Electrical Conductivity of Titanium Oxide (Rutile) Plasma Sprayed Coatings†

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Abstract

Plasma spraying has been used to prepare n-type polycrystalline TiO_2 coatings on substrate. The infuluence of plasma spray process on the mixture of phases of coatings (corundun type Ti_2O_3, monoclinic Ti_3O_5, triclinic magneli phases, and tetragonal rutile) and the relation between deoxidation and the electrical conductivity of plasma sprayed coatings have been studied.

The amount of oxygen loss in the plasma sprayed TiO_2 coatings is infuluenced greatly by auxiliary hydrogen gas. Accordingly, the electrical conductivity of plasma sprayed TiO_2 coatings increases with the increase of oxygen loss. The reduction amount of plasma sprayed TiO_2 coatings increases with a drop of atmosphere pressure and an increase in quantity of hydrogen. The formation amounts of Ti_3O_5 and Ti_2O_3 phases increasesd with the deoxidation of plasma sprayed TiO_2 coatings.

KEY WORDS : (Plasma Spraying) (Electrical Conductivity) (Magneli Phase) (Auxiliary Gas) (Oxygen Loss) (TiO_{2-X}) (LPC) (Ti_3O_5 Phase) (Ti_2O_3 Phase)

1. Introduction

Plasma spraying is a well known technique in aeronautic and elsewhere to obtain the reliable coatings of metals, alloys and ceramics.

If the good quality policrystalline TiO_2 coatings are obtained easily by an economical process, the TiO_2 coatings will play on important part on the electronic and electrical industries.

When the titanium dioxide is treated so as to cause easily a loss of oxygen in the lallice either by heating in a low oxygen pressure or in hydrogen, the material becomes a n-type semiconductor whose property depends on the extent of oxygen loss. Therefore, rutile-TiO_2 is turned into non-stoichiometric TiO_{2-X}, Ti_nO_{2n-1} magneli series of homologous compounds, Ti_3O_5, and Ti_2O_3 by reduction, and its physical properties is changed.

Non-stoichiometric TiO_{2-X} has a complex defect structure. The reduced oxide TiO_{2-X} contains extended defects known as crystallographic shear planes whose formation can be described in terms of elimination of planes of oxygen[1].

The compound Ti_nO_{2n-1} have raised considerable interest, because of their unusual electric properties[2].

The oxides Ti_nO_{2n-1} with $n = 4 \sim 9$ form a magneli series of homologous compounds built of TiO_6 octahedra which share corners and edges to form rutile slabs[3,4]. They are bounded by monoclinic Ti_3O_5 on the one side and by reduced rutile (TiO_{2-X}) on the other.

In this study, an industrial coating technique, plasma spraying, has also been used to produce TiO_2 polycrystalline coatings from TiO_2 powders on SUS304 steel. The physical and chemical properties of TiO_2 plasma sprayed coatings depend greatly on plasma spray condition, and so, the electrical resistivity, oxygen concentration, and crystal structure of the plasma sprayed TiO_2 coatings have been investigated.

This work was done to know the relation between phases, oxygen concentration and electric conductivity of the plasma sprayed TiO_2 coatings by changing the plasma spray atmosphere and the amount of auxiliary gas, H_2.

2. Materials and Experimental procedure

Materials used in this investigations was commercially available TiO_2 powders (K-30M) (99% pure and particle sige, $10 \sim 44\ \mu$ m) and showed the rutile and a little magneli structure by X-ray diffraction as shown in **Fig. 1.**

Plasma spraying was performed with a plasma spray system (METCO 7M). As plasma spray conditions, spraying atmosphere were air and 100 Torr Ar, and plasma gas were Ar(7kg/min) and H_2 ($0 \sim 11.8$ l/min).

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Plasma powers were 30 ~ 49 kW, spraying distances were 100mm in the conventional plasma spraying and 200mm in the LPC plasma spraying. SUS304 steel plate (60mm×50mm×6mm) was used as substrate.

The van der Pauw technique[5] was followed to perform the conductivity measurements of TiO_2 coatings sprayed on alumina coatings that were projected on SUS304 steel as shown in **Fig. 2.**

The change in the deoxidized concentration of TiO_2 coatings after plasma spraying was determined by the change of weight of the coatings before and after annealing of 1000 °C - 5 hour in air.

The crystal structures of the plasma sprayed TiO_2 coatings (magneli, Ti_3O_5, Ti_2O_3, rutile, and anatase) depending on the spray conditions and auxiliary gas (H_2) were determined by X-ray diffractions.

3. Results and Discussion

3.1 Effect of plasma spray condition on crystal structure of plasma sprayed TiO_2 coatings.

Figure 3 is XRD results of conventional plasma sprayed TiO_2 coatings showing the mixtures of phases depending on plasma H_2 gas flow rates in air. X-ray diffraction showed that the conventional plasma sprayed TiO_2 coatings had the structure of rutile containing of anatase and magneli phase depending on the flow rate of auxiliary

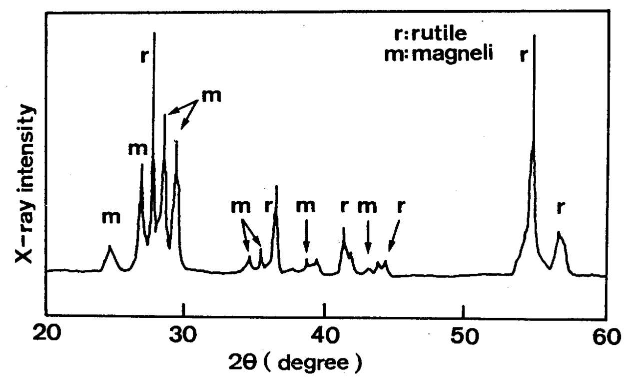

Fig. 1 XRD result of TiO_2 powder before spraying.

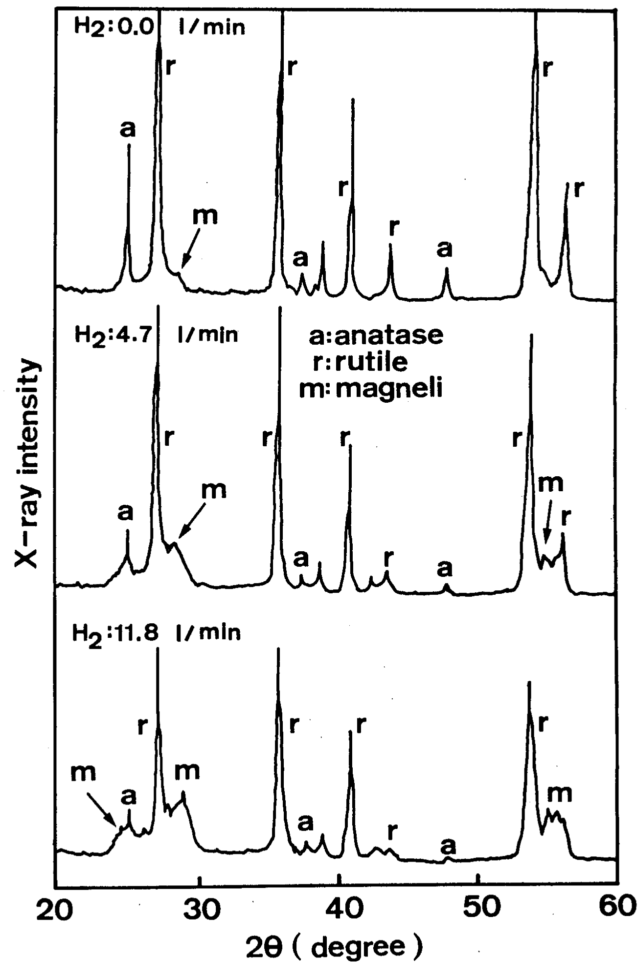

Fig. 3 XRD results of plasma sprayed TiO_2 coatings sprayed in air at various H_2 gas flow rates. (plasma power: 42kW, spraying distance: 100mm)

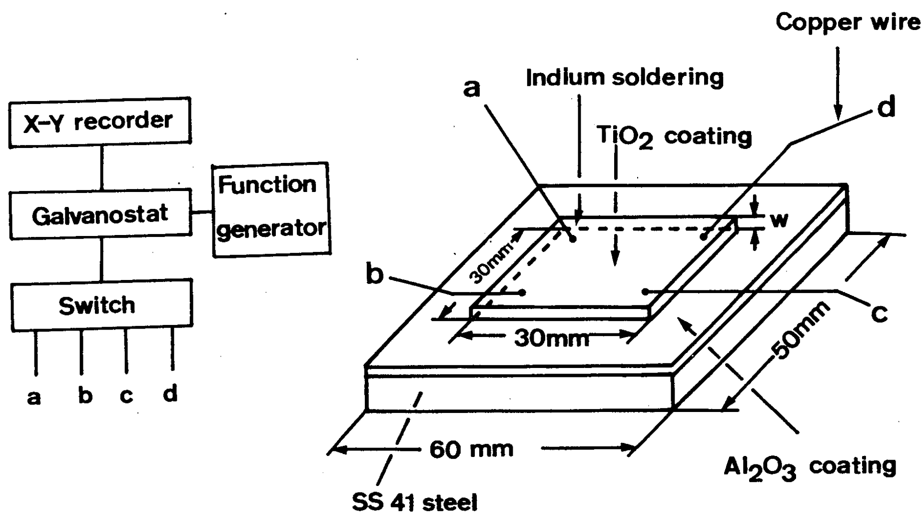

Fig. 2 Method for measuring electrical conductivity.

gas, H_2. With increase of H_2 gas flow rate, anatase decreased and magneli increased. Amounts of magneli of sprayed coatings is smaller than that of TiO_2 spray powder, because it is oxidized by plasma spraying, and

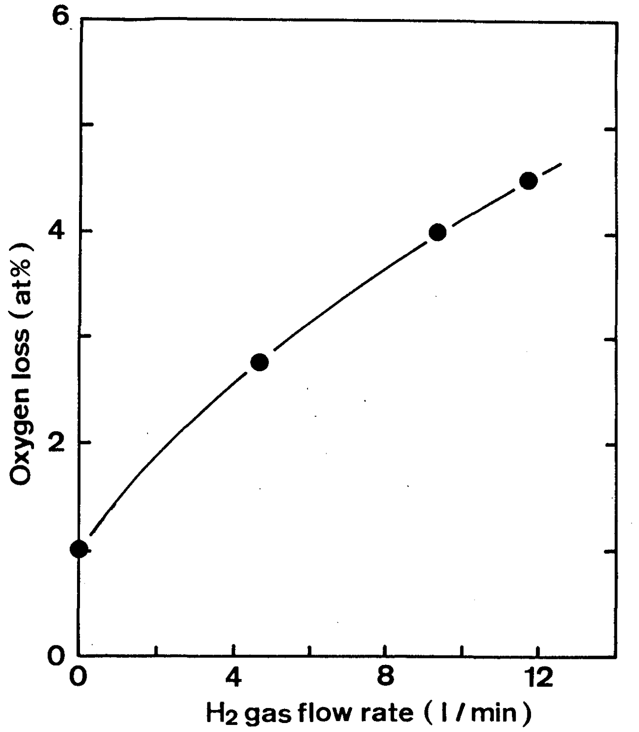

Fig. 4 Relation between oxygen loss of coatings and plasma H_2 gas flow rates in conventional plasma spraying. (plasma power: 42kW, spraying distance: 100mm)

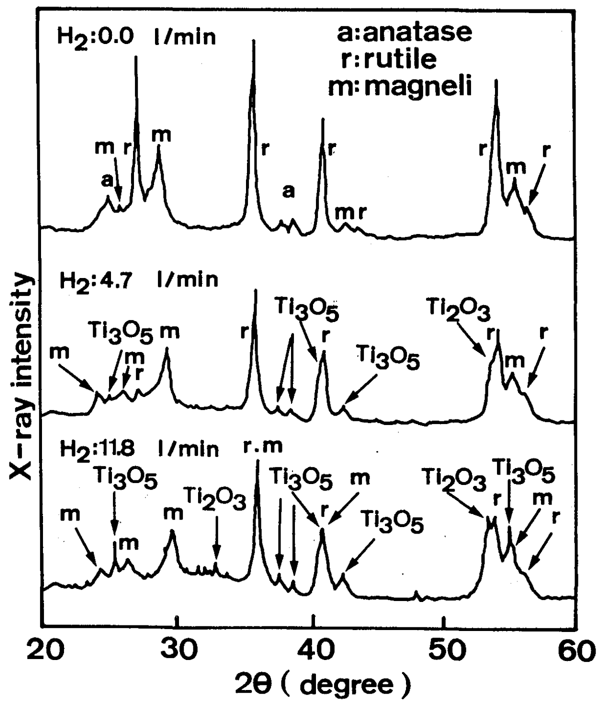

Fig. 5 XRD results of LPC plasma sprayed TiO_2 coatings at various H_2 gas flow rates. (pressure of sprying atmosphere: 100 Torr (Ar), plasma power: 42kW, spraying distance: 200mm)

amounts of magneli decreased. The ratio of rutile to anatase increased with increasing oxidation atmosphere and the decrease of H_2 in plasma gas.

Figure 4 shows a relation between oxygen loss of coatings and H_2 gas flow rates in conventional plasma spraying (air). The oxygen loss were increased with increase of H_2 gas flow rate, because TiO_2 powder reacted with hydrogen of plasma gas during plasma spraying. The smaller H_2 gas flow rate became the more plasma spraying particles were reoxidized easily by air.

Figure 5 is XRD results of LPC plasma sprayed coatings showing the mixture of phases depended on plasma H_2 gas flow rates at the Ar atmosphere of 100 Torr. X-ray diffraction showed that LPC plasma sprayed TiO_2 coatings had the structure of rutile containing of various phases (magneli, Ti_3O_5 and Ti_2O_3) depending on the flow rate of auxiliary gas, H_2. With the increase of H_2 gas flow rate, amounts of rutile decreased greatly and magneli, Ti_3O_5 and Ti_2O_3 phases increased. As it is reduced more easily by plasma spray gas in low pressure Ar atmosphere, amounts of low oxygen oxide increased in TiO_2 coatings. And, amounts of anatase of the sprayed coatings decreased in reduction atmosphere.

Figure 6 is a relation between oxygen loss of TiO_2 coatings and H_2 gas flow rates in LPC spraying atmosphere (100 Torr Ar). The oxygen loss increased with the increase of H_2 gas flow rate and the oxygen loss of these coatings is higher than that of conventional plasma sprayed coatings shown in Fig. 4, because TiO_2

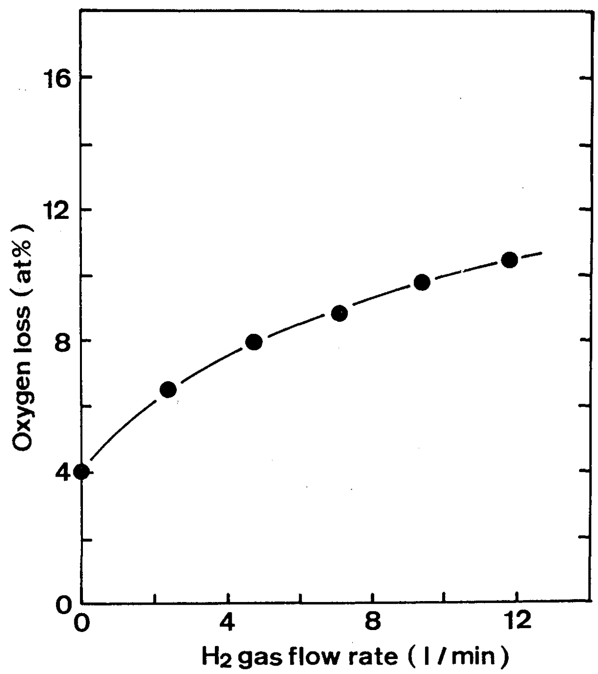

Fig. 6 Relation between oxygen loss of coatings and plasma H_2 gas flow rates in LPC plasma spraying. (pressure of spraying atmosphere: 100 Torr (Ar), plasma power: 42kW, spraying distance: 200mm)

powder reduced highly by hydrogen at low pressure during plasma spraying. Accordingly, amounts of Ti_2O_3 and Ti_3O_5 increased.

3.2 Electrical conductivity of plasma sprayed TiO_2 coatings.

It was reckoned that the structure of plasma sprayed TiO_2 coatings was influenced greatly by the plasma spray conditions, such as the spray condition and the quality of plasma gas (H_2). In this section, the effect of plasma spraying conditions on electrical conductivity of TiO_2 coatings was examined.

Figure 7 shows the change in the electrical conductivity of conventional plasma sprayed TiO_2 coatings with the plasma H_2 gas flow rates during the spraying in air. **Figure 8** is the change in electrical conductivity of LPC plasma sprayed TiO_2 coatings with the plasma H_2 gas flow rates in Ar atmosphere of 100 Torr.

The electrical conductivity with the increase of the plasma H_2 gas flow rate increased in both atmospheres.

The electrical conductivity of low pressure plasma TiO_2 sprayed coatings becomes higher than that of conventional plasma TiO_2 sprayed coatings from these figures.

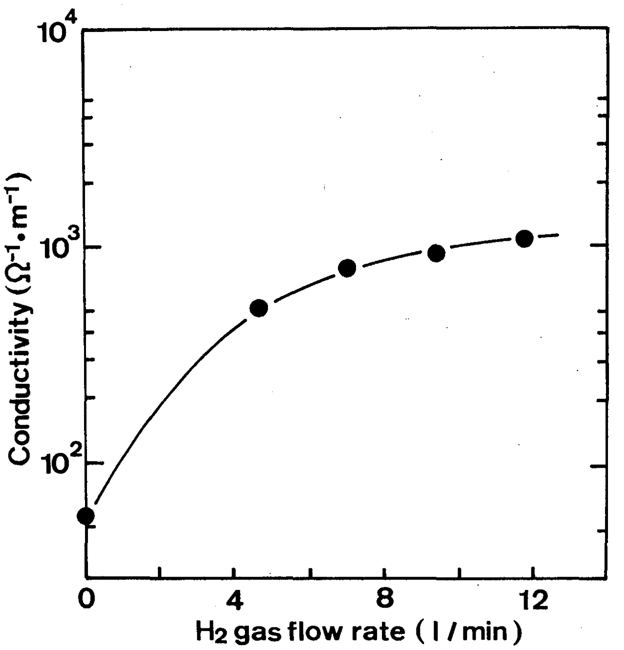

Fig. 7 Effect of plasma H_2 gas flow rate on electrical conductivity of conventional plasma sprayed TiO_2 coatings. (plasma power: 42kW, spraying distance: 100mm)

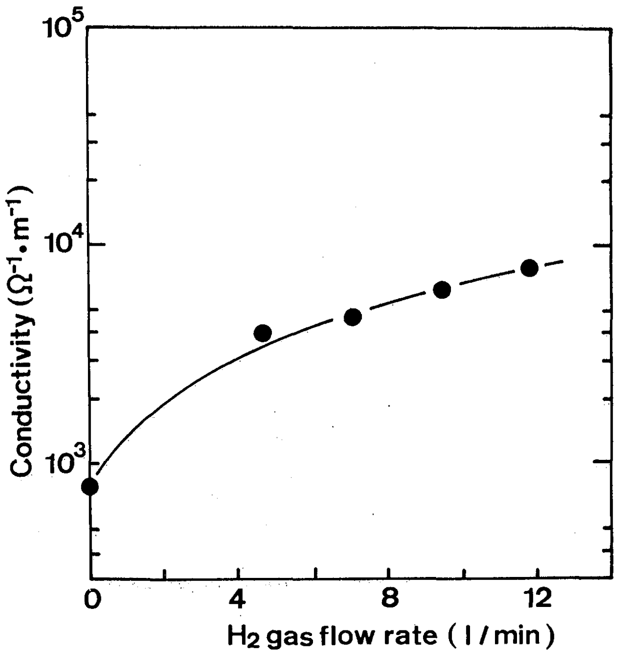

Fig. 8 Effect of plasma H_2 gas flow rate on electrical conductivity of LPC plasma sprayed TiO_2 coatings. (pressure of spraying atmosphere: 100 Torr (Ar), plasma power: 42kW, spraying distance: 200mm)

3.3 Relationship between the electrical conductivity and the structure of TiO_2 coatings.

The electrical conductivity of plasma sprayed TiO_2 coatings increased with the increase of plasma H_2 gas amount for both plasma spraying in air and in LPC. The conductivity of LPC plasma sprayed TiO_2 coatings showed larger value than that of air plasma sprayed TiO_2 coatings. **Figure 9** shows the relation between oxygen loss and the electrical conductivity of plasma sprayed TiO_2 coatings. From the figure, it is reckoned that the electrical conductivity increases with the increase of oxygen loss of TiO_2 coatings. The electrical conductivity is controlled by the concentration of oxygen loss in the plasma sprayed coatings.

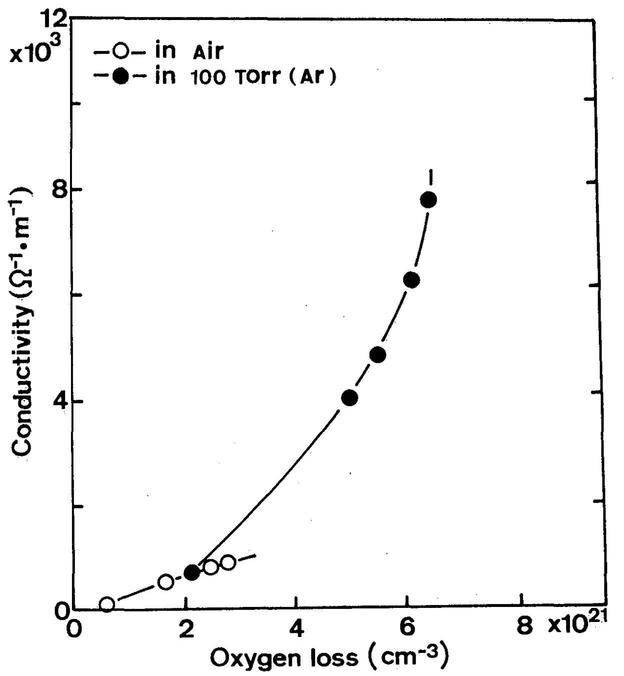

Fig. 9 Relation between electrical conductivity and oxygen loss of TiO_2 plasma sprayed coatings.

For nonstoichiometric oxides, a total electrical conductivity (TC) is given by following equation[6].

$$TC = 2e\ V_o\ U_o + e\ n\ U_n \qquad (1)$$

Where e is the eleconic charge, V_o is the vacancy concentration of oxygen atom, U_o is the mobility of oxygen vacancy, U_n is the electron mobility, and n is the number of electrons.

Two free electrons are created by one oxide vacancy, based on the theory of electrical neutrality, and following equation is given.

$$n = 2\ V_o \qquad (2)$$

The values of electron mobility is much larger than that of oxygen vacancy mobility. Accordingly, TC can be given by the following equation[7].

$$TC = 2e\ V_o\ U_n \qquad (3)$$

Then total electric conductivity (TC) is in proportion to the vacancy concentration of a oxygen atom (V_o) and the electron mobility (U_n). From Fig. 9, TC increases linearly with the increase of oxygen loss amount of TiO_2 coatings produced plasma spraying in air. As shown in Fig. 3 ane Fig. 4, magneli and the oxygen loss of TiO_2 coatings increases with the plasma H_2 gas amount.

The increase of TC may be dependent on magneli amount of TiO_2 coatings. From Fig. 3, TiO_2 coatings produced by plasma spraying in air, are composed mainly of rutile, anatase and magneli.

For TiO_2 coatings produced by LPC plasma spraying, TC increases greatly with the increase the oxygen loss. As shown in Fig. 5, the TiO_2 coatings are composed of rutile, magneli, Ti_3O_5 and Ti_2O_3. The increase of oxygen loss of the TiO_2 coatings, is due to the decrease of rutile, and the increase of Ti_3O_5 and Ti_2O_3.

The electron mobility (U_n) of Ti_2O_3 (2.5 $cm^2/v.s$)[8] in equation 3 is larger than those of Ti_3O_5 (0.21 $cm^2/v.s$, 450K)[9] and magneli (0.6 ~ 0.9 $cm^2/v.s$)[9] at room temperature. So, the electrical conductivity increased depending on the increase of Ti_2O_3 in TiO_2 plasma coatings.

4. Conclusion

The electrical conductivity for TiO_2 coatings produced by plasma spraying in air and LPC plasma spraying was studied.

The oxygen loss of TiO_2 coatings increases with the increase of plasma H_2 gas quantity. The oxygen loss of conventional plasma sprayed TiO_2 coatings becomes smaller than that of LPC plasma sprayed TiO_2 coatings.

TiO_2 coatings produced by plasma spraying in air, are composed of rutile, anatase and magneli, and LPC plasma sprayed TiO_2 coatings are composed mainly of magneli, Ti_3O_5 and Ti_2O_3.

The electrical conductivity increases with the oxygen loss of TiO_2 coatings. For conventional plasma sprayed TiO_2 coatings, the electrical conductivity increases with the increase of the magneli amount in TiO_2 coatings. For LPC plasma sprayed TiO_2 coatings increases with the increase of Ti_2O_3 amount in TiO_2 coatings.

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