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Relationships Between the Microstructure and Properties of Thermally Sprayed Deposits

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Thermally sprayed deposits have layered structure composed of individual splats. The individual splats have quenching microstructure of quasi-stable preferred fine grains. However, this fine-grained microstructure of the deposits is usually not reflected by improved performance of the deposits because a layered structure with two-dimensional voids occurs between lamellar interfaces.

The microstructure of the thermal spray deposits with the emphasis on the layer structural parameters is reviewed. Conventionally, one of the most common quantitative parameters used to characterize the microstructure of the thermally sprayed deposits is the porosity, measured by different methods. However, it is illustrated that the relationships between properties and porosity for bulk porous materials processed by conventional processes cannot be applied to thermally sprayed deposits owing to the two-dimensional characteristics of voids. The total porosity in the deposits is not meaningful from the viewpoint of prediction of the deposit properties. An idealized structural model and related parameters, instead of porosity, are proposed to characterize quantitatively the microstructure of the thermally sprayed deposit. The relationships between the properties and the structural parameters are presented for the plasma-sprayed ceramic deposits based on the proposed microstructure model. The properties include the Young's modulus, fracture toughness, erosion resistance, and thermal conductivity of the plasma sprayed ceramic deposits. The correlations of theoretical relationships with reported experimental data are discussed.

An agreement of theoretical with observed values suggests that the lamellar structure of the deposit with limited interface bonding is the dominant factor controlling the performance of the deposit.

Keywords Al_2O_3 deposit, ceramic deposit, erosion wear, fracture toughness, lamellar interface bonding, lamellar structure, microstructure/property relationship, porosity, thermal conductivity, Young's modulus

1. Introduction

The properties of materials, in particular, mechanical properties, are generally a sensitive function of their microstructure. The relationships between the microstructure and the properties form a central theme of materials science. Undoubtedly, thermally sprayed deposits are no exception. The establishment of comprehensive relationships between the microstructure and the properties of the deposits requires quantitative structural parameters, which can effectively characterize the structural features of thermal spray deposits.

However, for the thermal spray deposits the quantitative studies of the relationship between deposit structure and properties are limited. A major reason is the complexity of the deposit microstructure, which is composed of a complex void network, and a lack of quantitative characterization methods with effective and meaningful parameters.

Because the voids are easily identifiable, generally, the volume fraction of the voids, often referred to as the porosity, has been commonly accepted as a typical structure parameter. The porosity is usually estimated by qualitative examination from a cross-sectional microstructure and also estimated quantitatively by the image analysis technique. The detailed study into lamellar structure of the sprayed deposit has revealed the existence of the "void" in the interfaces between the lamellae in the deposits. Therefore, the voids in the thermal spray deposits should include what are commonly referred to as pores, which are often identifiable from the optical microstructure, interlamellar voids, and the open space from microcracks, which are often observed in the deposits from brittle materials. The interlamellar voids present the semi-two-dimensional (2D) type of geometrical feature, which is significantly different from those in porous materials, processed by conventional powder metallurgical process. Moreover, such interlamellar voids are often beyond the limitation of the observation when optical microscopy is used for the examination of the microstructure of the deposits. Accordingly, the characterization of the microstructure of a thermally sprayed deposit and examination of structural dependency of deposit properties should be approached in a completely different way from the characterization of conventional porous materials.

In this article, the current characterization methods to elucidate the microstructure of thermal spray deposits are reviewed. Emphasis is given to the quantitative characterization of the microstructure, useful and meaningful structural parameters are proposed, and their relationships to deposit properties are examined.

2. The Voids in a Thermally Sprayed Deposit

A thermally sprayed deposit is formed by a stream of molten droplets impacting on the substrate followed by flattening, rapid

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solidification, and cooling processes. The individual molten droplets spread to thin lamellae, the stacking of which constitutes the deposit. A thermally sprayed deposit is generally of lamellar structure. A fraction of voids from several percent up to 20% can be formed in the deposit.[1] Some of the voids result from insufficient filling and incomplete wetting of molten liquid to previously formed rough deposit surfaces. The microcracks can be formed easily in the splats of brittle materials (in particular, ceramic materials) because of quenching stress that occurs in the splats.[2] Such microcracks are also a kind of void that appears in the deposits and constitutes a fraction of porosity. Because the porosity in porous materials processed by conventional methods such as sintering influences significantly their performance,[3] it is believed that the porosity in the deposit will influence many parameters such as mechanical (e.g., elastic modulus and stress at failure) and physical properties (e.g., thermal conductivity and dielectric break down voltage) of the deposits.[4] Currently, the evaluation of porosity volume is the major method of the characterization of the thermal sprayed deposit microstructure.

The voids in the deposits can generally be divided into three types on the basis of the dimensions of voids, i.e., three-dimensional (3D) type, two-dimensional (2D) type, and microcrack type, especially in ceramic deposits.[5,6] 3D-type voids are similar in morphology to those in the materials processed by the powder metallurgical method, and are coarse voids in a size from sub-micrometer to more than 10 μm, with similar dimensions spatially. 2D-type voids correspond to the interlamellar gap, and are in the sub-micrometer dimension at the direction perpendicular to splat plane, but they are in the size comparable with the size of splat in the other two directions. Therefore, such voids present typically the "coin"-shape morphology. Figure 1 illustrates the interlamellar voids revealed by the distribution of copper electroplated into an Al_2O_3 deposit.[7] Because the cracks are perpendicular to splat plane, the microcracks within the splats have different sizes in three dimensions. The size in the direction perpendicular to cracking, e.g., the width of crack, is in the sub-micrometer range, whereas in the direction along the thickness of splat, the size of the void is comparable to the thickness of splat (Fig. 1). In the direction of cracking its dimension depends on the intersecting of a complex crack network and may range from about 10 μm to several tens of micrometers.[8,9] It should be noted that microcrack-type voids only occur in the deposits from brittle materials.

Generally, the porosity in thermal spray deposits is characterized qualitatively by microstructure observation and quantitatively by the mercury intrusion porosimetry (MIP) technique in addition to deposit density measurement. The direct examination of deposit microstructure from a cross section of a deposit using optical microscopy and scanning electron microscopy (SEM) is usually used for qualitative comparison of porosity. With the application of the digital imaging technique, the porosity could be quantitatively measured from cross-sectional microstructure.[10] However, because the removal of loosely bonded particles in the deposit and smear-out for ductile materials may occur during grinding and polishing processes, such quantitative characterization may lead to a misleading result.[11] Therefore, to minimize those influences, the infiltration of resin into the voids in deposits during the evacuated condition before grinding was proposed.[12] Another problem with the quantitative estimation of the porosity using cross-sectional microstructure is the limitation of such direct observation methods to reveal the voids in the sub-micrometer range.[7]

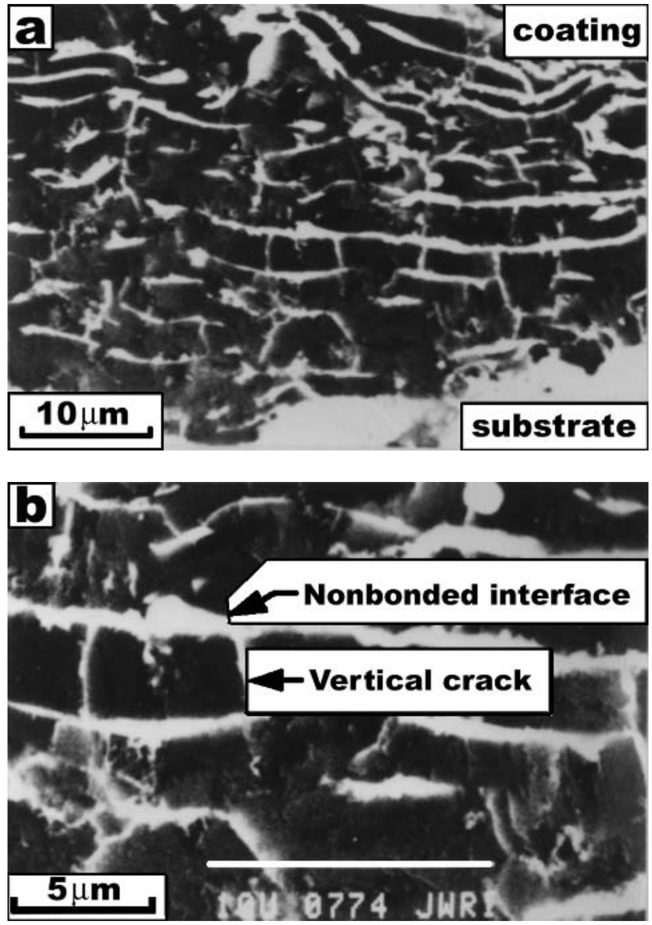

Fig. 1 Typical microstructure of copper-plated Al_2O_3 coating. White strings are copper plated into the coating, the distributions of which indicate the 2D voids in the coating corresponding to the interlamellar gaps and vertical microcracks.

Using the MIP measurement, not only total porosity for open voids, but also the distribution of void size could be evaluated quantitatively.[13] The MIP measurement indicated that the voids in thermal spray deposits appeared as a bimodal distribution.[14,15] However, because the intrusion of mercury into voids in the deposits will be controlled by the small dimension of the channel interconnecting small and large voids, the MIP can result in misleading results in the void distributions.[16,17] Kuroda[17] examined the effect of sample preparation methods on the results of MIP measurements of plasma sprayed Ni-Cr deposits by covering the deposit surface with polyester to limit the deposit surface contacting with mercury. Compared with the ordinarily prepared sample, the plastic-covered samples show almost no voids larger than 1 μm. However, the porosity volumes of the small size voids are almost the same despite the sample preparation methods. Therefore, it was suggested that the porosity volume of those voids larger than 1 μm is an artifact resulting from the surface roughness of the deposits. It is evident that the porosity fraction corresponding to small voids gives the measurement of the deposit porosity volume. This does not mean, however, that there are no voids larger than 1 μm in the deposits. Therefore, it was suggested that the deposits should be encapsulated or surface-polished to diminish the effect of sample preparation on the MIP result.[6,17]

Recently, small angle neutron scattering (SANS) was used to characterize the specific void surface area of ceramic deposits with the information about anisotropic features of the voids.[18] However, the examination of the relationship between the specific void surface area and mechanical properties of deposit (for example wear resistance[19]) yielded a very poor dependence. This fact may suggest that it is necessary to abstract the other form of characteristic parameters from the SANS signal rather than the total specific void surface area to interpret successfully deposit properties using the SANS technique.

3. Influence of Porosity on Properties of the Deposits

For conventionally processed bulk materials in which the void has a 3D spherical shape, the mechanical properties of materials are generally related empirically to porosity by the following equation:[3]

$$S_p = S_0 \cdot \exp(-bp) \quad \text{(Eq 1)}$$

where S_p is one of mechanical properties of materials with porosity p, such as Young's modulus, hardness, tensile strength, compressive strength, and fracture toughness; S_0 is the corresponding individual properties of dense material; and b is a constant for a certain property. For porous materials with spherical voids, the above equation can empirically depict the relationship between porosity and mechanical properties satisfactorily.[3]

Similar consideration could be applied to thermal sprayed deposits. However, the dependence of mechanical properties on the porosity would be greatly influenced by the shape of the voids. In thermally sprayed deposits, because of the unique void geometry as mentioned in the previous section, the above exponential relationship becomes difficult to apply. For example, Young's modulus and compressive strength of yttria stabilized zirconia deposit of 7% porosity were measured to be about 37 GPa and 400 MPa, respectively.[20] At the same time, the Eq 1 yields 135 GPa and 1087 MPa, on the basis of the exponential relation[1] assuming that $b = 4.1$ for Young's modulus and 7.2 for compressive strength with a spherical-shaped void,[3] Young's modulus and compressive strength of identical void-free materials are 180 GPa and 1800 MPa,[20] respectively. Clearly, there is a considerable discrepancy between the observed values and the values predicted by the formula.[1] It is evident that the relationship given by Eq 1 is not applicable to thermal spray deposits.

For thermal conductivity, Loeb derived the theoretical relationship between thermal conductivity and porosity. For porous materials with spherical voids, this relationship can be simplified to the following equation:[21]

$$\lambda_p = \lambda_0 \cdot (1 - bp) \quad \text{(Eq 2)}$$

where λ_p is the thermal conductivity of porous materials with porosity of p, λ_0 is the thermal conductivity of dense material, and b is a constant. For randomly distributed spherical voids, b is equal to 1.[22] For thermal sprayed deposit with porosity of 5-15%, Eq 2 predicts thermal conductivity higher than 80% of dense bulk materials. However, the thermal conductivity of thermal sprayed deposits is usually about 10-20% of dense bulk materials.[23,24]

Therefore, it is clear that the general relationships between porosity and properties for conventionally processed porous materials cannot be applied to thermally sprayed porous deposits. This is because total porosity or the specific void surface area estimated by the SANS could not represent the characteristics of the microstructure of thermally sprayed deposit owing to the 2D feature of void geometry despite great efforts made for the evaluation of porosity of the deposit as reviewed in previous section.

4. Characterization of Layer Structure of Thermal Spray Deposit

Examinations of the fractured deposit surface after the fracture mechanics test[25] and shear strength test[26] suggested that cohesive fracture easily occurs and the lamellar interface area is the weakest part in the deposit. Therefore, taking into account the layered structure of porous thermal spray deposits, the bonding at the interface between flattened particles (i.e., lamellar cohesion) is the most important factor in controlling deposit properties. The fracture mechanical test results suggested that only a limited interface area in the deposit is in real contact.[25] This fact was experimentally confirmed through the direct observation of plasma-sprayed Al_2O_3 deposit using transmission electron microscopy (TEM) by McPherson and Shafer.[27] The comparison of Young's modulus of Al_2O_3 deposits with identical bulk material suggested a real contact lamellar interface area of about one fifth (bonding ratio).[27] The bonding ratio here is defined as the ratio of total bonded lamellar interface areas to the total apparent interface areas between flattened splats in the deposits.[7,28] This was further confirmed by a microstructure model for thermal conductivity of ceramic deposits proposed by McPherson.[23]

Such limited interface contact between lamellae was visually revealed when copper was electroplated into a plasma sprayed Al_2O_3 deposit by Arata et al.[7,28] The typical microstructure of a copper-plated Al_2O_3 deposit is shown in Fig. 1, where the white strings in the microstructure are the copper plated into voids in the as-sprayed deposit. The copper strings clearly reveal the void structure in the sprayed ceramic deposit, and indicate the existence of a substantial nonbonded interface area between lamellae. The nonbonded interface areas constitute the 2D voids in the deposits. Accordingly, the structure of plasma sprayed Al_2O_3 deposits was intensively studied using copper plating into the deposits and structural parameters other than porosity.[7-9,28-30]

Because the infiltration of copper into the Al_2O_3 deposit can reveal its detailed lamellar structure, the infiltration technique has been used to visualize the structure of thermal spray deposits.[31-36] The impregnation of epoxy resin into voids before polishing was attempted to characterize the microstructure of Ni-Al deposits by quantitative metallography.[31] Such a technique can

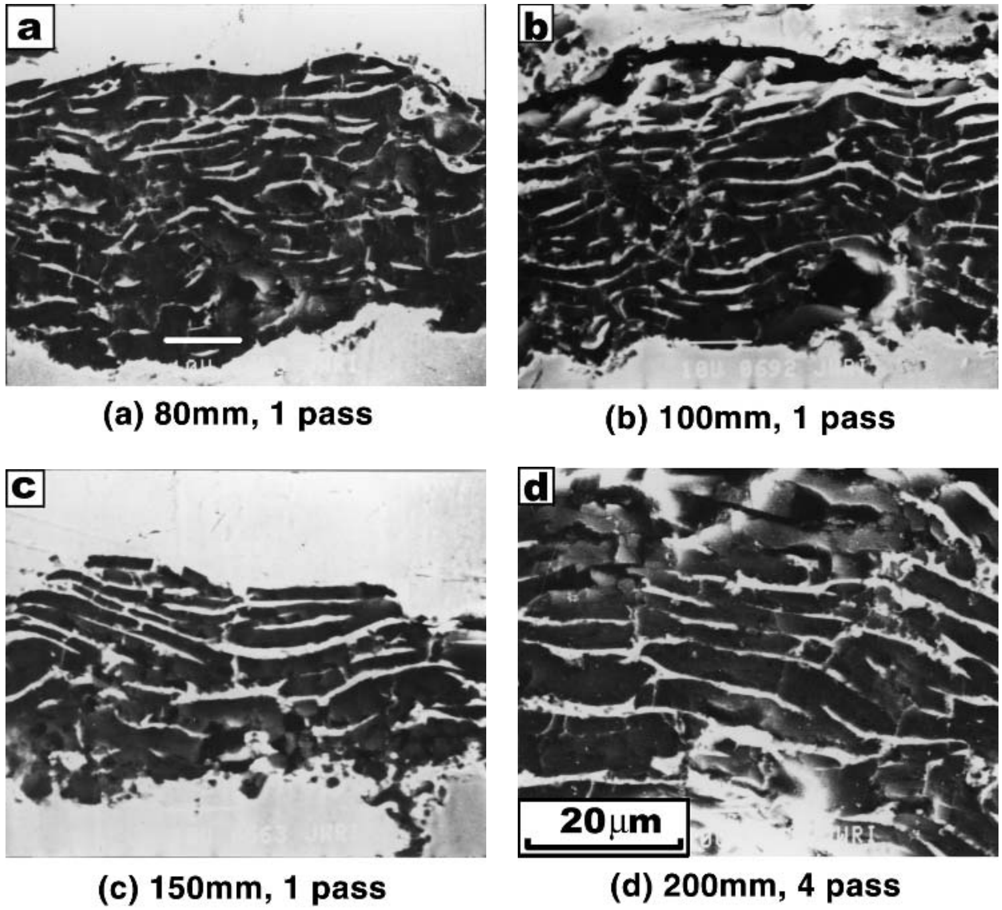

Fig. 2 Microstructures of copper-plated Al_2O_3 coatings. The coatings are sprayed at different spray distances. White strings represent the copper plated into interlamellar gaps and vertical microcracks in as-sprayed coatings.

improve the repeatability of the microstructure characterization of the thermal spray deposit.[37] The infiltration of Cr_2O_3 by chromium acid into an Al_2O_3 deposit was used to strengthen the deposit properties.[38] Recently, this technique was used to visualize the deposit microstructure, which provided a similar image to that revealed by the copper plating technique.[32,33] For metallic deposits such as Ni-Cr, the infiltration of molten Bi-alloy with low melting point assisted by high pressure, instead of Cr_2O_3, confirmed the existence of the limited interface bonding in the deposits.[34] The detailed microstructure of refractory tungsten deposits was also delineated by the infiltration of molten copper into the deposit.[35] By the infiltration of epoxy resin into a thermal barrier coating deposit, Bengtsson and Johannesson[36] characterized the microcracks using a point-counting technique, and the vertical crack density reported reasonably agreed with those for Al_2O_3 deposits.[8,9]

All of these studies successfully revealed the detailed void network in corresponding deposits and the existence of the limited bonding at the lamellar interface, and proved the usefulness of such infiltration techniques. Most of these studies were ultimately limited to void structure characterization using parameters such as porosity volume and void size. However, these void-related parameters cannot satisfactorily be used to characterize the dependence of the properties on the microstructure for thermal spray deposits of lamellar structure, as mentioned previously. Only the infiltration of copper into the tungsten deposits measured the interface bonding ratio rather than void-related porosity.

The systematically quantitative characterization of the structure of plasma sprayed Al_2O_3 deposits clarified the dependency of structural parameters on process parameters using structural parameters such as the mean lamellar thickness, the mean bonding ratio, and vertical crack density.[7-9,28-30] Figure 2 shows typical microstructure of copper-plated Al_2O_3 deposits sprayed at different spray distances at the plasma power of 28 kW.[8,9] The microstructures show that all deposits exhibit lamellar structure and are composed of well-flattened particles. The existence of substantial nonbonded interface area can be clearly observed in either deposit, indicated by the distribution of copper area in the Al_2O_3 deposits. A quantitative measurement of bonding ratio for the above deposits shows that a rapid decrease of bonding ratio occurs when the spray distance is increased from 100-150 mm (Fig. 3).

The effect of plasma power during plasma spraying reveals that the bonding ratio is rapidly saturated to about 32% with an increase in plasma power (Fig. 4).[8,9] This result implies that the increase in power of plasma spraying equipment does not contribute to an increase in interface bonding. The systematic inves-

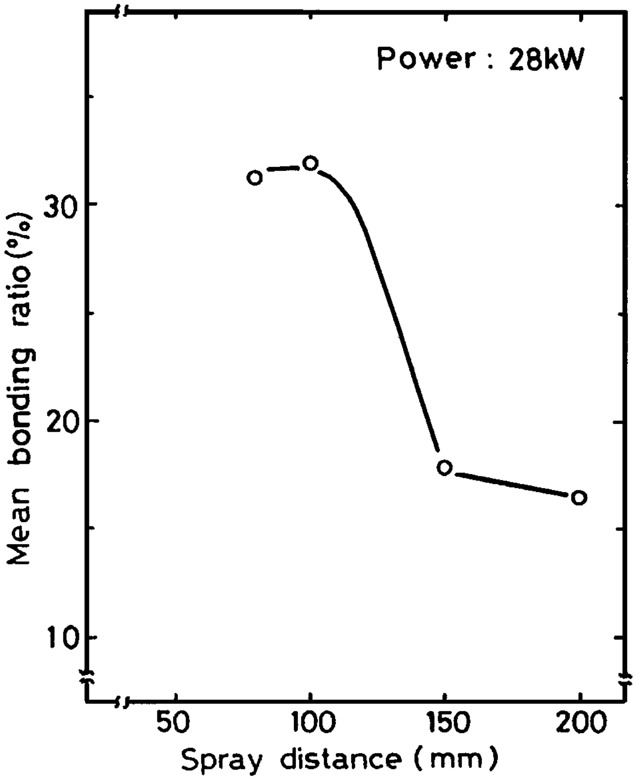

Fig. 3 Effect of spray distance on the mean bonding ratio of plasma sprayed Al_2O_3 coating

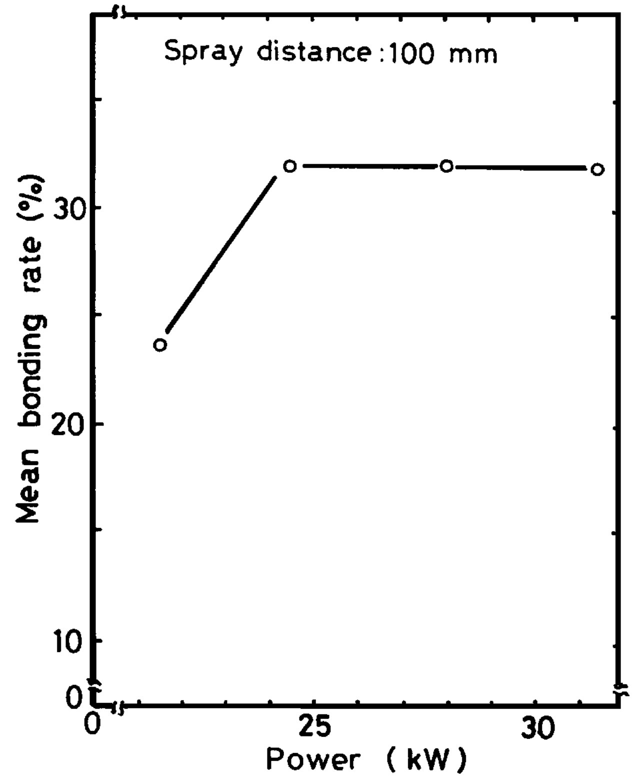

Fig. 4 Effect of plasma arc power on the mean bonding ratio of plasma sprayed Al_2O_3 coating

tigation into lamellar bonding revealed that bonding ratio up to around 32% could be achieved for plasma sprayed ceramic deposit. This implies that two-thirds of the interfaces between lamellae in ceramic deposit are separated by an interlamellar gap in sub-micrometer dimension.

On the basis of the effect of spray conditions on the particle temperature and velocity reported,[39,40] it can be suggested that the bonding ratio is mainly influenced by the particle temperature rather than particle velocity.[8,9] The fact that the Al_2O_3 coating deposited by the detonation gun (D-gun) process yielded an interface bonding less than 10% provided support for the above speculation.[30] All of these results quantitatively reveal that only a limited bonding exists at the interfaces between flattened particles.

In addition to the bonding ratio, the effects of spray parameters on the mean lamellar thickness and vertical microcrack density were also characterized with the copper plating method using Al_2O_3 deposits.[8,9] The results showed that the mean lamellar thickness was changed from 1.5 to about 3 μm in plasma sprayed Al_2O_3 deposits with the powder size from 10-44 μm. For most spray conditions the mean thickness ranged from 1.5 to about 2.5 μm.

Although the copper as the tracer can be plated into the small voids larger than the size of a Cu anion,[41] this copper plating method can only be applied to electrically insulating ceramic deposits such as Al_2O_3 and ZrO_2. It cannot be applied to TiO_2 and Cr_2O_3 deposits, because these materials become electrically conductive after plasma spraying. Consequently, the copper was plated on the surface of the deposits rather than into the deposit.[41] Therefore, the visualization of the microstructure with another effective infiltration method, such as Cr_2O_3, which would combine the detecting technique of the infiltrated materials should be developed.[5] The quantitative characterization of the microstructure using structural parameters (such as the bonding ratio and lamellar thickness) for Al_2O_3 deposit makes it possible to examine the structural features that control the deposit properties.

5. Idealized Model for the Microstructure of Thermally Sprayed Deposit and Introduction of Structural Parameters

The recent progress of splat formation research revealed that the disk-like splat of evenly distributed thickness could be formed with a molten droplet on a flat substrate surface when the substrate temperature exceeds 200 °C.[42-44] On the basis of the systematic investigation of the structure of plasma sprayed Al_2O_3 deposits, it can be suggested that for the deposits sprayed with completely molten droplets and composed of well-flattened splats, a splat in deposit is of evenly distributed thickness. In a splat of brittle material the vertical microcracks are distributed in individual splats in a net-like form, which break vertically through the splat. For ductile metallic splat the periphery of splat can be regarded as the only vertical crack. The flattened splats are bonded to underlying splat through bonding areas of radius

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a, which are distributed evenly between lamellae. By neglecting the tortuosity of lamellae, an idealized microstructure model can be described (Fig. 5).[1,23]

Generally, the porosity volume and void size and its distribution are used as the microstructural parameters to characterize the microstructure void features of thermal spray deposits. As illustrated in the previous section, all of these parameters cannot successfully characterize the 2D type of voids in the deposits to interpret the properties of the deposits. On the other hand, such 2D type of voids (i.e., nonbonded interface area) can also be regarded as the cracks in addition to the vertical microcracks in individual lamellae from the viewpoint of fracture mechanics.[7] To characterize the structure shown in Fig. 5 and to characterize the relationship between the structure and properties of the deposits, the following proposed parameters[5] are more suitable:

- mean lamellar thickness (δ);
- vertical crack density (ρ_c);
- splat diameter (D);
- average width of crack (β_c);
- bonding ratio between lamellae (α);
- size of bonded region ($2a$); and
- average width of nonbonded lamellar interface gap (β_i).

In addition to the above parameters, the information for the curvature of splat resulting from tortuosity may also be necessary. The porosity in thermal spray deposits can be calculated by the above-mentioned parameters except for coarse voids.

6. Relationship Between Properties and Structural Parameters

6.1 The Relationship Between Thermal Conductivity and Structural Parameters

The first attempt to establish the quantitative relationship between the deposit structure and properties was made for thermal conductivity of ZrO_2 deposits using an idealized structure model by McPherson.[23] On the basis of the proposed model of thermal contact resistance, the relative thermal conductivity can be derived in the following equation when the thermal convection and radiation in the void are neglected[45]:

$$\frac{\lambda_c}{\lambda} = \frac{2\alpha}{\pi}\frac{\delta}{\alpha}\left(1 + \frac{2\alpha\delta}{a\pi}\right)^{-1} \qquad \text{(Eq 3)}$$

where λ_c and λ are thermal conductivities of deposit and splat materials, respectively. Neglecting the second term in the denominator, the above equation is reduced to the original equation derived by McPherson.[23]

It is obvious that the thermal conductivity also depends on the geometric dimensions of bonded area. For Al_2O_3 deposits, typical structural parameters are $\alpha = 0.32$ and $(\delta/a) = 0.5$. Eq 3 yields $(\lambda_c/\lambda) = 0.102$.

For bulk dense Al_2O_3, the thermal conductivity ranges from 29-36 W/mK at 300 K.[46-48] The thermal conductivity of Al_2O_3 deposits is 2.72-3.64W/mK.[49,50] This yields the value of (λ_c/λ) = 0.076-0.126, which is consistent with the above estimated value, although the deposit consists of γ-Al_2O_3 (the thermal conductivity of which is unknown). A higher thermal conductivity was observed by Ault for a flame sprayed Al_2O_3 deposit.[51]

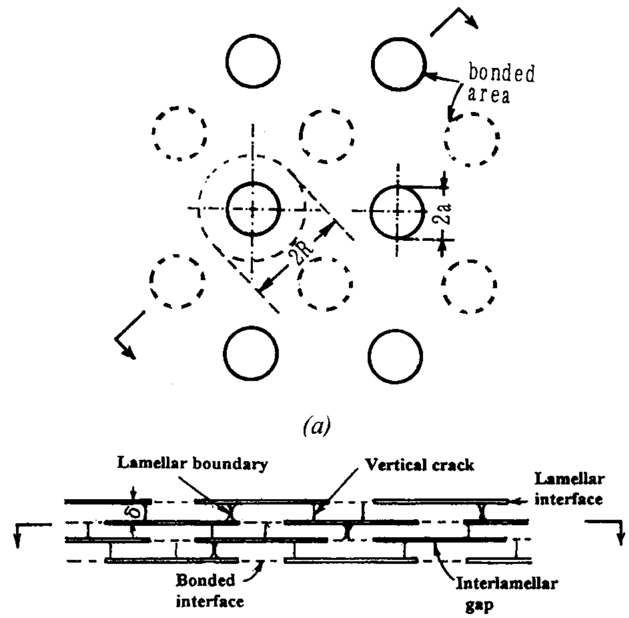

Fig. 5 Idealized model of the microstructure of the thermal spray deposit. **(a)** Plan view of lamellar interface and **(b)** cross section of coating.

Therefore, the comparison between predicted values using Eq 3 with observed values yields good agreement.[23,45]

When there exist gases in the voids such as nonbonded interface area and microcracks under elevated temperature, the heat transfer from convection of gases and radiation between lamellae will increase the apparent effective thermal conductivity.[23,52] In such a case, the parameters such as the gap of nonbonded interface area and the width of vertical cracks must be known to calculate the thermal conductivity of the deposits, in addition to the parameters required by Eq 3.[23]

It should be noted that the above relationship of the thermal conductivity with the microstructural parameters was derived on the basis of the thermal contact resistance model of localized contact area. Such a model was originally used to calculate the electric contact resistance.[53] Therefore, the above relationship also should be valid for the electric conductivity of the deposit. This may be used to interpret the dependency of the electric conductivity of the deposit or the limited critical current density of high temperature superconducting oxide deposits formed by thermal spraying on the basis of the structural parameters; in particular, the limited bonding at the interfaces.

6.2 The Relationship Between Young's Modulus and Structural Parameters

When a load is applied perpendicularly to the plane of the deposit, the stress will be transferred from one lamella to the other through the bonded interface area. Figure 6 shows schematically the loading at a cross section of one lamella.[1,54] Under such stressed conditions, the lamella will experience tension at the bonded interface area and bending at the nonbonded area.

The idealized model for microstructure of the deposit was used and the effect of vertical cracks was neglected to establish

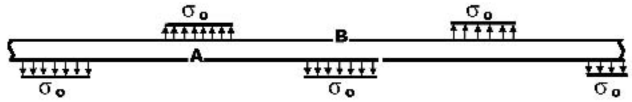

Fig. 6 Schematic diagram of the loading between lamellar by stress σ_0 at bonded regions

the relationship between Young's modulus perpendicular to the deposit plane and structural parameters based on the plate theory. The relative Young's modulus of thermally sprayed deposit can be expressed as follows[1]:

$$\frac{E_c}{E} = \alpha \left[1 + 2\pi \left(\frac{a}{\delta} \right)^4 \beta^2 f(\beta) \right]^{-1} \qquad \text{(Eq 4)}$$

where E_c and E are Young's modulus of deposit and splat materials, respectively; $\beta = \sqrt{(\pi/8\alpha)}$; and $f(\beta)$ is a function of β, i.e., a function of the interface bonding ratio. When α becomes larger than 40%, the bending effect of lamella during transfer of load can be neglected and the above equation then is reduced to $E_c/E = \alpha$. Figure 7 shows the relationship between the relative Young's modulus of the deposits and the bonding ratio calculated under different values of a/δ.[1] If this result and the bonding ratio data described in the previous section are considered, it can be found that the Young's modulus of the deposits will range from about 10% up to the bonding ratio of bulk materials, depending on the a/δ.

If one assumes an a/δ value about 2 and γ-Al_2O_3 content in the Al_2O_3 deposit, the Young's modulus of Al_2O_3 deposits are estimated using the above equation in Fig. 8,[1,54] compared with the data reported in literature. Although the effect of the vertical cracks on the Young's modulus is neglected in the present model, it is obvious that the above model explains reasonably the observed Young's modulus of a thermally sprayed deposit.[1,54]

Note that the increase in microcrack density will lead to the decrease in the Young's modulus. The calculation in Eq 4 showed that the individual relative bonding area (a/δ) has significant influence on the Young's modulus, as shown in Fig. 8.[1] Therefore, it is necessary to obtain the sizes of bonded areas for individual deposits to examine quantitatively the effect of crack density on the Young's modulus of the deposits.

The anisotropy of Young's modulus of the thermal spray deposits is obvious with regard to the layered microstructure.[50,55] The present model explains reasonably the Young's modulus at the direction perpendicular to the lamellar surface of the deposits. Moreover, the Young's modulus in this direction should be the lowest of the entire deposit.

More recently, Leigh and Berndt[56] and Sevostianov and Kachanov[57] have used the other theoretical approaches to characterize the relationship between the Young's modulus and the microstructure of the thermal spray deposits with a spheroid-shaped voids model. All of these approaches explained the dominant effect of the thin crack type of void on the Young's moduli and the anisotropy of the elastic properties of the thermal spray deposits. To predict the elastic moduli of the thermal spray deposits with those models, however, a characterizable microstructural model must be developed.

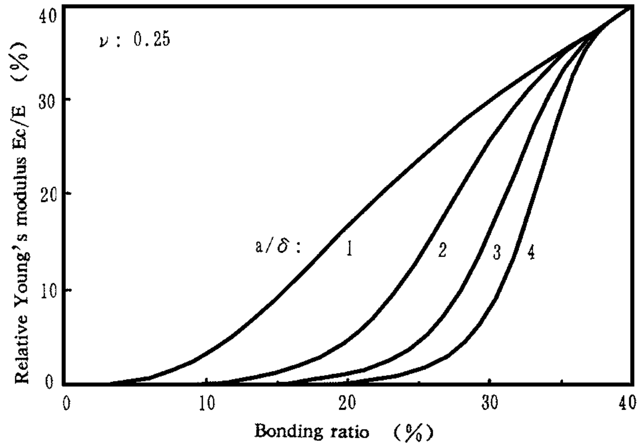

Fig. 7 Effects of the bonding ratio and a/δ on the Young's modulus of the thermal spray deposits

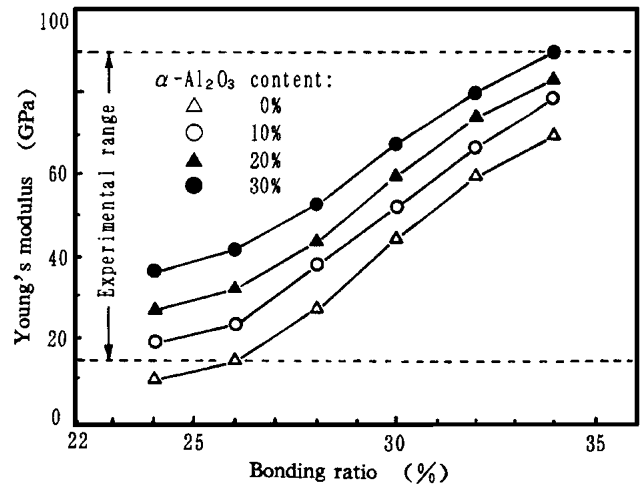

Fig. 8 Comparison of Young's modulus estimated as a function of bonding ratio and α-Al_2O_3 content in Al_2O_3 coating with those observed

6.3 The Relationship Between Fracture Toughness and Structural Parameters

For bulk ceramic materials, the critical kinetic strain energy release rate G_{1c} is generally expressed as[58]

$$G_{1c} = 2\gamma_e \qquad \text{(Eq 5)}$$

where γ_e is the effective surface energy.

For the cohesive fracture of the deposit, G_{1c} can be simply expressed by the following equation[59]:

$$G_{1c} = 2C_p\gamma_e\alpha \qquad \text{(Eq 6)}$$

where C_p is a fracture path-related constant, which depends on the tortuosity of flattened particle in a thermally sprayed deposit. For the deposit consisting of well-flattened particles, $C_p \approx 1$. The

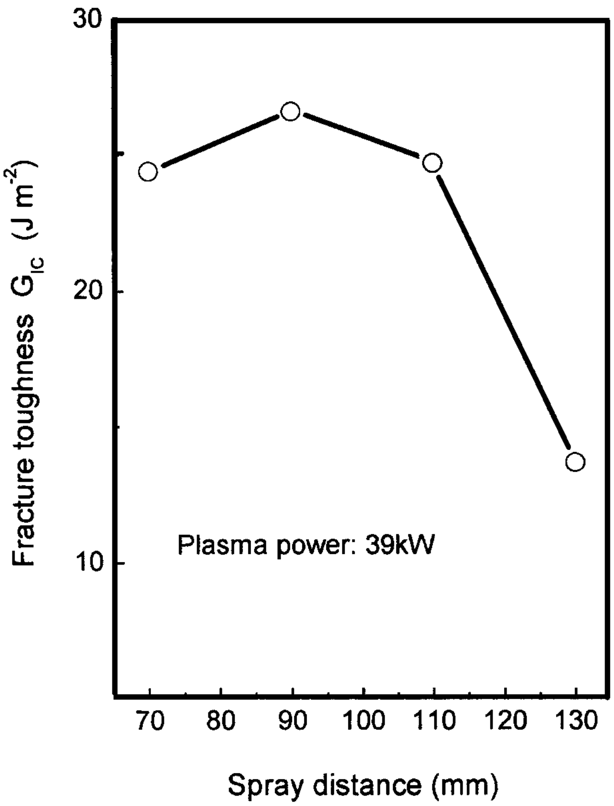

Fig. 9 Effect of spray distance on the fracture toughness of plasma sprayed Al_2O_3 coating

plasma sprayed ceramic deposits, such as those shown in Fig. 2, can be considered to belong to such a case.

For bulk Al_2O_3, γ_e is increased from 25-45 J/m^2 as grain size is decreased from about 20 to less than 2 μm.[60] This yields a G_{1c} of around 90 J/m^2 for bulk Al_2O_3 with fine grain structure of about 2 μm. With the fine structure observed (i.e., G_{1c} value of 90 J/m^2) and bonding ratio of 16-32%,[8,9] a G_{1c} value from 14.4-29 J/m^2 can be expected for the α-Al_2O_3 deposit from Eq 6.

A G_{1c} value of 12-26 J/m^2 was observed for an Al_2O_3 deposit using the double cantilever beam (DCB) method.[25] However, the Al_2O_3 deposit mainly consists of γ-Al_2O_3. Although the data of effective surface energy of γ-Al_2O_3 are not available, the value may be expected to be lower than that of α-Al_2O_3. Accordingly, the reported G_{1c} is reasonably consistent with the expected value. The recent measurement of G_{1c} of an Al_2O_3 deposit using a modified DCB test has also yielded similar results. As shown in Fig. 9,[61] it was evident that the change of G_{1c} of an Al_2O_3 deposit with spray distance takes place at the same dependency as that observed for the interface bonding shown in Fig. 3, despite different plasma spray equipment. These facts suggest that the fracture toughness of a ceramic deposit is mainly governed by the interface bonding between flattened particles.

From the cohesive fracture surface of the deposits after the DCB test, the translamellar propagation of the crack was also observed in addition to the propagation along the lamellar interfaces.[61] With ceramic deposits, such translamellar propagation tended to occur from the pre-existing vertical cracks. Therefore,

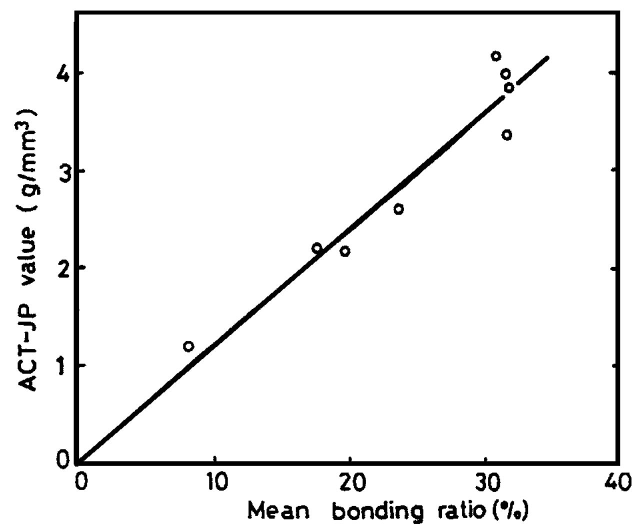

Fig. 10 Effect of mean bonding ratio on the ACT-JP value of plasma sprayed Al_2O_3 coating

it can be considered that the substantial occurrence of the vertical cracks in individual lamellae limits the effect of the translamellar propagation on the dependence of the G_{1c} on the interface bonding. This implies the limited effect of the vertical cracks in individual splats on the relationship between G_{1c} and bonding ratio.

6.4 The Relationship Between Erosion Resistance and Structural Parameters

For the ceramic deposit of lamellar structure with limited bonding at the interface between flattened particles, the erosion of the deposits occurs through the separation of flattened particles from the interface after impact by an erosive particle, in particular, at 90° impact.[62] If one assumes that a fraction of kinetic energy of an impacting particle absorbed by the deposit contributes to the debonding of bonded interface area of the lamella exposed directly to impact, which leads to the separation of surface lamella from the deposit, the erosion rate can be related to the structural parameters by the following equation[63]:

$$A_c = \frac{2\gamma_e \alpha}{K E_m \delta} \qquad \text{(Eq 7)}$$

where A_c is referred to as the ACT-JP value in the Arata coating test with jet particles (ACT-JP) value, γ_e is the effective surface energy of lamellar materials, E_m is the kinetic energy of the erosive particle, and K is an effective energy-absorbing coefficient. Here, the ACT-JP value is defined as the reciprocal of volume erosion rate of the deposit tested using the ACT-JP tester, which is the modified particle erosion tester with the erosive particle conditions strictly monitored.[64]

On the basis of the above relation, the erosion of the deposit is inversely proportional to interface bonding and directly proportional to the lamellar thickness. The correlation with experimental data shows excellent agreement (Fig. 10).[63] Therefore, the lamellar bonding will be significantly important in determining the erosion of deposit.

7. Conclusions

Thermally sprayed deposits are characterized by layered structure. There are voids inevitably in the thermal spray deposits. The voids in the deposits consist of large voids of size corresponding to lamellar thickness larger than 10 μm, nonbonded interface area, and vertical cracks (in particular, in individual ceramic lamella which are in the sub-micrometer size range).

The porosity is a commonly used parameter to characterize the deposit microstructure. However, the total porosity of the deposit does not have significant meaning from the viewpoint of quantitative interpretation of deposit properties, mainly because of the 2D characteristics of voids in the deposits.

Therefore, despite the fine grain structure within individual lamella in the thermally sprayed deposits, the properties of the deposits generally exhibit much lower property values compared with identical bulk materials of the same porosity level. The empirical relationships between properties and porosity for conventional processed porous bulk materials cannot be successfully applied to represent the dependency of the deposit property on the microstructure.

The quantitative structural parameters have been proposed to characterize the deposit lamellar structure instead of porosity. The most important parameter proposed is the bonding ratio at the interfaces between lamellae.

The bonding at the interface between flattened particles is much less than the apparent total interface area. It has been revealed using the copper electroplating technique that for Al_2O_3 deposit the bonding ratio can be achieved up to 32%. The spray parameter (in particular, spray distance) was found to largely affect the interface bonding.

The establishment of relationships between the proposed structural parameters and the properties, including thermal conductivity, Young's modulus, fracture toughness, and erosion resistance, has been attempted using an idealized microstructural model with parameters. The good correlation of experimental results with the theoretical relationships suggests that the properties of the thermally sprayed deposits are determined by the lamellar structure of the deposits. Therefore, the quantitative characterization of the deposit structure using the structural parameters other than total porosity is of major importance.

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