Formation of vertical cracks in solution-precursor plasma-sprayed thermal barrier coatings

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Abstract

When tailored to make durable thermal barrier coatings (TBCs), the Solution Precursor Plasma Spray (SPPS) process produces a microstructure containing uniformly vertical cracks. These cracks provide a high degree of strain tolerance to the ceramic top coat. In order to understand the formation of vertical crack in SPPS process, coatings of various thicknesses were deposited on a variety of substrates with vastly different thermal properties. These coatings were characterized in the as-sprayed state and after heat treatment. It has been determined that the tensile stress derived from the pyrolysis of precursor occurring during coating deposition or post heat-treatment is the major driving force for the formation of vertical cracks in SPPS TBCs.

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1. Introduction

Ceramic thermal barrier coatings (TBCs) of 6–9 wt.% Y₂O₃–ZrO₂ (7YSZ) are widely used to protect and to insulate metallic components in gas-turbine engines from high temperatures, which can prolong the lifetime of the component and/or increase the allowable operating temperatures (see, e.g., overview articles by Miller [1,2], Jones [3], Evans et al. [4], and Padture et al. [5] and references therein). TBCs are subjected to cyclic thermal environment in service. As a result, residual stresses are generated in the coating due to the differences in the coefficient of thermal expansion (CTE) between the ceramic coating and the metallic substrate. In order to achieve high durability in TBCs, the ceramic top-coat is required to have some capability to tolerate the resulting thermal strain or to be “strain tolerant”.

The two commercial processes used for the deposition of TBCs are air plasma spray (APS) and electron-beam physical-vapor deposition (EB-PVD). APS TBCs are relatively low-cost, have lower thermal conductivities relative to EB-PVD TBCs, but are generally less durable [1–5]. In order to increase the durability of APS TBCs by improving the strain tolerance of the coating, Taylor [6] developed dense vertically cracked (DVC) APS TBCs. The DVC TBCs have a density greater than 88% of the theoretical density. A majority of vertical cracks runs normal to the ceramic/metal interface and has a length greater than half of the coating thickness. Improved thermal cyclic durability has been reported for the DVC TBCs compared to the normal APS TBCs [6].

In the APS process, the coating is formed by the accumulation of splat layers deposited each time the plasma torch passes over the substrate. The vertical cracks in DVC TBCs are generated through the alignment of micro vertical cracks produced in each splat layer due to shrinkage of the deposited splats [6]. It was found that if the coating density is less than about 88% of the theoretical density, the shrinkage strain can be absorbed or compensated by the porosity, which prevents the formation of the vertical cracks [6]. The improved stain tolerance of DVC TBCs is partially offset by the higher thermal conductivity associated with the higher coating density.
Recently, it has been demonstrated that Solution Precursor Plasma Sprayed (SPPS) TBCs also possess vertical cracks [7–10], which contribute to their superior thermal cyclic durability [11,12]. In the SPPS process, an aqueous chemical precursor, containing Zr and Y, is injected directly into the plasma jet. The atomized precursor droplets undergo rapid evaporation and breakup in the plasma flame. This is followed by precipitation or gelation, pyrolysis and melting in the plasma flame. Together with the pyrolyzed and/or molten 7YSZ ceramic particles or droplets, precursor at various reaction stages also reaches the substrate. When a coating thicker than 150 μm is sprayed, most of the precursor on the substrate is pyrolyzed during coating deposition process due to the continuous heating of the plasma flame. In contrast to DVC coatings, the vertical cracks are formed in SPPS TBCs when the density of the coating is less than 85% of the theoretical limit [7–12]. Therefore, the mechanism for vertical crack formation in SPPS TBCs appears to be different from what is observed in the DVC TBCs. This research is aimed at understanding the mechanism for vertical crack formation in SPPS TBCs.

2. Experimental procedures

In order to understand the mechanism of vertical crack formation in SPPS TBCs, a series of experiments have been conducted where substrate material, coating thickness, and post-coating heat treatment were systematically varied.

All coatings were sprayed using a direct current (DC) plasma torch (Metco 9 MB, Sulzer Metco, Westbury, NY). The plasma power used was in the range 35 to 45 kW. Ar and H₂ were used as the primary and the secondary plasma gases, respectively, whereas N₂ was used as the solution-precursor atomizing gas. The precursor used here was aqueous acetate and nitrate salts, to result in a 7 wt.% Y₂O₃–ZrO₂ (7YSZ) in the coating [7]. Substrates used in this work include: (i) copper, (ii) bond-coated Ni-base superalloy (NiCoCrAlY bond-coat, CMSX-4 single crystal superalloy), and (iii) fully-dense polycrystalline alumina. The thermal physical properties of these substrates, along with 7YSZ ceramic, are presented in Table 1. The thicknesses of the coatings were varied from 70 to 200 μm. The coatings on bond-coated Ni-base superalloy substrates were heat-treated at 300, 600, or 1121 °C for 1 h. All SPPS TBCs are deposited under the same processing conditions, the details of which can be found in previous publications [7–10].

All as-sprayed and heat-treated SPPS TBCs were cut to prepare the cross-sections. These cross-sections were then polished to a 1 μm finish using routine metallographic methods. The polished cross-sections of the SPPS TBCs were characterized using a scanning electron microscope (SEM) (ESEM 2020, Philips Electron Optics, Eindhoven, The Netherlands). Hardness measurements (Vickers indenter, 100 g load) were performed at random locations on the polished cross-section of the

Table 1

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Coefficient of thermal expansion (×10⁻⁶/°C)</th>
<th>Thermal conductivity (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>20.3</td>
<td>401.0</td>
</tr>
<tr>
<td>Superalloy (CMSX-4)</td>
<td>16.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Alumina</td>
<td>8.0</td>
<td>11.8</td>
</tr>
<tr>
<td>7YSZ</td>
<td>9.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Fig. 1. Microstructure of SPPS TBC on bond coated superalloy substrate. (a) 70 μm, (b) 100 μm, (c) 200 μm.
TBCs. The reported hardness value for each specimen is an average of 10 measurements.

The coating surface temperature was measured during the SPPS deposition process using a single-wavelength (7.92 μm) infrared pyrometer (Model 38-99C99, Ircon Corp., Niles, IL) that was previously calibrated against a black body oven in the temperature range 300 – 1000 °C. The pyrometer was fixed at a distance of 1m away from the substrate and was focused at the center of the sample (spot diameter 8 mm). The raw data output from the pyrometer was corrected to take into account the emissivity of ZrO₂ by using the data published by Liebert [13], which is a function of temperature and the coating thickness. The emissivity of the coating is given by [13]:

\[ e = 4.52e^{4.4x}T^{-0.725x+0.28} \quad 0.00 \leq x \leq 0.51 \text{ mm} \quad (1) \]

where, \( e \) is the emissivity; \( x \) is the thickness of the coating in mm; and, \( T \) is the actual surface temperature of the coating.

3. Experimental results

3.1. Effect of coating thickness

Fig. 1 shows the microstructures of the SPPS TBCs of thicknesses 70, 100, and 200 μm on the bond-coated Ni-based superalloy substrates. No vertical cracks are observed in the 70-μm coating. In contrast, vertical cracks appear in the 100 and 200 μm coatings, and the vertical crack density of the latter is higher. It was found that the average of the vertical crack spacing, the distance between two adjacent vertical cracks, decreases with increasing coating thickness, which is plotted in Fig. 2. It was also observed that majority of the vertical cracks connect to the top surface of the coating, but do not always connect to the ceramic/metal interface.

Fig. 3a is a schematic illustration showing the temperature measurement procedure. Fig. 3b shows the coating surface temperature during deposition of 70 and 100 μm thick coatings. Since the pyrometer is focused on a fixed spot (a diameter of 8 mm), the temperature increases as the plasma jet approaches that spot and then decreases as the jet moves away. It can be seen that the maximum coating surface temperature is ~700 °C for the 70 μm thick coating and 800 °C for the 100 μm thick coating. Coating surface temperature increases with increasing coating thickness due to the heating effect of the plasma jet. As shown in Fig. 4, the coating hardness is also found to increase with increasing coating thickness.

3.2. Effect of heat treatment

In order to study the effect of heat treatment, the 70 μm crack-free coating (Fig. 5a) was heat-treated for 1 h at three different temperatures. No vertical cracks were observed for a heat-treatment temperature of 300 °C (Fig. 5b). However, when the heat-treatment temperature was increased to 600 °C, vertical cracks can be observed in the coating (Fig. 5c). With a further increase in heat-treatment temperature, the vertical crack density increases significantly. Fig. 5d shows the effect of heat treatment on the coating hardness. It can be seen that the coating hardness increases with increasing heat-treatment temperature.

Fig. 2. Effect of coating thickness and 1-h post heat treatment at 1121 °C on vertical crack spacing (for coatings on bond coated superalloy substrate).

Fig. 3. Coating surface temperature profile during deposition of 70 and 100 μm thick coatings on bond coated superalloy substrate.

Fig. 4. Change of coating hardness with coating thickness for coatings on bond coated superalloy substrate.
increase in the heat-treatment temperature to 1121 °C, the density of vertical cracks was found to increase (Fig. 5d). The vertical-crack spacing for TBCs heat-treated at 1121 °C for 1 h is also shown in Fig. 2. It can be seen that the vertical-crack spacing attains a steady state value of ~115 μm, independent of the coating thickness. The coating hardness was found to increase slightly after the 1-h heat treatment at 300 °C. A significant increase in the coating hardness was noted at the higher heat-treatment temperatures (Fig. 6).

3.3. Effect of substrate properties

In order to determine the effect of thermal-expansion-mismatch stresses on the vertical cracking in SPPS TBCs, substrates of different coefficients of thermal expansion (CTE) were arranged side-by-side and coated at the same time. Table 1 lists the CTEs and the thermal conductivities of the three substrates used in this study: copper, Ni-base superalloy, and alumina [14,15]. Fig. 7 shows the microstructures of the coatings on the three different substrates. While no vertical cracks are visible in coatings on the Ni-base superalloy and copper substrates, vertical cracks can be seen in the coating on the alumina substrate. The hardness of the coating on alumina substrate is much higher than that of coatings on both the copper and Ni-base superalloy substrates (Fig. 8).

The maximum specimen surface temperature during the SPPS process was found to be 580 °C for the coating on copper substrate, 680 °C for coating on Ni-base superalloy substrate, and 780 °C for coatings on alumina substrate (Fig. 9).

Coatings of various thicknesses were also deposited on copper and alumina substrates, under identical conditions. It was found that a 20-μm coating on alumina substrate had no vertical crack, but vertical cracks did appear for a coating with a thickness of 40 μm. For coatings on copper substrates, no vertical cracks were visible for a 100 μm thick coating. However, when coating thickness exceeds 150 μm, vertical cracks were observed in the coating.

4. Discussion

The driving force for the formation of uniformly spaced vertical cracks in the 7YSZ TBCs is the in-plane tensile stress. During the deposition of SPPS coatings, in-plane tensile stresses can be generated as a result of: 1) thermal expansion mismatch between the ceramic top coat and the metallic substrate, 2)
transient cooling following deposition, and 3) pyrolysis of precursor incorporated into the coating. Stresses from thermal expansion mismatch and transient cooling are generated in APS coatings, as well. However, APS coatings deposited under similar conditions do not have vertical cracks. Therefore, stresses from pyrolysis of precursor incorporated into the coating are probably the major driving force for the formation of vertical cracks in SPPS TBCs. In order to confirm this conclusion, the contribution to vertical-crack formation of the stresses generated from the above-mentioned three sources are analyzed in the following section.

4.1. Thermal expansion mismatch stress

The thermal expansion coefficient of metallic substrate (16×10$^{-6}$ to 20×10$^{-6}$ °C$^{-1}$) is larger than that of the 7YSZ top-coat (9×10$^{-6}$ °C$^{-1}$) [14,15]. Therefore, thermal expansion mismatch stresses will be generated during coating deposition when the ceramic coating and metallic substrate are heated and cooled during successive passes of the plasma torch and after final cooling to room temperature.

During deposition, the temperature of the substrate and the coating increase with time (Fig. 9). As a result, in-plane tensile stresses are generated in the coating due to the larger CTE of the substrate. In order to investigate the contribution of tensile stress from substrate expansion, three substrates having different coefficients of thermal expansion (CTE) were plasma sprayed at the same time with a 70 µm thick coating. It should be mentioned that since the coating is thin and compliant compared to the substrate, the elastic modulus of the substrate is not important. For copper and superalloy substrates, the resultant stress is tensile upon heating since their CTE is larger than that of the 7YSZ.
than that of YSZ. The stress is compressive for the coating on the Al$_2$O$_3$ substrate due to Al$_2$O$_3$'s smaller CTE relative to that of YSZ.

If the tensile stress from substrate expansion on heating is the major driving force for vertical crack formation, it would be expected that vertical cracks would form most readily on the sample where the difference in CTE with the substrate multiplied by the temperature change is the largest, which in the present case would be the copper substrate. However, the results indicate that the coating on the Cu substrate, the one with largest CTE, contains no vertical cracks; while the coating on the Al$_2$O$_3$ substrate, which has the lowest CTE, has many vertical cracks. This observation indicates that thermal expansion mismatch stress generated during coating deposition when the ceramic coating and the metallic substrate are heated is not a major driving force for the formation of vertical cracks in SPPS coatings.

After the completion of coating deposition, the ceramic top coat and substrate are cooled from 400–800 °C to room temperature. The resulting thermal expansion mismatch stress in the coating on the metallic substrates is compressive since the CTE of substrate is larger than that of YSZ. Therefore, this thermal expansion mismatch stress on cooling will not contribute to the formation of vertical cracks.

Based on the above analysis, it can be concluded that thermal expansion mismatch stresses are not a major driving force for the formation of vertical cracks in SPPS coatings.

4.2. Transient cooling stress

As it can be seen in Fig. 9, the coating surface temperature increases and then decreases rapidly when the plasma torch passes over the coating. During the transient cooling stage, the coating surface cools down first and the resulting contraction is restricted by the relatively hotter underlayer, which leads to the generation of in-plane tensile stresses. The amplitude of this stress depends on the temperature gradient through the coating thickness, given the same CTE of the coating. Since the temperature gradient is caused by the repetitive heating of the plasma flame and surface cooling, the gradient is determined by the heating capability of the plasma flame and the surface cooling condition. Hotter plasma and stronger surface cooling give rise to higher temperature gradients through the coating during the transient cooling stage. For the same processing condition, the temperature difference between the coating surface and substrate generated during transient cooling is less than 40 °C and not sufficient to explain cracking by itself. In addition, for 100-μm and 70-μm coatings, the temperature difference between coating surface and the substrate is similar. However, the 100-μm coating has vertical cracks while the 70-μm coating does not, which suggests that the tensile stress generated during transient cooling, as a result of the thermal gradient, is not the major driving force for the formation of vertical cracks in SPPS TBCs.

4.3. Precursor pyrolysis stress

In SPPS process, precursor at various reactions stages, like evaporation and gelation, reaches the substrate. The deposition of unpyrolyzed precursor has been confirmed by TGA and DTA analysis [7]. Unpyrolyzed precursor starts to decompose at temperatures above ~350 °C [7]. When the unpyrolyzed precursor is exposed to a temperature higher than 350 °C, during deposition or post-deposition heat-treatment, the precursor will decompose and crystallize (pyrolysis). However, pyrolysis of the precursor will not be completed until a much higher temperature, like 700 °C at a heating rate of 20 °C/min, due to kinetics of the reactions. As a result, unpyrolyzed precursor was observed in thin SPPS coatings though the maximum coating temperature is higher than 350 °C (Figs. 3 and 9).

The pyrolysis of precursor is accompanied by large volume shrinkage due to the evaporation of remaining water and pyrolysis of acetate and nitrate salts [7,8]. The extent of volume shrinkage depends on the nature and amount of the unpyrolyzed precursor in the coating. Both factors can change rapidly during the deposition process. It is estimated that the volume shrinkage can be as large as 2% to 3%, based on thermogravimetric (TGA) analysis of crushed free-standing SPPS coatings [7]. This would result in an in-plane tensile stress of the order of 400 MPa, assuming an elastic modulus of 40 GPa for the SPPS coating. The tensile strength of SPPS TBCs is about 25 MPa [12], therefore, the stress resulting from precursor pyrolysis in the coating is sufficient to create vertical cracks in SPPS TBCs.

It is also consistent with experimental observations that stresses from precursor pyrolysis in the coating play a dominant role in the formation of vertical cracks in SPPS TBCs. Vertical cracks are generated in coatings with a thickness larger than a critical value that increases with the thermal conductivity of the substrate, as described in Section 3.3. During coating deposition, the coating temperature is higher than the precursor decomposition temperature (~350 °C) [7] after the first 2–3 passes and it increases with time. Therefore, precursor incorporated into the coating will start to decompose during coating deposition. Precursor pyrolysis occurs more extensively in thicker coatings due to longer spraying time and higher coating temperature (Fig. 3), which leads to the generation of higher tensile stress that promotes the formation of vertical cracks. The coatings on substrates of lower thermal conductivity experience higher temperatures during coating deposition; therefore, the critical coating thickness for vertical crack generation is smaller.

Moreover, the effect of precursor pyrolysis on vertical crack formation is verified in post-heat treatment experiments. When a 70 μm thick crack-free sample is subjected to heat-treatment at temperature (300 °C) below the precursor decomposition temperature (350 °C), no vertical cracks are generated after the heat-treatment due to the absence of tensile stress resulting from pyrolysis. If the heat-treatment temperature is higher than the precursor decomposition temperature, e.g., 600 and 1121 °C, vertical cracks are generated in identical samples due to the pyrolysis of precursor remaining in the coating. In addition, APS coatings on identical substrates do not contain vertical cracks after same post-heat treatment.

Based on the experimental observations and the above discussion, the following mechanism of vertical crack formation is proposed. During deposition, the unpyrolyzed
precursor incorporated into the coating starts to decompose when the coating temperature is higher than the precursor decomposition temperature. Precursor decomposition produces shrinkage and tensile stress which is the primary cause of cracking in the coating acting in conjunction with other sources of tensile stress mentioned above. Once the total tensile stress primarily caused by the precursor decomposition exceeds the tensile strength of the coating, vertical cracks form at the external surface of the coating (Figs. 1b and 5c). These cracks extend further into the coating with the continuation of precursor decomposition during deposition or post heat treatment (Figs. 1c and 5d).

5. Summary and conclusions

Coatings of various thicknesses were deposited on a variety of substrates with vastly different thermal properties. These coatings were characterized in the as-sprayed state and after heat treatment. It has been determined that the tensile stress, derived from the pyrolysis of precursor occurring during coating deposition or post heat-treatment, is the major driving force for the formation of the vertical cracks in SPPS TBCs. It is proposed that during deposition, the precursor in the coating starts to decompose when the coating temperature is higher than the precursor decomposition temperature. Once the tensile stress caused by the precursor decomposition exceeds the tensile strength of the coating, vertical cracks form at the top surface. These cracks extend further toward the coating/substrate interface with the continuation of precursor decomposition during deposition or post heat treatment.

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