Effect of substrate materials on the rutile crystalline orientation in plasma-sprayed TiO₂ coatings

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Abstract: TiO₂ coatings are of technical importance owing to their promising applications to photocatalytic, electrical, optical and tribological coatings. Thermal spraying process has been widely used to deposit both metallic and nonmetallic coatings. During thermal spraying, spray particle at fully or partially melted condition is deposited to a substrate and subsequently flattens, rapidly cools and solidifies. Therefore, a coating in lamellar structure is usually formed as a quenched microstructure. In this study, TiO₂ coatings were deposited on different substrates through plasma spraying with fused-crushed powder in rutile phase as feedstock to reveal the crystalline orientation in the coatings. XRD results showed that the coatings consisted of rutile phase with a fraction of anatase phase, and the rutile phase presented a preferable crystalline orientation along [101] direction. It was found that the orientation factors of rutile phase in the thin coatings were significantly influenced by substrate materials. The thick coatings yielded the same orientation factors of 0.22 to 0.23 on all substrates in spite of substrate materials. It is considered that the thermal properties of substrate materials are the dominant factors for the preferable crystalline orientation in rutile phase within plasma-sprayed TiO₂ coating.

Key words: titanium oxide; thermal spray; coatings; rutile, orientation

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1 INTRODUCTION

TiO₂ coatings are very important industrial materials owing to their promising applications to photocatalytic, electrical, optical and tribological coatings [1-7]. The property and performance of the TiO₂ coatings are affected by their microstructures including crystalline structure. Moreover, owing to the different property at different crystalline directions, the preferable orientation is of great researching interest. Preferable orientation is considered useful for device applications [8]. For example, the permittivity value of TiO₂ coating deposited through an ion beam assisted deposition technique was proportional to the preferable orientation factor [9].

TiO₂ coatings are deposited through many processes such as vapor deposition, Sol-Gel, sputtering and thermal spraying [7-17]. Among these methods, thermal spraying is characterized as a flexible and efficient process which has been widely used to deposit both metallic and nonmetallic coatings. During thermal spraying, spray particle at fully or partially melted condition is deposited to a substrate followed by flattening and rapid cooling and solidification. Accordingly, thermally sprayed coatings consist of lamellar splats. The coating in lamellar structure is usually formed as a quenched microstructure resulting from the cooling at a very high cooling rate about 10⁶ K/s. For instance, amorphous phase was observed in high velocity oxy-fuel (HVOF) sprayed WC-Co coating [18].

For thermally sprayed TiO₂ coatings, the preferable orientation in rutile phase was observed by Li et al. [19-21]. They reported the rutile preferable orientation at (101) direction in plasma-sprayed coating deposited on the glass and stainless steel substrates [19]. Zhang et al. tried to explain the preferable orientation in plasma-sprayed TiO₂ coating through analyzing the valence electron structure of TiO₂ [22]. However, their model could not explain the results reported by Lima et al. [20-21]. Few literature can reasonably explain all results concerning with the preferable orientation in thermally sprayed TiO₂ coatings. In this study, TiO₂ coatings were deposited on different substrates through plasma spraying with fused-crushed powder in rutile phase as feedstock to reveal the dominant factor for the preferable orientation in plasma-sprayed TiO₂ coatings.

2 EXPERIMENTALS

2.1 Materials

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Rutile TiO₂ powder (Shenyang, China) in size from 10 to 20 µm prepared by fusing and crushing was utilized as a feedstock. Several solid plates were employed as substrates, including glass, titanium alloy, stainless steel, mild steel, brass, Si (111) single crystal and copper. Prior to spraying, the substrates were polished, except for glass and the substrate in single crystal.

2.2 Plasma spraying

The coatings were sprayed by an commercial atmosphere plasma spray system (GP-80, Jiujiang, China). The spray gun was manipulated by a robot (Motoman) and traversed at a relative speed of 500 mm/s over the substrate. Nitrogen was used as the powder carrier gas. The spraying parameters are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar pressure (MPa)</td>
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<tr>
<td>Ar flow (SLPM)</td>
<td>70</td>
</tr>
<tr>
<td>H₂ pressure (MPa)</td>
<td>0.4</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>50</td>
</tr>
<tr>
<td>Current (A)</td>
<td>400</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
<td>100</td>
</tr>
</tbody>
</table>

2.3 Coating characterization

The crystalline structure of the as-sprayed coatings was characterized using X-ray diffraction (XRD) (Rigaku D/max-2400) by Cu Kα radiation at 40 kV and 100 mA with a scan speed of 2°/min for 2θ. The topographic morphology of the as-sprayed TiO₂ coating was characterized using scanning electron microscopy (SEM) (Hitachi, S2700).

3 RESULTS

3.1 XRD analysis of the thick TiO₂ coatings

Figure 1 shows the XRD pattern of the starting rutile powder. The strongest diffraction peak appeared at (110) crystal face, which was in accord with the standard pattern of rutile TiO₂ [23]. To reveal the crystalline structure of plasma-sprayed TiO₂ coatings, samples with a thickness of 50 µm was sprayed on four substrates, i.e. glass, rutile (110) single crystal, stainless steel and copper. Fig. 2 shows the XRD patterns of TiO₂ coatings deposited on four different substrates. The coatings consisted of rutile TiO₂ and a fraction of anatase TiO₂. The surface morphology of the as-sprayed TiO₂ coating, shown in Fig. 3, suggested that spray particles were fully melted, for the particles were well flattened resulting from the impacting of molten particles on the substrate surface and the surface of the pre-formed coating. It is obviously observed that the coatings presented a preferable orientation at (101) crystal face.

![Fig. 1 XRD pattern of rutile powder obtained by powder diffraction.](image1)

![Fig. 2 XRD patterns of the TiO₂ thick coatings on different substrates.](image2)

![Fig. 3 Surface morphology of plasma-sprayed TiO₂ coating.](image3)
To quantitatively characterize the extent of crystalline orientation in the TiO$_2$ coating, Lotgering orientation factor $f$ was employed, which is defined as [24]

$$f = \frac{P - P_0}{1 - P_0}$$  \hspace{1cm} (1)

$$P_0 = \frac{\sum I(101)}{\sum I(hkl)}$$  \hspace{1cm} (2)

The values of $P$ and $P_0$ were calculated from the ratio of (101) peak intensity to that of all the (h k l) intensities for the TiO$_2$ coatings and the TiO$_2$ powder, respectively, over a 20 range from 20 to 60$^\circ$. Through fitting in Lorentzian model using commercially available Origin software, the peak area was estimated as the peak intensity. With increasing orientation, $P$ increases from the value $P_0$ for the non-oriented sample to the value 1.0 for an ideally oriented sample. The value of $f$ is therefore a measure of the degree of preferable orientation. The results shown in Fig. 4 indicate that the coatings presented similar $f$ values of 0.22 to 0.23.

![Fig. 4 Effect of substrate materials on the preferable orientation factors of the thick coatings.](image)

The present results are not consistent with those reported by Li et al. [19]. They pointed out that the latter cooled and solidified splats could keep the crystalline orientation of the formerly deposited coatings based on the experimental results that the orientation factor was independent of the thickness of the coatings. The microstructure investigation in plasma-sprayed ceramic coatings through copper electroplating technique visualized the limited bonded lamellar structure [25]. The mean bonding ratio at interfaces between the lamellae in plasma-sprayed ceramic coatings varied in a range from 16% to 32%, which was influenced by spraying parameters [26]. Even if a splat can keep the orientation in the pre-formed splats similar to the case of epitaxial growth of TiO$_2$ [8], it should be occur at the bonded area of interface between two splats. Since the bonded area is only 16% to 32% of the whole interface, the orientation from the epitaxial growth will disappear after several lamellae. Therefore, the results of all the thick coatings with the similar $f$ values are more rational.

### 3.2 Effect of substrate materials on the orientation in the thin coatings

During XRD analysis of the coatings, X-ray penetrates in a limited depth of TiO$_2$ coating before diffracting from crystal faces, and the diffracted X-ray comes from the lamellae within this depth. Accordingly, the XRD pattern can be attributed to several lamellae of the TiO$_2$ coating according to the results reported by Selvaraj [8], since the thickness of splats in plasma-sprayed ceramic coatings is about 1 to 5 µm. Therefore, the XRD analysis of TiO$_2$ coatings with a thickness of 50 µm, in fact, reveals the crystalline structure of several lamellae near the surface of the coating. To reveal the crystalline orientation in the lamellae near the substrate, thin coatings were deposited on different substrates. The coating was sprayed so that the whole surface of the substrate was almost covered by TiO$_2$ splats.

Figure 5 shows the XRD patterns for the thin coatings. The phase composition was the same as that in the thick coatings. All coatings presented preferable orientation at [101] crystalline direction. The orientation factors are shown in Fig. 6. It was found that the thin coatings deposited on different substrates presented different $f$ values. This difference reveals that the orientation depends on substrate materials. It is reported that the orientation in the coatings was independent of coating thickness when the coatings thickness increased from 20 to 300 µm [19]. According to the calculation by Selvaraj [8], the effective depth of X-ray penetration at rutile [110] direction is around 12 µm. It may be concluded that for coatings with thickness from 20 to 300 µm, the XRD patterns characterize the top lamellae in the coatings. The present study revealed the difference of crystalline orientation in the lamellae near the substrate.

When a molten particle flattens and solidifies on the surface of a glass sheet substrate, the grain often grows perpendicularly to the substrate surface. Therefore, plasma-sprayed coatings are of columnar crystals microstructure [27-29]. Since the (110) surface is the surface of the lowest energy for rutile TiO$_2$, the grains in plasma-sprayed TiO$_2$ coatings are expected to grow along [110] direction. However, thermally sprayed TiO$_2$ coatings presented a preferable orientation at the crystalline direction, i.e. [101] direction. Zhang et al. argued that the grains with {110} faces being not perpendicular to the surface of coatings turned their orientation faces to be perpendicular to the surface, which resulted from the pressure acting perpendicularly on the pre-formed coatings by the impacting of spray particles [22]. According to their conclusion, the larger the pressure, the more severe the preferable orientation is. It may be concluded that the
preference orientation in HVOF sprayed TiO\textsubscript{2} should be more prominent than that in plasma-sprayed one, and furthermore, the preferable orientation in plasma-sprayed coating should be more prominent than that in flame-sprayed one. However, these are not consistent with the experimental results reported. Therefore, the preferable orientation of thermally sprayed TiO\textsubscript{2} was not reasonably explained yet in all published reports [19-22].

On the other hand, the present results clearly showed that the orientation factor was significantly influenced by the materials of substrate. This may be due to the difference in splats cooling condition when different materials were used. Further investigation is necessary to clarify the mechanism of the preferable orientation in plasma-sprayed rutile TiO\textsubscript{2} at [101] direction.

4 CONCLUSIONS

Thick and thin TiO\textsubscript{2} coatings were plasma-sprayed on different substrates with rutile TiO\textsubscript{2} powder as a feedstock. SEM observation suggested that the coatings consisted of well flattened splats. XRD analysis revealed the binary phase composition of TiO\textsubscript{2} coatings of mainly rutile with a fraction of anatase. The rutile phase in all TiO\textsubscript{2} coatings presented a preferable orientation at (101) crystalline face. The thick coatings on different substrates exhibited the same orientation factor of 0.22 to 0.23. However, the thin coatings showed different orientation factors from 0.19 to 0.26 for different substrates. The results showed that the orientation factor in the thin coatings was significantly influenced by substrate materials. It was found that the latter cooled and solidified splats can not keep the crystalline orientation of the formerly sprayed coatings. It was considered that the thermal properties of substrate materials are the dominant factors for the crystalline orientation in rutile phase during plasma spraying.

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REFERENCES


