A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 50 2005 Issue 3

A. PAWŁOWSKI*, T. CZEPPE*, L. GÓRSKI**, W. BALIGA*

STRUCTURE CHANGES OF THE PLASMA SPRAYED Al_2O_3-TiO_2 LAYER AND ITS ADHESION TO THE SUBSTRATE AFTER THERMAL SHOCKS

ZMIANY W BUDOWIE WARSTWY Al_2O_3-TiO_2 NATRYSKIWANEJ PLAZMOWO ORAZ Z JEJ PRZYCZEPNOŚĆ DO PODŁOŻA PO WSTRZĄSACH CIEPLNYCH

The results of investigation of Al_2O_3+40 wt.% TiO_2 oxide layer plasma sprayed on steel-substrate with Ni-Cr-Al-Ti interlayer have been presented. The coating was subjected to thermal-shocks from 1400 K down to 300 K. The oxide layer was examined using scanning (SEM) and transmission (TEM) electron microscopy along with chemical analysis in microareas with (EDS) techniques. The X-ray phase analysis of the layer was applied to observe changes at different distances from the substrate. The structural stress in the oxide layer was examined using X-ray techniques. The strongest reflections from Al_2TiO_5 phase were recorded in the mid-distance from the substrate, which corresponded to the most refined morphology of the Al_2TiO_5 of 1 μm-size. The fine grains and columnar crystals of Al_2TiO_5 phase were observed near the structure, while equiaxial ones (8 μm-size) near the surface. No cracking was observed near the substrate. The stresses in the layer were measured to be of order of 250 MPa.

W pracy przestawiono wyniki badań struktury warstwy tlenkowej o składzie Al_2O_3 + 40% cięż.TiO_2 natryskiwanej plazmowo na podłożu ze stali nierdzewnej z międzywarstwą Ni-Cr-Al-Ti. Złącze poddano następnie oddziaływaniu szoków termicznych od 1400K do 300K. Stosowano techniki skaningowej (SEM) i transmisyjnej (TEM) mikroskopii elektronowej wraz z analizą składu chemicznego w mikroobszarach techniką (EDS). Prowadzono także rentenowską analizę fazową warstwy tlenkowej na różnych odległościach od podłoża, jak również badania wartości naprężeń w warstwie metodą X-ray. Stwierdzono silniejsze refleksy fazy Al_2TiO_5 w połowie grubości warstwy. Odpowiada to rozdrobnionej strukturze (1 μm) tej fazy. W pobliżu podłoża obserwuje się drobnokrystaliczną fazę oraz kryształy kolumnowe, zaś przy powierzchni ziarna równoosiowe (10 μm). Nie stwierdzono zjawiska pękania przy podłożu. Pomiary wykazały wartości naprężenia w warstwie na poziomie 250 MPa

* INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, 30-059 KRAKÓW, UL. REYMONTA 25, POLAND
** INSTITUTE OF ATOMIC ENERGY, OTWOCK-ŚWIERK, POLAND

1. Introduction

The Al_2O_3 based ceramic-metallic coatings become thermal barriers for the metallic substrate and are often used for the turbine blades in jet engines. They have good abrasive properties and their can work in temperatures more than 1000 K. They also should adhere well to the substrate.

Pawłowski and co-workers [1] found in the structure of plasma sprayed Al_2O_3+40wt%TiO_2 layer three sublayers from the substrate side: fine frozen crystallites and columnar crystals, fine crystalline sublayer originated from the dissolved columnar crystals and layers of equiaxial grains near the surface. The X-ray analysis registered reflections from Al_2TiO_5 as well as corundum and rutile [1, 2], which is consistent with the results of Górski [2], who found that the orthorhombic Al_2TiO_5 appeared above 10% TiO_2 in the amount depending on the cooling rate of the substrate. It was established in work [1], that annealing at 1400 K for 10 hs brings about not only the dissolution of columnar crystals at the sublayer boundary but also the homogenization of equiaxial grains. The heating may also be applied in order to stabilize the supercooled phases obtained during plasma spraying.

Another form of the thermal treatment of a ceramic-metallic coatings is a process of thermal shocks. Such material was examined by Woynowski and Serkowski [3], who observed the resistance of Al_2TiO_5 to thermal shocks. The examination of similar ceramics were the subject of works [4, 5], in which transformations γ Al_2O_3 $\rightarrow$ α-Al_2O_3 were observed at temperatures 1170 K and 1470 K.

The aim of this work was to analyse the structure of the Al_2O_3+40 wt.% TiO_2 ceramic layer after thermal shocks from 1400 down to 300 K. They were thought to simulate the conditions, of practical applications for example as a thermal barrier turbine blades, made of ceramic layer with the Ni-Cr-Al-Ti interlayer on the stainless steel. The influence of thermal shocks on structure of another layer, which was ZrO_2-Y_2O_3, was investigated by Górski [6], who observed microcracks and scaling of the layer as the effect of thermal strains and the appearance of a monoclinic phase on cooling. That is why in the present work, apart from structure analysis (SEM (EDS) and TEM (EDS) as well as X-ray), the strains in the material were also examined as a factor of adherence.

2. Experimental procedure

The plasma spraying of a ceramic powder melted in an electric arch in plasma hydrogen and argon atmosphere was carried out in PN-120 plasmothrone in Świerk, Poland according to parameters given in the work of Górski [2]. The ceramics was introduced as Al_2O_3 corundum and TiO_2-rutile powders (at 1:1 ratio) with grains 10-80 μm in size. It took several milliseconds to reach temperature about 10^4 K, while the cooling rate of the layer obtained on the metallic substrate, was assessed to be 10^5-10^6 K/s. The stainless steel was the substrate, which was plasma sprayed with a

Ni-20 Cr-5 Fe-2 Al wt.% interlayer, to improve the adherence of the ceramic cover. The thickness of the ceramic layer obtained varied from 50 up to 150 μm. The coating was subjected to thermal shocks in a special device, which provided numerous cyclic heating by a stream of hot gases [6] up to 1400 K during 20-120 sec and cooling with a compressed air down to 300 K during 60 sec. The analyses of grain morphology and chosen areas of the layer as well as the composition of the ceramic and transition layer at cross-sections were realized using a Philips XL 30 scanning microscope (SEM) together with a LINK X-ray dispersive spectrometer (EDS).
The analyses of composition in microareas were carried out on thin foils in a Philips CM20 Twin transmission electron microscope using ion thinning technique for the sample preparation. The X-ray analysis was carried out at different distances from the substrate at a Philips PW 1710 diffractometer using Cu α radiation.
The strain analysis in the layers was performed at X-ray diffractometer Philips XL 30.

3. Results and discussion

3.1. SEM microstructure and chemical composition EDS analyses

The changes of structure in the plasma sprayed ceramic layer after annealing at 1400 K were compared with the results of the layer subjected to thermal shocks 1400/300 K.
The microstructure observations of the Al_2O_3+40% wt.%.TiO_2 ceramic layer annealed at 1400 K for 10 hours revealed the existence of several sublayers (Fig. 1). Fine

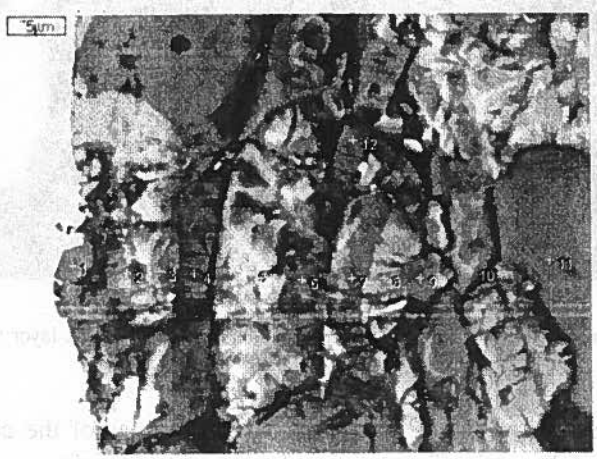

Fig. 1. SEM microstructure of the plasma spayed Al_2O_3+40wt% TiO_2 ceramic layer after annealing at 1400 K

frozen crystallites of 1 μm size were observed at the metallic substrate. The following sublayers consisted of partially dissolved columnar crystals with fine crystalline

areas, which appeared as the effect of dissolution at the sublayer boundary. Equiaxial grains 10 μm big were spotted at the side of the ceramic layer. Such arrangement was caused by the high cooling rate of the melted Al_2O_3-TiO_2 ceramics at the substrate, which decreased when approaching the surface, at which equiaxial crystals appear due to uniform cooling. The dissolution of columnar crystals at the sublayer boundaries proceeded similarly to the discontinuous dissolution of lamellar or rod-like products of discontinuous precipitation in the area of the cell.
The after-thermal-shock ceramic layer (Fig. 2) revealed the appearance of three sublayers: narrow one of frozen crystallites and columnar crystals and a wide fine crystalline one due to the dissolution of the columnar crystals. Near the surface, equiaxial crystals of 10 μm diameter were observed. It was concluded that the three sublayers of partially dissolved columnar crystals (Fig. 1) were substituted by a wide (20 μm) fine crystalline layer (Fig. 2). It seems, that the thermal strains induced by the 1400 /300 K thermal shocks derived energy, which facilitated diffusion on the sublayer boundaries of the columnar crystals, and thus enhanced the process of dissolution. Meanwhile, the dissolution process brought about the relaxation of the strains and that it why no cracks were observed in the layer. Moreover, even secondary microcracks which might have occurred due the material fatigue did not appear at the substrate.

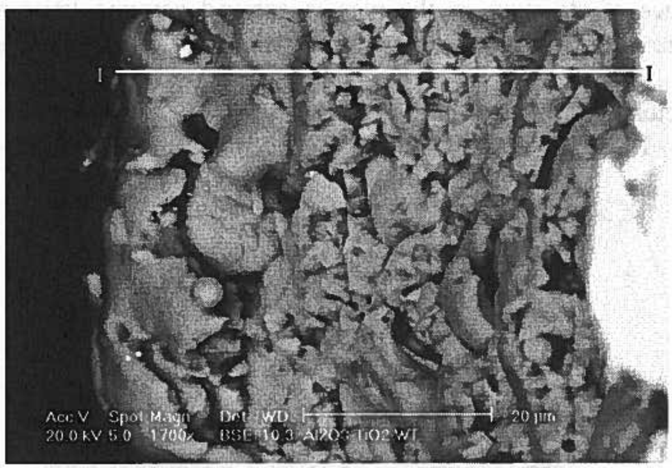

Fig. 2. SEM microstructure of the plasma sprayed Al_2O_3+wt%TiO_2 ceramic layer after thermal shock at 1400K/300K

The EDS chemical analysis (Fig. 3) in the microareas of the ceramic layer after the thermal shocks shown in Fig. 2 seemed to confirm that frozen crystals of Al_2O_3 and TiO_2, prevailed in the area of fine crystalline phase close to the substrate (to be seen on the right side of the microstructure), while the Al_2TiO_5 phase occurred in the area of columnar crystals as an effect of directional cooling. The fine crystalline region, which appeared due to the dissolution of columnar crystals was found to be also rich in Al_2TiO_5, which was detected in the equiaxial grains apart from the Al_2O_3

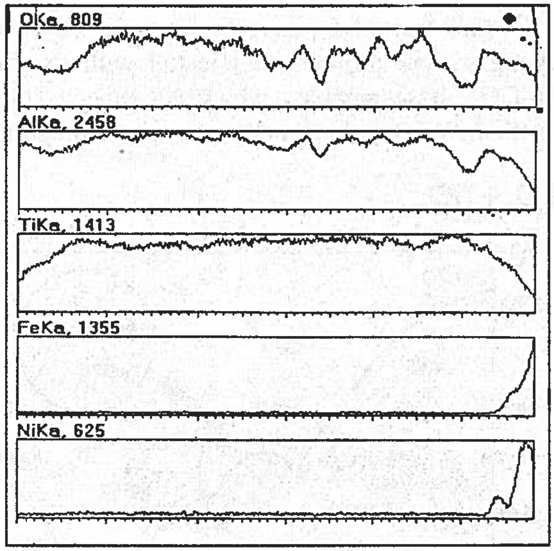

Fig. 3. EDS analysis of ceramic layer in the area show in the area show in Fig. 2

phase. The diffusion of Ti and Fe from the substrate to the ceramic layer improved the adherence of the layer and the substrate, being the reason for the lowering of the susceptibility to microcracks.

3.2. The X-ray phase analysis

The existence of the orthorhombic nonstechiometric [7]- Al_2TiO_5 (022) phase, hexagonal corundum Al_2O_3 and tetragonal rutile TiO_2 was observed in the plasma sprayed and annealed at 1400 K. Al_2O_3–TiO_2 ceramic using the methods of X-ray phase analysis (Fig. 4). Cell parameters from [7] a=3.5929 b= 9.6472 c= 9.4392. The

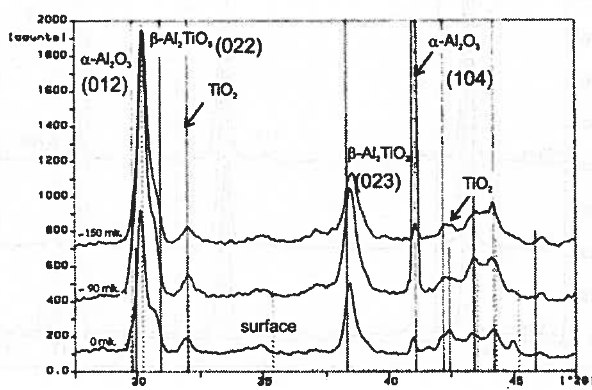

Fig. 4. X-ray diffraction pattern of the plasma sprayed Al_2O_3+40wt% TiO_2 after annealing at 1400 K

reflections of Al_2TiO_5 (023) and Al_2O_3 were found to be the strongest in the middle of the layer. The changes were probably connected with the rate of cooling after solidification. The Al_2TiO_5 phase prevailed, which was expected due to the composition of the alloy (Al_2O_3 +40 wt.% TiO_2) indicated in the phase diagram [8] (Fig. 5). When

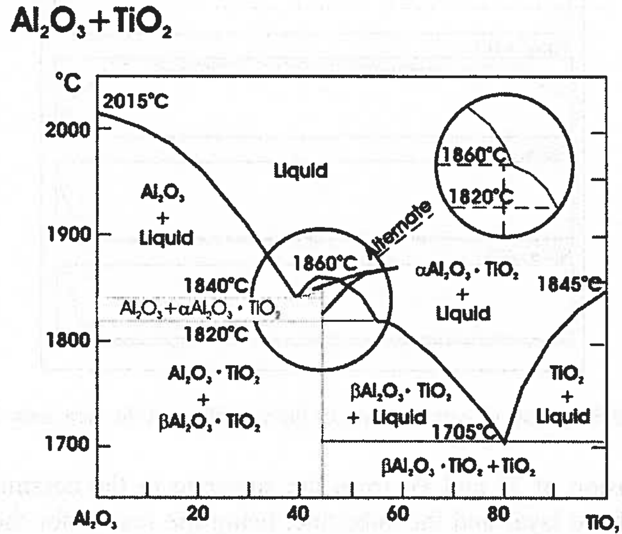

Fig. 5. Equilibrium system of Al_2O_3-TiO_2 [8]

analyzing the ceramic layer submitted to the thermal shocks, only traces of Al_2O_3 and TiO_2 were seen in the phase analysis (Fig. 6). The equilibrium Al_2TiO_5 phase

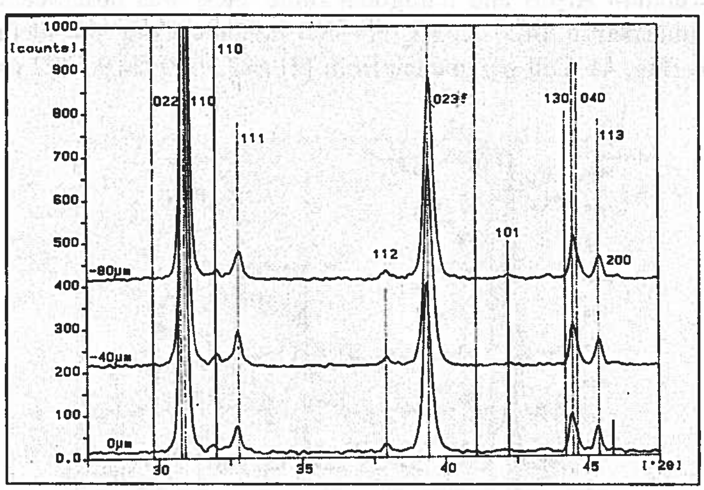

Fig. 6. X-ray diffraction pattern of the plasma sprayed Al_2O_3+40wt% TiO_2 ceramic layer after thermal shock at 1400 K/ 300 K

[9] prevailed exhibiting the strongest reflections (023) at the substrate as well as in the middle of the layer, where columnar crystals and the areas of their dissolution were observed. Cell parameters from [9] a=3.591 b=9.429 c=9.636. The results are in accordance with the EDS analysis carried out in the scanning microscope. This suggests that the thermal shocks enhanced the transition of the Al_2O_3 and TiO_2 phase in the equilibrium Al_2TiO_5.

3.3. TEM microstructure and chemical composition EDS analysis

The ceramics achieved full stability of the layer, after it was subjected to thermal--shocks from 1400 K down to 300 K.
The microstructure of the plasma sprayed layer consisted of many sublayers oriented roughly parallel to the substrate and mixed with the microcrystalline areas (Fig. 7). Their microstructure was composed of the parallel-spaced columnar crystals. In the sub-

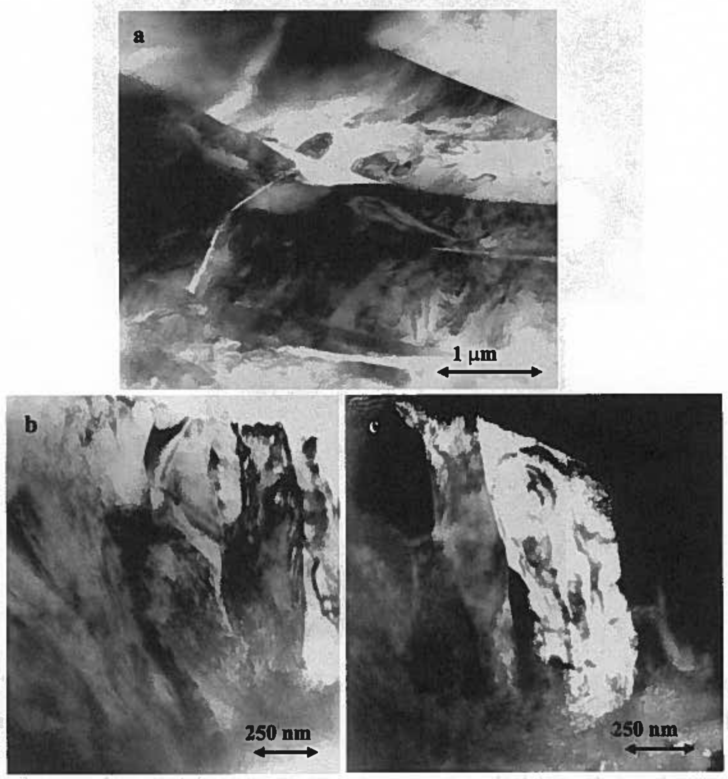

Fig. 7. TEM- microstructure of plasma sprayed layer on metallic substrate; a)- a group of the most external sublayers; b, c)- microstructure of an individual sublayer in ligh and dark field technique

strate direction, below the group of external sublayers, the micro-crystalline structure was observed. The atomic plane distances of microcrystals fitted well to the mixture of α- Al_2O_3 and rutile TiO_2 oxides. Next sublayers, also built of the columnar crystals were observed between the substrate and polycrystalline oxide areas. The results of EDS analysis performed in several points inside the individual sublayer as well as in subsequent sublayers showed that they were composed of two kinds of crystals, revealing variable compositions: I- 50 % Ti, 30 % Al, 20 % O and II- 70 % Ti, 30 at.% O, or the composition of Al_2O_3 with a few percent of Ti and Fe. In some places this phase was identified as γAl_2O_3, a metastable structure of Al oxide, by SADP. The artificially formed layer of the Ni-25 Cr-5 Al-1 Ti composition was not found. The layer nearest to the substrate was composed of the columnar crystalline Al_2TiO_5 and Al_2Ni_3 phases (Fig. 8).

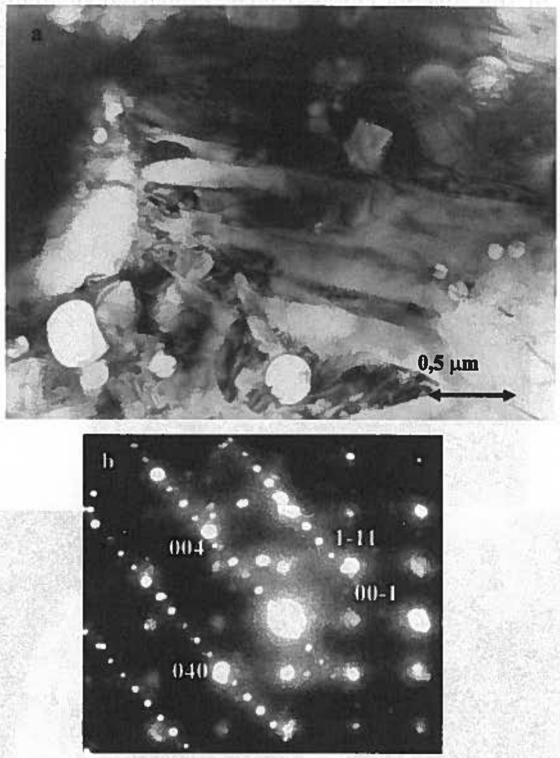

Fig. 8. TEM microstructure- a, and b-SADP of the sublayer nearest to the substrate: Al_2TiO_5 (zone axis [100]). Al_2Ni_3 (zone axis [100]) and rapidly crystallized Al_2O_3 droplets are visible

The presented results added some understanding to the problems of structure and composition of plasma–sprayed and thermal shocked layers. The layer was alternatively composed of sublayers α-Ti (Al, O) solid solutions and Al_2O_3 oxide. Ti-rich sublayers were built of the columnar crystals representing, two different solid solutions of Ti, $Ti_x(Al_2O_3)y$ and Ti(O) of typical composition in at. %: 65 Ti-21 O – 14 Al and 66 Ti-33 O-1 Al respectively, or similar microstructure of Ti_x $(Al_2O_3)_y$ and Ti (Al, O) solid solutions [10]. The second type of the sublayers was essentially composed of Al_2TiO_5 columnar crystals. Near to the sublayers, alternative Ti (Al, O) and Al_2O_3 were observed. The layer composed of polycrystalline phases Al_2O_3 and TiO_2 or Ti(Al,O) solid solution was observed roughly at the middle distance to the substrate. The reason for such a structure was probably a poorer heat transfer from this layer. All these observations are in good agreement with the X-ray diffraction investigations of the phases formed in the annealed mixtures of Al_2O_3 and TiO_2 oxide powders [7] showing that Ti solid solutions predominantly form of compositions according to the α-Ti-Al_2O_3 pseudobinary cross-section in the Al-Ti-O system.

3.4. X-ray strain measurements

The technique of X-ray diffraction using classical $\sin^2\Psi$ method was applied to obtain the level of strains in the plasma sprayed Al_2O_3+40 wt.% TiO_2 ceramic layer after the thermal shocks. The substrate was a stainless steel with Ni-Cr-Al-Ti interlayer. The penetration distance was 23 μm while the layer thickness was from 50 up to 150 μm. The average strain value was 250 MPa. Such a relatively low value of strain resulted from the phase transformations like the dissolution of the columnar crystals, appearance of the fine crystalline layer as well as the diffusion between the frozen crystallites and the metallic substrate. This behavior was confirmed by microstructure observations and phase analysis.

4. Conclusions

1. a. The structure of the Al_2O_3+40 wt.% TiO_2 ceramic layer plasma sprayed on the metallic substrate subjected to 1400 K/300 K thermal shocks consisted of three basic layers observed by the SEM technique:
   - frozen and columnar crystals at the substrate
   - fine crystalline central zone as the effect of the dissolution of the columnar crystals.
   - equiaxial grains at the surface.
1. b. The structure differs from the morphology of the layer after annealing at 1400 K by three times broader fine crystalline zone of the dissolved columnar crystals.
2. a. The Al_2TiO_5 equlibrium phase is the prevailing phase in the central part as well as in columnar crystals of the layer after the thermal shocks. Its weakest intensity was observed in the area of equiaxial grains at the surface, where traces of the Al_2O_3 phase were found. The effects of the Ni and Fe diffusion to the ceramic layer were seen at the substrate.
2. b. The structure of the Al_2O_3+40 wt.% TiO_2 ceramic layer plasma sprayed on the metallic substrate and annealed revealed apart from the nonequilibrium Al_2TiO_5 phase quite a volume of Al_2O_3 and TiO_2 ones, which did not undergo the reaction in the process of plasma spraying and annealing at 1400 K.

3. The TEM and electron diffraction techniques enabled us to establish the existence of the fine frozen Al_2O_3 and TiO_2, crystallites firmly adhered to the substrate. The columnar Al_2TiO_5 crystals grew surrounded by the Al_2O_3 phase. They were also occasionally spotted at the Al_3Ni substrate. Additionally, two nonequilibrium solid solutions based on Ti ($Ti_x(Al_2)O_3$) were found.
4. The thermal shocks at 1400 K / 300 K, which simulated the changes of temperature of the ceramic layer on the turbine blades in the propeller during the exploitation, brought about even more complete transformation of nonstechiometric Al_2TiO_5 phase and the Al_2O_3 and TiO_2 into the equilibrium phase Al_2TiO_5 due to the induced thermal strains. These strains, introducing additional plastic energy, intensified the diffusion in the boundaries of sublayers being the reason for the discontinuous dissolution of the columnar crystals and the formation of the fine, broad crystalline central sublayer.
5. The strains induced by the thermal shocks were only about 250 MPa, because they were relaxed by diffusional phase transformations protecting the structure from the ccurrence of the microcracks, which is promising for this kind of treatment.

The work was carried out within research IMIS PAS supported by State Commitee for Scientific Research in cooperation with IEA, Świerk Poland.

REFERENCES

[1] A. Pawłowski, T. Czeppe, L. Górski, W. Baliga, XVII Phys.Metall. and Materials Sci.Mat.Conf.ATM 2004. Inż.Mater.3(140)XXV, 626-628 (2004) .

[2] L. Górski, Inż.Mater. 1, 78 (1994).

[3] M. Voynowski, S. Serkowski, Inż.Mater. **4-5**, 110 (1992).

[4] S. Vaurinen, L. Karson, Thin Solid Films **214**, 72 (1992).

[5] R. Mc Pherson, Surf.Coat Technol. **50**, 213 (1991).

[6] L. Górski, Inż.Mater. **5**, 112 (1999).

[7] W. Sywiński, G. McCarthy, North Dacota State University Fago, ICDD Grant-in-Aid (1989).

[8] S.M. Lang, C.L. Fillmore, L.H. Maxwell, J.Res.Natl.Bur.Stand.(US) 48, 298 (1952).

[9] C.E. Holcombe, A.L. Coffey, J.Am.Ceram.Soc. **56**, 220v (1973).

[10] E.S. Zhmud, A.E. Shmelew, Neorgan. Mater. IH **10**, 1733-1737 (1973).

Received: 10 November 2004.