JTTEE5 6:449-455

Plasma-Sprayed Duplex and Graded Partially Stabilized Zirconia Thermal Barrier Coatings: Deposition Process and Properties

J. Musil, M. Alaya, and R. Oberacker

(Submitted 15 September1996; in revised form 14 June 1997)

Atmospheric plasma spraying of duplex and graded ZrO_2 (8% Y_2O_3) thermal barrier coatings (TBCs) on Inconel 617 substrate with a NiCrAlY bond coat is described in terms of a deposition process of controlled coating structure. Special attention is devoted to the dominant spray parameters and the injector configuration for powder feeding, which play a fundamental role in graded coating deposition with controlled formation of a graded metal-ceramic (GMC) intermediate zone. The results of the graded coating spraying allow: (a) suppression of step-interface effects, (b) suppression of large differences (misfit) between physical and mechanical constants of the coating and those of the substrate material, and (c) favorable intergrowth of crystallites for a microstructurally integrated structure. Sprayed TBCs were investigated and compared with regard to their thermal cycling, oxidation behavior, and mechanical properties.

The influence of crystal anisotropy changes on the resulting coating structure and properties is shown. On the basis of finite element (FE) calculations, the stress distribution within thermally cycled coating systems was analyzed. It is confirmed that the graded coating structure relaxes considerably the stresses resulting from the internal constraint due to thermal expansion difference between both metallic and ceramic materials. This stress distribution also decreases the gradient of elastic deformation and/or residual stresses between the metal bond coat and top ceramic coating, and hence leads to a better thermal cycling behavior of the graded TBC systems. However, this advantage is not practical in every case, since the rapid oxidation of the metallic lamellae causes the ceramic phase in the GMC zone to undergo tensile stresses within a short thermal exposure time. The lifetime of duplex TBC systems that are under steady-state thermal load conditions is much higher than that of graded ones.

Keywords duplex coatings, graded coatings, interface zone, mechanical properties, oxidation, stresses, texture, thermal cycling

1. Introduction

The development of thermal barrier coatings (TBCs) has led to highly efficient thermal barrier systems for gas turbines, diesel and natural gas engines, and fuel burners. Plasma spray deposition is a most attractive method to form TBCs of thicknesses between 400 and 3000 μm. Thermal barrier coating development has focused on partially stabilized zirconia (PSZ) coatings, which typically consist of ZrO_2 ceramics alloyed with stabilizing additions of Y_2O_3, MgO, CaO, $2CaO\text{-}SiO_2$, CeO_2, or Sc_2O_3. These oxide TBCs give optimum performance with about 8 to 20% porosity by adding to the insulating value of the coating and increasing the apparent toughness, stemming from its intrinsic network of microcracks and pores that absorbs crack energy (Ref 1).

In systems operating under a high thermal flux and large thermal gradient, in addition to thermal stability, the coatings should have good resistance to damage under thermal cycling. A number of approaches have been tried to improve the thermal cycling resistance, mechanical properties, and oxidation resistance of TBCs. These can be divided into three targets: (a) lowering the Young's modulus of the TBCs, (b) reducing the mismatch between the coefficients of thermal expansion (CTE) of the bond and the top ceramic coat, and (c) increasing the high-temperature oxidation resistance. So far, many methods of improving coating properties have been performed by using PSZ. Techniques include the promotion of segmented and microcracked structures (Ref 2-4), further development of stabilizing elements (Ref 5), advanced ceramics (Ref 4) using residual stress control (Ref 6), phase-composition controlled deposition (Ref 7, 8), microcrack formation and coating densification by laser irradiation (Ref 9), and formation of graded coating structures (Ref 10-12).

This paper summarizes a spraying process for graded coatings. Attention is devoted to the reproducible formation of a graded metal-ceramic (GMC) zone and top ceramic coat with prescribed properties. The experiments compare a graded TBC with a conventional duplex TBC, taking into consideration the transient and steady-state temperature loading conditions. The thermal cycling and oxidation behavior and basic mechanical properties of both types of TBC systems are compared and discussed on the basis of results of thermal cycling and thermal aging tests, FE calculations, x-ray powder diffraction (XRD),

J. Musil, SKODA a.s., Tylova 57, 316 00 Plzen, Czech Republic, and **M. Alaya** and **R. Oberacker,** Institute of Ceramics, University of Karlsruhe, Haid-und-Neu-Str. 7, D-76131 Karlsruhe, Germany.

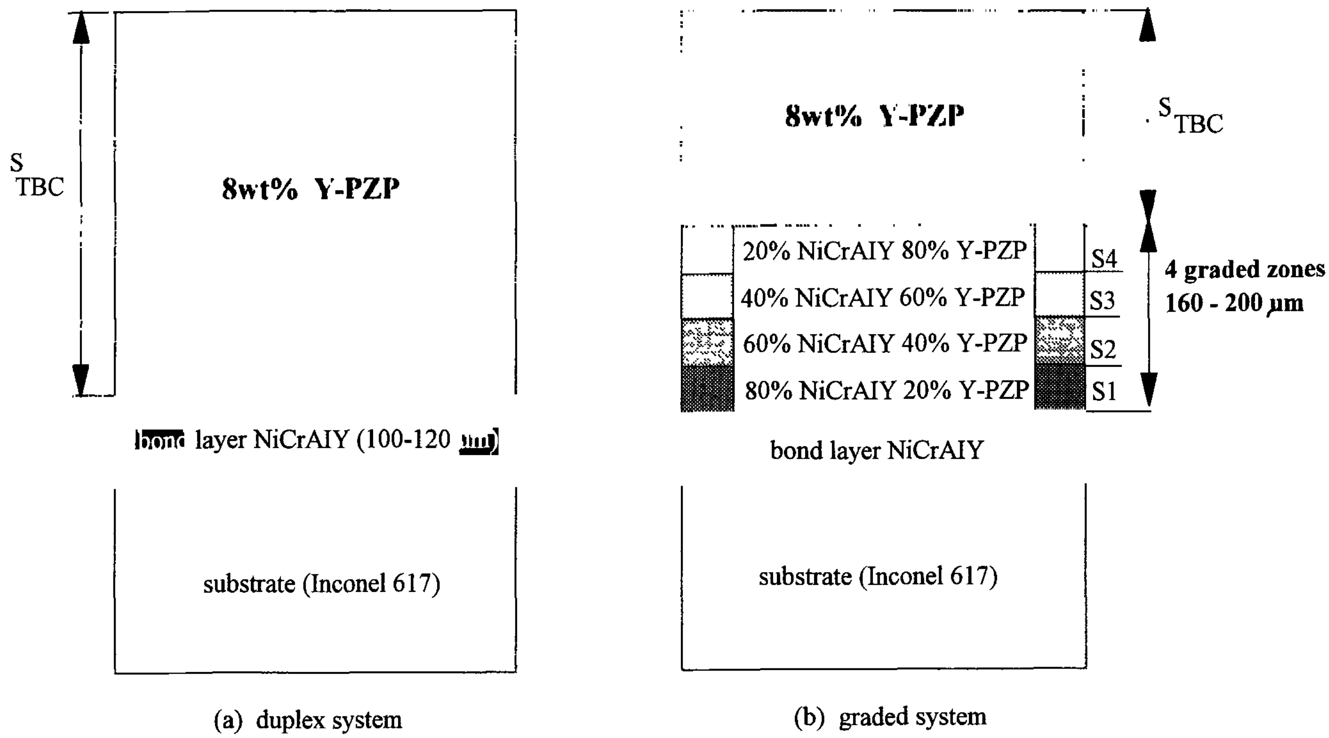

Fig. 1 Concept of TBC PSZ coatings. (a) Duplex system. (b) Graded system

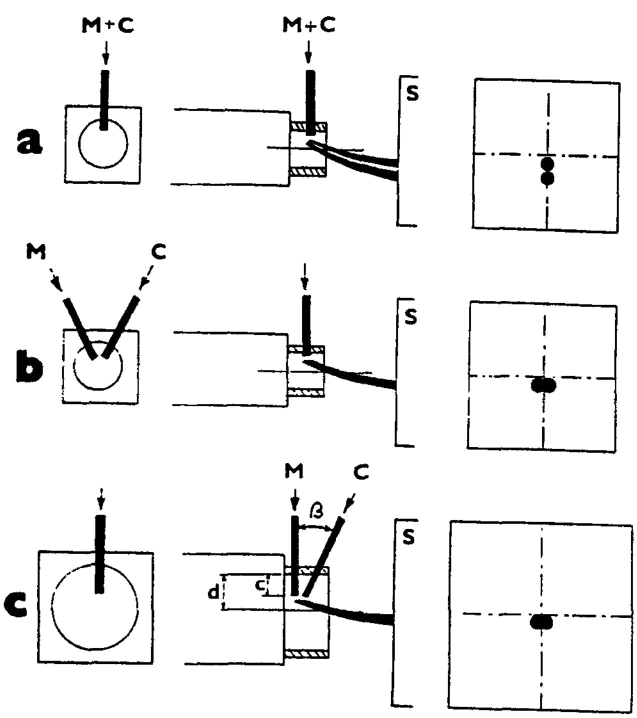

Fig. 2 Injector configuration and scheme of simultaneous deposition of metal and ceramic particles. (a) Premixed powder feeding. (b) Individual parallel injection ports. (c) Individual series injection ports (present work). M, NiCrAlY powder; C, ZrO_2 (Y_2O_3) powder; S, substrate

texture and scanning electron microscopy (SEM) structural analysis, and adhesive-cohesive measurements.

2. Experimental Details

2.1 *Spraying Process*

The TBCs were sprayed using a PT A 3000 S microprocessor-controlled atmospheric plasma spraying (APS) system. The relative movement between the plasma torch and substrate was performed by a robotic system. In our experiments Amdry 962 NiCrAlY (Cr = 22 wt%, Al = 10 wt%, Y = 1.0 wt%) and PT 1085 ZrO_2 (8% Y_2O_3) powders were used for APS spraying onto Inconel 617 superalloy. The duplex TBCs were plasma sprayed by a conventional procedure, whereas the graded coatings were plasma sprayed with the composition varying from 100% metal applied directly to the substrate to 100% ceramic for the top coat (Fig. 1). The substrate temperature distribution was measured by a multichannel measuring instrument, and substrate temperature (T_S) was held constant during spraying in all experiments (130 to 150 °C). The powder feed rate was controlled by computerized mass flow of the twin powder feeder.

The main goal in the production of graded coatings is the reproducible deposition of a GMC zone through controlled flight and impingement of metal and ceramic particles, and their mutual mixing, overlapping, spreading, and distribution in the growing GMC zone. The correlation between the dominant deposition parameters and the impingement of the particles, their spreading, mutual overlapping, and distribution is described by the coefficient of homogeneity (COH) (Ref 11):

$$\mathrm{COH} \sim k \cdot \frac{1}{ctg\beta} \cdot \frac{P_e \Phi_{Ar}}{d_{S-T} \Delta\Phi_{PG}} \cdot \frac{1}{\Delta\lambda\Delta T} \quad \text{(Eq 1)}$$

where k is a constant ($k = \pi_i k_i$) including limiting deposition and scale factors of individual spray parameters i; $1/ctg\beta$ (see Fig. 2) is the influence of the injector arrangement and geometry of powder feeding; $P_e\phi_{Ar}/d_{S\text{-}T}\Delta\phi_{PG}$ is the influence of the dominant spray parameters: P_e (kW) electrical power, ϕ_{Ar} (L/min) argon plasma gas flow rate, $d_{S\text{-}T}$ (mm) spraying distance, $\Delta\phi_{PG}$ (L/min) magnitude difference of carrier gas flow rates of metal and ceramic powder feeding; and $1/\Delta\lambda\Delta T$ is the basic properties of the sprayed powder (i.e., magnitude differences of melting temperatures and thermal conductivities of metal and ceramic powder materials, ΔT (K) and $\Delta\lambda$ (W/mK), respectively).

For our experiments, when $k = 6.5 \times 10^{-4}$ and the injector arrangement is fixed at $\beta = 20°$, $c = 5.10^{-3}$ m, and $d = 8.5 \times 10^{-3}$:

$$\text{COH} \sim 3.57 \times 10^{-1} \cdot \frac{P_e\Phi_{Ar}}{d_{S\text{-}T}\Delta\Phi_{PG}} \cdot \frac{1}{\Delta\lambda\Delta T} \qquad \text{(Eq 2)}$$

For example, COH = 1 when metal and ceramic particles are sprayed onto the same spot on the substrate, where the mutual overlapping is 100%, and COH = 0.5 where the metal and ceramic particle overlapping is 50%.

2.2 *Analysis and Evaluation of TBCs*

2.2.1 Structural Analysis

Coating structure was studied by XRD texture analysis using a D-500 Siemens diffractometer with Euler four-circle arrangement, Siemens/Tex software, and orientation distribution function (ODF) analysis. For residual stress measurement, the low x-ray penetration depth due to a high absorption and structural defects and heterogeneity imply that the $\sin^2\varphi$ relationship commonly used to analyze macroscopic stresses is ineffective and/or misleading for plasma-sprayed coatings. An alternative method, which assumed a residual strain estimation of $\varepsilon = (d_i - d_0)/d_0$ normal to the surface, was therefore chosen (Ref 13). The terms d_i and d_0 are the interplanar spacings of measured and standard specimens, respectively. Further, standard procedures of SEM observation (JEOL JSM 840) and electron dispersive x-ray analysis (EDAX, LINK 860) were used.

2.2.2 Thermal Cycling and Oxidation Behavior

Thermal cycling tests were conducted on a burner rig with a C_2H_2/O_2 torch. The specimens were intermittently heated to a well-defined temperature of the substrate T_S (e.g., 1000 °C) and cooled to 60 °C by forced air. The specimens were removed from the test when they exhibited 30% ceramic coating spallation or when the number of cycles reached 1000 without any spallation (Ref 14).

In order to assess the level of thermal stresses that resulted from thermal cycling, FE analyses were carried out with the ABAQUS code. The components of the TBCs were assumed to be isotropic and homogeneous and their elastic and thermophysical parameters were assumed to be temperature independent. The generalized plane-strain state was adopted to simplify the calculations. Linear elastic behavior of all components was assumed. The temperature distribution during the heating and cooling phases is shown in Fig. 3.

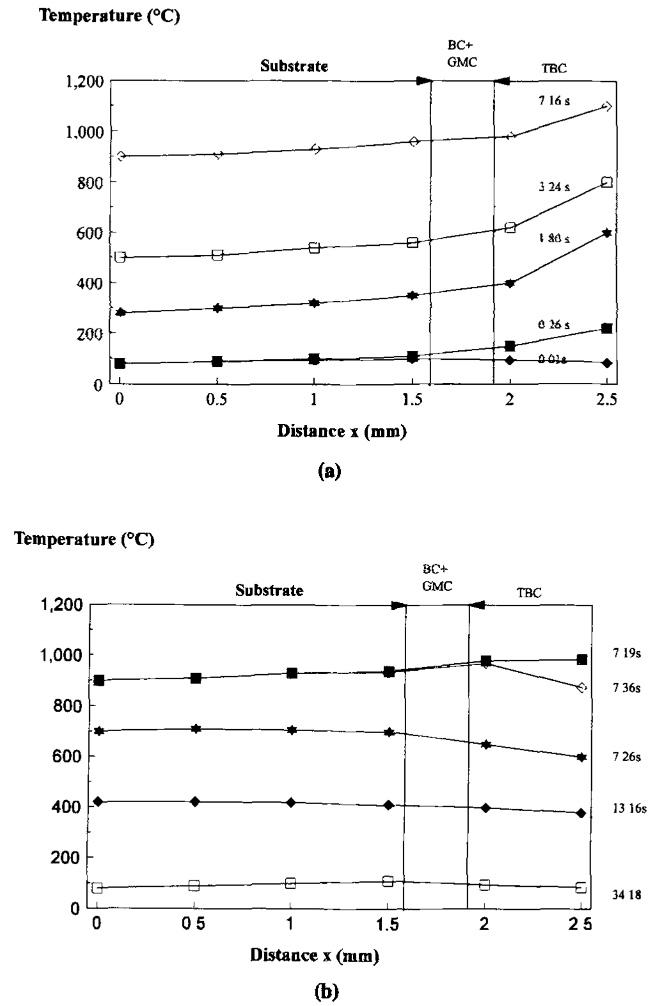

Fig. 3 Temperature distribution in the coating-substrate system. (a) During the heating phase. (b) During the cooling phase

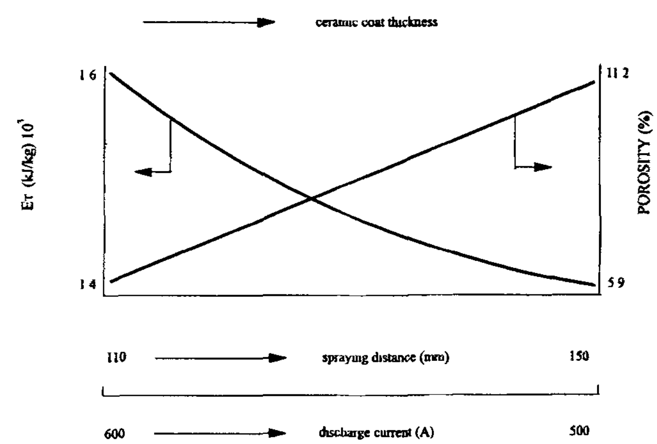

Fig. 4 The deposition conditions for spraying of the ceramic top coat

The results of the thermal cycling tests shown do not take into account the effect of long-term oxidation, because the thermal cycles do not include a dwell time at high temperature. Duplex and graded systems were thermally aged at 950 and 1000 °C in air for different exposure times (1, 10, 100, and 250 h) (Ref 14).

2.2.3 Mechanical Properties

The adhesive-cohesive strength was determined by a standard tensile test and by measuring fracture toughness by analyzing the half-cone fracture formation on a coating cross section during scratch test measurements (AMI scratch tester CSEM-Revetest, Micro Photonics Inc., Allentown, PA) (Ref 11).

3. Results and Discussion

3.1 *Plasma Spray Process*

The following conclusions for the APS spraying of graded TBC PSZ coatings are valid:

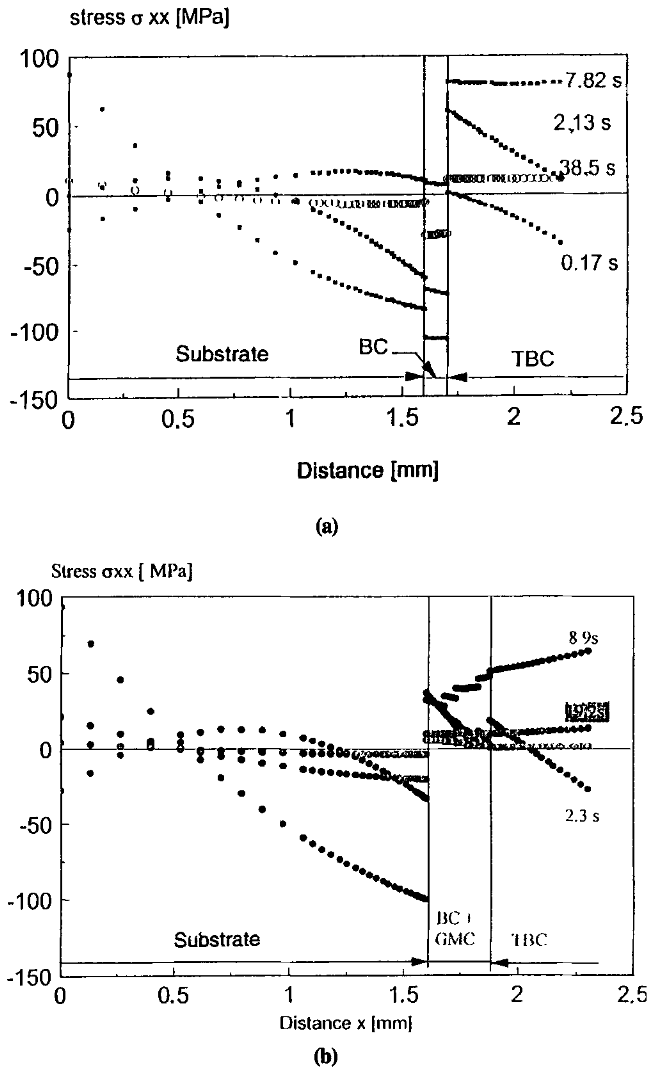

Fig. 5 Calculated stress distributions. (a) For a duplex coating. (b) For graded coating

- Increasing plasma current I_D (electric power P_e), I_D ~ 500 → 700 A, increases particles velocity and improves the homogeneous overlap and mutual mixing and distribution of metal and ceramic particles in the growing GMC zone. Furthermore, the efficiency and regularity of particle melting increases. Particle melting is also affected by increasing the high-temperature region in the radial direction of the plasma stream. Increasing I_D also increases the electrical conductivity and power and enthalpy of plasma. Increasing I_D from 500 to 700 A increases the COH from 0.5 to 0.8.
- Increasing ϕ_{Ar} from 42 to 50 L/min accelerates the dc arc; therefore, particle velocity increases and the required overlap for mutual mixing is higher, so that the COH approaches 0.8.
- Increasing ϕ_{H2} from 8 to 15 L/min increases the plasma enthalpy and heat transfer to particles and is responsible for undesirable separation of overheated metal particles during their spreading. Further, when the hydrogen content increases the isocontour diameter is smaller and plasma stream constriction increases, which increases the separate focusing of the impinging particle spots.
- Decreasing I_D (from 700 to 500 A) and increasing the deposition distance $d_{S\text{-}T}$ (from 110 to 150 mm) during the spraying of the top ceramic coat, together with intensive cooling, decreases the thermal energy E_T brought to the substrate and keeps the surface temperature of the growing ceramic coat constant (T_S ~ 120 °C), which increases the coating porosity (Fig. 4).
- Decreasing I_D is very favorable from the point of view of the growth structure of zirconia. PSZ coatings sprayed at I_D = 500 to 550 A have smaller columnar grains than those sprayed at I_D = 700 to 750 A. Coatings with splats composed of smaller columnar grains exhibit better lifetime and reliability under thermal and mechanical stresses.
- Decreasing the electrical power into the plasma P_e by decreasing I_D (to 500 A) allows more passes of the plasma torch with less thickness of layer per pass. Intensive cooling and the greater substrate mass influence the reduction of residual stresses in the coating.
- The choice of P_e needs to be determined very carefully, because increasing P_e (increasing I_D) by 20 to 30% decreases the monoclinic phase in PSZ coating from 7 to 1 wt%. This

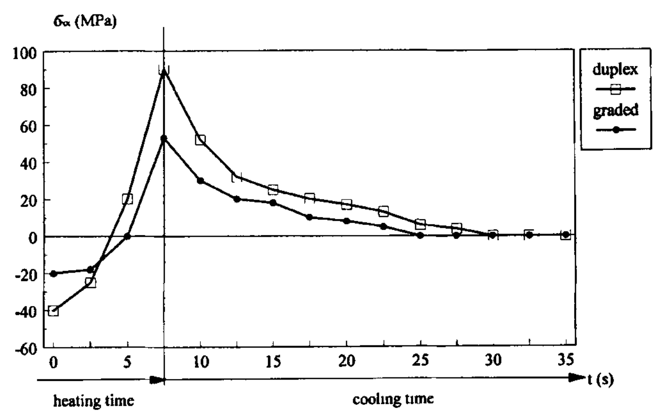

Fig. 6 The thermal stress course vs. time for duplex and graded TBC coatings

phase change is important, for example, when I_D is changed from 500 to 600 A.

3.2 *Thermal Cycling Behavior*

The calculated stress distributions at different times of the same thermal cycle are shown in Fig. 5. The selected times are the beginning, the end of the heating phase, and the end of the cooling phase. The stress level in the bond coat is higher than the yield strength, and thus the resulting plastic deformation of the bond coat at high temperature leads to a reduction of the tensile stresses in ceramics during cooling (Ref 14, 15).

Further FE calculations indicate that it is possible to eliminate or reduce the discontinuities in the stress distributions that result from the transient load conditions and the mismatch between the CTEs of the components if there is a GMC zone between the bond coat and the ceramic top coat. As well, the stress concentrations are reduced at free edges. From Fig. 6, where the course of the stress on the top surface of the ceramic coating is shown for both the graded and the duplex systems, it can be seen that the resulting thermal stresses are lower for the graded TBC system than for the duplex one (Ref 15).

Orthogonal cracks open in the ceramic top coat and grow due to tensile stresses during cooling. The number and the growth rate of the orthogonal cracks depend on the load level. With further thermal cycling, a bifurcation of one or a few cracks can be observed 40 to 50 μm above the bond coat (for the duplex TBC) or above the graded zone (for the graded TBC).

The better thermal cycling resistance of graded TBC systems is demonstrated in Fig. 7. A degradation due to the thermal cycling can be seen in the graded zone only at temperatures above 800 °C, while cooling from this temperature leads to instantaneous failure of the duplex systems. This fact may be ascribed to the reduction of tensile stresses in the ceramic and the mismatch of the CTEs of the ceramic top coat and the bond coat.

Based on texture analysis and an ODF calculation, the distribution of crystallographic planes was determined. It was found that decreasing the metal particle content affected preferential growth of (111) planes of PSZ ceramics owing to heat removal and, consequently, a change of solidification and crystallization processes. It is demonstrated that the graded zone decreases the texture intensity of PSZ (Fig. 8) by providing a randomless crystal orientation and, therefore, suppressing a low-energy path for possible crack growth inside the grade zone. The XRD measurement shown in Fig. 9 confirms the important role of a graded zone that decreases the gradient of elastic deformation and/or residual stresses between NiCrAlY bond coat and ZrO_2 top coating (Ref 15).

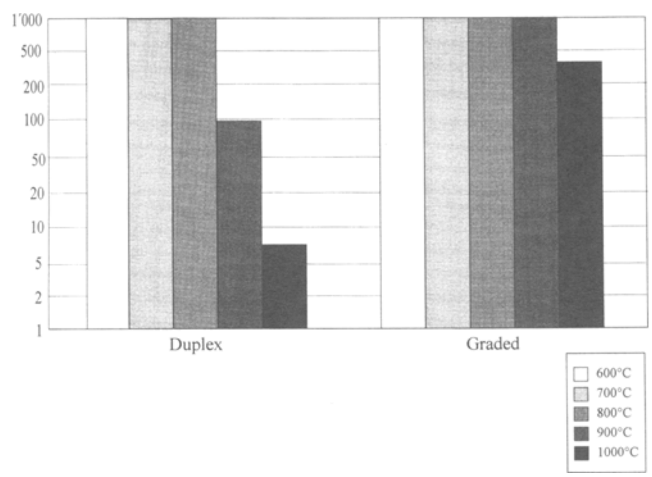

Fig. 7 Number of cycles to failure vs. temperature

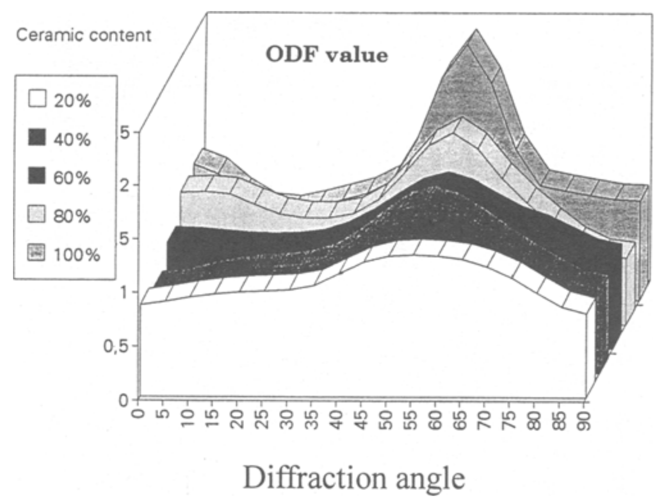

Fig. 8 Orientation distribution function of texture intensity vs. metal-ceramic ratio in graded coating

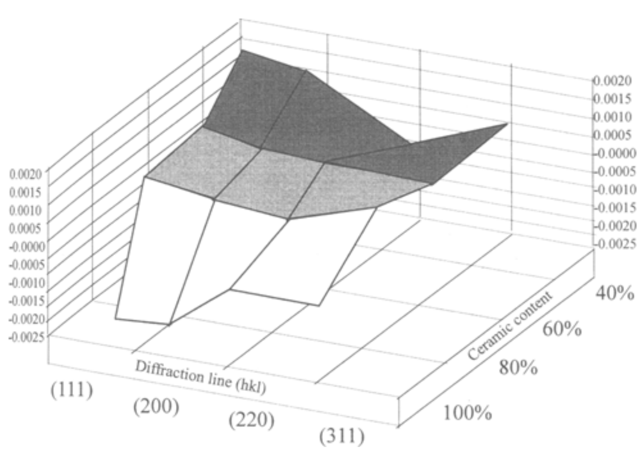

Fig. 9 Elastic deformation vs. metal-ceramic ratio in graded coating

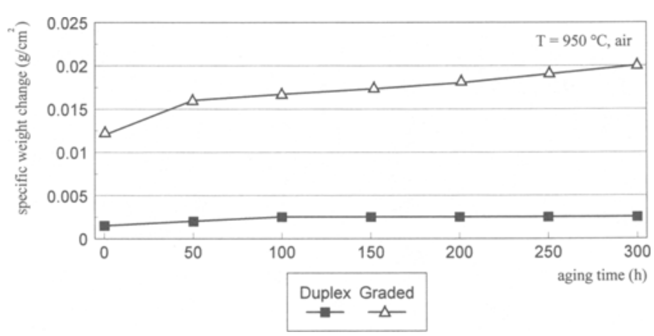

Fig. 10 Specific weight change vs. aging time for duplex and graded TBC coatings

3.3 *Oxidation Behavior*

The results of the thermal cycling tests shown do not take into account the effect of long-term oxidation, because the thermal cycles are without any dwell time at high temperature. For this reason, duplex and graded systems were aged at 950 and 1000 °C in air for different exposure times (1, 10, 100, and 250 h).

Figure 10 shows the specific weight change versus exposure time for the graded and duplex TBC systems. The difference in specific weight change can be attributed to the structure of the graded zone, where the isolated metallic particles with a high surface-to-volume ratio rapidly oxidize. Different stages of oxidation can be observed, depending on the size of the metallic particles. Based on XRD analysis and SEM and EDAX observation, it is possible to explain the degradation process by reference to Fig. 11.

At up to 250 h the oxidation does not seem to affect the integrity of duplex TBC systems. In contrast to oxidation of duplex TBC systems, the oxidation of the graded zone is a lifetime-limiting factor and affects the integrity of graded TBCs, even after a rather short exposure. Many lateral cracks appeared in the graded zone of a TBC after thermal exposure at 1000 °C/250 h in air. This occurred in the upper part of the graded zone and arose from a change in the residual stress state caused by the oxidation of the metallic lamellae in the graded zone. Oxidation is also a lifetime-limiting factor for duplex TBC systems, but the lifetime of duplex TBC systems that are under steady-state thermal load conditions is much higher than that of graded ones (Ref 15).

Table 1 Tensile test (*P*) and fracture toughness (K_c) of graded and duplex coatings (12 tested samples for each coating)

	P, MPa	K_c, MN/m$^{3/2}$
Graded coatings	27-30	6.0-6.4
Duplex coatings	18-20	3.7-3.9

3.4 *Mechanical Properties*

The adhesive-cohesive mechanical strength of the coatings was obtained from the tensile test and by measuring fracture toughness by analyzing the halfcone fracture formation during scratch test measurements on cross sections of coating-substrate systems (Ref 11). The results, shown in Table 1, confirm the importance of a graded structure in improving the strength of TBCs.

4. Conclusions

The expected improvement of thermal cycling resistance and strength due to the gradation in composition between the ZrO_2 coat and the bond coat in TBC systems has been demonstrated, described by XRD texture analysis, and quantitatively explained from numerically derived stress distributions during thermal cycling tests. However, this advantage may not be prac-

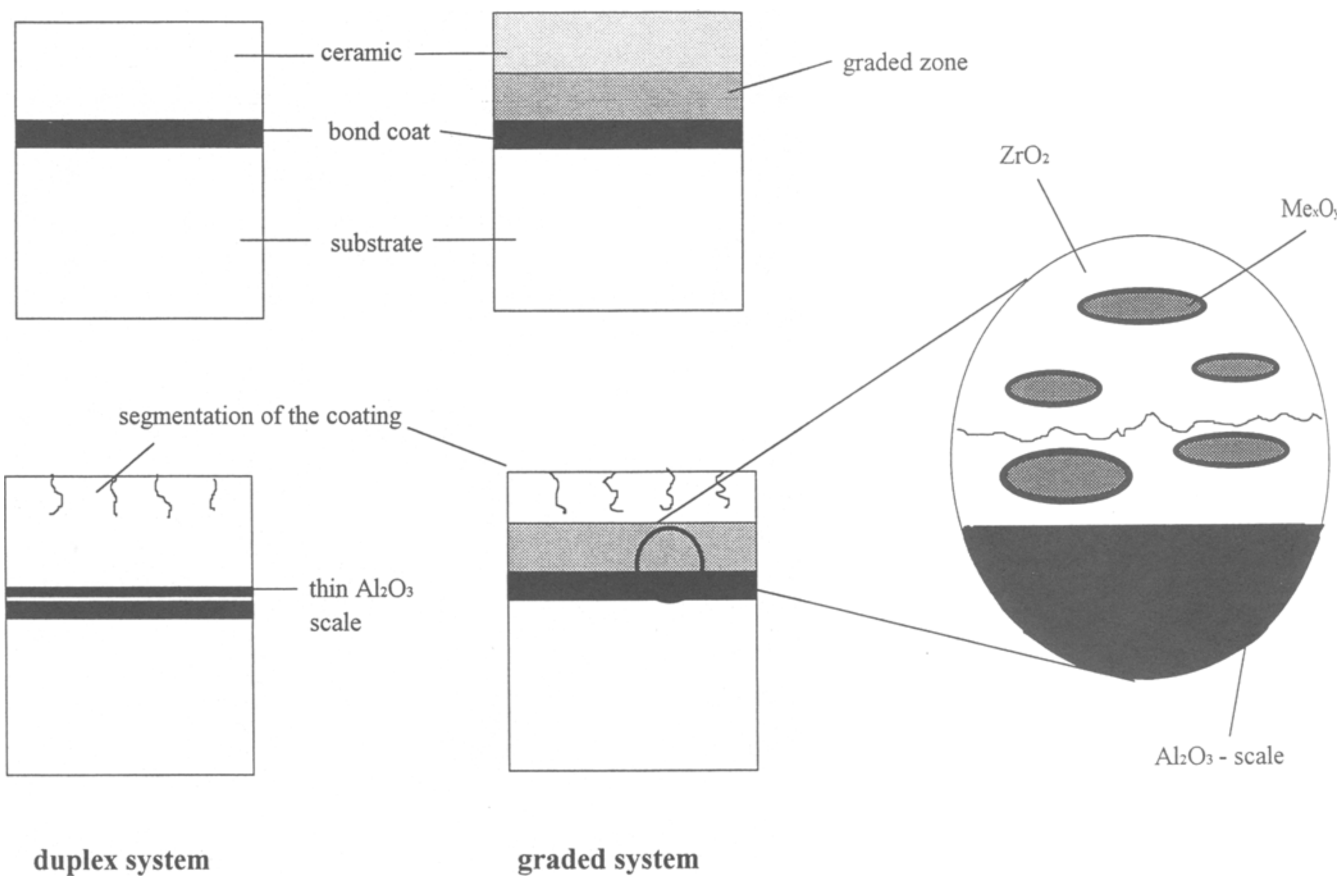

Fig. 11 Scheme of degradation process under steady-state thermal load condition

tical in every case, because rapid oxidation of the metallic lamellae causes the ceramic phase in the graded zone to undergo tensile stresses within a short thermal exposure time. The tensile stresses lead to delamination of the ceramics in the upper part of the graded zone. Moreover, the rapid growth of the oxide scale at the metallic lamellae leads to a reduction of the metallic component in the graded zone and changes the ratio of metallic to ceramic phase, therefore affecting the gradient of elastic and thermophysical properties of the graded zone.

References

1. R.W. Smith and R. Novak, Advances and Applications in U.S. Thermal Spray Technology, Part I: Technology and Materials, *Powder Metall. Int.*, Vol 23 (No. 3), 1991, p 147-155
2. R.J. Bratton and S.K. Lau, Advances in Ceramics, *Science and Technology of Zirconia*, Vol III, A.H Heuer and L.W. Hobbs, Ed., American Ceramic Society, 1981, p 226-248
3. P.E. Hodge, S. Stecura, M.A. Gedwill, I. Zaplatynsky, and S.R. Levine, "Thermal Barrier Coatings: Burner Rig Hot Corrosion Test Results," NASA TM-79005, NASA Lewis Research Center, Cleveland, OH, 1978
4. H. Nakahira, Y. Harada, N. Mifune, T. Yogoro, and H. Yamane, Advanced Thermal Barrier Coatings Involving Efficient Vertical Microcracks, *J. Therm. Spray Technol.*, Vol 2 (No. 1), 1993, p 51-57
5. J.D. Reardon and M.R. Dorfman, Advanced Thermal Barrier Coating System, *J. Mater. Energy Syst.*, Vol 8 (No. 4), 1987, p 414-419
6. M.K. Hobbs and H. Reiter, Residual Stresses in ZrO_2-8% Y_2O_3 Plasma Sprayed Thermal Barrier Coatings, *Proc. National Thermal Spray Conf.*, D.L. Hauck, Ed., ASM International, 1987, p 285-290
7. N.R. Shankar, C.C. Berndt, and H. Herman, Phase Analysis of Plasma Sprayed Zirconia Yttria Coatings, *Ceram. Eng. Sci. Proc.*, Vol 3 (No. 9-10), 1983, p 784-791
8. M.C. Foujanet, J.P. Lumet, and J.L. Derep, Structural Analysis of Zirconia-Alumina Plasma Sprayed Coatings, *Proc. First Plasma Technik Symposium*, Vol 2, H. Eschnauer, P. Huber, A.R. Nicoll, and S. Sandmeier, Ed., Plasma-Technik AG, 1988, p 357-366
9. K. Nezaki, Y. Nakanishi, R. Katsutani, N. Morishige, T. Irisawa, and T. Ota, Effect of Laser Cracking Method: Improvement of Failure Characteristics of Thermal Barrier Coatings, *Proc. Jpn. Welding Soc.*, Vol 47, 1990, p 184-185 (in Japanese)
10. D.S. Duvall and D.L. Ruckle, "Ceramic Thermal Barrier Coatings for Turbine Engine Components," Paper 82-GT-322, ASME, 1974, p 1-9
11. J. Musil and J. Fiala, Plasma Spray Deposition of Graded Metal-Ceramic Coatings, *Surf. Coat. Technol.*, Vol 52, 1992, p 211-220
12. J. Musil, J. Filipensky, J. Ondrácek, and J. Fiala, Plasma Spraying Deposition of Graded Thermal Barrier Coatings, *ASM Advances in Coating Technology: Proc. Int. Thermal Spray Conf.*, C.C. Berndt, Ed., ASM International, 1992, p 525-530
13. J. Zeman, M. Cepera, J. Musil, and J. Filipensky, Grinding Induced Effects in Plasma Sprayed Zirconia Coatings, *J. Therm. Spray Technol.*, Vol 2 (No. 4), L'Ecole Polytechnique, 1993, p 351-356
14. M. Alaya, G. Grathwohl, and J. Musil, A Comparison of Thermal Cycling and Oxidation Behaviour of Graded and Duplex ZrO_2 Thermal Barrier Coatings, *Third Int. Symposium on Functional Gradient Materials Proc.*, L'Ecole Polytechnique, 1994, p 524-530
15. J. Musil, M. Alaya, and R. Oberacker, Thermal Cycling, Oxidation Behaviour and Mechanical Properties of Graded and Duplex PSZ TBC Coatings, *Proc. 12th Int. Symposium on Plasma Chemistry*, Vol II, J.V. Heberlein, D.W. Ernie, and J.T. Roberts, Ed., University of Minnesota, 1995, p 915-920