AMORPHISATION AND CRYSTALLISATION OF PHASES IN PLASMA SPRAYED Al₂O₃ AND ZrO₂ BASED CERAMICS

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The susceptibility to glass formation in the group of four Al₂O₃-SiO₂, Al₂O₃-TiO₂, Al₂O₃-ZrO₂ and ZrO₂-Y₂O₃ ceramics alloys plasma sprayed on a metallic substrate, commonly used for thermal shields of diesel engine parts, were studied in the work. In the ceramic layers produced in such a way amorphous sublayer solidified on a surface of the substrate. The layers were analysed using techniques of electron microscopy (SADP and EDX). It was established, that although all studied alloys revealed amorphous sublayers, the Al₂O₃-SiO₂ materials were more prone to glass formation than the ZrO₂-Y₂O₃ ones. An annealing of the amorphous layers resulted in their partial crystallisation.

Keywords: thermal barrier coatings, plasma spraying, phase transitions

Chemical properties of the investigated alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Liquidus temp. [°C]</th>
<th>Eutectic comp. [wt.%]</th>
<th>Eutectic temp. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃+SiO₂</td>
<td>30 wt.% SiO₂ 42 mole fraction SiO₂</td>
<td>1860</td>
<td>22 SiO₂</td>
<td>1840</td>
</tr>
<tr>
<td>Al₂O₃+TiO₂</td>
<td>40 wt.% 50 mole fraction TiO₂</td>
<td>1840</td>
<td>40 TiO₂</td>
<td>1840</td>
</tr>
<tr>
<td>Al₂O₃+ZrO₂</td>
<td>40 wt.% 40 mole fraction ZrO₂</td>
<td>1900</td>
<td>40 ZrO₂</td>
<td>1900</td>
</tr>
<tr>
<td>ZrO₂+Y₂O₃</td>
<td>20 wt.% Y₂O₃ 20 mole fraction Y₂O₃</td>
<td>2805</td>
<td>20 Y₂O₃</td>
<td>2380</td>
</tr>
</tbody>
</table>

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Using general measure of the alloy tendency to amorphisation, the values of e/a, where \( a_k \) is a diameter of the alloy addition, were calculated.

- **Alloy (1)**: \( e/a = 20 \), \( e = 15.2 \), \( a_{Si} = 0.76 \) Å
- **Alloy (2)**: \( e/a = 12.6 \), \( e = 15.2 \), \( a_{Ti} = 1.2 \) Å
- **Alloy (3)**: \( e/a = 10.1 \), \( e = 15.6 \), \( a_{Zr} = 1.54 \) Å
- **Alloy (4)**: \( e/a = 6.1 \), \( e = 9.4 \), \( a_{Y} = 1.54 \) Å

The \( Tl/Tg \) criterion (ratio of melting temperature to the amorphisation temperature) could not be applied, because of the lack of reliable data of the amorphisation temperatures. Inoue [3] and Dutkiewicz [4] established that the higher the e/a ratio the easier the amorphisation in metallic alloys. The phenomenon of the increase of susceptibility to amorphisation with the increase of the atom diameter of some metals was explained at least for AgCuCe, AgCuGe, AgCuSb alloys produced with melt spinning method. It was found, that large atoms promoted amorphisation as they obstruct the nucleation of crystallite from the liquid phase. The e/a values were 1.8, 1.84, and 2.44 for Ce, Sb and Ge additions, respectively. The \( Tl/Tg \) was 0.63. The problem is more complex in ceramic alloys because of the formation of glassy phases from metal oxides. In this case, sizes of atoms and their ions as well as the size of oxygen atoms have to be dealt with. Assuming the ratio of atom diameter of the alloy addition to that of the metal oxide it seems that the tendency goes the other way round, that is, the tendency to amorphisation increases with the decrease of the atom size of alloy addition.

The most favourable conditions to form the amorphous phase can be obtained in eutectic or semi-eutectic alloys such as alloys 1–3, studied in this research. Apart from these, the fourth alloy was quite far in composition from the eutectic one, but anyway all the selected materials find commercial application and thus they are worth to be studied.

Based on the calculated e/a values it was proposed, that material (1) \((\text{Al}_2\text{O}_3+\text{SiO}_2)\) should become glassy in the easiest way during plasma spraying, while material (4) \((\text{ZrO}_2+\text{Y}_2\text{O}_3)\) should be the most difficult to transform into an amorphous state. The amount of the material transformed could be the measure of the susceptibility to amorphisation.

In order to gain the data on the process of crystallite formation in the amorphous phase, the plasma sprayed samples were annealed according to the following schedule:

- **Alloy (2)**: \( Ta = 1150^\circ \text{C} \) for 15 hrs
- **Alloy (3)**: \( Ta = 1350^\circ \text{C} \) for 15 hrs
- **Alloy (4)**: \( Ta = 900^\circ \text{C} \) for 50 hrs.

These conditions were established experimentally as the most suitable to ensure optimal decrease of stresses in the plasma sprayed layers as well as in the sublayer of the glassy phase.

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 [5]. The ceramics was introduced into the plasmothrone as \( \text{Al}_2\text{O}_3\), \( \text{ZrO}_2\), \( \text{Y}_2\text{O}_3\), \( \text{SiO}_2 \) powders at appropriate fractions with grains 10–50 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 \( 10^3–10^6 \) K/s. A Ni-based super-alloy or stainless 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. The thicknesses of the ceramic layers obtained were about 200 µm. The joints were annealed at 900 up to 1350°C in order to decrease stresses of the material.

The detailed phase morphology analyses of the ceramic layers were carried out at cross-sections using a transmission microscope (TEM) Philips CM20 TWIN. Thin foils were produced with mechanical polishing using so called Trog 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 10 nm wide beam measured as full width at high maximum and energy dispersive X-ray spectrometer (Phoenix EDAX) and EDX HAADF Detector.

The heat effects were recorded during crystallisation of the \( \text{Al}_2\text{O}_3+40 \text{ wt.}% \text{ TiO}_2 \) alloys plasma sprayed and annealed at 1150°C for 15 hrs using DSC-TGA microcalorimeter (TA Instruments SDT Q 600).

3. **Results and discussion**

3.1. **Microstructure of the \( \text{Al}_2\text{O}_3+30 \text{ wt.}% \text{ SiO}_2 \) ceramics**

The TEM microstructure of the ceramic layer of composition \( \text{Al}_2\text{O}_3+30 \text{ wt.}% \text{ SiO}_2 \) plasma sprayed on a metallic substrate obtained with the FIB technique is shown in Fig. 1a. It can be seen that the \( \text{Al}_2\text{O}_3 – \text{SiO}_2 \) based amorphous phase existed close to the substrate between the transition NiCrFeAl layer visible in right, upper corner of the photograph and etched out particles visible in the left side. A selected area diffraction pattern SAED taken in the centre of the microstructure confirmed its amorphous morphology. The chemical composition analyses (EDX) are shown in Fig. 2a and 2b. Fig-
ure 2a shows the Al₂O₃ enrichment in the area marked with a cross, while Fig. 2b presents the area rich in SiO₂ in the lower part of the micrograph. These facts suggested a strong differentiation of the composition in the plasma sprayed ceramic material. Some crystallites in the amorphous phase did not appear.

3.2. Microstructure of the Al₂O₃+40 wt.% TiO₂ ceramics

The TEM microstructure of the plasma sprayed ceramic Al₂O₃+40 wt.% TiO₂ layer close to the metallic substrate is shown in Fig. 4a, in which fragments of the Al₂O₃-ZrO₂ based amorphous phase less than 1 µm wide are visible on the metallic transition surface. SAED in Fig. 4b taken from the area marked with arrow shows a circle consisting of reflections corresponding to the amorphous phase.

3.3. Microstructure of the Al₂O₃+40 wt.% ZrO₂ ceramics

The TEM microstructure of the plasma sprayed ceramic Al₂O₃+40 wt.% ZrO₂ layer close to the metallic substrate is shown in Fig. 4a, in which fragments of the Al₂O₃-ZrO₂ based amorphous phase less than 1 µm wide are visible on the metallic transition surface. SAED in Fig. 4b taken from the area marked with arrow shows a circle consisting of reflections corresponding to the amorphous phase.
The TEM microstructure of $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ based amorphous phase observed on cross-section close to the substrate is visible in Fig. 5 a, together with maps of element distributions (Figs. 5 (b-d) and the changes of Zr content along the line marked in d, e.

3.4. Microstructure of the $\text{ZrO}_2$+20 %$\text{Y}_2\text{O}_3$ ceramics

The observations of TEM microstructure of the plasma sprayed ceramic $\text{ZrO}_2$+20 wt.%$\text{Y}_2\text{O}_3$ layer close to the metallic substrate is shown in Fig. 6, in which the $\text{ZrO}_2$-$\text{Y}_2\text{O}_3$ based amorphous phase can be seen. A area in Fig.6a its presence was confirmed by the rings of reflections in the corresponding SAED, in which also reflections from nanocrystalline particles of tetragonal $\text{ZrO}_2$ phase resulted from the annealing of the joint at 900°C for 50 hrs could be observed (Fig. 6c). The SAED taken of the area away from the amorphous phase (marked K) showed reflections from the same particles (Fig. 6b).

3.5. Measurements of heat effects

The example of heat effect measurements using DSC-TGA instrument during crystallisation of the $\text{Al}_2\text{O}_3$+40 wt.%$\text{TiO}_2$ alloy plasma sprayed and annealed at 1150°C for 15 hrs is presented in Fig.7. Temperature of crystallisation has been assessed to be 1233°C, while the temperature of the glass formation could not be determined unambiguously. I may only be suggested to be 1207°C. On the heat effects curve 1285°C was marked as the crystallisation temperature of $\text{Al}_2\text{O}_3$-$\alpha$ (corundum), and 1435°C for the crystallisation of $\text{Al}_2\text{TiO}_5$.

The presented results of the study of microstructure, crystallography and chemical (EDX) composition using TEM were generally in accordance with the calculated tendencies to amorphisation of the analysed ceramic materials, which were plasma sprayed on an air cooled (100°C) substrate of Ni super alloy or alloyed steel.

It was established, that the sublayer of amorphous phase prevailed in the structure appeared at plasma spraying of material (1) $\text{Al}_2\text{O}_3$+30 wt.%$\text{SiO}_2$, which resulted from the influence of the Si atoms of small diameter 0.76Å and high e/a ratio=20. Thus, it seemed, that the small diameter of the Si atoms and high value of e/a ensured the high tendency to amorphisation. The differentiation of the composition of the amorphous phase as regards the amount of the $\text{SiO}_2$, showed that there was more $\text{Al}_2\text{O}_3$ than $\text{SiO}_2$ in the vicinity of the substrate.

In material (2) of $\text{Al}_2\text{O}_3$+40 wt.%$\text{TiO}_2$ composition, the amorphous sublayer was quite wide (about 5μm, which suggested its high susceptibility to amorphisation at e/a parameter equal to 12.6 and the Ti atom size equal to 1.2 A. The annealing of the joint at 1150°C for 15 hrs brought about the appearance of great number of $\text{Al}_2\text{O}_3$-$\alpha$ and $\text{TiO}_2$ nanocrystallites on the expense of the amorphous phase. This indicated that the temperature of its transition in crystalline form is lower than 1150°C.

In material (3) of $\text{Al}_2\text{O}_3$+40%$\text{ZrO}_2$ composition, the amorphous sublayer was relatively narrow (about 1-2 μm,) which could result from lower value of parameter e/a=6.1 and
atomic diameter of Zr = 1.54 Å. The composition of the amorphous layer close to the substrate was inhomogeneous; enrichments in ZrO$_2$ or even its tetragonal particles were observed. The annealing at 900°C for 50 hrs induced the formation of nanocrystalline phases in the amorphous area probably as an effect of prolonged annealing.

4. Conclusions

Based on the presented results and their discussion the following conclusions have been formulated:

- The tendency to amorphisation analysed through microstructure investigation of plasma sprayed Al$_2$O$_3$ and ZrO$_2$ materials with TiO$_2$ and Y$_2$O$_3$ additions seemed to depend on the value of e/a parameter as well as the size of atom diameter of the alloy addition. The susceptibility to amorphisation increased with higher e/a parameter and the smaller atom size. Such a relation was confirmed for all four alloys examined in such a way, that the Al$_2$O$_3$+30%SiO$_2$ with e/a=20 was the most prone to amorphisation. The Al$_2$O$_3$+40%TiO$_2$ alloy with e/a=12.6 was less prone and even less susceptible was the Al$_2$O$_3$+40%ZrO$_2$ with e/a=10.1. The lowest tendency for amorphisation was observed in the ZrO$_2$+20%Y$_2$O$_3$ with e/a=6.1.

- The diameter of silicon atoms was the smallest (a=0.76 Å) at the greatest tendency of the Al$_2$O$_3$+30%SiO$_2$ alloy to amorphisation, while that of iridium the biggest (1.54 Å), which meant the least susceptibility to amorphisation of the alloy ZrO$_2$+20%Y$_2$O$_3$. The diameter of oxygen (2.92 Å) was not considered as its influence was the same for all the alloys.

- Crystallisation of the amorphous phase in the investigated alloys seemed to depend on temperature and time of annealing. Prolonged annealing of the alloy (4) ZrO$_2$+20%Y$_2$O$_3$, ensured the partial transformation of the amorphous phase into a crystalline one.

- Partial crystallisation of the amorphous phase was observed in alloys (2 with Ti) and (4 with Y), which had the highest values of atomic diameters (Ti and Y). It seemed that the higher atom size of the alloy addition and smaller tendency to amorphisation the easier is the reverse transition from amorphous into crystalline phase.

REFERENCES

[3] A. I n o u e, I. P a r t, T. M a s s u a n m o t o, Formation of Amorphous CuAgCe Alloys by Rapid Solidification and Transformed Thermal and Mechanical Properties, Mater. Trans. JIM 35, 227 (1994).
[4] J. D u t k i e w i c z, T. M a s s a l s k i, Research for Metallic Glasses of Eutectic Crystallisations in the AgCuCe, AgCuSb and AgCuGe Systems, Metall.Trans. 2A, 773 (1981).

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