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DIFFRACTION AND MICROSCOPIC STUDIES ON THE STRUCTURE OF PLASMA SPRAYED COATINGS CONTAINING COMPOSITES BASED ON AL_2O_3

DYFRAKCYJNE I MIKROSKOPOWE BADANIA STRUKTURY POWŁOK NATRYSKIWANYCH PLAZMOWO ZAWIERAJĄCYCH KOMPOZYTY NA BAZIE AL_2O_3

Plasma sprayed coatings of thermal barrier type (TBC) based on Al_2O_3 and ZrO_2 with metallic bondcoat are studied by X-ray diffraction, scanning and transmission electron microscopy. Phase transitions and presence of various layers : amorphous, nano and polycrystalline of equiaxial and columnar shape are observed. Local fluctuations of chemi-cal and phase composition are mainly connected with the conditions of plasma spraying process. In the result of thermal treatment changes directed to more ordered state occur.

Keywords: thermal barrier coatings, phase transitions, X-ray diffraction, transmission electron microscopy

Powłoki natryskiwane plazmowo typu barier termicznych na bazie Al_2O_3 i ZrO_2 zawierające metaliczną warstwę wiążącą badane były metodami dyfrakcji rentgenowskiej oraz skaningowej i transmisyjnej mikroskopii elektronowej. Zaobserwowano występowanie przemian fazowych oraz obecność oddzielnych warstw: amorficznych, nanokrystalicznych oraz polikrystalicznych charakteryzujących się równoosiowymi i kolumnowymi kształtami krystalitów. Lokalne fluktuacje składu chemicznego i fazowego są związane z warunkami procesu natryskiwania plazmowego. Zmiany zachodzące w wyniku obróbki termicznej powłok prowadzą do stanu bardziej uporządkowanego.

1. Introduction

The presented paper is connected with the works on high temperature resistant protective coatings of thermal barrier type (TBC). This type of coatings being a product of advanced technology has numerous applications in different branches of industry and technology among others in heat and gaseous turbines, aircraft and high compression engines [1-3]. Therefore it needs a choice of special materials as components for preparing the suitable coatings. First is a substrate from superalloys based on Ni or Fe. Second is the metallic bondcoat of MCrAlY type (where M = Ni, Fe, Co). The third essential component is an external ceramic layer based on Al_2O_3 and/or ZrO_2. Sometimes additional mixed metal-ceramic layer is used between ceramics and metal. Coatings of TBC type due to the insulat-ing properties of ceramics reduce the temperature attained by the substrate and act as a barrier against it degradation by hot gaseous and liquid streams. The plasma spraying process is the main method for deposition such type of coatings. The essential features of this process are short time of high temperature action and subsequent high cooling rate. Material in the form of powder introduced to plasma arc (temperature about !0^4 K) mostly melts and flies by a few ms and as a result the cooling rate in the contact with cold substrate is 10^5 – 10^6 K/s. Under such conditions distant from thermodynamic equilibrium amorphous, nanocrystalline and unordered areas in the coatings appear and different phase transitions are observed.

Various research methods such as X-ray diffraction (XRD), scanning and transmission elec-tron microscopy (SEM, TEM) combined with selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) have been applied in order to reveal the above effects. The aim of the presented work has a twofold character. The first research side is to deter-mine all changes in coatings structure and phase transitions especially in the areas near to the ceramics - metal interface important for the coatings resistance. The second practical side is

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to obtain coatings with good adherence to the substrate and high resistance as a thermal barrier.

2. Experimental

The studied coatings consist of two layers:

I. metallic bondcoat – NiCrAlY Cr 15 – 25 wt %
Al 6 – 14 wt %
Ni – balance Y 0.5 – 1 wt %
thickness 50 –100μm

II. ceramic layer
Al_2O_3 + 40 wt % ZrO_2
thickness 150 - 300 μm
substrate – Ni and Fe based superalloys.

Coatings are deposited by the method of atmospheric plasma spraying (APS) with the use of Polish plasmatrone PN – 120 at the Institute of Atomic Energy. The process parameters and experimental details are described elsewhere [4,5].

First test of coatings thermal resistance is a long time annealing (50-100 h at 1200-1800 K). The next are thermal shocks experiments performed on special arrangement described in earlier works with multiplies short time (10-120 s) cycles of heating by oxygen-acetylene burner and cooling by air blow [4,5,6].

Coatings structure before and after thermal treatment was studied by XRD methods. Micro-structure is studied firstly by SEM and next ion milling technique with the use of focused ion beam is applied to obtain specimens with thickness suitable for transmission electron microscopy. TEM methods combined with SAED with the use of CM 20 Twin microscope are carried on at the Institute of Metallurgy and Material Sciences. Local composition analysis with 10 nm diameter beam are performed by EDS methods.

3. Results and discussion

First experimental results show that coatings structure is generally rather polycrystalline with some visible effects of disorder and changes in crystallite sizes. The level of diffraction pattern background is often higher in comparison with pattern of the same material before spraying. Coatings microstructure observed by SEM methods is characterized by the existence of numerous pores and microcracks [7,8]. This microstructure desirable for thermal insulation may however cause lower values of coatings elastic properties. But either scanning microscopy or X-ray diffraction give information involving coatings surface or adjacent areas. We need however structural data from the coatings interior especially from the areas near to the interface metal – ceramics with higher resolution and connection between microscopic image and identification. Therefore attempt of applying TEM methods combined with SAED is performed. Using of transmission microscopy with higher resolution made possible microstructure observations in the nanometric range but needs overcoming the experimental difficulties with preparing sufficiently thin specimens especially for brittle materials such as ceramics. As already mentioned tthe special ion milling technique with the use of focused Ga ion beam (FIB) has been developed [9]. In the course of coatings thinning possibilities of X-ray identification on various depths occur.

In this work. some new results obtained for coatings from special composite Al_2O_3 + 40% ZrO_2 are described. X -ray diffraction patterns made before and after plasma spraying are shown in fig. 1. As can be seen material in the form of powder before spraying contains two separate phases: Al_2O_3 in α form and ZrO_2 in monoclinic form (fig. 1A).These are the most thermodynamic stable forms of both polymorphic oxides. After plasma spraying some changes in the diffraction pattern are observed (fig. 1B). An interesting effect is visible for ZrO_2 particularly in the area .near $2\upsilon = 30°$. Between two strongest peaks of the monoclinic form new peak corresponding to the higher symmetry forms (cubic and tetragonal) occurs. After coatings annealing (50 h at 1200K) the intensity of this peak is growing and becomes almost equal to that of monoclinic form (fig. 1C). In such a manner we can observe the effect of coexistence of three crystalline ZrO_2 forms. Both oxides remain however as separate phases without forming neither common phase nor solid solution. Phase transitions for Al_2O_3 are similar to described earlier [5,6]. After plasma spraying α form transforms to metastable γ form which partly returns to stable α form in the result of coatings annealing.

The above described phase composition occurs on the coating surface. Diffraction patterns made in the course of coating thinning at different depths show some fluctuations in phase composition for both oxides connected with difference in the cooling rate between coating surface and interior [10,11].

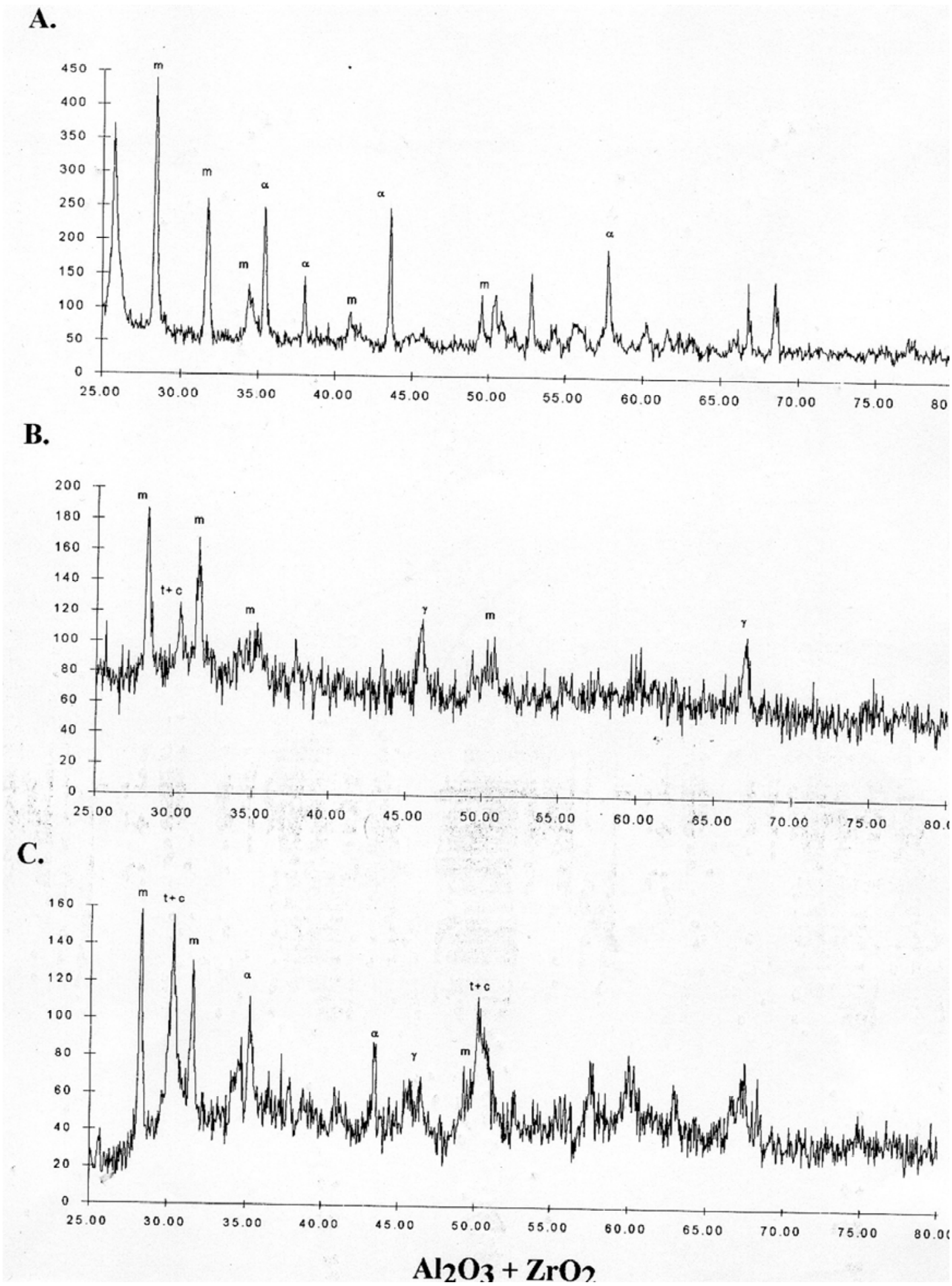
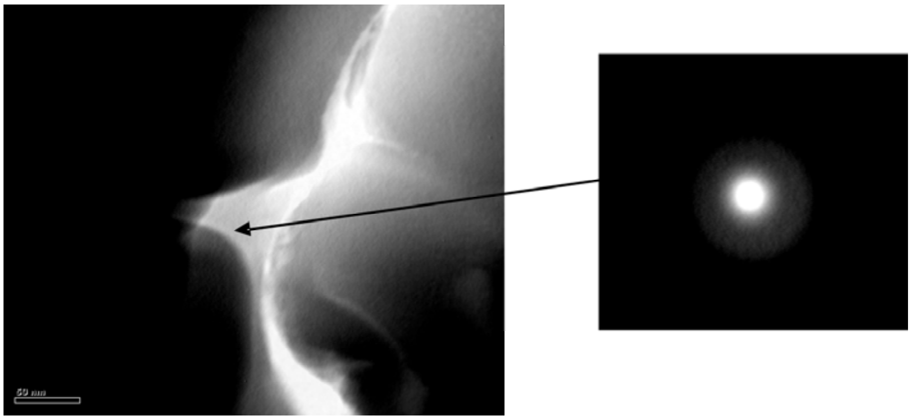


Fig. 1. Diffraction patterns: A – powder before spraying, B – as sprayed coating, C – coating after 50h annealing at 1200 K. Forms of ZrO_2: c-cubic, m-monoclinic, t-tetragonal,α,γAl_2O_3polymorphs

Microstructure seen in TEM images is rather complex. Several alternating layers, amorphous and crystalline, differing in composition are observed. In some cases these layers are separated, in other may be slightly mixed. In figure 2a eutectic amorphous phase Al_2O_3 – ZrO_2, placed near to the interface with bondcoat, is shown. Image contrast is somewhat different for amorphous and crystalline layers. Distribution of Al, .O and Zr within amorphous layer is presented in figure 2b.

a.)



b.)

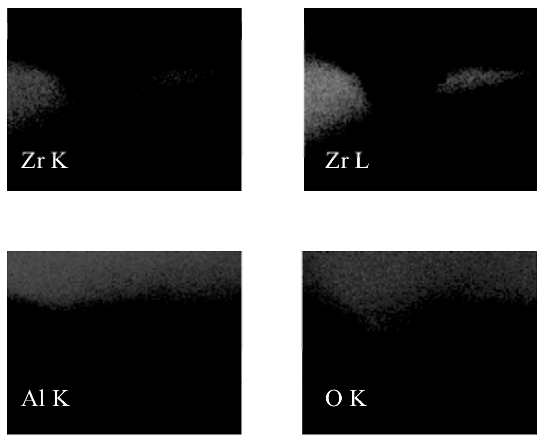


Fig. 2. a) TEM microstructure with indication of eutectic amorphous phase
b) Distribution of Al, O and Zr in amorphous phase

Adjacent layers consisting of crystalline single oxides are visible in the figure 3. Cubic ZrO_2 is identified among others in elongated form aligned parallel and close to the boundary with metal. In the next area crystalline ά – Al_2O_3 exists. The ribbons of γ – Al_2O_3 nanocrystalline with amorphous fragments are also observed. Nearer to the coatings interior the columnar crystals shown in figure 4a are encountered. The image of individual such crystal is shown in fig. 4b. Columnar crystals contain more monoclinic ZrO_2 and less of γ – Al_2O_3. Local agglomerations of both oxides in different crystal forms are also observed.

Under the influence of annealing the areas of amorphous phases decrease and small crystallites occur mainly in the platelike shape. Some dislocations and other structural defects partly disappear. The columnar crystals partly dissolve in equiaxial crystal matrix..

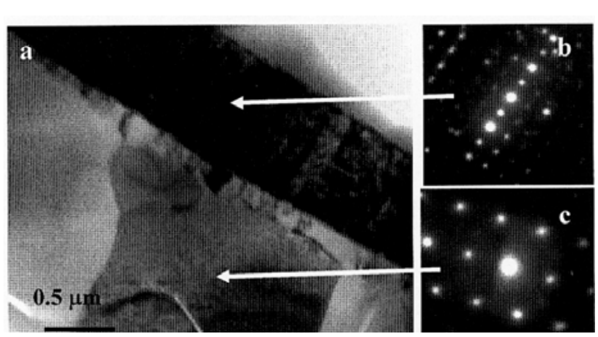
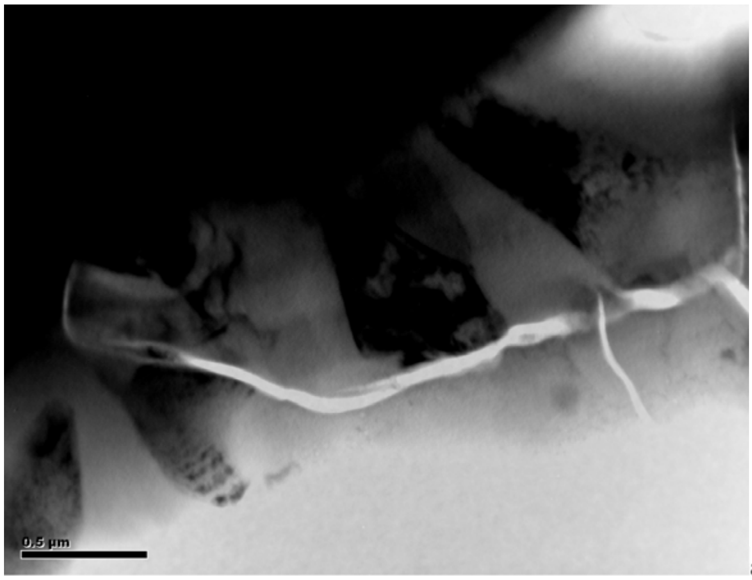
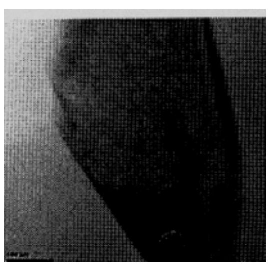


Fig. 3. Crystalline areas of ά – Al_2O_3 [113] (c) and ZrO_2 (cubic) [200] (b).
a-TEM,
b-electron diffraction for ZrO_2,
c- electron diffraction for Al_2O_3



a)



b)

Fig. 4. a) Columnar crystals within the ceramic Al_2O_3 – ZrO_2 layer
b) Enlarged image of individual crystal

4. Concluding remarks

The above mentioned specific conditions of plasma spraying process cause differences in phase composition and some properties between coatings and bulk materials. It is worthwhile to notice that both involved ceramic oxides exist in several crystal modifications differing in stability. For instance in Al_2O_3 the ά crystal form is thermodynamically most stable, other forms are rather metastable. But in plasma sprayed coatings the main phase is γ form even material before spraying exists in ά form. Mc Pherson suggests that in spraying conditions forming of the γ phase may be thermodynamically more favourable especially for smaller particles [12]. After coatings annealing above 1200 K transition to stable ά modification is observed. This phase transition causes internal stresses due to volume changes resulting from different density values for each crystal form. Therefore coatings stability is more or less decreased and we try new composites in order to counteract phase transitions in coatings or at least to decrease its extent.

Application of transmission electron microscopy combined with electron diffraction brings some new data about plasma sprayed coatings structure. Local inhomogeneities and appearing of several alternating layers: amorphous, nano and polycrystalline have been revealed. Existing of these effects is caused by two factors. First is connected with the nature of used material composites, second (more important) with the above mentioned conditions of plasma spraying process distant from the thermodynamic equilibrium. Coatings adherence and stability is dependent on its microstructure especially in the areas near to the ceramics-meta interface.l. Some recently performed experiments show coatings microstructure dependence on plasma spraying parameters which is important from the application point of view.

The microstructure observed in nanometric range in studied composites is similar but some differences can be noticed. In ZrO_2 – Y_2O_3 composites the extent of amorphous layer is limited mainly to the metallic bond-coat. Cubic and tetragonal crystal forms are coexisting. Local fluctuations of phase and chemical composition have been observed. In Al_2O_3 – ZrO_2 more local amorphous layers are visible in TEM image. It may cause higher back-ground level in X-ray diffraction patterns of this composite in comparison with that of material before spraying. Other interesting effect in this composite is existing of cubic and tetragonal crystal ZrO_2 forms in ambient temperature without stabilising additions. These higher symmetry forms appear in the coatings and its amount grow after annealing with monoclinic form still remaining. It seems to be some kind of stabilisation higher symmetry forms of zirconia by the presence of alumina. Similar effects were observed for coatings obtained by solgel method [13,14]. The coexistence of monoclinic ZrO_2 with higher symmetry forms may cause toughening effect known in so-called partially stabilised zirconia due to martensitic transformation in a little extent. Therefore the studied composite is suitable as a component for thermal barrier coatings.

The following conclusions may be expressed on the basis of performed works.

1. Specific coatings microstructure in nanometric scale with local disorder and fluctuations of chemical and phase composition is mainly caused by the conditions of plasma spraying process.
2. After coatings thermal treatment changes directed to more ordered state occur.
3. The appearance of stable cubic and tetragonal ZrO_2 crystal forms without stabilising additions only in the presence of Al_2O_3 has been observed.
4. The obtaining of stable coatings from Al_2O_3 – ZrO_2 composite containing in common cubic, tetragonal and monoclinic forms of ZrO_2 is an important effect from the application point of view in TBC.

Further works on described composites and other possible components of TBC are still in progress.

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