Experimental study of insulating properties and behaviour of thermal barrier coating systems in thermo cyclic conditions

Mihailo Mrdak, Marko Rakin, Bojan Medjo, Nikola Bajic

Abstract

The aim of this study was to improve the resistance of turbo jet engine parts exposed to high temperatures and overheating and sudden changes in temperature. For this purpose, three thermal barrier coating (TBC) systems NiCrAlCoY2O3, NiCrAlCoY2O3, and NiCrAlCoY2O3 were tested. They were deposited using the atmospheric plasma spray process (APS). In order to develop a TBC with the best thermal insulating properties and the highest reliability in relation to aging of materials under the influence of sudden changes in temperature, TBC systems that were deposited on cold and preheated substrates were tested. The network of microcracks on the surfaces of the ceramic layers in deposited condition was analyzed using scanning electron microscopy (SEM). Insulating characteristics of TBC systems were examined by measuring the temperature difference between the top and bottom surfaces of the samples at a temperature of 1200 °C. Testing of TBC for resistance to thermal cyclic behaviour was performed by exposing samples to alternate heating at 1200 °C and rapid cooling of the samples to 180 °C. Microhardnesses of the TBC system, after completion of thermal cycles, were compared with the values in deposited state. Analyses of thermal insulation properties and thermal cyclic behaviour have shown a correlation between the substrate temperature and quality of the TBC system in thermal cyclic conditions.

1. Introduction

The increasing demand for improving the efficiency of gas turbine parts of turbo-jet engines, both in the civilian and military sector, led to the development of new materials for thermal barrier coatings (TBC). The need to develop TBC systems resulted from the more stringent conditions of the new generation of gas turbines and higher temperatures of gases [1] (of course, they are also used in other industries, e.g. in automotive industry for spark ignition engine production [2]). Parts of the gas turbines are exposed to high-temperature oxidation, hot corrosion, gas erosion and foreign particle emissions, as well as rapid changes in temperature. The TBC should not only limit heat transfer through the coating, but also protect engine components from oxidation and hot corrosion. No single coating is able to fulfil these multifunctional requirements. As a result, a coating system was developed consisting of two or three coatings in order to achieve long-term efficiency at high temperatures, oxidation and corrosion protection of the base material. TBC systems are the only class of materials that can be applied to such working conditions [3]. Typical thermal barrier coatings for gas turbines and diesel engines consist of a top layer of ZrO2 stabilized by other oxides and bond coating of NiCrAlY [4]. The basic material for making the ceramic thermal barrier coating layer is ZrO2 oxide.

Selection of ZrO2 compared to other oxides was done because of its good mechanical properties (high strength and fracture toughness) and physical properties, such as thermal conductivity (λ ≈ 1.7 W/m°C), thermal expansion coefficient (α ≈ 9 × 10⁻⁶/°C) and melting temperature of 2710 °C [5,6]. An important feature of pure ZrO2 is its polymorphism [7]. At atmospheric pressure, there are three crystallographic phases: monoclinic, tetragonal and cubic. When alternating heating and cooling, thermal fatigue of ZrO2 material occurs due to volume changes caused by phase transformation.

As a result of the reversible transformation of the monoclinic to the tetragonal phase in the temperature range of 950–1170 °C, occurrence of microcracks that spread and turned into macro cracks was observed [8,9]. For this reason, pure ZrO2 is not suitable for the production of thermal barrier coatings. In order to reduce the effect of tetragonal to monoclinic transformation, other oxides are added to pure ZrO2, such as CaO, MgO, Y2O3 and recently CeO2, HfO2, and In2O3. These additions stabilize the ceramic layer...
The separation of TBC layers along the edges can occur as a result of the temperature gradient in the marginal zone. On the surface of the ceramic coatings, the networks of microcracks are formed due to compressive stress induced by phase transformations accompanied by volume changes [15]. Networks of microcracks tend to connect with the number of thermal cycles, and cause segment separation of ceramic particles from the surface [16].

In this paper, three types of TBC systems (NiCrAlCoY2O3/ZrO2MgO, NiCrAlCoY2O3/ZrO2Y2O3 and NiCrAlCoY2O3/ZrO2CeO2/Y2O3) were tested in thermal cyclic conditions to determine which coating system provides the greatest temperature drop through the layer. In order to develop a TBC with the best thermal insulating properties and the highest reliability in relation to aging of materials under the influence of sudden changes in temperature, TBC systems deposited on cold and preheated substrates were tested. Analyses of the results of the examinations allowed choosing TBC systems with the best thermal insulating properties and highest reliability.

2. Materials and experimental details

Materials for testing are TBC systems that are deposited on steel substrates of stainless steel X15Cr13 (EN 1.4024). Coatings systems were deposited with atmospheric plasma spraying using powders: Metco 461NS (NiCr–Al–Co–Y2O3), Metco 210 (ZrO2MgO), Metco 202NS (ZrO2Y2O3) and Metco 205NS (ZrO2CeO2Y2O3) [17–20]. Three ceramic powders with different thermal conductivity coefficients were used, as follows: ZrO2MgO with thermal conductivity coefficient 1.5 W/m°C, ZrO2Y2O3 with thermal conductivity coefficient 1.3 W/m°C and ZrO2CeO2Y2O3 with thermal conductivity coefficient 0.9 W/m°C. In the experiment, these systems were tested: TBC system 1 (NiCrAlCoY2O3/ZrO2MgO), TBC system 2 (NiCrAlCoY2O3/ZrO2Y2O3) and TBC system 3 (NiCrAlCoY2O3/ZrO2CeO2Y2O3). The same bonding layer (NiCrAlCoY2O3) was used for all the TBC systems. It was selected because it belongs to the new generation of bonds, and it has been widely used due to the good thermo-mechanical properties. Its important advantage is pronounced toughness.

Labels of tested samples, total thickness of the coatings and amount of pores in the ceramic layers were: for TBC system 1 samples (2–1)/(2–2), thickness (504 μm/490 μm), amount of pores (24%/14%), for TBC system 2 samples (3–1)/(3–2), thickness (420 μm/406 μm), amount of pores (29%/23%), for TBC system 3 samples (4–1)/(4–2) thickness (490 μm/476 μm) and amount of pores (29%/23%). For TBC deposited on substrates with temperatures of 21–23 °C, the labels are (2–1), (3–1) and (4–1), and on substrates with temperatures of 160–180 °C the labels are (2–2), (3–2) and (4–2).

Testing for presence of microcracks on the surfaces of ceramic layers was carried out on samples with dimensions 70 × 2 0 × 1.5 mm. The presence of microcracks on the surfaces of the ceramic coatings after depositing powders was examined by scanning electron microscopy (SEM), in order to determine their effect on the behaviour and durability of the TBC in thermal cyclic conditions. Thermal insulation properties of TBC systems were investigated by measuring the temperature difference ΔTe through the sample in the direction perpendicular to the substrate surface. ΔTe values for the sample are obtained by measuring the surface temperature of the TBC and the bottom surface of the substrate. This method is usually applied for stationary conditions and, above all, it provides information on the temperature drop through the thickness of the TBC. Samples for testing of thermal barrier coatings are made by pairing two samples of the same type of TBC-s which were deposited on substrates with different temperatures. Between the samples, a metal plate was positioned. The inner thermocouple passed through this plate, measuring the temperature of the bottom surface of the substrate.

The external thermocouple was placed on the upper surface and at the same distance as the internal thermocouple which measured the temperature on the upper surface. Connecting of the samples was done with stainless steel bolts that were protected by thermal barrier. Internal and external thermocouples were separated by alumina ceramic tubes that went through a larger ceramic tube. That tube was used as a sample holder. For sealing the furnace, a cap of special insulating mass was made through which the larger ceramic tube passed. Fig. 1 shows one of the prepared samples for testing. In this figure, one can see: a sample (1), an external thermocouple (2), an alumina ceramic tube (3) and the special insulating mass cap for sealing the furnace (4).
A steel sample was also made, with the same size as the samples on which TBC systems were deposited to establish a temperature difference in the top and bottom surfaces of the substrate $D_{T_s}$. Temperature difference through the layers, $D_{TTBC}$, perpendicular to the surface of the substrate, is obtained as the difference $D_{TTBC} = D_{Tu} - D_{Ts}$. Investigation of thermal insulating properties of TBC (temperature drop in the layer depths) and the behaviour of layers in thermal cyclic conditions is done at 1200 $^\circ$C. In order to perform sample testing, a differential thermocouple Pt/Rh–Pt was made from wire 0.3 mm thick; a dedicated software and hardware (AD converter) was used to convert the heat flux into electrical values. The equipment used for testing of samples is shown in Fig. 2.

The equipment consists of: a screen for tracking test results (1), a computer (2), an AD converter (3), a heating furnace (4), a tunnel for rapid cooling of the sample (5) and a sample for testing (6). The furnace in which the sample testing was done was calibrated at 1200 $^\circ$C. The measuring was carried out with an error of ±20 $^\circ$C, due to temperature rise and fall while turning the furnace on and off. Before inserting the sample into the furnace, the temperature difference between the surface of the ceramic coating and the substrate bottom surface was $D_{Tu} = 0$. After inserting the sample into the furnace, $D_{Tu}$ slowly begins to rise due to the heating of surface of the ceramic coating. The surface temperature of the coating increases more rapidly than the temperature of the base, due to ceramic coating insulation. $D_{Tu}$ value reaches a maximum when the temperature of the surface of the ceramic coating reaches 1200 $^\circ$C, and then decreases because the temperature of substrate rises until it reaches the furnace temperature.

After equalizing the temperature, the samples are extracted from the furnace and rapidly cooled in the tunnel with a fan to a temperature of 160–180 $^\circ$C. The time for heating of the samples was two minutes, while cooling lasted three minutes. The number of completed cycles depended on the occurrence of macro cracks.

Microstructures of the TBC systems were analyzed after thermal cyclic tests with an optical microscope (OM). Samples were prepared using the standard method of grinding and polishing, without etching.

Measuring of microhardness of layers of the TBC system after thermal cyclic tests was performed using a Vickers diamond pyramid indenter and 100 gram load (HV0.1). The measuring was carried out in the direction along the lamellae in the middle and at the ends of the sample. At all three sites, five value readings were conducted and averaged subsequently. The values of microhardness after thermal cyclic tests were compared with the values of hardness before the tests.

### 3. Results and discussion

On the surfaces of all the ceramic coatings in deposited condition, identified networks of microcracks were examined using scanning electron microscopy (SEM). Presence of networks of microcracks on the surfaces of the ceramic coatings is the result of stress occurring during deposition of molten powder particles. Stresses on the surface of the deposited ceramic particles depend on the temperature at which the molten particle droplets are extinguished, particle hardening speed, substrate temperature and the ratio of thermal expansion coefficients of substrate and coating. The presence of microcracks on the surface of the deposited ceramic particles was described by Vardelle et al. [21] and the cause of their occurrence explained. This type of error is something that can not be avoided. The causes of the microcracks are stresses resulting from thermal gradients in the particles during cooling and differences of the expansion coefficients of layers. The substrate and the previously deposited layer restrict shrinking of the deposited particle after extinguishing. Another reason is the difference in thermal expansion of deposits and substrate during cooling of deposits to the substrate temperature. Figs. 3–5 show microcracks on the surfaces of ceramic particles $\text{ZrO}_2\text{MgO}$, $\text{ZrO}_2\text{Y}_2\text{O}_3$ and $\text{ZrO}_2\text{CeO}_2\text{Y}_2\text{O}_3$ deposited on preheated samples.

The most prominent networks of microcracks were present on the surface of the completely molten ceramic $\text{ZrO}_2\text{MgO}$ particles.
For completely molten particles there is a greater temperature difference between the particles that are cooled on the surface of the coating and the previously deposited layers. Also, there is a greater difference in the expansion coefficients between the substrate and the surface layer of the coating. Therefore, the ceramic ZrO₂ MgO particles on the surface of the coating are exposed to greater tensile stresses which are opposing the particle contracting during cooling [21]. On the micrograph, it is clearly shown that the molten particle in collision with the base is properly deformed, it is almost smooth, and that compared to the other two ceramic particles has the highest degree of plastic deformation.

Investigating differences between the temperature at the top and bottom surface of the substrate thickness 1.5 mm, a drop in temperature $\Delta T = 150 ^\circ C$ was measured. The values of temperature difference $\Delta T_{b}$ through the tested samples for TBC system 1 (NiCrAlCoY₂O₃/ZrO₂MgO) are shown in Fig. 6, for TBC system 2 (NiCrAlCoY₂O₃/ZrO₂Y₂O₃) in Fig. 7 and for TBC system 3 (NiCrAlCoY₂O₃/ZrO₂ CeO₂Y₂O₃) in Fig. 8. The average value of the temperature drop through samples (2–1)/(2–2) for TBC system 1 (NiCrAlCoY₂O₃/ZrO₂MgO) is $\Delta T = 460 ^\circ C$, through samples (3–1)/(3–2) for TBC system 2 (NiCrAlCoY₂O₃/ZrO₂Y₂O₃) is $\Delta T = 390 ^\circ C$ and through samples (4–1)/(4–2) for TBC system 3 (NiCrAlCoY₂O₃/ZrO₂ CeO₂Y₂O₃) is $\Delta T = 560 ^\circ C$.

The real value of temperature drop through TBC system 1 is $\Delta T_{TBC-1} = 460 ^\circ C - 150 ^\circ C = 310 ^\circ C$, through TBC system 2 it is $\Delta T_{TBC-2} = 390 ^\circ C - 150 ^\circ C = 240 ^\circ C$ and through TBC system 3 it is $\Delta T_{TBC-3} = 560 ^\circ C - 150 ^\circ C = 410 ^\circ C$. All types of TBC systems have lowered the actual temperature of the top surface of the substrate for $\Delta T = 240–410 ^\circ C$. The best insulation properties and the most prominent drop in temperature are obtained for ceramic layers ZrO₂ CeO₂Y₂O₃, although these layers had the lowest proportion of pores and were the most dense.

Fig. 4. SEM photomicrographs ZrO₂Y₂O₃ surface.

Fig. 5. SEM photomicrographs ZrO₂ CeO₂Y₂O₃ surface.

Fig. 6. $\Delta T$ for TBC system 1 and samples (2–1)/(2–2).

Fig. 7. $\Delta T$ for TBC system 2 and samples (3–1)/(3–2).

Fig. 8. $\Delta T$ for TBC system 3 and samples (4–1)/(4–2).
It is well known that thicker layers have a lower thermal conductivity and a lower temperature drop through the layer. The cause of such low thermal conductivity and increased temperature drop through ZrO$_2$ CeO$_2$ Y$_2$O$_3$ layers is an extremely low thermal conductivity coefficient of ceramics: 0.9 W/m°C. Ceramic layers ZrO$_2$ MgO, although more dense than ZrO$_2$ Y$_2$O$_3$, showed better insulating properties due to thicker 84 μm layers. The measured values indicate that thermal conductivity coefficient and the ceramic layer thickness have more significant impact on the insulating properties of ceramic layers than the amount of pores.

The microhardness values of bond coating NiCrAlCoY$_2$O$_3$ layers before and after thermal cyclic tests are shown in Fig. 9. Lower values of microhardness are related to bond coatings in the deposited state, and higher values after completion of thermal cycles.

The measured values of microhardness are directly related to the number of thermal cycles performed. The largest increase in microhardness is observed for the layers with the highest number of cycles performed (34). The cause of a larger increase in the microhardness of samples is prolonged exposure to high temperature. At 1200°C inter-diffusion of chemical elements occurs due to different content of chemical elements in the coating and the substrate and the diffusion of oxygen from the atmosphere through the porous ceramic layers.

Occurrence of oxygen diffusion into the bond coating and diffusion of iron from the substrate into the bond coating was described by Zhu et al. [22]. In the coating, there is probably present a Fe$_2$O$_3$ type oxide due to Fe diffusion from the substrate into the coating and Fe reaction with oxygen that diffuses into the coating [22].

The microhardness of ceramic layers ZrO$_2$ MgO, ZrO$_2$Y$_2$O$_3$, ZrO$_2$ CeO$_2$ Y$_2$O$_3$ before and after thermal cyclic tests is shown in Fig. 10.

Lower values of microhardness are related to ceramic coatings in the deposited state. For all types of ceramic coatings, microhardness values were increased. The highest values and increase of microhardness are obtained for ZrO$_2$ MgO layers. For a small number of completed cycles (7), ceramic layer ZrO$_2$MgO showed microhardness values from 916 to 1027 HV$_{0.1}$. This indicates that the oxide MgO at 1200°C is a bad stabilizer for ZrO$_2$ ceramics and that there is a ceramic ZrO$_2$MgO layer fatigue due to rapid transformation of the tetragonal phase into a monoclinic phase (t → m). The increase in microhardness of the ceramic layer ZrO$_2$MgO deposited on a cold substrate was 422 HV$_{0.1}$, and on the preheated substrate 379 HV$_{0.1}$. Higher growth of microhardness is also affected by higher pore content (24%). Larger contents of porosity significantly affect the level of developed thermal stresses in ceramic coatings and accelerated fatigue of coatings subjected to thermal stresses. Ceramics Y$_2$O$_3$ and CeO$_2$ have proven to be more reliable stabilizers for ceramics ZrO$_2$.

Microhardness increase is not as high as in TBC system 1, which indicates that in these coatings there was no fatigue or complete transformation of the tetragonal phase into the monoclinic phase (t → m). The increase in microhardness of ceramics ZrO$_2$Y$_2$O$_3$ for 34 completed cycles was 62 HV$_{0.1}$ and 43 HV$_{0.1}$. A larger increase was obtained for the layers deposited on a cold substrate with a higher content of pores (~29%). For layers ZrO$_2$CeO$_2$Y$_2$O$_3$, increase in microhardness for 10 completed cycles was low, 46 HV$_{0.1}$ and 43 HV$_{0.1}$. A slightly greater increase in microhardness was observed in layers with higher pore content (18%). Otherwise, ZrO$_2$CeO$_2$Y$_2$O$_3$ layers were deposited with the smallest pore content. Generally, for all TBC systems, greater increase in microhardness was observed for layers deposited on cold substrates with higher pore content.

Metallographic examination of samples with deposited TBC systems have shown that the high thermal load at 1200°C caused the deformation of the substrate, growth and expansion of existing microcracks into macrocracks, and the emergence of new microcracks in the ceramic layers. Figs. 11–13 show the microstructure of TBC systems deposited on preheated samples after thermal cyclic tests. Generally, for all TBC systems there was no flaking of lay-
Results of experimental examination of the TBC system 1 (NiCrAlCoY2O3/ZrO2MgO), TBC system 2 (NiCrAlCoY2O3/ZrO2 CeO2Y2O3) and TBC system 3 (NiCrAlCoY2O3/ZrO2 CeO2Y2O3) enable evaluation of insulating properties and behaviour of coatings in thermal cyclic conditions. It is shown that stabilizers MgO, Y2O3 and CeO2 have great influence on the stability of ZrO2, insulating properties and behaviour of the TBC systems in cyclic conditions.

On the surfaces of all ceramic coatings in deposited state, there was a network of microcracks as a result of stress that occurs during deposition. The causes of formed microcracks are stresses arising from the difference of thermal gradients in the particles during cooling and expansion coefficients of the previously deposited layers. Substrate with a pre-deposited layer limits the contraction of deposited particles after extinguishing.

The best insulation properties and the largest drop in temperature \( \Delta T = 410 \, ^\circ C \) were obtained for ceramic layers ZrO2CeO2Y2O3, although they had the smallest proportion of pores and were the most dense. The worst insulation properties, \( \Delta T = 240 \, ^\circ C \), are obtained for ceramic layers ZrO2CeO2Y2O3, because they were thinner than the previous two layers. The thermal conductivity and thickness of the ceramic layers had the most significant effect on the insulating properties of ceramic layers.

The microhardness values of bond layers NiCrAlCoY2O3 after thermal cyclic tests were directly related to the number of thermal cycles performed. The largest increase in microhardness was obtained for layers with the highest number of cycles performed. The cause of the increase in microhardness is exposing samples to high temperatures, which leads to oxygen diffusion and inter-diffusion of the chemical elements on the interface between the coating and substrate.

Of the ceramic coatings, the largest increase of microhardness was observed for ZrO2MgO layers with the lowest number of completed cycles. Oxide MgO proved to be a bad stabilizer for ZrO2 ceramics at 1200 \( ^\circ C \). Ceramics ZrO2Y2O3 and ZrO2CeO2Y2O3 with a larger number of completed cycles showed significantly lower microhardness increase, indicating that Y2O3 and CeO2 and Y2O3 together are good stabilizers for ZrO2 ceramics. The increase in microhardness is also influenced by the higher content of pores in the coating. Higher porosity significantly affects the level of stress in the ceramic coatings that accelerate fatigue of coating subjected to thermal stresses.

Metallographic studies showed that the high thermal load at 1200 \( ^\circ C \) caused the deformation of the substrate, the growth and expansion of existing microcracks into macrocracks and the emergence of new microcracks in the ceramic layers. Ceramic layer ZrO2MgO showed the worst microstructure. Microstructure indicates that in some places there was destruction and fatigue of the ceramic due to tetragonal phase transformation to monoclinic phase (t \( \rightarrow \) m). The largest number of macrocracks and microcracks were present in the ceramic layer ZrO2Y2O3 with the maximum number of completed cycles. The most pronounced vertical macrocracks were present in ZrO2CeO2Y2O3 layers because this type of ceramics has the lowest thermal expansion coefficient compared to the substrate.

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References


