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
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A. PAWŁOWSKI*, J. MORGIEL*, M. FARYNA*, L. GÓRSKI**, J. GRZONKA*

# STRUCTURE ANALYSIS OF THE PLASMA SPRAYED $Al_2O_3$-$SiO_2$ COATING ON METALLIC SUBSTRATE

# ANALIZA STRUKTURY NATRYSKIWANEJ PLAZMOWO WARSTWY $Al_2O_3$-$SiO_2$ NA PODOŁOŻU METALICZNYM

The results of investigations of structure of $Al_2O_3$ + 30 wt.% $SiO_2$ oxide layer plasma sprayed onto a steel substrate with a NiCrFeAl transition layer were presented in the work, in which scanning (SEM) and transmission (TEM) techniques along with electron diffraction (SAED) and analysis of composition in microareas (EDX) were applied. Based on the X-ray phase analysis of the oxide layer at various distances from the surface it was showed that mulite (25 wt.% $SiO_2$ ) and corundum ($Al_2O_3$ -$\gamma$) was found at 10 $\mu$m depth as well as across the whole 200 $\mu$m thickness of the layer. The change of the background intensity confirmed the occurrence of the amorphous phase. Its appearance was also observed in TEM examinations together with differentiated composition of the phase based on $Al_2O_3$ with $SiO_2$ addition.

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. Do badań zastosowano techniki skaningowej (SEM) i transmisyjnej (TEM) mikroskopii elektronowej wraz z dyfrakcją elektronową i analizą składu w mikroobszarach techniką EDX. Przeprowadzono także rentgenowską analizę fazową warstwy tlenkowej na różnych odległościach od powierzchni. Stwierdzono, iż w jej sąsiedztwie tj. na głębokości 10 $\mu$m jak i na całej grubości warstwy do 200 $\mu$m występuje mulit (25%cięż.$SiO_2$) oraz korund $Al_2O_3$-$\gamma$ a zmiana intensywności tła wskazuje na obecność fazy amorficznej. Jej występowanie potwierdzają obserwacje TEM wykazując także zróżnicowany skład fazy na bazie $Al_2O_3$ z dodatkiem $SiO_2$.

## 1. Introduction

The ceramic coatings plasma sprayed on metallic substrate have found their application as thermal barriers in diesel engines and turbine blades. The $ZrO_2$ based ceramics has been a material of particularly high insulating properties [1]. There are also cheaper coatings like $Al_2O_3$+$TiO_2$ [2] or $Al_2O_3$+$ZrO_2$ [3], which reveal similarly valuable properties. The investigations carried out so far showed that flattened grains close to the substrate occurred due to plasma spraying. In the direct vicinity of the substrate an amorphous phase was observed. Simultaneously, unidirectional cooling resulted in the appearance of the columnar crystals, which was typical for the $ZrO_2$+$TiO_2$ ceramics. The grains which solidified last were equiaxial and strongly segregated [2]. The coatings based on $Al_2O_3$ and $ZrO_2$ often consisted of several sublayers. The examination using electron diffraction technique enabled to find an $Al_2O_3$ based amorphous phase enriched in $TiO_2$ or $ZrO_2$ close to the substrate [2, 4]. R.F. Davis and J.A. Pask [5] established the presence of two eutectics in the equilibrium diagram of $Al_2O_3$-$SiO_2$. One contained 20 wt.% $SiO_2$ and another 90 wt.% $SiO_2$. At 25 wt.% $SiO_2$ the occurrence of the oxide compound called mulite could be seen. There was neither solubility in the solid state from the side of the $Al_2O_3$ nor from the side of $SiO_2$ in the equilibrium diagram. Earlier studies using X-ray phase analysis technique carried out on $Al_2O_3$+30 wt.% $SiO_2$ ceramics by Górski [6] derived contents which corresponded to the compositions in the phase diagram [5].

The aim of this work was to analyse the phase composition of the plasma sprayed ceramics $Al_2O_3$+30 wt.% $SiO_2$ on the steel substrate at various distances from the surface based on the electron diffraction and examination of chemical composition in microareas.

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

## 2. Experimental procedure

The plasma spraying of ceramic powders 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 [6]. The ceramics was introduced into the plasmothrone as $Al_2O_3$ and $SiO_2$ powders in amount 30 and 70 wt.%, respectively with grains 10-50 $\mu m$ 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 $10^5$-$10^6$ K/s. A stainless steel was the substrate, which was first plasma sprayed with a Ni-20 Cr-5 Fe-2 Al to improve its adherence to the ceramic cover. The thicknesses of the ceramic layers obtained were about 200 $\mu m$.

The X-ray phase analysis of the coating at the starting stage (without annealing), of which layers 10 $\mu m$ thick were removed subsequently (mechanical polishing), was performed using Philips PW1710 diffractometer with the radiation Cu $K\alpha$.

The detailed phase morphology analyses of the ceramic layers were carried out at cross-sections using a scanning microscope Philips XL 30 with an LINK EDX device, as well as transmission microscope Philips SM 20 TWIN. Thin foils were produced with mechanical polishing using so called Tripod device followed by thinning with focused $Ga^+$ ion beam (FIB) technique in a Quanta 3D thinning instrument. Local analyses of chemical composition were performed using 10nm wide beam in Phoenix EDAX device. The experiments referred to the areas close to the substrate.

## 3. Results

### 3.1. SEM microstructure and EDX analyses

The observation of the microstructure of the $Al_2O_3$ + 30 wt.% $SiO_2$ ceramic cover before annealing using SEM technique on crossections confirmed its layer-like morphology characteristic by its numerous sublayers separated sometimes with voids (Fig. 1 a). Grains 30 m in size were seen in the vicinity of the Ni-20Cr-5Fe-2Al transition layer in areas of 10-30 $\mu m$ away from the substrate. The EDX analysis suggested the existence of mulite containing 25 wt.% $SiO_2$ (Fig. 1 b) in the alloy with similar contents of $SiO_2$ (Fig.1d). The analysis of composition, visible in Fig. 2, showed the increase of the Fe and Ni contents in the ceramics near the substrate, which must have diffused from the transition layer into the coating. In the subsequent sublayers little changes of the Si content were detected in the $Al_2O_3$- $SiO_2$ matrix apart from several $Al_2O_3$ inclusions (Fig. 2). It was observed that the size and number of $Al_2O_3$ grains – which became equiaxial – increased at the distance of 60 $\mu m$ and 160 $\mu m$ from the surface.

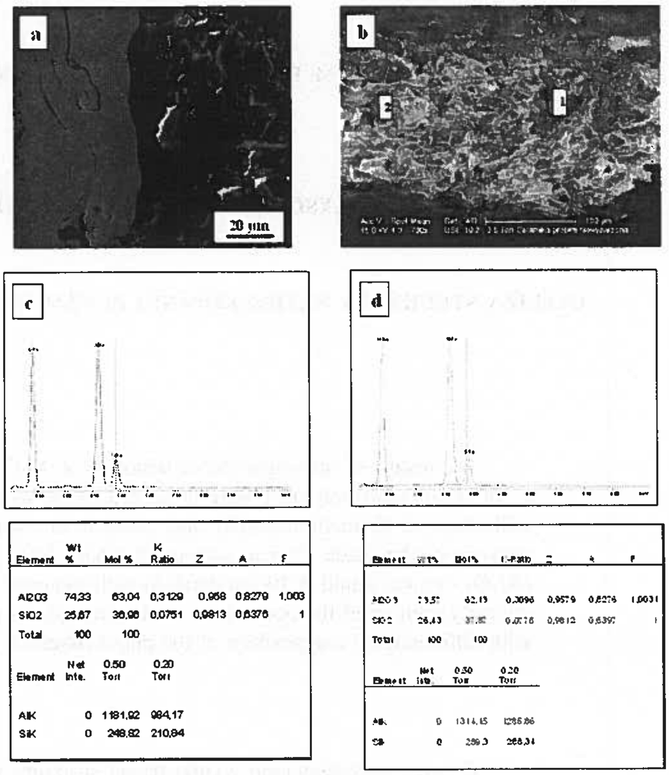


Fig. 1. SEM microstructure of plasma sprayed $Al_2O_3$+30 wt.% $SiO_2$ coating on a crossection, (a); SEM microstructure showing the area of EDX analysis, (b); point analysis of the chemical content in the triangle-like inclusion, (c); point analysis of the chemical content around the inclusion examined in Fig. c,(d)

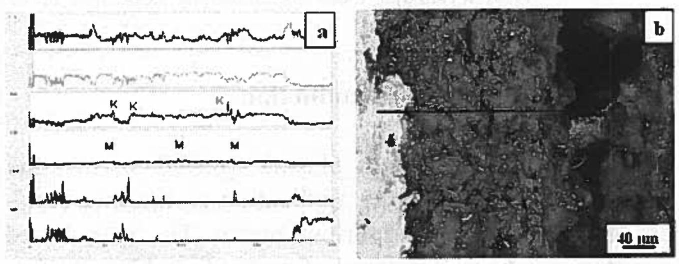


Fig. 2. Linear analysis of the C, O, Al, Si, Fe, Ni contents (a) in the ceramic coating (b)

### 3.2. The X-ray phase analysis

The X-ray phase analysis carried out at various distances from the coating surface showed that the mulite amorphous phase gave the background with increased intensity, lines of mulite crystals of orthorhombic lattice and also lines from the cubic $Al_2O_3$-$\gamma$ corundum. The mulite lines from (001), (220) (130), (201) (230) planes presented the highest intensity in the vicinity of the coating surface as well as at the depth of 10 $\mu m$ (Fig. 3).

The lines of the $Al_2O_3$-$\gamma$ phase from the (012) (104) (110) planes exhibited similar intensity across the whole thickness of the coating. Its phase composition is shown in the phase diagram in Fig. 4. The average 30 wt.% $SiO_2$ composition of the ceramic alloy should have fallen on the left side of the mulite. However, the EDX and X-ray phase analyses derived that large areas of the alloy contained more $Al_2O_3$ than predicted and fell on the right side from the mulite containing 25 wt.% $SiO_2$.

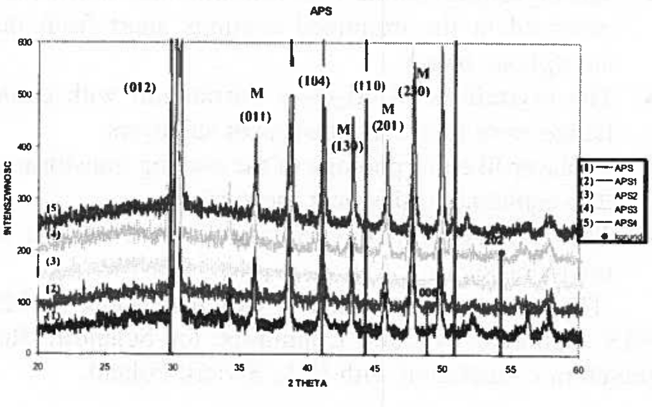


Fig. 3. X-ray diffraction pattern of the plasma sprayed $Al_2O_3$+30 % $SiO_2$, 2Θ range 20-60°; (1) the surface of the sample, (2)- 10 $\mu$m, (3)-20 $\mu$m, (4)-30 $\mu$m (5) -140 $\mu$m below the surface

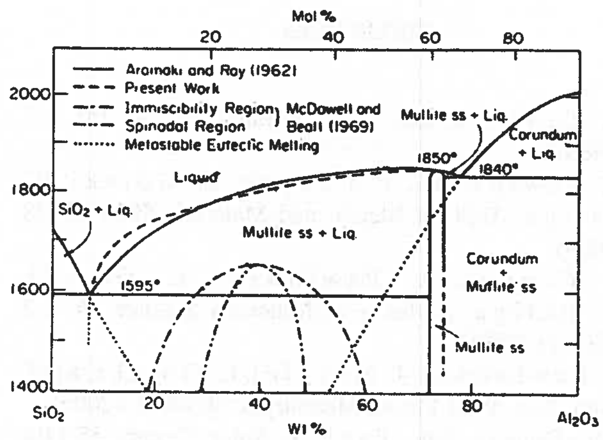


Fig. 4. Phase equilibrium diagram of $Al_2O_3$-$SiO_2$ [2]

### 3.3. TEM microstructure and EDS analysis

The observations using transmission electron microscopy were performed on thin foils obtained by thinning with a focused $Ga^+$ ion beam (FIB) technique, which is a suitable tool when the analysis of composition in microareas close to the substrate is to be carried out.

The TEM microstructure of the plasma sprayed ceramic $Al_2O_3$+30wt.%$SiO_2$ coating produced in such a way is contained in Fig. 5 a, in which a NiCrFeAl transition layer can be seen on the right side, while amorphous areas, confirmed by the appropriate electron diffraction, lie on the left (Fig. 5. b).

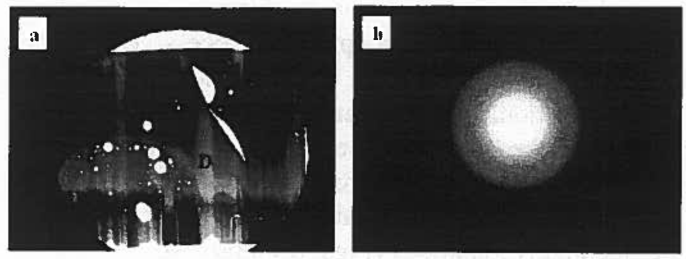

Fig. 5. TEM microstructure of plasma sprayed $Al_2O_3$+30 wt.% $SiO_2$ coating, near the substrate, crossection,(a); corresponding SAED of area marked D, (b)

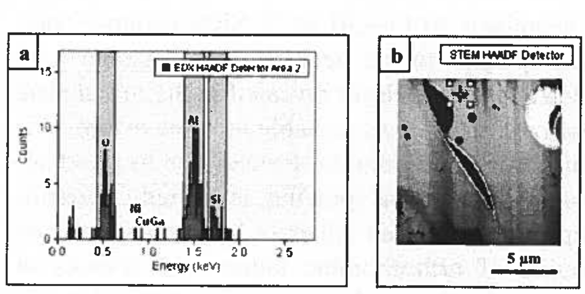


Fig. 6. TEM microstructure of plasma sprayed $Al_2O_3$+30 wt.% $SiO_2$ coating, near the substrate, point 1, crossection, (a); analysis of content in the area marked with cross in (a)

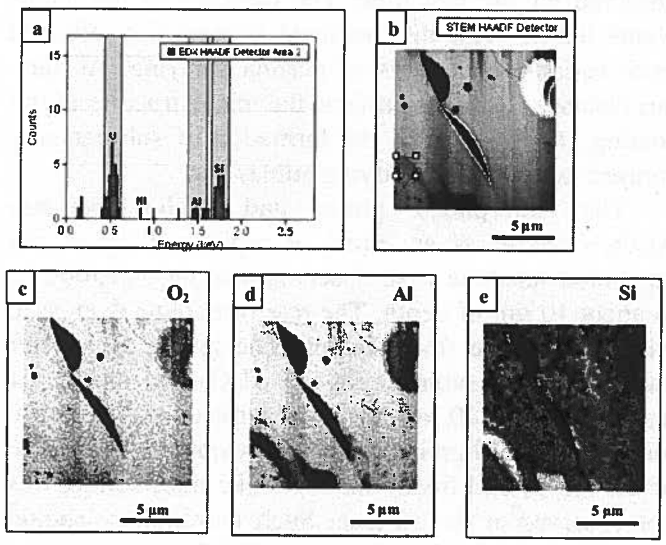


Fig. 7. TEM microstructure of plasma sprayed $Al_2O_3$+30 wt.% $SiO_2$ coating, point 2, crossection, (a); analysis of composition in the area marked with cross, (b); map of O distribution, (c); Al, (d); Si, (e)

The analysis of the chemical composition in the area presented in Fig. 6a, marked with cross is visible in Fig. 6b, which shows an area of the amorphous phase of the mulite composition judging from the high content of Al.

The changes of composition in the area presented in Fig. 7 a, marked with cross are visible in Fig. 7 b, and analysis of the diffraction pattern confirmed that the area was amorphous too, but at much higher Si content and lower that of Al compared to the results discussed above. The examined amorphous phase revealed a shift from the mulite composition in different areas, which resulted from the plasma spraying process. The analysis was reliable due to the FIB technique of the thin foil preparation, which ensured the same foil thickness throughout the sample. The maps of O, Al and Si distributions in the amorphous areas showed in Figs. 6 a and 7 a contained in Figs. 7 c, d, e, respectively confirmed the quantitative analyses (Figs. 6 b and 7 b.

## 4. Discussion of results

The examined $Al_2O_3$+30 wt.% $SiO_2$ ceramic coating plasma sprayed on the steel substrate together with the NiCrFeAl transition layer revealed in the initial state phase structure, which was unstable to some extent. The amorphous structure of mulite, formed due to rapid solidification during plasma spraying, exhibited differentiated composition enriched either in Si or Al. The crystalline mulite of orthorhombic lattice and crystals of $Al_2O_3$-$\gamma$ corundum) of cubic symmetry were also observed using X-ray technique by Górski [6]. However, the supercooled M phase of mulite composition was observed for the first time. The presence of the amorphous mulite with differentiated composition effected from variable conditions of plasma spraying. At various distances from the surface, the microstructure of the coating changed due to the formation of subsequently sprayed layers and solidifying sublayers.

The amorphous phase and high-temperature $Al_2O_3$-$\gamma$ phase as an effect of rapid cooling of the air-cooled substrate were observed near the substrate up to about 10 $\mu$m of depth. The rate of cooling decreased with the distance from the substrate giving as a result alternate, wider sublayers of the $Al_2O_3$ and mulite. At distance about 100 $\mu$m from the surface, mulite, in the form of equiaxial grains, began to prevail on the expense of the $Al_2O_3$ and finally the layer-like morphology was not observed at the surface. Such morphology should ensure good thermal resistance and high properties.

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## 5. Conclusions

The following conclusions were formulated based on the experiments carried out:

- The amorphous phase of composition $Al_2O_3$+26 wt.% $SiO_2$ approaching that of mulite formed in the vicinity of metallic substrate as a result of rapid cooling during plasma spraying. The $SiO_2$ content varied in the areas of the amorphous phase.
- The crystalline mulite with orthorhombic lattice was observed in the examined coatings apart from the amorphous phase.
- The crystallites of $Al_2O_3$-$\gamma$ corrundum with cubic lattice were found in subsequent sublayers.
- Sublayer-like morphology of the coating transformed into equiaxial grains near the surface.
- The examined coatings revealed a small amount of microcracks.

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