INSIDE:

– Transparent Super-Hydrophobic Cold-Sprayed Coatings
– Novel Online Diagnostic in Cold Spray
– Bonding Strength of Cold-Sprayed Metal Coatings on Ceramic
– Interplay between Adhesion Strength and Tensile Properties of Coatings
– Failure Analysis of Suspension Plasma-Sprayed Thermal Barrier Coatings
– and much more....

Armelle Vardelle
Editor-in-Chief
Announcement

Kuroda Retires as Associate Editor; Hussain and Shinoda Join Editorial Team 243

Science of Thermal Spray Processes

Nanostructured Photocatalytic TiO₂ Coating Deposited by Suspension Plasma Spraying with Different Injection Positions
X. Liu · K. Wen · C. Deng · K. Yang · C. Deng · M. Liu · K. Zhou 245

Epitaxial Growth and Cracking Mechanisms of Thermally Sprayed Ceramic Splat
L. Chen · G. Yang 255

Modeling of Rapid Solidification with Undercooling Effect During Droplet Flattening on a Substrate in Coating Formation
R.K. Shukla · V. Patel · A. Kumar 269

Modeling of Thickness and Profile Uniformity of Thermally Sprayed Coatings Deposited on Cylinders
Z. Yanjun · L. Wenbo · L. Dayu · X. Jinkun · Z. Chao 288

Coating Analysis and Characterization

On the Interplay Between Adhesion Strength and Tensile Properties of Thermal Spray Coated Laminates—Part I: High Velocity Thermal Spray Coatings
X. Luo · G.M. Smith · S. Sampath 296

On the Interplay Between Adhesion Strength and Tensile Properties of Thermal Spray Coated Laminates—Part II: Low-Velocity Thermal Spray Coatings
X. Luo · G.M. Smith · S. Sampath 308

Imaging Slit Pores Under Delaminated Splat by White Light Interference
L. Chen · L. Gao · G.-J. Yang 319

An Effective Electrical Resonance-Based Method to Detect Delamination in Thermal Barrier Coating
J.M. Kim · J.-H. Park · H.G. Lee · H.-J. Kim · S.-J. Song · C.-S. Seok · Y.-Z. Lee 336

Microstructural Characteristics and Performances of Cr₂O₃ and Cr₂O₃-15%TiO₂ S-HVOF Coatings Obtained from Water-Based Suspensions
F.-L. Toma · A. Potthoff · M. Barbosa 344

Phase and Microstructure Evolution and Toughening Mechanism of a Hierarchical Architectured Al₂O₃-Y₂O₃ Coating under High Temperature
J. Rong · K. Yang · Y. Zhuang · J. Ni · H. Zhao · S. Tao · X. Zhong · C. Ding 358

Microstructural Analysis and Transport Properties of Thermally Sprayed Multiple-Layer Ceramic Coatings
H. Wang · G. Muralidharan · D.N. Leonard · J.A. Haynes · W.D. Porter · R.D. England · M. Hays · G. Dwivedi · S. Sampath 371

Cover photo: Optical microscope observation of LZ (La₂Zr₂O₇) splats on 8YSZ single crystal substrate at 600°C with appearance of Newton's rings. “Imaging Slit Pores under Delaminated Splat by White Light Interference,” by Lin Chen, Li-li Gao, and Guan-Jun Yang, pp. 319–335 in this issue.
Imaging Slit Pores Under Delaminated Splat
s by White Light Interference

Lin Chen - Li-li Gao - Guan-Jun Yang

Abstract The slit pores under delaminated films significantly contribute to the properties of the film and the coating. In the present study, a novel and practical technique, the white light interference method, is proposed to characterize the slit pores covered by the 8YSZ and LZ splats. In this method, only an ordinary optical microscopy (OM) is used. Interestingly, colorful Newton’s rings and parabolic shapes of the slit pores were clearly observed by OM. The crack spacing and the shapes of the slit pores captured by OM were in good agreement with those obtained by scanning electron microscopy and focus ion beam. Moreover, this is the first time when successful quantitative imaging of the slit pores under the thermal spray splats is achieved. Besides, mechanical analyses were carried out, and the results were consistent with those obtained by OM. In addition, the essential fact that the slit pores were mainly caused by transverse cracking/delamination in the thermal spray coatings was clarified. These results indicate that white light interference is an excellent method to characterize the slit pores under smooth and transparent films.

Keywords crack patterns · crack spacing · delamination · parabolic shapes · slit pores · white light interference

Introduction

Delamination is one of the main failure modes in layered materials, which significantly deteriorates the functional performance, such as thermal and electric conductions, and the lifetime of thin films. Up to now, significant attention has been paid to delamination, and a large number of mechanical models have been proposed to establish the relationship between delamination parameters (such as delamination length and crack opening displacement) and the energy release rate and stress (Ref 1-8). However, accurate description of delamination parameters, such as delamination length and crack opening displacement, remains difficult to be achieved because the slit pores are usually covered by the films. Generally, the focus ion beam (FIB) method is used to determine the delamination length; however, it is quite expensive and not conveniently available.

In the case of thermally sprayed coatings, which have been widely used as thermal/environmental barrier coatings (TBCs/EBCs) (Ref 9, 10), functional layers in solid oxide fuel cells (SOFCs) (Ref 11), and abradable seal coatings (Ref 12, 13), the two most important features are numerous vertical cracks and transverse pores between lamellae (Ref 14). In addition, TBCs are indispensable and vital components of blades in gas turbines, as thermal insulation cells. Every centigrade improvement in thermal insulation produces significant economic benefits. The distribution and shape of the transverse pores directly affect the thermal insulation and service life of TBCs. Therefore, it is important to investigate and control the distribution of transverse pores. However, imaging internal transverse pores in coatings is always difficult. King (Ref 15) directly studied the transverse pores in a ceramic thin splat by scanning electron microscopy (SEM). However,
the result was ambiguous and only applicable for dielectric sputtered coatings on conductive substrates. Li (Ref 14) characterized the structure of Al₂O₃ coatings by copper electroplating. However, this method was only applicable to insulated coatings, had low contrast, and also not environmental friendly. Moreover, the formation mechanism of transverse pores still remains unclear. It is widely believed that transverse pores are formed during the formation process of sputtered coatings due to reasons such as low-impact pressure (Ref 15, 16) or condensates and adsorbates on the surface of the substrate (Ref 17, 18). All models mentioned above suggest that transverse pores only exist at the edge of the sputtered coatings. However, Chraska and King (Ref 20-22) reported that transverse pores clearly existed in almost every fragment in both the central and peripheral regions of the sputtered coatings. This reveals that the above models are actually a simplified version of the reality. Compared to the high tensile stress (several GPa), residual stress in sputtered coatings is usually in the order of ~ 100 MPa (Ref 23-26). As a result, the relief of stress and strain energies should be considerably large. It is widely accepted that the existence of vertical cracks is due to stress relaxation during rapid cooling (Ref 25, 27). This indicates that delamination can also act as an effective mode of stress relaxation in sputtered coatings (typical layered materials).

In the present study, the formation mechanism of the transverse pores, transverse cracking/delamination, is proposed. More importantly, the distribution and shape of the lamellar pores are investigated quantitatively. Understanding the formation mechanism of the transverse pores has great importance for structure tailoring and evolution process control under high-temperature or complex stress service conditions in TBCs and EBCs.

**Experiment**

**Materials**

Considering that a thermal spray coating is formed through successive deposition of lamellar sputtered splats, understanding the microstructure of a single sputtered splat can provide a rational understanding of the underlying fundamental mechanism. In this study, two kinds of splats, i.e., yttria-stabilized zirconia (ZrO₂-8 mol.% Y₂O₃, 8YSZ, Fujimi, Japan) and lanthanum zirconia (La₂O₃-ZrO₂, LZ, Tianyao, China) were used as demonstration materials for TBCs. The fused and crushed 8YSZ powder had a particle size ranging from 5 to 25 μm with a mean size of 17.8 μm, measured by a laser particle size analyzer (LS230, Beckman Coulter, USA) with a measuring range from 0.04 to 2000 μm, and the LZ agglomerate powder had a particle size ranging from 15 to 45 μm with a mean size of 30 μm. Additionally, in order to avoid the influence of surface roughness of the substrate (which can result in the formation of gas pockets) and to easily identify the crystallographic orientations of the splats, all splats were deposited on the (001) plane of a single-crystal 18YSZ (ZrO₂-18 mol.% Y₂O₃) substrate with a well-polished surface (Ra < 0.5 nm). All substrates were square, with a width of 10 mm and a thickness of 500 μm. The side face of the substrate was oriented along the <100> direction.

**Splat Deposition**

A commercial plasma spray system (GP-80, Jiujiang, China) and an external powder feeding injector were used. In addition, the detailed spraying parameters are listed in Table 1. It was reported that the deposition temperature had an obvious effect on the sputtered/coating structure (Ref 28-30). In addition, the high substrate temperature contributed to the elimination of the adsorbates and gas pockets. In this study, the substrates were preheated to a different temperature of (henceforth denoted as deposition temperature, from 100 to 600 °C with intervals of 100 °C) by a copper plate heater on which the substrates were placed. To avoid the extra calefaction of the substrate by the plasma arc, a shielding plate with several small holes was placed on the substrate. Additionally, the substrate surface temperature was monitored in real time by a calibrated thermocouple (NiCr/NiCrSi, Type N) with a thermal response time of ~ 1 s and data precision of ~ 2 °C. The temperature could maintain the set value with a variation less than 10 °C over a 5-min time interval. After the sputtered deposition, the splat and the substrate were cooled down to room temperature in air.

| Table 1 Deposition parameters for thermal sprayed YSZ and LZ sputters |
|----------------|-------|
| Parameters     | Values |
| Arc current, A | ~ 630  |
| Arc voltage, V | 70     |
| Primary plasma gas, Ar/slpm | 50 |
| Secondary plasma gas, H₂/slpm  | 7 |
| Powder feed gas, N₂/slpm | 3 |
| Spray distance, mm  | 80 |
| Traverse speed of torch, mm/s | 1200 |
| Deposition temperature, °C | 100-600 |
Characterization of Splats

We observed the splat morphologies by SEM (VEGA II-XMU, TESCAN, Czech Republic) and confirmed the epitaxial growth of the splats by electron back scattered diffraction (EBSD, AZTEC, OXFORD INSTRUMENTS, UK). All crack spacings were measured by the Demo VegaTC software integrated in the SEM.

Most importantly, for the characterization of the transverse pores covered by the splats, we proposed the white light interference, which was a simple and practical method. In this method, only ordinary optical microscopy (OM, ECLIPSE MA200, NIKON, JAPAN) was used to observe the interference fringe on the splat surfaces. The schematic of white light interference is shown in Fig. 1. A beam of light has the following wave function (Ref 31):

$$\tilde{E}_1(x,t) = \tilde{E}_0 \cos \left[ 2\pi f_1 \left( t - \frac{x}{u} \right) + \varphi_1 \right], \quad (\text{Eq 1})$$

where $\tilde{E}_0$, $f_1$, and $u$ is the basis vector, frequency, and light wave velocity, respectively. When two beams of the light meet, interference occurs. The resultant intensity of interference light can be expressed as

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \Delta \varphi, \quad (\text{Eq 2})$$

where the phase difference $\Delta \varphi$ follows $\Delta \varphi = \varphi_1 - \varphi_2 - \frac{2\pi(r_2 - r_1)}{\lambda}$. Furthermore, $r_1$ and $r_2$ denote the path of reflected lights I and II, respectively. If the two interfered light beams come from the same light source as shown in Fig. 1, the phase difference and light intensity can be reduced to

$$\Delta \varphi = \frac{2\pi(r_2 - r_1)}{\lambda}, \quad (\text{Eq 3})$$

$$I = 2I_0(1 + \cos \Delta \varphi). \quad (\text{Eq 4})$$

Considering the half-wavelength loss, the condition of light interference can be rewritten as (Ref 31)

$$2d + \frac{\lambda}{2} = \left\{ \begin{array}{ll} (2k)\frac{\lambda}{2}, & I = I_{\text{max}} \\ (2k + 1)\frac{\lambda}{2}, & I = I_{\text{min}} \end{array} \right. \quad (\text{Eq 5})$$

where $k$ and $\lambda$ represent a random integer and the wavelength, respectively, and $d$ refers to the width of the slit, as shown in Fig. 1. When the light intensity reaches its maximum, a bright region emerges. Inversely, a dark region is produced. Therefore, based on the positions of the interference fringes, the shapes of the slit pores (the slit width) can be accurately distinguished.

Results

Splat Morphologies by SEM

The surface morphologies of 8YSZ and LZ splats on a single-crystal 18YSZ substrate at a deposition temperature from 100 to 600 °C were observed by SEM, as shown in Fig. 2. The splats at all deposition temperatures presented regular and smooth crack pattern morphologies. During the SEM observation, the substrate edge always kept parallel with the edge of the SEM view field. It was found that, at all deposition temperatures, vertical cracks were generally oriented at a 45° angle to the substrate <100> direction (side face), which revealed a <110> orientation for the vertical cracks. This was consistent with the close-packed direction of face-centered-cubic (FCC)-structured 8YSZ and LZ splats. Due to regular cracking patterns, an array of nanochannels (see insets in Fig. 2) was successfully fabricated. It was found that substrate spallation occurred for all 8YSZ splats deposited at different temperatures, while both interfacial and substrate spallation occurred for LZ splats deposited at temperatures below 300 °C, and only substrate spallation occurred at deposition temperatures above 300 °C. In addition, there were many intact disk-shape splats without vertical cracks and large quantities of residual vertical cracks retained on the bare substrate (where the splat had fell off) for all kinds of LZ splats. These residual vertical cracks clearly revealed that transverse pores followed up with vertical cracking. Besides, the orientation maps of 8YSZ and LZ splats were identified by EBSD, as shown in Fig. 3. The inverse pole figures (IPFs, see insets in Fig. 3) and the identical colors between the splat and single-crystal substrate revealed that epitaxial growth along the <001> orientation had readily occurred for all types of 8YSZ and LZ splats. Consequently, the cracks were quite straight and sharp due to the lack of intergranular cracking, which significantly contributed to accurate measurement of the crack spacing and further estimating the cracking stress.
Moreover, the size of the rectangular crack patterns was measured by using the Demo VegaTC integrated in the SEM. At least 900 patterns for every kind of splat and deposition temperature were counted. Then, the equivalent crack spacing, which was the square root of the crack pattern size, was obtained, and the statistical results are shown in Fig. 4. It was found that the mean crack pattern size changed only slightly for epitaxial 8YSZ and LZ splats at the deposition temperature from 100 to 600 °C. However, for each kind of epitaxial splats, the crack spacing varied in an exceptionally broad range, as shown in Fig. 4(b) and (c). The broad range revealed that delamination substantially occurred in most crack patterns. Epitaxial growth indicates the chemical bonding (complete contact) between the splat and substrate. This clearly demonstrates the slit pores result from transverse cracking/delamination.

Additionally, it was found that numerous residual pits or hills existed on the bare substrates, as shown in Fig. 5(a) and (b) by red arrows. A high number of residual pits or hills were formed on substrates without any splat deposition.
pits or hills on the backside of delaminated lamellae were also observed, as shown in the insets in Fig. 5(b). Apparently, these residual pits or hills were the regions where the delamination occurred last. The equivalent width, which was the square root of the residual region size (i.e., the size of the residual pits or hills), was also determined by using Demo VegaTC software. At least 100 residual regions for each kind of splat and deposition temperature were counted, and the results are shown in Fig. 5(c)-(e). As the deposition temperature increased from 100 to 600 °C, the residual crack spacing increased slightly for both epitaxial 8YSZ and LZ splats, as shown in Fig. 5(c).

In brief, 8YSZ and LZ splats grew epitaxially on the 18YSZ substrate at all deposition temperatures. In the
meantime, transverse spallation was ubiquitous in epitaxial splats. The crack pattern size was also determined and the result presented an exceptionally broad range, which revealed severe delamination readily occurred. Furthermore, residual pits or hills on bare substrate were observed. These observations revealed that the slit pores between the splats and substrate resulted from transverse cracking.

**Splat Morphologies by White Light Interference**

More importantly, the transverse pores in epitaxial 8YSZ and LZ splats were characterized by using the white light interference method with an ordinary OM. Interestingly, colorful Newton’s rings clearly appeared under white light imaging by OM, as shown in Fig. 6 and 15 (in “Appendix”). As expected, almost every crack pattern had both bonded region (dark region) and unbonded region (colored/bright region), which was consistent with the results reported by King et al. (Ref 15, 21).

In addition, the size of the bonded regions under OM was counted by using the Demo VegaTC software. The boundary of the bonded regions was defined as the region with the brightness of 50% (the average of the black and the white). At least 1000 patterns for every kind of splat and deposition temperature were counted. Then, the equivalent crack spacing, which was the square root of bonded area size, was obtained, and the statistical results are shown in Fig. 7. As the deposition temperature increased from 100 to 600 °C, the equivalent crack spacing increased slightly for 8YSZ splats, while this showed little variation for LZ splats. It was worth noting that the equivalent crack spacing of the bonded area size captured by OM (Fig. 7a) was much smaller than that of the crack patterns by SEM (Fig. 4a) but comparable with that of the residual patterns by SEM (Fig. 5c). This further confirmed that the slit pores were the result of transverse cracking.

Most importantly, based on the order of the interference fringes (see Fig. 1 and 6 and Eq 5), the shape of the slit pores can be determined. Herein, cyan fringes (with a wavelength of 480 nm) on the 8YSZ splat surfaces at the deposition temperature of 600 °C were used. Seventy-seven splats were counted for the fitting of the shapes of the slit pores. As a result, a second-order polynomial fitting was applied with an average $R$-square of 0.99999 (value “1” means perfect) as shown in Fig. 8, which clearly indicated a parabolic shape.

In summary, the position and distribution of the slit pores in 8YSZ and LZ splats were successfully observed by white light interference. Colorful Newton’s rings clearly appeared under white light imaging by OM. Moreover, the bonded area size and the shape of the slit pores were determined under the white light interference method. The results of the bonded area size by OM (Fig. 7a) were consistent with those obtained by SEM (Fig. 5c).
a parabolic shape for the slit pores was successfully obtained. These results indicated that white light interference was an excellent method to characterize the slit pores covered by the delaminated splats.

**Cross-Sectional Morphologies by SEM**

To confirm the shapes of the slit pores covered by the fragments, the inclined cross-sectional morphologies were observed by SEM. As expected, the tile and parabolic shapes were clearly observed for all splats and deposition temperatures, as shown in Fig. 9. A further quantitative confirmation was also performed by using FIB, as shown in Fig. 10. As a result, perfect parabolic shapes were observed (Fig. 10a-f), and the fitting result (Fig. 10g) was in good agreement with the result by OM (Fig. 8).

The thickness of the splat/substrate lamellae (d) and the epitaxial splat (h) was also determined by using the Demo VegaTC software, and the dimensional thickness ratio (d/h) was shown in Fig. 11. The splat thickness remains almost unchanged as the deposition temperature increases from 100 to 600 °C. The thickness of epitaxial 8YSZ and LZ splats in the present study is 0.49 ± 0.1 and 0.6 ± 0.17 μm, respectively. The dashed red line with d/h = 3.86 in Fig. 11 represents the equilibrium depth where the steady state trajectory occurs in the case that the splat and the substrate have identical properties (Ref 1, 3). It is found that the thickness ratios in the present study fluctuate strongly, which can be attributed to the nonlinear and dynamic effects of cracking. The nonlinear effect by the change of geometry (Ref 32, 33) in the present study can be generated by the residual stress in the delaminated...
splat/substrate composite lamellae, when the cracks become considerably long. The dynamic effect (Ref 34, 35) of cracking may result from the high cooling rate $10^6$-$10^8$ °C/s (Ref 36, 37) during the thermal spraying.

In brief, the shapes of the slit pores covered by the crack patterns were demonstrated by SEM (Fig. 9) and FIB (Fig. 10). A high number of tile-shaped segments and parabolic-shaped slit pores were observed as shown in Fig. 9 and 10, which were consistent with the results by white light interference as shown in Fig. 8. This further verifies that white light interference is suitable for the accurate characterization of the slit pores under the delaminated splats.

**Discussion**

**Transverse Spallation**

In combination with the epitaxial growth, the slit pores clearly reveal the forming mechanism by transverse cracking/delamination. Compared to the splat thickness
The delamination length is estimated to be several tens of microns from the crack pattern size (Fig. 4a) and bonded area size (Fig. 7a). It is found that the crack reaches steady state when the crack length is only a few times larger than the thickness of the film (Ref 4, 38). Apparently, the steady state approximation is appropriate in the present study. For thin splats bonded on a semi-infinite substrate, the stress intensity factors for substrate spallation are given by (Ref 1-3, 5)

\[ K_I = \frac{P}{\sqrt{2U}} \cos \omega + \frac{M}{\sqrt{2V}h} \sin \omega, \]  
\[ K_{II} = \frac{P}{\sqrt{2U}} \sin \omega - \frac{M}{\sqrt{2V}h} \cos \omega, \]  
(Eq 6)

where \( h \) is the splat thickness, \( P \) and \( M \) are the equivalent load and moment in splat/substrate system. Besides, nondimensional quantities \( U \) and \( V \) are geometrical factors related to the stiffness ratio and thickness ratio, and the angle \( \omega \) can be found in the publications by Suo et al. (Ref 1, 5). When the splat and the infinite substrate have identical properties, the stress intensity factors for substrate delamination can be reduced to

\[ K_I = 0.434 \frac{\sqrt{h}}{d/h} + 0.966 \frac{\sigma \sqrt{h}}{\sqrt{(d/h)^3/[(d/h) - 1]^2}}, \]  
\[ K_{II} = 0.558 \frac{\sqrt{h}}{d/h} - 0.752 \frac{\sigma \sqrt{h}}{\sqrt{(d/h)^3/[(d/h) - 1]^2}}, \]  
(Eq 8)

where \( \sigma \) is cracking stress in the splats, \( d \) and \( h \) are the thickness of delaminated splat/substrate composite.
lamellae and the splats (see inset in Fig. 9). Once the cracking stress and resistance are obtained, the crack behavior can be determined.

**Shapes of the Slit Pores**

In the present study, three aspects of deformations contribute to the shapes of slit pores. These are the crack opening displacement (COD), the displacement due to Euler buckling, and the bending deformation of the...
composite beam. The COD is generally affected by the length scale to the crack tip. When the position is extremely close to the crack tip (this region is usually known as the bond-breaking zone, where \( r_0 \leq 1 \text{mm} \) for linear elastic ceramics), the COD is proportional to the distance to the crack tip \( (r) \). When \( r \) is between \( r_0 \) and \( r_K \) (the length scale of fracture in materials), i.e., the \( K \) annulus as shown in Fig. 12a, the COD is usually proportional to the square root of the distance to crack tip \( (\sqrt{r}) \) and dictates (Ref 39)

\[
\delta_y + i\delta_x = \frac{8(K_I + iK_{II})}{E} \sqrt{\frac{r}{2\pi}},
\]

(Eq 10)

where \( K_I \) and \( K_{II} \) are the stress intensity factors for Mode I and II substrate cracking, respectively, and the quantity \( r \) is the distance to the crack tip. Obviously, once the stress intensity factors are obtained, the COD can be calculated. In the case of the splat and the substrate having identical properties, the displacement \( (\delta_y) \) follows \( \sim 0.0063\sqrt{r} \) when the cracking strain is \( \sim 0.5\% \). Based on dimensional analysis, all length units in the present study are tacitly unified to \( \mu m \). As shown in Fig. 12(b), the critical force for Euler buckling can be generally written as (Ref 40)

\[
F_{cr} = \frac{\pi^2EI}{(\mu l)^2},
\]

(Eq 11)

where \( l \) and \( I \) are the crack length and the bending rigidity of the composite beam, respectively. Moreover, the nondimensional quantity \( \mu \) is the length factor (here it is equal to 2 for the case shown in Fig. 12b). Then, the displacement due to Euler buckling can be expressed as

\[
v = C_1 \sin kx + C_2 \cos kx,
\]

(Eq 12)

where the coefficient \( k \) is related to the total crack length \( (l) \). In the case of the splat and the substrate having identical properties, the bending rigidity of composite beam \( (I) \) dictates

\[
I = \frac{bd^3}{12},
\]

(Eq 13)

where \( b \) and \( d \) are the width and thickness (see inset in Fig. 11) of the composite beam, respectively. As a result, the critical stress for Euler buckling is about 2.82 GPa. This indicates that Euler buckling can be ignored except in the case of extremely slender stripes. The bending deformation of the composite beam, as shown in Fig. 12c, usually follows (Ref 40)
\[ y = \frac{Mx^2}{2EI}, \]  
\text{(Eq 14)}

where \( M \) is the moment of the composite beam. As shown in Fig. 7(a) and 10(a), the bonded area size of the crack pattern measured by OM is similar to that measured by FIB. Additionally, a perfect parabolic fitting is obtained in the peripheral region of crack patterns, as shown in Fig. 8 and 10(g). When the splat and the substrate have identical properties, the moment of the composite beam (see Fig. 12c and see inset in Fig. 11) can be expressed by

\[ M = \sigma_1 h db / 2, \]  
\text{(Eq 15)}

where \( \sigma_1 \) is residual stress in the splat. In conjunction with Eq 13-15 and the second-order coefficient of the parabolic fitting (Fig. 8), the residual stress in the composite beam can be calculated and it is about 550 MPa for the 8YSZ splat at the deposition temperature of 600 °C. It should be noted that this stress is the result after cracking and stress redistribution take place; thus, the total stress in the case of no cracking and redistributing is larger than this value. It is also found that the cracks in the localized center region deviate the parabolic shapes, as shown in Fig. 10(c) and (f). It is difficult to obtain the shape of slit pores near the crack tip because both OM and FIB have limited image resolution in this region. Theoretically, the crack shapes in the localized center region follows the \( \sqrt{r} \) relation based on COD. In brief, a mechanical model was set up to describe the shapes of the slit pores. It was found that the bending deformation of the composite beam with the residual stress of \( \sim 550 \text{ MPa} \) was dominant in the formation of the parabolic shapes of the slit pores, which was consistent with the results by OM.

**Crack Spacing**

Based on fracture mechanics, the crack spacing has been widely investigated for various film/substrate combinations and cracking modes (Ref 1, 41-47). In the present study, three kinds of equivalent crack spacing were obtained. These were the equivalent crack spacing of the crack patterns obtained by SEM (Fig. 4a), of the bonded area size captured by OM (Fig. 7a), and the residual patterns (residual pits or hills) by SEM (Fig. 5c). Apparently, the former was much larger than the latter two. In addition, mainly three failure modes occurred, specifically, channeling (Ref 41-45), penetration (Ref 7, 39, 46), and spallation (Ref 1, 3, 5), as shown in Fig. 13(a).

For the splat and the substrate with identical properties, the crack spacing of channel cracks without substrate penetration and spallation can be written as (Ref 42)

\[ \lambda_{\text{eqi}} / h = 5.6 \sqrt{\frac{\Gamma_f / (E \epsilon_0 h)}{h}}. \]  
\text{(Eq 14)}

where \( \Gamma_f \) and \( \epsilon_0 \) are the fracture toughness and applied strain, respectively.

As both vertical and transverse cracking exist, the normal crack spacing \( (L, \text{see Fig. 4a}) \) in the present study has no contribution in maintaining the mechanical equilibrium configuration, as shown in Fig. 13(b). Inversely, the stress transfer from the splat to the substrate only takes place over the portion of the segment where no delamination propagates (i.e., the bonded region, see Fig. 6 and 15 in

![Fig. 13](image)
“Appendix”). This defines an effective length of the segments (Ref 46) \(l\), which can be considered as the equivalent crack spacing of the bonded area size by OM, as shown in Fig. 7(a).

In the case that both channeling and substrate penetration occur without spallation, the effective crack spacing is a function of

\[
l = f(h, d, \Gamma_s, \sigma, z, \bar{E}_l),
\]

(Eq 15)

where \(\Gamma_s\) and \(z\) are the substrate fracture toughness and Dundurs’ parameter (Ref 5, 48), respectively, related to the elastic mismatch. This indicates that crack spacing has multiple and complex configurations. Using the theory of weight functions and linear fracture mechanics, the effective crack spacing dictates (Ref 49)

\[
l = \frac{h}{20^{0.83} + 59.80R + \frac{0.2811}{R_c - R} - \frac{1.074 \times 10^{-4}}{(R_c - R)^2}},
\]

(Eq 16)

where \(R_c\) is the critical cracking resistance number (which gives 0.6607) (Ref 49). The cracking resistance number (\(R\)) follows

\[
R = \frac{2\gamma E}{\pi \sigma^2 h},
\]

(Eq 17)

where \(\gamma\) is the specific surface energy. By taking the fracture energies \((2\gamma)\) and elastic modulus \((E)\) of YSZ and LZ as 2.74 and 2.34 J/m\(^2\), and 205 and 175 GPa, respectively, the cracking stress \((\sigma)\) can be estimated, and the result is shown in Fig. 14. The average stress is about 820 and 680 MPa for the 8YSZ and LZ splats, respectively. It has been reported by TEM results (Ref 50) that an extremely high stress \((\sim 2\) GPa) arose due to the intrinsic lattice mismatch between the splat and the substrate, and vertical cracks still exist in the 8YSZ splat at the deposition temperature of 1200 °C (Ref 51) where the peak stress is estimated to be 950 MPa on the assumption of the interfacial solidification temperature of \(\sim 1650\) °C (Ref 50). These are consistent with the present values.

Similarly, if the cracking stress is known, the fracture energy can be calculated. It should be noted that the mechanical analysis described above does not consider the residual strain energies stored by the delaminated composite beams. This indicates that the actual value should be larger than the present value. In addition, it is found that all kinds of crack spacing (Fig. 4a, 5c, and 7a) change only slightly as the deposition temperature varies. This clearly indicates that the stress is large enough to drive cracking during splt deposition.

**Conclusions**

In the present study, it was found that all the 8YSZ and LZ splats grew epitaxially on the 18YSZ substrate, which clearly revealed that the ubiquitous lamellar pores resulted from transverse cracking.

Most importantly, a novel and practical and effective technique, the white light interference method was proposed to characterize the features of the slit pores under 8YSZ and LZ splats. The Newton’s rings, obtained by OM, revealed that almost every crack pattern had both bonded region and unbounded region (slit pores), as expected. In addition, both OM observation and SEM and FIB experiments confirmed the parabolic shape of the slit pores. The mechanical analysis indicated that the formation of the parabolic shape was dominated by the bending deformation of the composite beam, which was consistent with the OM and FIB observations. Based on the equivalent crack spacing obtained by OM, the cracking stress was estimated to be about 820 and 680 MPa for the 8YSZ and LZ splats, respectively. Thus, we can conclude that the lamellar pores in the thermally sprayed ceramic coatings mainly result from the high cracking stress. This reveals that the essential approach to promoting the performances of thermally sprayed coatings, such as TBCs and EBCs, is how to tailor the stress during the splt deposition.
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Appendix: Splat Morphologies by White Light Interference

See Fig. 15.

Fig. 15 The surface morphologies of (a-c) 8YSZ and (d-f) LZ splats at the deposition temperature of (a, d) 200, (b, e) 400, and (c, f) 500 °C by OM. Colorful Newton’s rings were widely observed.
References

17. C.J. Li and J.L. Li, Transient Contact Pressure During Flattening of Thermal Spray Droplet and Its Effect on Splat Formation, in *J. Therm. Spray Technol.*, 2004, 13(2), p 229-238