeared (Fig. 4b). In the result of 50 h annealing at 1200 K this peak of higher symmetry phases visible between two highest peaks due to monoclinic phase still exists and its intensity becomes almost equal to the intensities of neighbouring peaks (Fig. 4c). It means that contents of all these crystal forms of zirconia are similar. After annealing by 100 h the diffraction pattern is almost unchanged. It may be supposed that some form of partial stabilisation of higher symmetry ZrO_2 polymorphs under the influence of Al_2O_3 appear. It is worthwhile to remark that this latter oxide existing as a separate phase undergoes transitions: $\alpha \rightarrow \gamma$ in the result of spraying and in the reverse direction after annealing. Full interpretation of this effect will be a subject of further works and therefore thermal shock experiments performed on the above-mentioned arrangement are planned for materials of both groups (with silica and zirconia).

On the basis of the described works the following results may be pointed out:

1. Coatings containing materials with NiO show after 150 thermal cycles an inhomogenous phase transition which occurs in the coatings center.

2. Coatings containing aluminum titanate show resistance up to 150 thermal shocks.

3. Coatings with polycrystalline mullite type of structure are stable to applied thermal treatment. Some differences in few peaks intensities connected with crystallite sizes and ordering changes and probable polytypism are registered.

4. Complex phase transitions concerning both oxides due to plasma spraying and subsequent coatings annealing are observed for the materials from Al_2O_3–ZrO_2 system.

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