Microstructure of thermal barrier coatings deposited by APS method with application of new type ceramic powders

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ABSTRACT

Purpose: The paper presents results of structural research into thermal barrier coatings obtained by the APS. For the base the Rene 80 alloy was used, whereas a MeCrAlY-type multicomponent alloy was used for an interlayer.
Design/methodology/approach: Throughout the research an optic microscope as well as a scanning electron microscope were employed. Measurements of the formed structure’s porosity were taken.
Findings: It has been observed that application of novelty ceramic powders allows for a possibility of forming thermal barrier coatings, which can be used for protecting of the combustion chamber’s surface as well as turbine’s blades in an aircraft engine.
Research limitations/implications: Further research into resistance to oxidation of these coatings seems necessary for experimental determination of their actual work temperature.
Practical implications: They can be successfully applied in automotive industry for coating of petrol or diesel engine’s components.
Originality/value: Investigation into possible applications of two-layer and composite coatings, which may improve the work temperature of thermal barrier coatings, is feasible.
Keywords: Ceramics and glasses; Corrosion; Erosion; Material science; Thin and Thick Coatings; Surface treatment

Reference to this paper should be given in the following way:

1. Introduction

Improving efficiency of engine combustion and reducing fume emission has caused the turbine temperature in aircraft engines to grow significantly over the last 30 years.

In engines, work temperature of a rotating blade is about 1050°C where maximum temperatures may reach 1150°C [1,2].
In gas turbines, temperatures are slightly lower (800-950°C) but these stem from severe work conditions [3,4]. Continuous temperature growth was observed at the turbine inlet, up to 2000K (1723°C). This development in the production has been achieved...
thanks to designing of new materials, improvement of blade coating methods as well as introduction of new production technologies [2,3,5]. This influenced development of turbine blades as well as alloys used for their production. Common heat-resistant alloys have been replaced with nickel-based alloys. The rise of temperature brought about a need of improving the resistance to oxidation and hot corrosion.

Aluminide coatings were the first protective coatings introduced in the 1960s. These coatings were formed through chemical vapour deposition carried out with the use of the pack cementation method. In the early 1970s [4,6-9] there were developed MCrAl-type multialloy coatings protecting from corrosion and high temperatures. Further development was connected with introducing Thermal Barrier Coatings (TBC). These protect from hot gases. Coatings consist of two layers, an external ceramic (\(Y_2O_3\) - or \(MgO\) - stabilized ) \(ZrO_2\) and an MCrAlY metallic interlayer, where M will mostly be Co, Ni, Fe. The role of an interlayer is to improve adhesion of a ceramic layer to the base and to decrease stresses caused by coefficients of thermal expansion of the coating and base material. Thermal barriers were at first used for static components and only recently have been applied for rotating elements.

The APS, EB-PVD and LPPS methods based on thermal spraying of ceramics are the most popular methods of coating deposition. Application of protective coatings improves reliability and lengthens the engine’s work time. Most popular thermal barrier coating methods are:

- APS (Air Plasma Spraying) - plasma spraying at atmospheric pressure,
- LPPS (Low Pressure Plasma Spraying),
- EB-PVD (Electron Beam - Physical Vapour Deposition).

In plasma spraying powder is first injected into the burner and then deposited. Plasma-generating gas is run through the burner - most often it is argon (sometimes supplemented with hydrogen, nitrogen or helium). Placed in the central part of the burner, a tungsten cathode is encircled with a copper anode. Stress difference between the anode and the cathode in the presence of argon results in electric arc discharge inside of the burner. Rapid heating of argon caused by flow of electric current through the arc results in its turning to plasma density and escaping through the burner’s nozzle, combined with heated powder. The burner is water-cooled due to a high temperature of gases produced during the process. Most usually, the burner is supplied with direct current (DC) [10]. If the APS procedure is carried out appropriately, the base will not heat up. Deposition of high-melting point materials such as tungsten and zirconium is possible thanks to the fact that the temperature of the plasma burner may reach a temperature of 14000K. This method allows for use of powders and rods (though used rarely in this method). There is a possibility of spraying low-melting point substances if the burner is replaced with other material-feeding component.

The LPPS method (Low Pressure Plasma Spraying) used for formation of thermal barrier coatings is carried out by means of plasma spraying at low pressure.

Basic features of the LPPS procedure are:

- no reduction of metal and gas,
- a quick procedure of coating deposition,
- very low porosity of coating,
- self-cleaning during the procedure,
- very good coating’s adhesion to the base.

Coatings obtained by the LPPS method enjoy very good quality due to their high density as well as fine-grained and homogenous character. High quality of coatings can be obtained through appropriate surface preparation and coating temperature. Plasma flow is deposited at low pressure approx. 50 mbar (in Ar, He or Ar+He atmosphere).

Comparison of the LPPS and EB-PVD methods shows that the methods are complementary. The LPPS method is used for large components, while a big amount of small components can be coated by the EB-PVD method. However, there is a significant cost difference between the two methods. Although the EB-PVD method is more expensive than the LPPS method, it offers higher quality of the coating’s surface. Porosity of the surface is not closed.

Extensive research into developing new ceramic coatings of better properties than those of commonly used yttrium-stabilized zirconium oxide is now being carried out. Currently, most valued are ceramic powders based on pyrochlorals, rare earth metal oxides, hexaluminates and pervoskites [11].

Research into application of novelty zirconium-stabilised oxides is also carried out. These oxides include magnesium oxides [12]. Currently producers of powders for plasma spraying offer magnesium- and calcium-stabilised zirconium oxide ceramic powders [13]. The paper presents results of plasma spraying of these powders.

### 2. Experimental

As the base material a Rene 80 foundry alloy was used; Table 1 shows its chemical composition. Plasma spraying procedure was carried out with the use of an F4 MB Sulzer Metco burner. For an interlayer AMDRY 997 powder was used; Table 1 presents its chemical composition. For forming of a ceramic layer three types of powder were used: common yttrium oxide-stabilized zirconium oxide and new types of powder - calcium- and magnesium-stabilized zirconium oxides. Chemical composition of the powders has been presented in Table 2.

Description of powders has been included in the paper [13]. Metallographic examination was carried out in accordance with methodology suggested by Moskal in the paper [14]. Metallographic and porosity tests were done along the procedure as described in the paper [15]. For selected coatings, microstructural research was carried out with the use of an S-3400 type scanning electron microscope by Hitachi, equipped with an X-ray add-on device for microanalysis of chemical composition by Thermo.

| Table 1. The nominal composition of base material and bondcoat powder |
|------------------|---|---|---|---|---|---|---|---|---|
| Alloy            | Ni | Co | Cr | W  | Mo | Al | Ti | Zr | C  | Ta | Y  |
| Rene 80          | 9.5| 14 | 4  | 4  | 3  | 5  | 0,06| 0,17|     |    |    |
| AMDRY 997        | 23 | 20 | -  | -  | 8.5| -  | 0   | 4   | 0.6 |

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Table 2.
The nominal composition of ceramic powders

<table>
<thead>
<tr>
<th>Phase composition (nominal wt. %)</th>
<th>Powder type</th>
<th>Metco 201 B NS</th>
<th>Metco 204 NS</th>
<th>Metco 210</th>
</tr>
</thead>
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<tr>
<td>ZrO</td>
<td>91.5</td>
<td>bal.</td>
<td>bal.</td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>-</td>
<td>8-9</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>4.5-5.5</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>-</td>
<td>15-30</td>
<td></td>
</tr>
<tr>
<td>other</td>
<td>bal.</td>
<td>approx. 1%</td>
<td>up to 7%</td>
<td></td>
</tr>
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</table>

3. Results

Trial spraying carried out with the use of flat and cylinder-shaped samples has rendered entire thermal barrier coating of the said samples. No sample has shown cracks or other surface failure upon coating deposition. The microstructure of layers has been presented in Fig. 1.

Thickness measurements were also taken. For standard TBC with YSZ layer (METCO 204) thickness of the external, that is ceramic layer was approx. 190 μm. The TBC with external calcium oxide-stabilized zirconium oxide layer (METCO 201) was approx. 250 μm thick. Magnesium-stabilized ceramic layer (METCO 210) was 300 μm thick.

Measurements of layers porosity have shown significant differences depending on the applied ceramic powder. A conventional YSZ ceramic layer displayed 10.5% porosity. Zirconium oxide ceramic layers stabilized by other elements display less porosity. In case of calcium oxide-stabilized zirconium oxide it was approx. 3.4%, while for magnesium oxide-stabilized yttrium oxide - approx. 5.3%.

![Fig. 1. Thickness measurement of thermal barrier coating obtained by the APS method with the use of calcium-stabilised (a) yttrium-stabilised (b) and magnesium-stabilised (c) zirconium oxides in the ceramic layer.](image)
Microstructure and chemical composition tests of thermal barrier coating with a ceramic layer obtained from zirconium oxide stabilized with calcium oxide were carried out (Figs. 2, 3 and 4). Tests on chemical composition of the external area have shown presence of oxygen zirconium and calcium zirconium.

In the interlayer area average aluminium content was approx. 3 at.%, cobalt amount was appr. 19 and chromium amount was 16.6 at.% (area 2 in Fig. 4a). Below, in the area indicated ‘3’ in Fig. 4a, chemical composition was analogous to the base material - the Rene 80 alloy. Thorough examination of the interlayer’s chemical composition was carried out in the area indicated in Fig. 4b. Spots marked ‘4’ and ‘5’ show most probably presence of oxides such as aluminium oxide. In area 6 no oxygen amount was reported, while aluminium content was increased - 30 at.%; chromium and cobalt amount was lower.

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Table 3.
Results of the EDS analysis of chemical composition in spots as indicated in Fig. 4

<table>
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<tr>
<th>Area</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Ca</th>
<th>Ti</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Y</th>
<th>Zr</th>
<th>Mo</th>
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<tr>
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<td>0.94</td>
<td>4.40</td>
<td>0.14</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>23.48</td>
<td>-</td>
<td>-</td>
<td>16.56</td>
<td>19.47</td>
<td>39.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.71</td>
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<td>3</td>
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<td>6.48</td>
<td>6.79</td>
<td>15.89</td>
<td>9.48</td>
<td>58.31</td>
<td>-</td>
<td>-</td>
<td>1.07</td>
<td>2.07</td>
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<tr>
<td>4</td>
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<td>20.77</td>
<td>-</td>
<td>-</td>
<td>13.99</td>
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<td>5</td>
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<td>-</td>
<td>14.31</td>
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<td>6</td>
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<td>-</td>
<td>-</td>
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<td>17.04</td>
<td>41.55</td>
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</table>

Fig. 4. Microstructure of thermal barrier coating with calcium-stabilised zirconium oxide ceramic layer (METCO 201) (a) and detailed construction of the McCrAlY-type interlayer (b) with indicated spots for chemical composition analysis.

### 4. Summary

Initial trials of thermal barrier coatings deposition with use of novelty calcium- and magnesium-stabilised zirconium oxide powders have proven that the powders can be easily deposited by the APS method. Both layers were significantly less porous - two and three times respectively - under the same deposition conditions. Fundamental limitation of application of these materials lies in low work temperature which should not exceed 800-900°C - much lower than in conventional YSZ.

Further research into resistance to oxidation of these coatings seems necessary for experimental determination of their actual work temperature. They can be successfully applied in automotive industry for coating of petrol or diesel engine’s components. Further investigation into formation of thermal barrier coatings will continue to use yttrium-stabilized zirconium oxide since it is rather irreplaceable. However, investigation into possible applications of two-layer and composite coatings, which may improve the work temperature of thermal barrier coatings, is feasible.

### Acknowledgements

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