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Effects of TiO_2 on the mechanical properties of the Al_2O_3–TiO_2 plasma sprayed coating

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Abstract

Plasma sprayed ceramic coatings are successfully used in many industrial applications, where high wear and corrosion resistance with thermal insulation are required. In this study, various types of Al_2O_3–TiO_2 plasma sprayed coatings in different compositions (Al_2O_3–13 wt.% TiO_2, Al_2O_3–40 wt.% TiO_2 and Al_2O_3–50 wt.% TiO_2) were prepared on an AISI 304L austenitic stainless steel substrate. The effects of TiO_2 addition on the properties of the coating were investigated in terms of microhardness and fracture toughness values. The results obtained from experimental work were evaluated with standard characterisation techniques. The results indicated that an increase in TiO_2 amount improves fracture toughness and lowers the microhardness values of the coatings.

Keywords: Al_2O_3; TiO_2; Toughness

1. Introduction

Ceramic materials with high hardness and high resistance to thermal and corrosive conditions and relatively low densities offer many advantages over metallic materials.[1] The use of ceramic coating is an effective way to protect some metal components in power and refractory industries against chemical corrosion, abrasive wear, and high temperature oxidation.[2]

Plasma spraying is one of the powerful techniques for preparing the coatings with variety of properties required for industrial applications. Ceramic coatings produced by thermal spray techniques are increasingly and widely used for a range of industrial applications to provide wear and erosion resistance, corrosion protection and thermal insulation.[3–7] Due to high flame temperature typically higher than 5000 °C, a satisfactory melting state can be achieved, which is beneficial for formation of a dense coating structure.

Al_2O_3 and Al_2O_3–TiO_2 plasma sprayed on a metallic substrate provide high thermal resistance and reduce the metal surface temperature, thus, increasing component durability in a harsh environment. Al_2O_3–TiO_2 coating can be used in various purposes such as textile industry.[8]

Microstructure and mechanical properties of the coating needed to be investigated using various characterisation techniques to find out correct processing parameters, which are to be used in plasma spraying, consequently, to develop mechanical properties of the coating. It is well known that the mechanical properties of the coating are usually strongly depended on their microstructure such as phase composition, grain size, porosity and its distribution. Microhardness and toughness values of the Al_2O_3 coating can be modified by changing its composition with addition of TiO_2 in plasma spraying in a way that this contribute the increase in toughness and wear resistance values of the coating.[5,9]

In the present work, the influence of TiO_2 in plasma sprayed alumina coating on the mechanical properties such as microhardness and toughness has been investigated using an AISI 304L austenitic stainless steel as a substrate material. Characterisation on the accomplished coatings was also performed. The results have been discussed with previously published works in literature.

2. Experimental procedure

2.1. Materials and coating parameters

In this study, an AISI 304L austenitic stainless steel was used as a substrate of the coating. Prior to deposition, specimens

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Table 1
Size range of powders used in this study

Material	Size range (μm)
Al_2O_3–13 wt.% TiO_2	+22–45
Al_2O_3–40 wt.% TiO_2	+5–45
Al_2O_3–50 wt.% TiO_2	+5–45
NiCr 80/20	+36–106

with dimension of 10 mm × 10 mm × 2 mm were sand blasted to provide surface roughness for better adherence between the ceramic coating and metallic substrate. Approximately 40 μm thick bond layer of NiCr 80/20 was applied on the surface of the steel substrate to obtain better performance of plasma sprayed Al_2O_3–TiO_2 coating. Total thickness of the coating on the steel substrate was about 400 μm. The coating was completed in eight or ten passes.

Metco 3 MB plasma gun with Metco 40 KW atmospheric plasma spray coating system was used for deposition of the bond and upper layer. The range of powder size used as based materials is given in Table 1. The parameters of the plasma spraying condition are summarised in Table 2.

2.2. Microhardness measurement, toughness determination and microstructural examination

For the metallographic examinations and the microhardness measurements, the coated samples were cut cross-section before grinding and polishing them with standard SiC grinding papers starting from 800 grid and finishing of with 1200 grid. The samples were then lightly polished using 1 μm diamond paste. Samples were finally washed with water and cleaned by alcohol before drying. Microhardness values of the specimens were taken from the cross-section of the polished samples at a load of 200 g using MH3 METKON microhardness equipment. Microhardness measurements were performed in air at room temperature with the load duration of 15 s. At least five different measurements were taken on each specimen to calculate the average microhardness values of the coating. Toughness values were calculated by measuring crack lengths after a Vickers indentation with a load of 3 kg applied for 30 s. The toughness values were calculated as described in an earlier study.[5]

Table 2
Plasma spraying parameters of the ceramic coating

Parameters	Bond coating	Ceramic coating
Operation conditions arc current (A)	500	500
Arc voltage (V)	70	70
Primary plasma gas	Ar	Ar
Flow rate of primary gas (ml/m)	100	100
Secondary plasma gas	H_2	H_2
Flow rate of secondary gas (ml/m)	15	15
Feeding gas	Ar	Ar
Flow rate of feeding gas (ml/m)	40	40
Powder feed rate (g/m)	60	70
Spraying distance (mm)	150	120

Optical microscopy examinations of the alumina coating were carried out using NIKON ECLIPSE L 150 model optical microscope. The phase composition of the coating was examined by X-ray diffraction (XRD) with nickel filtered Cu Kα (λ: 1.54056) radiation on a RIGAGU D/Max 2200 diffractometer with 2θ, 0–90°.

3. Results and discussion

3.1. Microstructural characterisation of the coating

Typical cross-section microstructure of the Al_2O_3–TiO_2 coating is shown in Fig. 1. The thickness of the upper ceramic coating is approximately 400 μm. The bond layer is NiCr 80/20 with the thickness of 50 μm. As clearly seen from the figure that the porosity is present in the coating. As previously reported by Fervel et al.[5] that the porosity is generally present in thermally sprayed coating in a range between 6 and 9%. Cross-section of Al_2O_3 coating with 13–50 wt.% TiO_2 addition is given in Fig. 2. The porosity exists in all coatings. Therefore, it can be said that TiO_2 in the coating does not contribute to decrease porosity in the coating. This is consistent with the previous studies.[5,10–12] Although colour of the phases is not distinguished in all the coatings, white regions in the coating are attributed to TiO_2 while grey ones are Al_2O_3.

The XRD analysis of the Al_2O_3 coating with 13 and 50 wt.% TiO_2 additions revealed that α-Al_2O_3, γ-Al_2O_3, Al_2TiO_5 and TiO_2 rutile phases are present (Fig. 3). Surprisingly, XRD analysis of 40 wt.% TiO_2 coating shows only γ-Al_2O_3 and Al_2TiO_5 phases. The missing of the α-Al_2O_3 and TiO_2 peaks could be because of the absence of those phases or using a solid form sample for the analysis instead of powder form. As mentioned by researchers,[6,7,10,11,13] the coatings consist of γ-Al_2O_3 and little amount of α-Al_2O_3. Actually, the powder used in the coating contains α-Al_2O_3. During the plasma spraying, α-Al_2O_3 transforms in to γ-Al_2O_3 due to fact that γ-Al_2O_3 has lower

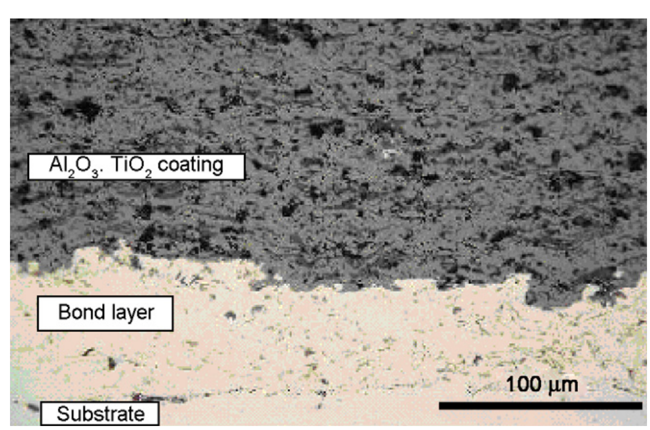

Fig. 1. Optical micrograph of cross-section view for the Al_2O_3–13 wt.% TiO_2 coating.

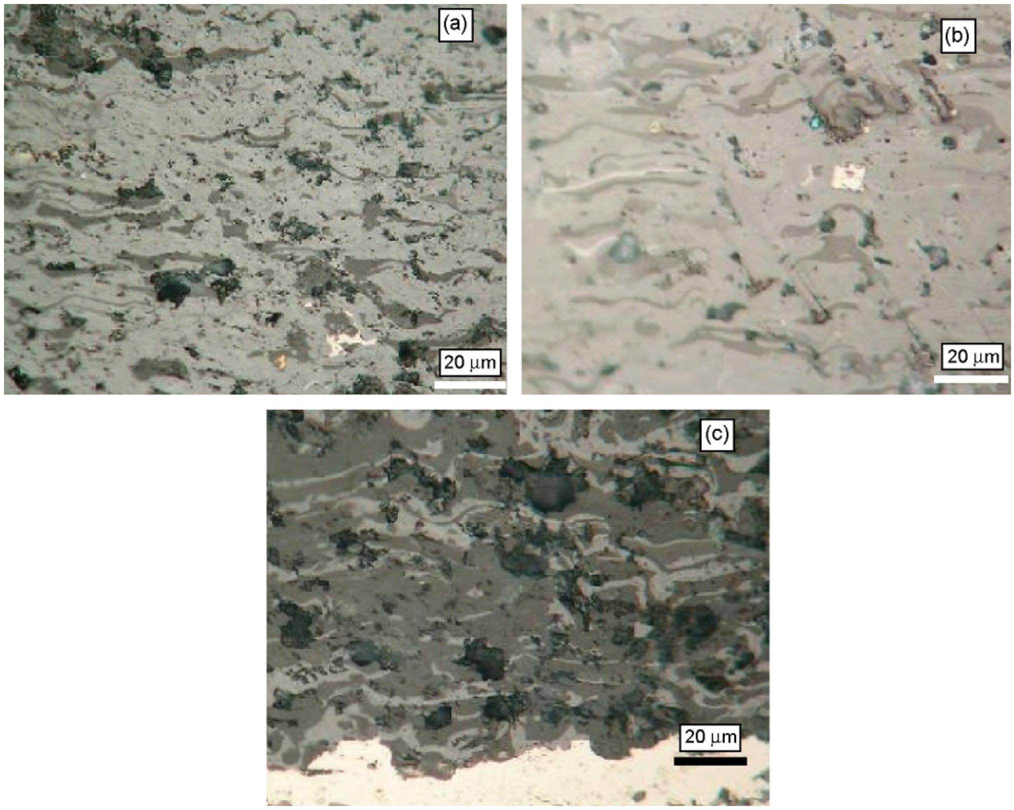

Fig. 2. Cross-section optical view of plasma sprayed coating: (a) Al_2O_3–13 wt.% TiO_2, (b) Al_2O_3–40 wt.% TiO_2 and (c) Al_2O_3–50 wt.% TiO_2.

nucleation energy and therefore, metastable γ-Al_2O_3 occurs through the melting and later rapid solidification.[13] As reported by Luo et al.[13] that γ-Al_2O_3 is nanosized phase while α-Al_2O_3 has micro-size dimension, therefore, α-Al_2O_3 can remain without transformation embedded in γ-Al_2O_3 matrix in the partially melted region during plasma spraying due to the fact that melting temperature of TiO_2 is lower than that of the α-Al_2O_3 with the value of 1854 and 2040 °C, respectively.[14] Al_2O_3 and TiO_2 are mixed and agglomerated before plasma spraying. Contact areas between two oxides are quite large due to their small size of dimensions. Thus, these react together during plasma spraying to form Al_2TiO_5. Agglomerated powder also allows improving the homogeneity of the coating.[7]

3.2. Mechanical properties of the coating

Fig. 4 depicts microhardness values of the Al_2O_3 coating. In principle, the microhardness values of Al_2O_3–TiO_2 coatings depend on their composition. Microhardness tends to decrease with TiO_2 addition to the coating.[5,7,15] In this study, the Al_2O_3–13 wt.% TiO_2 coating shows higher microhardness values than that of the samples having compositions of 40 and 50 wt.% TiO_2 additions. Fluctuation in microhardness values as seen in Fig. 4, especially with the sample 13 wt.% TiO_2 are typical of this sort of ceramic coatings. This may be attributed to the variation in microstructural differences, porosity and phase distribution. Although originally pure Al_2O_3 exhibits microhardness value of 1700 Hv,[16] Fervel

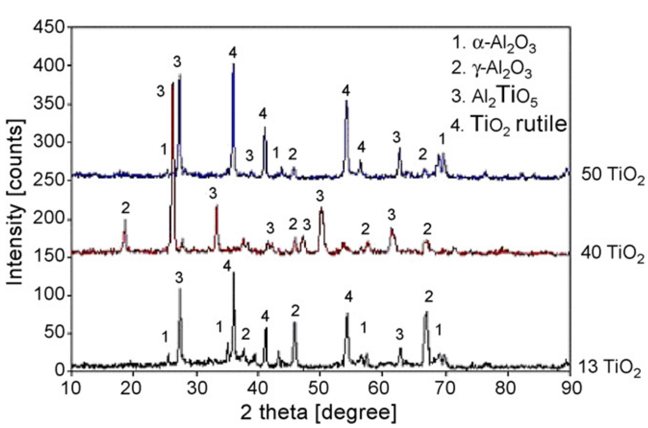

Fig. 3. XRD patterns of Al_2O_3–TiO_2 coatings.

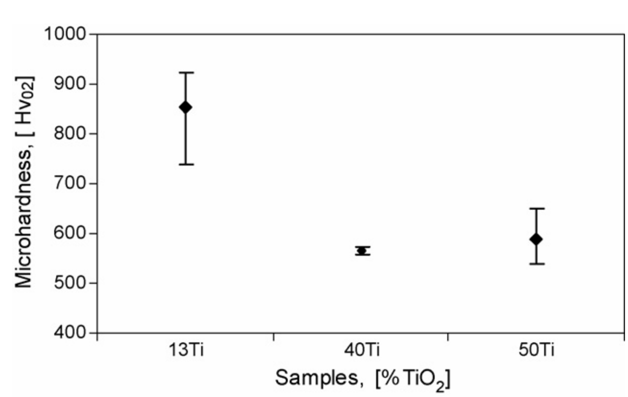

Fig. 4. Microhardness variation with TiO_2 addition to the Al_2O_3 coating.

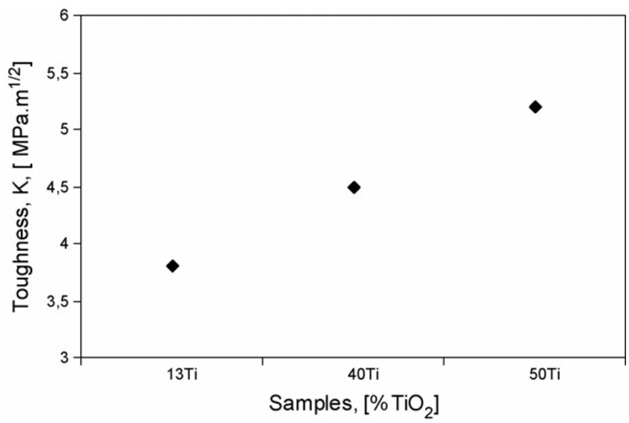

Fig. 5. Toughness variation with TiO_2 addition to the Al_2O_3 coating.

et al.[5] reported that the pure Al_2O_3 applied on to the substrates using plasma spraying technique gives the microhardness values much lower than this, i.e., about the range of 900–1100 Hv.

Microhardness values of the Al_2O_3–50 wt.% TiO_2 coating are a bit higher than that of the Al_2O_3–40 wt.% TiO_2. It is shown that microhardness values of the coating not depend on only the amount of TiO_2 in the coating, but also some another factors have an influence on the microhardness values of the coating as mentioned earlier. This is consistent with the previous studies.[5,6,11,12] The average microhardness value of the bond layer was 235 $Hv_{0.2}$ while that of substrate stainless steel has an average microhardness value of 190 $Hv_{0.2}$. On the other hand, microhardness of the sample increased to 853, 566, 587 $Hv_{0.2}$ for 13, 40 and 50 wt.% TiO_2 additions to Al_2O_3 coating, respectively. These values are almost three times higher than that of the substrate.

There were some limitations on the measurements of the coating. The measurement should be taken close to the centre of the ceramic coating and indentations should be parallel to the substrate. Otherwise, crack creation would be difficult during the measurement.

Fig. 5 shows the toughness variation versus the TiO_2 content in the coating. Those values of the coating strongly depend on TiO_2 addition to the coating. TiO_2 is a well known additive to increase the toughness of Al_2O_3. The pure Al_2O_3 coatings using plasma sprayed technique has low toughness value of 1.8 MPa $m^{1/2}$ as given elsewhere.[5] In this study an increase in toughness values compared to pure Al_2O_3 coating was obtained as 110, 150 and 190 for the 13, 40 and 50 wt.% TiO_2 addition to Al_2O_3, respectively. These toughness results obtained in the present study show slightly lower values than that of the values obtained in an earlier study.[5] The difference may be caused by plasma spray parameter variation used in those studies. The toughness of the plasma sprayed depends on the adhesion strength between splats and previously deposited layer.[11] Fully melted region in the coating is mainly composed of γ-Al_2O_3, while partially melted region contain γ-Al_2O_3 including α-Al_2O_3.[13] Cracks are propagated along the splat boundaries.[11] The increase in splat adhesion contributed to the toughness values of the coating. The presence of α-Al_2O_3 embedded in the γ-Al_2O_3 matrix may contribute to improve toughness behaviour of the coating.[11]

During the plasma spraying process α-Al_2O_3 and TiO_2 melt together and rapidly solidify to form γ-Al_2O_3 containing dissolved TiO_2. This type of microstructure was relative to the melting degree of the powder and contributed to the improvement of fracture toughness of the coating.[11,17]

4. Conclusion

Characterisation of the Al_2O_3 coatings with the addition of TiO_2 was performed and the effects of TiO_2 addition to alumina base plasma sprayed coatings were studied. It was found that TiO_2 addition lowered significantly the microhardness of the alumina coating. Since the toughness is related to the hardness of the coatings, therefore, a decrease in hardness values resulted in an increase in toughness values of the alumina coatings. In addition to that, the coating of a substrate with Al_2O_3–TiO_2 ceramics resulted in a profound increase in the microhardness values of the sample.

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