Origin of preferential orientation of rutile phase in thermally sprayed TiO₂ coatings

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Abstract

In order to elucidate the origin of the (101) preferential orientation of rutile phase in thermally sprayed TiO₂, both plasma spraying and high velocity oxy-fuel spraying of TiO₂ were conducted. The rutile phase in plasma-sprayed TiO₂ presented a much more significant preferential orientation than that in high velocity oxy-fuel sprayed TiO₂. The significant difference in the surface morphologies of both deposits suggests that the orientation factor is significantly influenced by the tensile stress in the individual splats. (101) planes may change their orientations parallel to the coating surface under tensile stress at high temperature during splat cooling. The crystalline plane rotation leads to the preferential orientation of the rutile phase in thermally sprayed TiO₂ deposit.

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1. Introduction

TiO₂ attracts much attention owing to its promising applications to photocatalytical, electrical, optical and tribological coatings [1–6]. The performance of TiO₂ is significantly influenced by preferential crystalline orientation [4–14]. Therefore, the orientation of TiO₂ coating is of essential importance to control the performance of TiO₂ coatings. It is reported that the rutile phase in plasma-sprayed TiO₂ coating presented a preferential orientation along (101) [15–17]. However, no reasonable explanation was found on the origin of the preferential orientation of rutile phase. To elucidate the mechanism of rutile phase orientation in thermally sprayed TiO₂, two different processes were employed to deposit TiO₂ with significantly different extent of preferential orientation. A mechanism resulting in the orientation of rutile phase in thermally sprayed TiO₂ was proposed.

2. Experimental

TiO₂ powder in pure rutile phase prepared by fuse-crushing was utilized as a feedstock. The powder size was ranged from 10 to 20 μm. TiO₂ coatings were deposited by plasma spraying (GP80) and high velocity oxy-fuel (HVOF) spraying (CH-2000). Ar/H₂ was employed to create a plasma jet in plasma spray. The arc voltage and arc current were 50 V and 400 A, respectively. The pressure of argon and hydrogen was 0.7 MPa and 0.4 MPa, respectively. The flow of argon and hydrogen was 2000 l/h and 10 l/h, respectively. The spray distance was 100 mm. During HVOF spraying, propane at flow of 36 l/min and oxygen at flow of 402 l/min was used to create a supersonic flame. The spray distance was 130 mm.

The crystalline structure of the coatings and the spray powder was characterized using X-ray diffraction (XRD) (Rigaku D/max-2400, Cu-Kα radiation). The topographic morphology of the coatings was examined using scanning electron microscopy (SEM) (Hitachi, S2700).

3. Results and discussion

Fig. 1 shows the XRD patterns of thermally sprayed TiO₂ coatings in comparison of those of TiO₂ powders. It can be found that both deposits were composed of rutile phase and a fraction of anatase phase. Anatase phase in both coatings showed no preferential orientation. The first strongest peak of rutile phase in XRD pattern of the plasma-sprayed TiO₂ was from (101) plane, while that for rutile powder was...
from (110) plane. It is clear that rutile phase in plasma-sprayed coating presented significant preferential orientation along (101). Moreover, rutile phase in HVOF coating presented a limited orientation. To quantitatively characterize the extent of preferential orientation of rutile phase in the coatings, Lotgering orientation factor was employed [17,18]. Lotgering factors were calculated to be 0.26 and 0.1 for plasma-sprayed coating and HVOF coating, respectively.

To further investigate the difference between plasma-sprayed TiO$_2$ coating and HVOF coating, coating topographic morphology was examined. Plasma sprayed coating, shown in Fig. 2, was composed of well flattened splats. During plasma spraying of TiO$_2$ coating, a stream of molten droplets impacts on a substrate followed by flattening, rapid solidification, and cooling processes [19]. The individual molten droplets spread into thin splats, the stacking of which constitutes the thermally sprayed deposit. Therefore, plasma-sprayed coating is typically of lamellar structure. Moreover, microcracks were formed in individual splats as observed in Fig. 2. Shrinkage of splats would occur when it cools down from high temperature once the solidification completes. However, since the substrate was kept at a low temperature and had dimensions several orders larger than sput in thickness, the splat shrinkage is restrained, although the bonding between the splats was not perfect [19–23]. Consequently, tensile stress is increased with the decrease of sput temperature. As the tensile stress reach the level of fracture strength at a certain temperature, cracks will occur because of brittleness of TiO$_2$. Since cracks were clearly observed in the splats as the result of tensile stress that occurred in the splats during cooling, it was possible to observe that the splats suffered restrain during cooling.

The tensile stress $\sigma$ in a sput is discribed as [24],

$$\sigma = E \alpha \Delta T$$

where $E$ is the Young’s modulus (290 GPa), $\alpha$ is the coefficient of thermal expansion ($7 \times 10^{-6}$ K$^{-1}$), $\Delta T$ is the temperature difference between the sput temperature and melting point. Here the tensile strength of TiO$_2$ was taken as 200 MPa. Basing on this equation, the tensile stress corresbonding to a small temperature drop of 100 K was calculated to be 203 MPa, which was higher than the tensile strength of TiO$_2$. It indicates that a small temperature drop of 100 K can lead to the fracture of the splats which results in the cracks perpendicular to the coating surface. Although the occurrence of cracks decreased the residual stress in splats, the further cooling of the splats can increase the tensile stress in the splats. In addition, the possible phase transformation from anatase to rutile could also increase the tensile stress owing the larger density of rutile phase comparing with anatase phase.

It must be pointed out that these cracks occurred at high temperature. Therefore, these cracks clearly demonstrated that the tensile stress in splats was ever larger than fracture strength of TiO$_2$ at high temperature during sput cooling process. The surface morphology of HVOF sprayed coating, shown in Fig. 3, is obviously dfferent from that of plasma-sprayed one. HVOF coating is composed of small particles in size from 1 to 3 $\mu$m. This morphology is similar to that observed with detonation gun sprayed ceramic coatings [25]. There are no evident cracks observed on the surface morphology. This suggests that the largest tensile stress in the sput was smaller than fracture strength of TiO$_2$ during cooling process. Accordingly, it can be considered that the tensile stress in plasma-sprayed coating was much larger than that of HVOF sprayed one. Possibly, the preferential orientation factor of two coatings is significantly influenced by the tensile stress. The larger preferential orientation is associated with a larger tensile stress.

During solidification of a molten TiO$_2$ splat, columnar grains grow perpendicularly to coating surface [19]. Considering surface energy, the close-packed (110) plane should be favored thermodynamically because (110) plane has the smallest surface energy in all planes of rutile phase [26]. (101) preferential orientation of thermally sprayed coatings suggested that there may be other force to change favorable (110) plane to (101) plane.

Rutile TiO$_2$ has a tetragonal unit cell, in which $a = b = 4.584 \AA$ and $c = 2.953 \AA$ [27]. Ti atoms occupy the body-center positions and eight corners in each unit cell. Each Ti atom is coordinated to six neighboring O atoms. One Ti atom and its six surrounding O atoms make up an
octahedron. Therefore, the crystalline structure of rutile can also be described as chains of TiO₆ octahedra. In each octahedron, Ti atom forms four first strong bonds, marked with thick line in Fig. 4, with its four nearest O neighbors, and two second strong bonds, marked with thin line in Fig. 4, with other two second near O neighbors [16]. These first strong bonds are distributed on (110) and (-110) crystalline planes.

When a tensile force is applied over rutile phase, the TiO₆ octahedra will prefer to be elongated along weak bonds, e.g. the second strong bonds shown in Fig. 4. These bonds are along the axes of the octahedra. Therefore, (110) and (-110) planes tend to be elongated under tensile stress. Since tensile stress in splats during cooling is parallel to the coating surface, both (110) and (-110) planes have a comparable ability to rotate their orientation parallel to coating surface. However, these two planes can never simultaneously be parallel to coating surface because they are perpendicular to each other. There must be another crystalline plane which can balance the two planes. To endure the tensile strain, this plane needs to make the smallest angles with the two planes such that the two planes can have the largest cast shadow on this plane. Fortunately, (101) and (-101) planes are suitable for serving as this balance planes. Since (101) and (-101) planes have the same atom arrangement owing to the symmetry of rutile unit cell, we can consider that (101) is most endurable to tensile stress and tensile strain.

Under the tensile stress at high temperature during splat cooling, some (101) planes in splat rotate their orientations parallel to coating surface. Although this change cannot be experimentally observed owing to very short time of several hundreds microseconds, rotation of (111) planes in Pb thin films under stress resulting from thermal cycling was experimentally reported [28]. The larger tensile stress leads to the more (101) planes change of their orientation. Consequently, thermally sprayed TiO₂ coatings present preferential orientation at (101) planes. Accordingly, the preferential orientation of rutile phase in plasma-sprayed TiO₂ coatings was larger than that of HVOF sprayed one, because the tensile stress in plasma-sprayed TiO₂ coating was much higher than that of HVOF sprayed one. Furthermore, the preferential orientation of the rutile phase in the HVOF sprayed coatings may also have been affected in a minor degree by the presence of semi-molten rutile particles embedded in the coating microstructure. Further analysis will be carried out to confirm this issue.

### 4. Conclusions

The anatase phase in thermally sprayed TiO₂ coatings presented no preferential orientation. The rutile phase in plasma-sprayed TiO₂ coating showed significant preferential orientation along (101) plane. The surface morphology of plasma-sprayed TiO₂ and HVOF sprayed TiO₂ suggests significantly difference tensile stress in magnitude in individual splats during cooling process. The difference of preferential orientation factor of the two coatings was attributed to tensile stress conditions during splat cooling. It was considered that some (101) planes rotate their orientations parallel to the coating surface under high tensile stress at high temperature during splat cooling. The crystalline plane rotation resulted in the preferential orientation of rutile phase within plasma-sprayed TiO₂ coatings.

### References