Effect of intersplat interface bonding on the microstructure of plasma-sprayed Al₂O₃ coating

Er-Juan Yang¹, Chang-Jiu Li¹*, Guan-Jun Yang¹, Cheng-Xin Li¹ and Makoto Takahashi²

¹State Key Laboratory for Mechanical Behaviour of Materials, School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an, Shannxi 710049, P. R. China
²Japan Welding and Joining Research Institute, Osaka University, Ibaraki 565-0871, Osaka, Japan

*: E-mail: licj@mail.xjtu.edu.cn

Abstract. The interface bonding between lamellae dominates the properties and performance of plasma-sprayed ceramic coatings. In this study, the interlamellar interface bonding and its effect on the splat microstructure were examined using TEM analysis of the microstructure of a plasma-sprayed Al₂O₃ coating. The obtained results revealed that the intersplat interface microstructure depends significantly on the intersplat bonding. An amorphous phase was observed in the interface region in which the bonding was formed, while the γ-Al₂O₃ phase was observed at the interface where no bonding was formed. In addition, it was found that the interface bonding significantly influenced the interface microstructure of the coating. After heat treatment, the phase of the bonding between adjacent splats was transformed from amorphous to γ-Al₂O₃. In the interface region in which the amorphous phase recrystallization occurred, nanosized pores evolved owing to the volume shrinkage accompanying the transformation of alumina from the amorphous to the γ-Al₂O₃ phase.

1. Introduction
Plasma spraying is a flexible process for producing thick coatings (thickness ranging from micrometers to millimeters) at a high deposition rate and has been employed extensively in different industrial fields. During plasma spraying, molten or semimolten particles successively impact on the substrate, followed by rapid spreading and subsequent solidification of the melt, thereby forming a deposit stacked with splats [1-4]. A splat is the basic unit constituting a plasma spray coating. The successive stacking of splats is required to deposit a thermal spray coating with a certain thickness. Thus, the resulting coating possesses a lamellar structure. It has been demonstrated that the intersplat bonding dominates the mechanical and physical properties such as strength and thermal or electrical conductivity of certain materials [5]. Therefore, bonding formation between splats is an important factor that affects the stacking of splats to form a coating. Accordingly, a systematic quantitative investigation of splat bonding was carried out by utilizing the bonding ratio [6]. It was found that the bonding ratio changes from ~10% in the case of D-gun alumina to a maximum value of ~1/3 for optimized plasma-sprayed ceramic coatings deposited by following a conventional routine [7]. This accounts qualitatively for the fact that most of the coating properties such as Young’s modulus [7, 8],
fracture toughness [9], thermal conductivity [5, 10], and electrical conductivity [5, 11] are found to range from one-tenth to one-third of those of bulk materials. Moreover, it is evident that the coating properties also depend on the crystalline structure of splats.

Aluminum oxide (Al$_2$O$_3$) coatings have been widely used as dielectric coatings, protective coatings, and corrosion-resistance barriers. However, aluminum oxide is a complex material even in the massive bulk form as it exhibits various crystalline structures. Several transient metastable phases (χ, κ, γ, δ, and θ) may evolve and only one thermodynamically stable phase (α-Al$_2$O$_3$ in a hexagonal close-packed (hcp) lattice) has been observed [12]. As mentioned previously, in a thermally sprayed ceramic coating, less than one-third splat interface area is bonded together [7] and the alumina coating mainly consists of metastable phases [10, 13]. This is because after the flattening of droplets, the cooling rate is dominated by the contact conditions between the droplets and underlying substrate. Assuming that the contact of the melt with solid splats before solidification is positively related to interface bonding, the cooling rate would differ in the bonded and unbonded zones, possibly resulting in different microstructures. Thus, it can be naturally considered that a local splat bonding state corresponds to the droplet–splat contact condition prior to solidification of the molten splat and thus influences the phase formation upon crystallization. However, little attention has been paid to the effect of splat bonding on the local splat microstructure. In this study, an alumina coating was deposited by atmospheric plasma spraying (APS), and high-resolution transmission electron microscopy (HR-TEM) analysis was performed to examine the local microstructures near the interfaces in both the bonded and unbonded zones. Further, microstructure changes resulting from heat treatment were also investigated.

2. Materials and methods

Commercial fuse-crushed Al$_2$O$_3$ powder with a particle size range of -45 to 15 μm was used as the feedstock. An Al$_2$O$_3$ coating was deposited on grit-blasted steel by atmospheric plasma spraying (APS, 80 kW class, Jiujiang, China) at a plasma arc power of 33 kW. During spraying, an air jet attached to the torch and oriented toward the substrate was employed by following a conventional routine to cool the sample by suppressing any rise in the sample temperature. Subsequently, post-spray heat treatment of the sample was carried out at 1073 K for 12 h.

The deposits were characterized using a variety of techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and HR-TEM (JEM-2100F JEOL) carried out at 200 kV. In order to distinguish the deposition direction in HR-TEM specimens, their substrate side was marked during sample preparation.

Vickers microhardness of the coating was measured from a polished cross-section at a load of 2.92 N and a loading time of 30 s. Young’s modulus was measured through the Knoop indentation approach as proposed in literature [14, 15] at a load of 9.8 N and a loading time of 50 s.

3. Results and discussion

3.1. Effect of interface bonding on interface microstructure

3.1.1. Microstructure characterization at unbonded intersplat interface in APS-sprayed alumina coating. A bright-field TEM image of a region near the unbonded lamellar interface zone in APS-sprayed alumina coatings is shown in Figure 1(a). A ~20–40-nm-wide crack at the splat interface can be easily observed. Such crack was presented as the unbonded splat interface. Moreover, the splat showed a columnar substructure. The columnar grains were perpendicular to the splat interface. Global pores possibly resulting from gas entrapment were also observed. Selected area electron diffraction (SAED) patterns taken from regions in two adjacent splats across the unbonded interface marked “A” and “B” in Figure 1(a) are shown in Figure 1(b) and 1(c), respectively. These patterns clearly indicate that both splats have a γ-Al$_2$O$_3$ lattice structure. This is in good agreement with the results widely reported in the literature [10, 13]. As expected on the basis of common knowledge on thermally sprayed coatings, substantial lamellar interfaces were present in the as-
sprayed alumina coatings as unbonded interfaces, as shown in Figure 1 (a). An investigation of the crystalline structure of two splats immediately across an unbonded interface confirmed the above-mentioned results.

3.1.2 Microstructure characterization at bonded intersplat interface in APS-sprayed alumina coating.

A bright-field TEM image of and SAED patterns corresponding to a region near the bonded interface in an alumina coating are shown in Figure 2. At the bottom of the image shown in Figure 2(a), the region marked “C” clearly shows columnar grains, which grew to the splat surface and became the interface between two splats. The columnar grains were confirmed to have a $\gamma$ phase. The SAED pattern corresponding to the region marked “B” in Figure 2(a) indicates the formation of an amorphous phase, as shown in Figure 2(c). The amorphous phase layer within a splat reached up to several hundreds of nanometers in thickness with a nanocrystal $\gamma$-Al$_2$O$_3$ phase extended throughout the remaining part of the splat, as indicated by the SAED pattern in Figure 2(b), which corresponds to the region marked “A” in Figure 2(a). The origin of the amorphous phase was attributed to the cooling rate in the bonded zone being higher than that in the unbonded zone owing to good contact of the molten alumina. The formation of nanocrystal $\gamma$-Al$_2$O$_3$ in the remaining part of the splat may be due to the decreased cooling rate resulting from droplet solidification by the release of fusion latent heat.

Figure 1. (a) Bright-field TEM image of an unbonded zone in an APS-sprayed alumina coating; (b) selected area electron diffraction (SAED) pattern corresponding to the region marked “A” in (a), which is in the unbonded zone; and (c) SAED pattern corresponding to the region marked “B” in (a), which is in the unbonded zone.

Figure 2. (a) Bright-field TEM image of a bonded zone in an APS-sprayed alumina coating; (b) SAED pattern corresponding to the region marked “A” in (a); and (c) SAED pattern corresponding to the region marked “B” in (a).
Amorphous structures are frequently observed in plasma-sprayed ceramic coatings owing to the rapid cooling rate of molten microsized powders [16, 17]. However, only a few studies have focused on the relationship between amorphous phase formation and intersplat bonding features. The results presented herein reveal that splat interface bonding significantly influences phase formation in the splat across the interface between bonded and unbonded regions. As mentioned above, in APS-sprayed alumina coatings, the $\gamma$ phase appears in $\text{Al}_2\text{O}_3$ splats over the unbonded interface while the amorphous phase appears in those over the bonded interface area.

3.2. Changes in microstructure at bonded intersplat interface through heat treatment

It has been confirmed that in APS-sprayed alumina coatings, the $\gamma$ phase appears in $\text{Al}_2\text{O}_3$ splats over the unbonded interface while the amorphous phase appears in those over the bonded interface area. This intersplat bonding features may change when the alumina coating is exposed to high-temperature conditions. Thus, heat treatment was carried out to investigate the changes in the microstructure of intersplat bonded zones resulting from high-temperature thermal exposure. The heat treatment was carried out at 1073 K for 12 h. During the treatment, the $\gamma$ phase of the alumina coating was stable [13] and the amorphous alumina phase could be crystallized [18].

A bright-field TEM image of a region near the bonded interface of an APS-sprayed alumina coating subjected to heat treatment at 1073 K for 12 h is shown in Figure 3(a). In the regions at the middle and bottom of the image marked “A” and “C,” respectively, the splat internal columnar substructure is still evident. This columnar substructure grew to the splat surface and became the interface between two splats. The columnar grains were confirmed to have the $\gamma$ phase. No columnar substructure was observed between the two internal columnar substructure splats. However, some nanosized pores were observed.

![Figure 3](image-url)

**Figure 3.** (a) Bright-field TEM image of the bonded zone in an APS-sprayed alumina coating subjected to heat treatment at 1073 K for 12 h; (b) magnified bright-field TEM image corresponding to the region marked “B” in (a); (c) SAED pattern corresponding to the region marked “B” in (a); and (d) magnified bright-field TEM image corresponding to the region marked “A” in (a).
In order to further examine the microstructure in the region marked “B,” a magnified bright-field TEM image was obtained and is shown in Figure 3(b). A number of nanocrystalline grains can be observed in this figure. Furthermore, many nanosized pores around these nanocrystals can also be observed. The SAED pattern corresponding to the region marked “D” in Figure 3(b) is shown in Figure 3(c). The pattern clearly indicates that the nanocrystals had a γ-Al2O3 lattice structure. The present observations reveal that the amorphous phase of the bonded zones in the APS-sprayed alumina coating was crystallized to nanocrystalline γ-Al2O3 after heat treatment at 1073 K for 12 h, and this phase transformation resulted in the formation of nanosized pores. As shown by a molecular dynamics simulation [19], the amorphous phase follows the same trend in the distribution of Al coordination numbers and ring distributions as that in the liquid phase. The density of both phases is almost equal at close to 3.175 g/cm^3 [19, 20]. Further, the density of γ-Al2O3 is 3.66 g/cm^3 [19, 21]. During the heat treatment at 1073 K for 12 h, the amorphous phase transformed to γ-Al2O3, resulting in a density difference of 3.175 and 3.66 g/cm^3 for amorphous alumina and γ-Al2O3, respectively. Thus, the dynamics of the heating process induced a volume shrinkage of about 13% and led to the formation of nanosized pores. The microstructure at the bonded intersplat interface after the heat treatment is shown in Figure 3(d). It can be concluded that the intersplat bonding phase changed from amorphous to nanosized γ-Al2O3, with a less dense microstructure.

3.3. Microhardness and Young’s modulus for as-sprayed and heat-treated alumina coatings

Figure 4 shows the microhardness of the as-sprayed and heat-treated alumina coatings. The as-sprayed alumina coating exhibited a mean hardness of 840 Hv0.3. However, the microhardness of Al2O3 coatings increased to 982 Hv0.3 after heat treatment.

![Figure 4. Comparison between microhardness of as-sprayed Al2O3 and that heat-treated at 1073 K for 12 h.](image)

The Knoop indentation method [14, 15] was employed to measure Young’s modulus of coatings deposited at different temperatures. The cross-sections of the samples were prepolished and subjected to Knoop indentation. The test was performed at a load of 1000 gf and loading time of 50 s to ensure sufficient deformation of the coating so that it yields in the direction perpendicular to the lamellae. Accordingly, obtained Young’s modulus was that for the direction perpendicular to the lamellar interface. Young’s modulus of the as-sprayed and heat-treated alumina coatings is shown in Figure 5. Clearly, Young’s modulus of the as-sprayed alumina coating was about 107 GPa, and increased to 124 GPa after heat treatment. The above-mentioned results show that although after heat treatment, the crystalline structure near the interface changed from amorphous to γ-Al2O3, only a little increase occurred in coating hardness and Young’s modulus. This is because the interface bonding was not
altered under the annealing conditions employed and because the region in which microstructure change occurred was limited to a small area. However, when interface areas are required to transfer mechanical or thermal loading, such changes in the interface microstructure may significantly influence the coating load-bearing ability.

4. Conclusions
The influence of interface bonding on the local microstructure near the interface of the as-sprayed and heat-treated alumina coatings was clarified through HR-TEM observations. The obtained results showed that over unbonded zones, splats exhibit a γ-Al₂O₃ phase. An amorphous phase was observed in the splat over the bonded interface area. The amorphous phase layer within a splat was several hundred nanometers thick with nanocrystal γ-Al₂O₃ extended throughout the splat. After heat treatment, the phase of the bonding between adjacent splats transformed from amorphous to nanosized γ-Al₂O₃, thereby resulting in amorphous phase recrystallization during heat treatment. Moreover, nanosized pores were observed in crystallized γ-Al₂O₃; these pores were formed because of the difference in the densities of the two phases involved in transformation. The microhardness and Young’s modulus of an as-sprayed alumina coating were 840 Hv 0.3 and 107 GPa, respectively, while these values increased to 982 Hv 0.3 and 124 GPa, respectively, after heat treatment. The small change in the values was attributed to the limited improvement in interface bonding after heat treatment.

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