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
olume 53 2008 Issue 4

. PAWŁOWSKI*, T. CZEPPE*, W. BALIGA*, L. GÓRSKI**, M. FARYNA*

THE MORPHOLOGY OF THE Al_2O_3 – SiO_2 LAYER PLASMA SPRAYED ONTO A METALLIC SUBSTRATE AFTER HEAT TREATMENT

BUDOWA WARSTWY Al_2O_3-SiO_2 NATRYSKIWANEJ PLAZMOWO NA PODŁOŻE METALICZNE PO OBRÓBCE TERMICZNEJ

The oxide layer composed of Al_2O_3 and 30 wt.% SiO_2 plasma sprayed on a steel substrate covered earlier with NiCrFeAl transition layer, annealed at 1150°C for 50 hrs, has been investigated in the paper. The material was studied using scanning (SEM) and transmission (TEM) electron microscopy techniques along with electron diffraction (SAED) and analysis of composition in microareas using EDX and X-ray methods. Mulite of 25 wt.% SiO_2 and Al_2O_3-α corundum was observed in the oxide layer down to the depth of 200 μm as well as near it up to 10 μm. As a result of annealing, small grains were observed to form in bands of the ceramic layer. Fine crystalline phases appeared in the vicinity of the substrate substituting the amorphous phase, which remained unaffected by the annealing in deeper layers of the cover. Some diffusional effects were observed in the direction from the ceramic layer towards the metallic interlayer.

Keywords: thermal barier coatings, Al_2O_3, mulite, plasma spraying, phase transformations

W pracy przedstawiono wyniki badań struktury warstwy tlenkowej o składzie Al_2O_3+30 %cięż. SiO_2 natryskiwanej plazmowo na podłoże ze stali stopowej z warstwą przejściową NiCrFeAl. Zastosowano wyżarzanie złącza w temperaturze 1150°C przez 50 godzin. Do badań użyto techniki skaningowej i transmisyjnej mikroskopii elektronowej wraz z dyfrakcją elektronową i analizą składu w mikroobszarach techniką EDX i dyfrakcji rentgenowskiej. Stwierdzono, iż w odległości 10 μm od podłoża jak i na całej grubości do 200 μm warstwy występuje mulit (25 %cięż. SiO_2) oraz korund Al_2O_3-α. Efektem wyżarzania jest powstawanie małych ziaren, w pobliżu podłoża występują fazy drobnokrystaliczne jako skutek krystalizacji uprzedniej fazy amorficznej. Zauważono efekty dyfuzji z warstwy ceramicznej do metalicznej międzywarstwy.

1. Introduction

Ceramic layers plasma sprayed onto either the Ni super alloy or alloy steel have been commonly applied in diesel engines and turbine blades as thermal shields. Most often, such insulating material is produced from oxides based on the ZrO_2 [1] or Al_2O_3 [2-4] with the addition of TiO_2 or ZrO_2. However, numerous papers report also SiO_2 [5] to meet the requirement for a thermal barrier at cheaper cost. The results obtained by Pawłowski et al. [5] showed, that the plasma sprayed layer of this material reveals sublayered morphology, which, forms equiaxial grains at the surface. The composition of the layers differs taking into account the content of corundum in the mulite matrix. As the effect of rapid solidification due to plasma spraying, an amorphous phase of composition close to that of mulite (Al_2O+26 wt.% SiO_2) appears in the vicinity of the metallic substrate. Large inhomogeneity of SiO_2 was observed within the amorphous phase. Because of brittleness of the sprayed layer, which made difficult the preparation of thin foils for TEM observations, annealing at 1150°C for 50 hrs was applied, following the work of Górski [6], who claimed it was successful, however without the explanation of reasons. The objective of the presented paper has thus been aimed at the determination of the phase composition of the plasma sprayed ceramics containing Al_2O_3+30 wt.% SiO_2 on steel substrate in order to find the structural reasons for the influence of annealing on its adhesion to the substrate. SEM, TEM and EDX techniques proved very suitable for such research.

* INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, 30-059 KRAKÓW, 25 REYMONTA STR., POLAND
** INSTITUTE OF ATOMIC ENERGY, 05-400 ŚWIERK-OTWOCK, POLAND

2. Experimental procedure

The ceramic cover was produced by spraying Al_2O_3 and SiO_2 powders melted in an electric arc using hydrogen – argon plasma in PN-120 plasmothrone in Świerk, Poland according to details given in the work of Górski [5]. The ceramics was loaded into the plasmothrone as 70 wt% corundum Al_2O_3, and 30 wt.% SiO_2 powders of grain size 10-50 μm. It took several milliseconds to reach temperature about 10^4 K, while the cooling rate of the layer obtained on the metallic substrate, was 10^5-10^6 K/s. A NiCrCoFe alloy steel was the substrate, which was first plasma sprayed with a Ni-20 Cr-5 Fe-2 Al to improve the adherence of the ceramic cover to the substrate. The thickness of the ceramic layer obtained was about 200 μm. The joints were annealed at 1150°C for 50 hrs.

X-ray phase analysis of the annealed cover, of which subsequent layers, about 10 μm thick, were removed by polishing, was carried out in Philips PW 1710 diffractometer at CuK radiation. Microstructure examination and chemical composition analysis were performed at cross-sections using Philips XL 30 electron microscope equipped with Link EDX device and Philips SM 20 TWIN electron transmission microscope. Thin foils were produced with ion thinning technique. Local analyses of chemical composition were performed using 10 nm wide beam in Phoenix EDAX device.

3. Results

3.1. SEM microstructure and chemical EDX analysis

The crossection of the annealed ceramic cover of average anticipated composition of Al_2O_3 + 30 wt.% SiO_2 examined by SEM technique revealed the lack of sublayer morphology so typical for not annealed layer [5]. Equiaxial grains of size about 20 μm similar to mulite in composition (25 wt.% SiO_2) were localized in bands, whose width (from 10 to 60 μm) corresponded to the primary sublayers observed in unheated samples.

A sample of a ceramic layer, shown in Fig. 1 consisted of a metallic transition layer enriched in Ni in the upper part and its surface is visible in the lower part. Inside, about 30-40 μm from the surface, darker, bigger grains of around 20-30 μm in size, marked 1 and 2, could be observed.

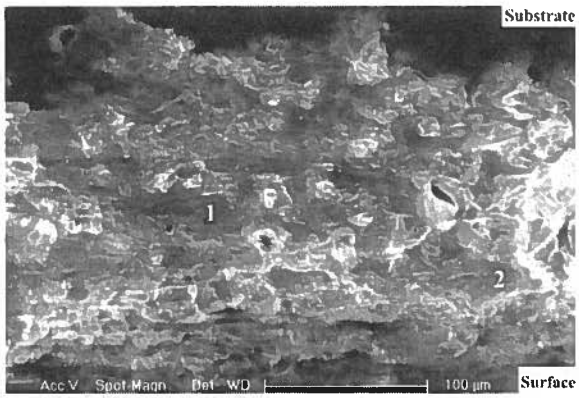

Fig. 1. SEM microstructure of a crossection of plasma sprayed Al_2O_3+30 wt.% SiO_2 layer after annealing at 1150 °C for 50 hrs; point analyses of composition at variable vacuum were carried out in grain 1 and 2

The composition of grain 1 was found to be: Al_2O_3 – 80.60 wt.% and SiO_2 – 19.40 wt.% (Fig. 1) and was determined at variable vacuum. The composition of the ceramic in between the grains was found to be Al_2O_3-70 wt.% and SiO_2-30wt.%. If the mulite was assumed to contain Al_2O_3 + 25 wt.% SiO_2 it meant that grain 1 exhibited excessive corundum.

On the other hand, grain 2 consisted of 71.83 wt.% Al_2O_3 and 28.17 wt.% SiO_2, which suggested excessive SiO_2. High accuracy of composition measurements was ensured by using variable vacuum of about 0.2 Torr without sputtering the specimen with carbon. The measured composition of the grains proved that a diffusion process during annealing at 1150 °C occurred as well as a reaction between mulite and the area rich either in corundum or in silicon oxide. A tendency to form larger grains during annealing in a zone of about 60 μm, located close to the substrate was observed in the upper part of Fig. 1. Next band below, of similar width, contained grain 1 with the analysed content. The following band in the same direction was more narrow (about 20 μm and consisted of fine (about 10 μm big), spherical subgrains. They resulted probably from the changes of subgrain shape in the region close to the surface of the

:over, which solidified a little faster due to heat flux hrough the surface of the cover. Grain 2 in, which the ıbove composition was analysed was located within that band. Crystals, similar to flattened beads of the melted ceramics are visible in lower part of Fig. 1.

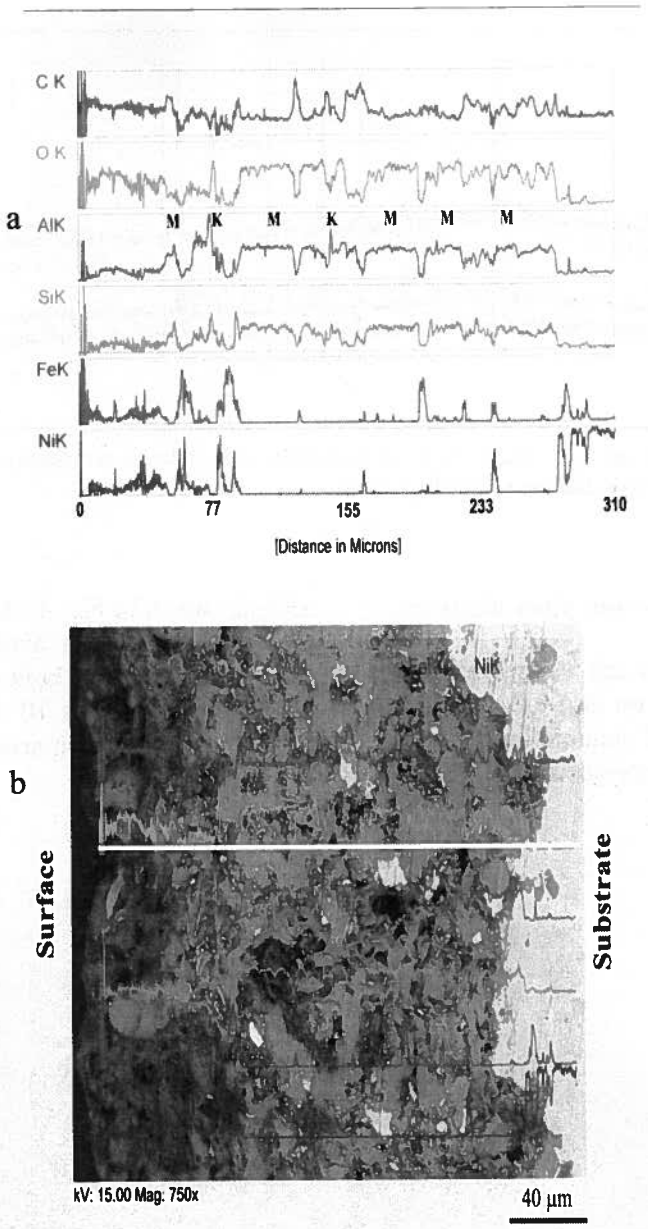

Fig. 2. Linear analysis of composition (C, O, Al, Si, Fe, Ni), (a); SEM microstructure with marked line of the analysis, (b)

If the microstructure of the annealed ceramic cover was analysed regarding its composition based on a continuous measurement (Fig. 2) it could be seen that the distribution of mulite and corundum differed on various depths from the substrate. Also nonuniform distribution of mulite grains enriched in SiO_2 or Al_2O_3 and various forms of crystals were observed.

3.2. The X-ray phase analysis

The X-ray phase analysis carried out on different distances from the cover surface enabled the phase identification exhibiting lines from mulite crystals of orthorhombic lattice and Al_2O_3-α corundum. The lines were a little shifted in respect to those observed in the unheated material [5], but they anyway corresponded to: mulite M- (001), (220), (130), (201), (121), while for

corundum to C – (012), (104), (110), (006) and (202) lines (Fig. 3). The intensities of lines were weakly diversified at various distances from the surface. Comparing that result with the composition analysis shown in Fig. 2 a and the microstructure in Fig. 2 b it seemed that corundum crystals were surrounded with mulite grains.

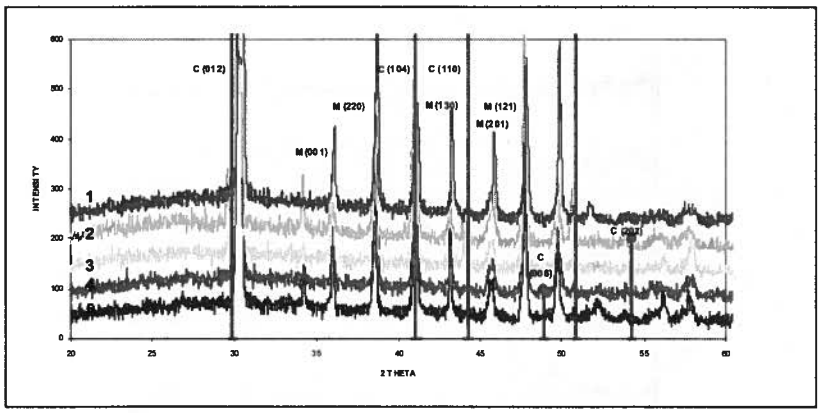

Fig. 3. X-ray diffraction pattern of the plasma sprayed Al_2O_3+30 wt.% SiO_2, (M-mulite, C-corundum), (1) – the surface of the sample, (2) – 10 μm, (3) – 20 μm, (4) – 30 μm, (5) – 140 μm below the surface

3.3. TEM microstructure and EDS analyses

The observations were carried out using transmission electron microscopy technique on thin foils prepared by ion thinning. A TEM image of ceramic layers stuck together with surfaces plasma sprayed with Al_2O_3+30 % SiO_2 is shown in Fig. 4, in which an image of a crossection of the ceramics annealed at 1150 °C for 50 hrs was obtained. It was built of bands 200 nm wide, which contained crystallites 10 times smaller and bands with scallops of 400 nm in size visible in Fig. 4.

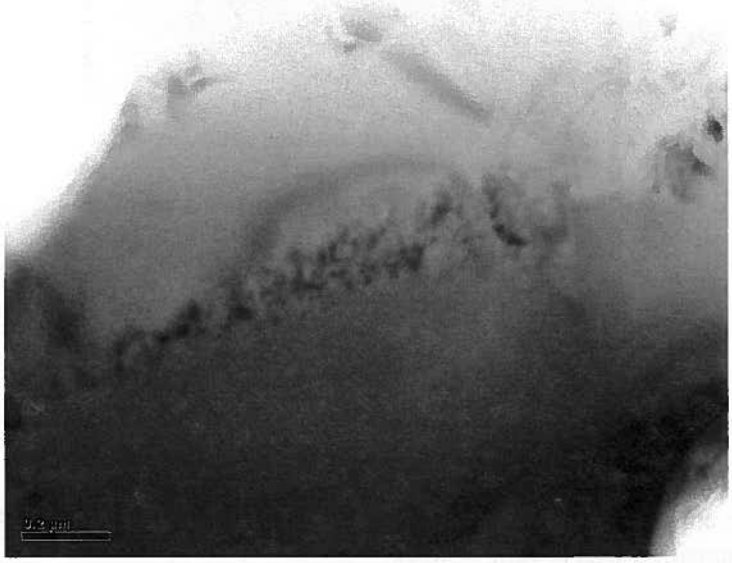

Fig. 4. TEM microstructures of the Al_2O_3-SiO_2 ceramic layer near the substrate observed on crossection

Fine crystalline lamellar precipitates 10 nm wide were observed within elongated grains close to the substrate (Fig. 5 a). Those precipitates grew for 100 nm perpendicular to the boundary of the amorphous phase, which was there before annealing. The grains, within which the above lamellas appeared, had elongated shapes as the effect of liquid ceramics flattening.

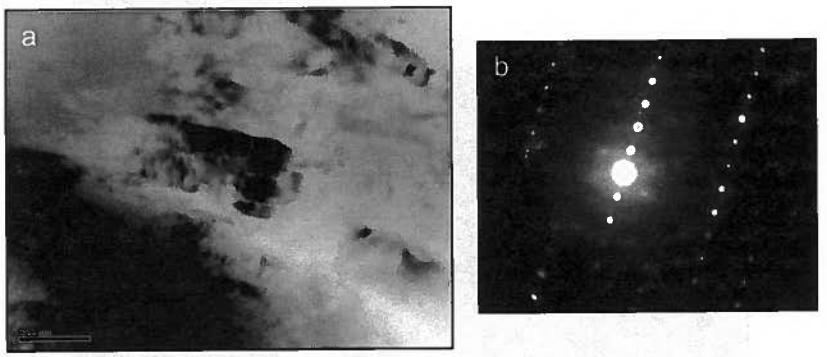

Fig. 5. TEM microstructure of bands with precipitates crystallizing from the amorphous phase, (a); corresponding SAED, (b)

Electron diffraction pattern obtained in such an area is presented in Fig. 5 b. The remnants of the amorphous phase were manifested by a centrally located circle, while the reflections from crystalline phases corresponded to Al_2O_3-α hexagonal phase and orthorhombic mulite. These were confirmed based on the analysis of composition (EDX) in nanoareas of mulite (10 nm in diameter), in which about 25 wt.% SiO_2 was recorded. Fig. 6 presents an image of a zone similar to that described above, in which bands with crystallites, whose electron diffractions confirmed the existence of the Al_2O_3-α phase can be seen. The amounts of Al-59.4 wt.% (55 at.%), Si-7wt.% (6.2 at. %) and O_2-21.4 wt.% (33.3 at.%) suggested prevailing of the A_2O_3-α phase precipitated from the amorphous one. The amounts of 7.1wt.% Fe and 3.4wt.% Ni detected in the zone indicated that the diffusion from the intermediate layer took place.

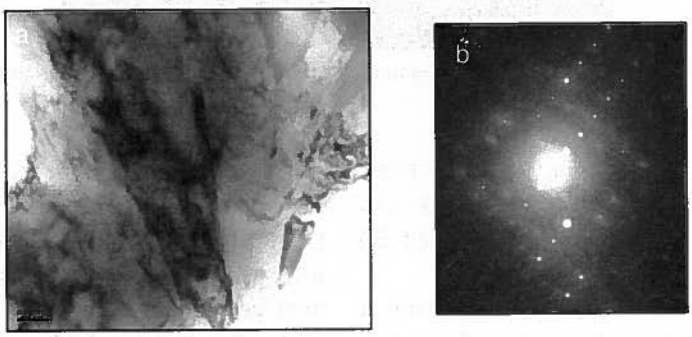

Fig. 6. TEM microstructure of the sublayer a little farther from the substrate than that shown in Fig. 5, (a); corresponding SAED from the band

In the next region the areas of crystallites adjacent to the amorphous phases were observed (Fig. 7 a). Upper part of the photo in Fig. 7 a referred to the amorphous phase, which gave a circle in the diffraction pattern (Fig. 7 b), while the lower part showed crystallites of the Al_2O_3-α according to the corresponding SAED pattern (Fig. 7 c). That zone lay at the distance of about 60 μm from the substrate, which was documented by lower contents of Fe – 2.2 wt.% and Ni – 1.3 wt.%. The amorphous phase contained Al – 50.5 wt.% (43.4 at.%) and Si – 14.8 wt.% (12.2 at.%) and O2 – 29 wt.% (42 at.%), while in the area 1 μm farther with precipitated crystalline phases, the EDX analysis detected the following contents: Al-60.8 wt.% (53.3 at.%), Si-10.7 wt.% (9 at.%) and O_2-24.3 wt.% (36 at.%). It seemed as if either increased content of Si by 4 wt.% was responsible for higher stability of the amorphous phase, or more probably, the increased concentration of strains and lattice defects were the reasons for the enhanced crystallization of the areas close to the substrate.

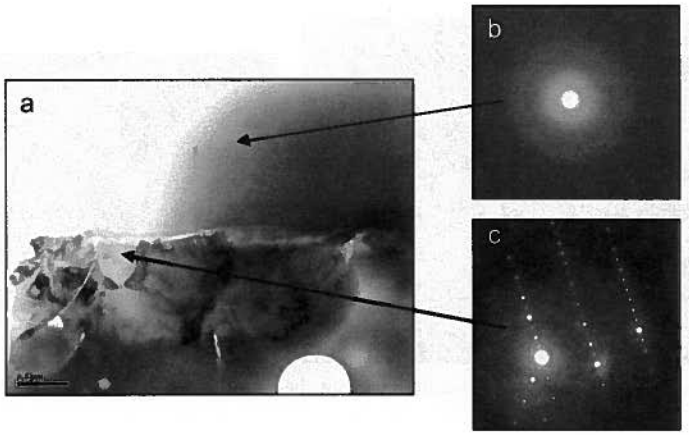

Fig. 7. TEM microstructure of a boundary between crystallites and the amorphous phase, (a); SAED taken of the amorphous phase marked with arrow, (b); SAED of the crystallite area marked with arrow, (c)

The central part of the cover at the distance of about 100 μm from the substrate contained crystallites, about 500 nm big, in irregular forms visible in Fig. 8 a. From a complicated electron diffraction image in Fig. 8 b, the Al_2O_3-α phase could be identified after all.

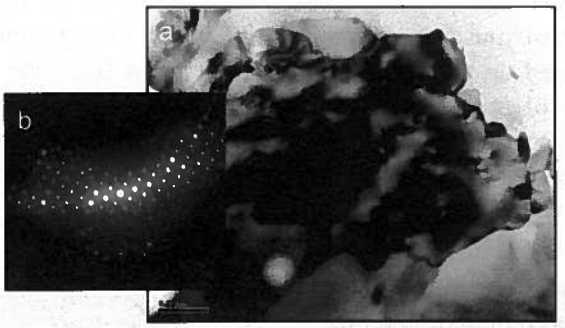

Fig. 8. TEM microstructure of an area in the middle of the ceramic cover, around 100 μm from the surface, (a); corresponding SAED, (b)

The sublayer contained: Al – 60.7 wt.% (52.8 at.%), Si – 12.1 wt.% (10.1 at.%) and O_2 – 24.5 wt.% (36 at.%) which corresponded to 80 wt.% Al_2O_3 and 20 wt.% SiO_2.

A 10 μm thick zone, which was observed in the nearest vicinity of the surface consisted of a band of crystals in the form of flattened drop of the melted mulite is shown in Fig. 9 a together with a corresponding SAED (Fig. 9 b), based on which Al_2O_3-α phase was identified as crystallites on a background of depleted mulite. That area contained: Al – 59.5 wt.% (51.6 at.%), Si – 10.2 wt.% (8.5 at.%) and O_2 – 26 wt.% (38.1 at.%).

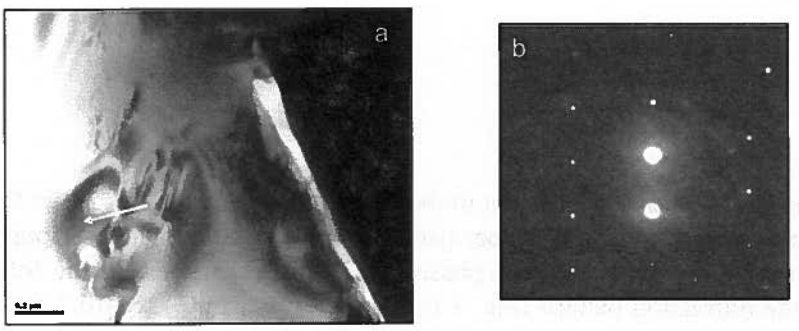

Fig. 9. TEM microstructure of a sublayer next to the surface of the ceramic cover, (a); corresponding SAED, (b)

Based on the results of analysis in nanoareas it was found that the precipitated crystallites consisted of about 60 wt.% Al, 21-26 wt.% O_2 and 7-12 wt.% Si, which corresponded to 80 wt.% Al_2O_3 and 20 wt.% SiO_2. Such composition was more or less the same in various sublayers due to the annealing of the cover.

The composition of the amorphous phase, which did not undergo crystallization, was 50 wt.% Al, 15 wt.% O_2 and 30 wt.% Si corresponding to 75 wt.% Al_2O_3 and 25 wt.% SiO_2. Such results suggested that in the area of the amorphous phase mulite prevailed, while the fine Al_2O_3 – precipitates dominated in the area of crystallites in the matrix of depleted mulite.

4. Discussion of results and conclusions

A model presented in Fig. 10 has been established based on the SEM, TEM and X-ray studies of microstructure of the plasma sprayed Al_2O_3+30 wt.% SiO_2 layer, annealed at 1150 °C for 50 hrs. It reflects the appearance of the following bands as a result of annealing:

- T(S) and T(B) bands, which replaced sublayers occurred due to plasma spraying,
- A amorphous phase band,
- A(C) one with nanocrystalline phases crystallized from the amorphous phase.

A zone, nearest to the substrate, consisted of the amorphous phase before the annealing, and was described by Pawłowski et al in work [5]. During annealing, in that area, crystallization occurred, resulting in the appearance of the fine lamellar crystalline – Al_2O_3 phases in the matrix of the depleted mulite.

Farther from the substrate up to the half of the cover, some amount of the amorphous phase resisted the crystallization. It means, that the amorphous phase near the substrate underwent the crystallization easier than that farther away. Such phenomenon may be explained by a greater short-range ordering, which appeared due to supercooling of the amorphous phase close to the substrate, transferring the heat out faster than within the layer. That was why, nucleation of crystallites was easier in that area of the amorphous phase. Similar phenomenon was observed in the Al_2O_3 + 40 wt.% ZrO_2 ceramics, annealed for 15 hrs, which crystallized with the precipitation of the α-Al_2O_3 and ZrO_2-t phases reported in work [4] by Pawłowski et al.

The presence of large grains of mulite with excessive Al_2O_3 (like 1) as well as grains 2 with the excess of SiO_2 was the third element of the structure confirmed by the X-ray analysis. Similar content of Al – 60.8 wt.% (55.3 at.%), Si – 10.7 wt.% (9 at.%) and O_2 – 24.3 wt.% (36 at.%) in different sublayers with crystallites was due to the homogenization of the cover during heating at 1150 °C for 50 hrs. The composition of the amorphous phase: 50 wt.% (43.4 at.%) Al, 14.8 wt.% (12.2 at.%) Si and 29 wt.% (42 at.%)O_2 corresponded to the supercooled mulite, which did not undergo crystallization, resulting from low concentration of vacancies inside the cover and high stability of the amorphous phase as the effect of high concentration of Si.

The particles of fine crystalline phases precipitated from the amorphous phase at the metallic substrate lowered its brittleness and improved its adherence to the substrate.

The T(S) and T(B) bands close to the surface contained grains obtained from flattened drops of the liquid ceramics and consisted of fine mulite grains with precipitates of corundum. It was observed, that the grains in the T(S) zone were of spherical shape due possibly to the effect of the thermal straining of the material.

The observed changes of microstructure studied using TEM and SEM techniques enabled building a graphical model of a ceramic cover submitted to annealing at 1150 °C for 50 hrs, which might make easier to predict changes of microstructure in plasma sprayed ceramic covers in wide range of compositions of Al_2O_3 – SiO_2 and with third additions (Fig. 10).

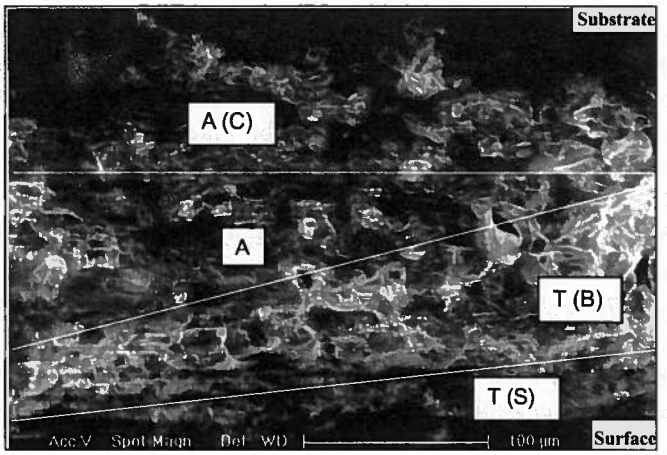

Fig. 10. The graphical model of structure changes of a plasma sprayed ceramic cover submitted to annealing at 1150 °C for 50 hrs

REFERENCES

[1] [1]. G. Cevales, Ber. Deut. Kerm. Ges. **45**, [5] 217 (1968).

[2] A. Pawłowski, T. Czeppe, L. Górski, W. Baliga, Archives of Metallurgy and Materials **50**, 719-729 (2005).

[3] T. Czeppe, A. Pawłowski, L. Górski, W. Baliga, Archives of Materials Science **26**, 1-2, 103-109 (2005).

[4] A. Pawłowski, J. Morgiel, L. Górski, Conference_of Com. Metall. PAN: Polska Metalurgia, 803-808 (2006).

[5] A. Pawłowski, J. Morgiel, M. Faryna, L. Górski, J. Grzonka, Archives of Metallurgy and Materials **53**, 3 (2008)

[6] L. Górski, Applied Crystall. 447-453 (1998).

Received: 10 March 2008.