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Electrical resistivity of plasma-sprayed titanium diboride coatings

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Plasma-sprayed TiB_2 coatings (50–600 μm thick) on alumina substrates have been developed and characterized. X-ray diffraction studies, thermal analysis and oxygen analysis of the coatings show that there is appreciable oxidation of TiB_2 during the spray process. Partial oxidation of the boride during spraying strongly influences the electrical conductivity of the coatings, which is found to be 100–1000 times less than that of pure TiB_2. Although use of argon as shield gas during the spray process brings down the resisitivity substantially, partial oxidation of TiB_2 could not be totally avoided.

1. Introduction

Titanium diboride is a refractory compound exhibiting a unique combination of many interesting and useful properties. By virtue of its high melting point (> 3200 K), excellent electrical conductivity (10– 55 μΩ cm in the range 300–1200 K), high degree of chemical inertness in many corrosive environments, high flexural strength and high strength to weight ratio, TiB_2 finds potential use in many high-temperature structural applications [1–4]. TiB_2 can be used as electrodes in metal extraction, as a high-temperature thermocouple element to measure the temperature of molten metals, corrosion- and wear-resistant coatings in the metallurgical and chemical industries, etc. Although the electrical conductivity of sintered TiB_2 has been studied [2], data on plasma-sprayed specimens are lacking. The present paper reports the preparation and study of the electrical conductivity of plasma-sprayed coatings of TiB_2.

2. Specimen preparation

Plasma-sprayed specimens (50–600 μm thick) of TiB_2 were prepared on sintered alumina substrates using a 40 kW air–plasma-spray system, details of which are described by Sreekumar *et al.* [5]. The substrate surface was roughened by sand blasting to improve the adhesion of the coating. A mixture of argon and nitrogen was employed as the plasma gas and the spray process was carried out at 8–15 kW. A few self-standing specimens, 800–1000 μm thick, were also prepared for thermoanalytical studies and density measurements. The spray parameters are given in Table I. In order to minimize oxidation during the coating process, argon was used as shield gas, the flow of which was continued even after the spraying process was completed until the sample temperature was below 500 K. The density of the sprayed samples, measured by the water immersion method, was found to vary from 3.9–4.1 $g\,cm^{-3}$, the corresponding variation in porosity being 15%–10%.

3. Experimental procedure

X-ray powder diffraction (XRD) technique using nickel-filtered CuK_α radiation was used to determine the phase composition of the coatings. The electrical conductivity of these specimens was measured in the temperature range 300–1000 K with a d.c. four-probe assembly in a flowing argon atmosphere. Details of the experimental apparatus are given by Patil *et al.* [6]. The sample temperature was monitored by a Pt/Pt–13%Rh thermocouple located in the vicinity of the sample. Electrical conductivity measurements were taken during the heating and cooling cycles. Resistivity measurements were also made on sintered specimens of TiB_2. Sintered specimens were prepared by compacting TiB_2 powder into wafers 25 mm diameter and 1 mm thick, followed by thermal treatment at 1473 K in flowing argon gas. The potential drop across voltage probes, in the case of the sintered samples, was measured using a nanovoltmeter.

4. Results and discussion

Variation of electrical resistivity with temperature of sintered TiB_2 is shown in Fig. 1. The values of resistivity at all temperatures are seen to be higher than those reported in the literature [2]. This is due to the presence of oxide impurities (boron oxide and titanium oxide) in the TiB_2 powder. Oxygen analysis of the TiB_2 powder, the results of which is summarized in Table I, shows the presence of oxygen to the extent of 2% by weight. This would suggest a much higher amount of total oxide impurity, which is responsible for the increased resistivity of the samples.

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The results of electrical resistivity measurements on plasma-sprayed samples are summarized in Fig. 2, which is a plot of resistivity, ρ, as a function of temperature. It is seen from the figure that resistivity of the samples, sprayed without any shield gas, is ~1000 times higher than that of sintered TiB_2 [2]. This is due to the fact that the high velocity plasma effluent acts as an aspirator and draws in air from the surrounding environment [7] resulting in partial oxidation of the boride to boric oxide (which is subsequently converted to H_3BO_3 by absorbing moisture) and titanium oxide. XRD patterns of the sprayed specimens indicate the presence of H_3BO_3 and TiO_2 apart from TiB_2, which was the major phase. Oxygen analysis (Table II) of the sprayed specimens showed as much as 14% by weight of oxygen, confirming the X-ray results.

Partial oxidation of the material during the spray process and the subsequent conversion of B_2O_3 to H_3BO_3 significantly affect the resistivity of the

TABLE I Plasma-spray parameters

Parameter	Operating value
Power (kW)	12
Plasma gas 1 (Ar–LPM)	20
Plasma gas 2 (N_2–LPM)	5
Powder gas (Ar–LPM)	8
Powder feed rate (g min^{-1})	20
Torch to base distance (mm)	100

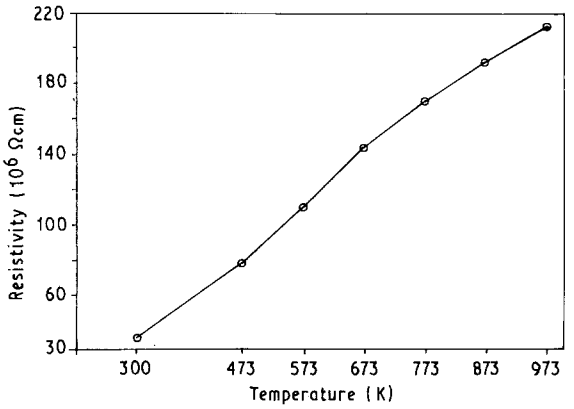

Figure 1 Variation of resistivity of sintered TiB_2 with temperature.

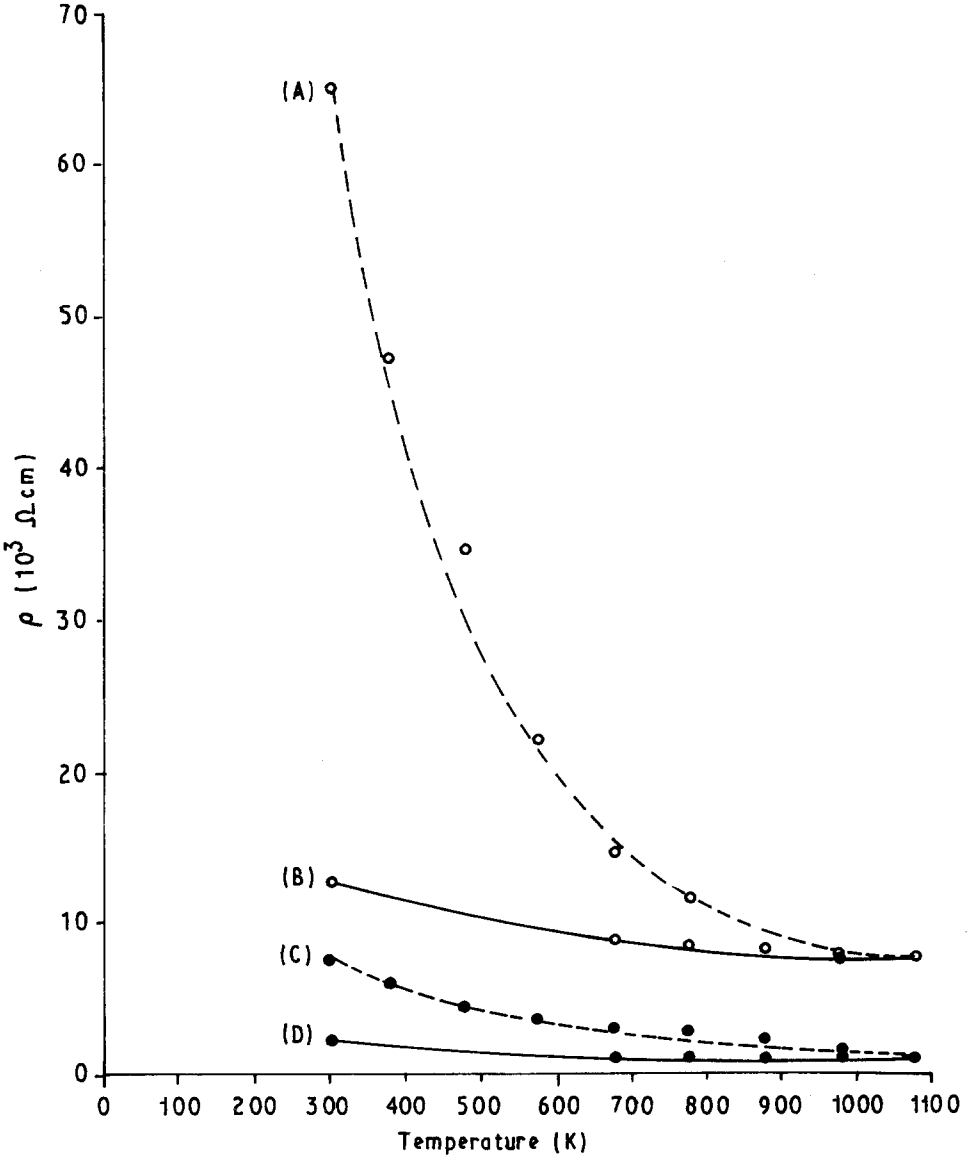

Figure 2 Variation of electrical resistivity with temperature of plasma-sprayed TiB_2.

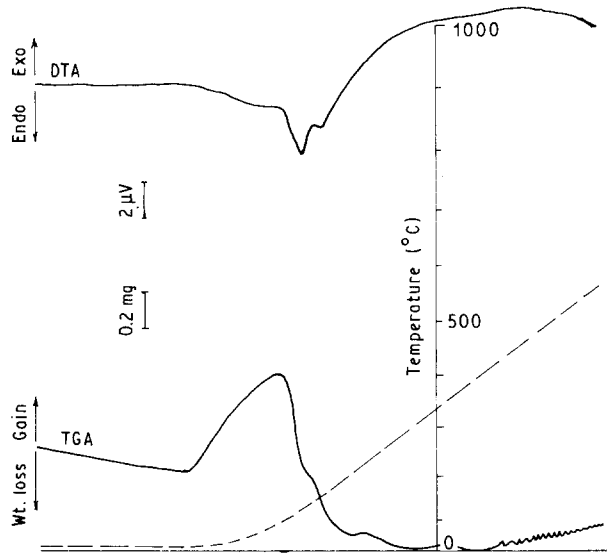

Figure 3 A typical TG–DTA curve of plasma-sprayed TiB_2.

sprayed specimens. Apart from increasing the magnitude of the resistance, it also affects the variation of resistivity with temperature, as can be seen from Fig. 2 curve A, which is a record of the resistivity values at different temperatures during the heating cycle. The resistivity is seen to decrease with temperature, although TiB_2 is known to have a positive temperature coefficient of resistivity (Fig. 1). Another important feature of the ρ–T curve is the sharp decrease in the resistivity values in the low-temperature range (300–700 K). After this initial steep change the resistivity values tend to level off. This is due to the decomposition of the boric acid present in the sample. The escape of water molecules leaves behind a material richer in TiB_2, thus lowering the resistivity.

The decomposition of H_3BO_3 to B_2O_3 involves a step-wise removal of water from the orthoboric acid according to the following reaction

$$H_3BO_3 \xrightarrow{-H_2O} HBO_2 \xrightarrow{-1/2H_2O} 1/2B_2O_3 \qquad (1)$$

This has been confirmed by simultaneous thermogravimetric (TGA) and differential thermal analysis (DTA) of the sprayed material, the results of which are shown in Fig. 3. It is seen from the figure that after the initial apparent gain in weight due to the buoyancy effect, there is a steady loss of weight due to removal of water molecules from H_3BO_3. The discontinuities in the TGA curve are due to the step-wise mechanism of the dehydration process as shown in Reaction (1). This is evident from the corresponding DTA curve which shows two well-defined endothermic peaks in the region of 350–500 K corresponding to the two-stage removal of water molecules from H_3BO_3. The above observations are in agreement with those reported by Duval [8], according to whom $B(OH)_3$ is stable up to 328 K. Above 328 K it begins to lose water to form metaboric acid, HBO_2, which is stable in the temperature range 408–441 K. Continued heating results in a gradual loss of weight, resulting in the formation of B_2O_3 which is the stable phase above 716 K. The steep decrease in resistivity in the temperature range

TABLE II Oxygen level in samples of TiB_2

Specimen	Oxygen (wt. %)
TiB_2 powder	2.0
TiB_2 sprayed without shield gas	14.0
TiB_2 sprayed with Ar shield gas	9.0

300–700 K is attributable to these reactions taking place in the sample. The removal of water molecules from the sample leaves behind a purer and better conducting surface.

Results of resistivity measurements taken in the cooling cycle are shown graphically in Fig. 2, curve B. It is seen that resistivity values are not appreciably affected down to 600 K. This is due to the fact that the rate of absorption of water and subsequent formation of boric acid is too slow to affect the resistivity. However, the resistivity value at room temperature taken 16 h after cooling shows appreciable increase in resistance, indicating the slow formation of boric acid.

The influence of shield gas on the electrical resistivity of the coating is evident from Fig. 2 curves C and D, which show the variation of ρ with T in the heating and cooling cycles, respectively, for a typical sample sprayed using argon as shield gas. It is seen that there is a ten-fold decrease in the resistivity. However, the magnitude of ρ as well as its variation with temperature suggests that the oxidation problem has not been totally eliminated. This is also seen from the results of oxygen analysis shown in Table II. It is seen that although the oxygen level in the specimen sprayed using argon as shield gas is much lower than that in the specimen sprayed without shield gas, it is still appreciably higher than that in the starting powder of TiB_2. A more effective way of shrouding or preparation of the coating in a controlled-environment chamber must be used to prevent the oxidation of the material completely.

5. Conclusions

1. TiB_2 undergoes partial oxidation during air–plasma spraying resulting in coatings with decreased electrical conductivity. Thermoanalytical studies indicate the presence of boric acid, which influences the temperature variation of electrical resistivity, as well as its magnitude. Although use of argon as a shield gas enhances the electrical conductivity of the coatings, oxidation could not be totally avoided.

2. Plasma spraying of TiB_2 in a controlled environment chamber can prevent the oxidation of the material and significantly improve the coating properties.

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