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Control of Oxygen Concentration in Plasma Sprayed TiO_2 Coating by CO_2 Laser Irradiation †

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Abstract

The effect of CO_2 laser irradiation treatment for a plasma sprayed TiO_2 coating on the crystal structure and oxygen concentration of the coating has been investigated by XRD and a measurement of the change in weight of the coatings before and after annealing in air. It was found that the laser irradiation deoxidizes the TiO_2 coating regardless of whether the irradiation atmosphere is air or argon at 1.33×10^4Pa. The re-oxidation layer was, however, observed near the coating surface when the laser irradiation atmosphere is air. The possibility of the control of oxygen concentration in the TiO_2 coating by CO_2 laser irradiation was demonstrated successfully.

KEY WORDS:(Oxygen Concentration)(TiO_2 Coating)(CO_2 Laser)(Irradiation Atmosphere)(Crystal Structure)(XRD)(Deoxidation)(Re-oxidation)

1. Introduction

There has been considerable practical concern in the application of titanium oxide to the functional materials such as catalysts, photo electrodes of wet solar batteries, anti-bacterial materials, dirt-free materials, etc. These concerns areise from the properties of titanium oxide, that is, its activity in photo-electric or photo-chemical energy transformation. There have been various investigations of titanium oxide from both the scientific point of view and the engineering one[1-4]. Especially in recent years, titanium oxide has gained more and more attention as an environmentally "friendly" materials.

Both the crystal structure and the oxygen concentration of the surface are expected to be important parameters that determine the performance of functional materials made from titanium oxide. In the engineering field of thermal spraying, some studies of the relation between the functional properties of titanium oxide coatings and the conditions of spraying, or additive treatment such as heat treatment, have been carried out[5-7]. However, to the authors' knowledge, the attempts to apply the laser irradiation treatment to the modification of titanium oxide coatings have not been reported. In this paper, experimental results concerning the effect of the CO_2 laser irradiation treatment for a plasma sprayed TiO_2 coating on the crystal structure and oxygen concentration of the coating are presented. The possibility of the control of the oxygen concentration of the coating surface by controlling the laser irradiation atmosphere is also discussed.

2. Materials and Experimental Procedure

The material used in this experiment was commercially available TiO_2 powder. The chemical composition of the powder was TiO_2:99.62, Al_2O_3:0.13, SiO_2:0.06, Fe_2O_3:0.02 in wt%. The particle size was 10-45 μm. The crystal structure of the powder was a composite of rutile and magneli as shown in **Fig. 1**. The rutile was the dominant phase and a bias of direction of crystal surface was not observed.

The schematic diagram of the experimental apparatus is shown in **Fig. 2**. TiO_2 coatings as the samples for CO_2 laser irradiation treatment were prepared by plasma spraying. The two samples of different oxygen concentration were prepared by two methods. One was obtained by conventional plasma spraying, which was carried out in air, and the other was obtained by low pressure plasma spraying which was carried out in argon at 1.33×10^4Pa. The thickness of the samples were 300-400 μm. The conditions of plasma spraying are shown in **Table 1**.

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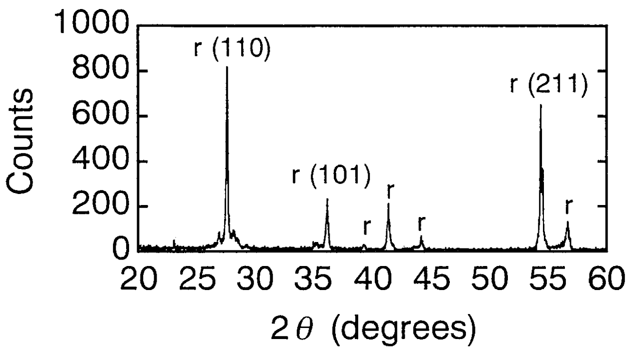

Fig. 1 XRD result of TiO_2 powder before spraying. 'r' in the figure denotes rutile.

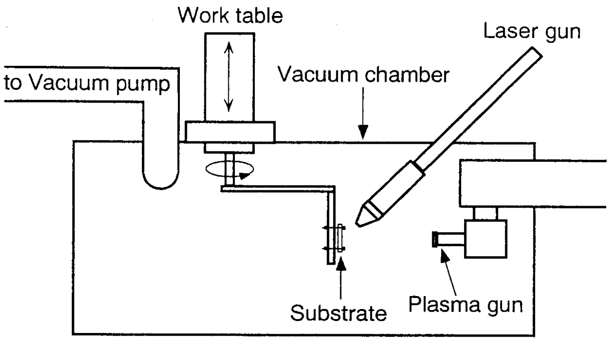

Fig. 2 Schematic diagram of experimental apparatus.

The two kinds of samples were treated by CO_2 laser irradiation. The laser irradiation condition is shown in **Table 2**. The method of irradiation was that the laser spot on the sample surface was scanned by the movement of work table to which the sample was fixed. The thickness of the fused layer formed by laser irradiation was 150-250 μm.

The crystal structure of the coating was investigated by XRD. The oxygen concentration of the coating was determined by the change in weight of the coating before and after annealing in air at 1273K for 18ks, where, for the as-sprayed coating, the coating was separated from the substrate and powdered before annealing, and for the laser-treated coating only the laser-fused layer of the coating was separated from the coating and powdered before annealing.

3. Results and Discussion

3.1 The typical morphology of the laser-treated coating

Fig. 3 shows typical examples of the cross sectional views of the as-sprayed coating(Fig. 3(a-1) and Fig. 3(a-2)) and the laser-treated coating(Fig. 3(b-1) and Fig. 3(b-2)). The porosity of micron order was drastically reduced by the laser irradiation and the Vicker's hardness increased from $800H_V$ to $1000H_V$, which shows that the laser irradiation caused densification of the coating. However, the densification of the coating brought about large cracks and in additon, the large pores emerged.

Table 1 Condition of plasma spraying.

Spraying atmosphere	Air	Ar at 1.33×10^4Pa
Ar gas flow rate (l/min)	47.2	50.0
H_2 gas flow rate (l/min)	2.4, 4.7, 9.4, 11.8	2.4, 9.4, 15.0, 20.0
Arc power (kW)	40	50
Distance between plasma gun and substrate (mm)	100	350
Substrate scan speed (mm/s)	100	100

Table 2 Condition of laser irradiation.

Irradiation atmosphere	Air, Ar at 1.33×10^4Pa
Irradiation power	150, 250, 350, 450
Defocus length (mm)	0
Spot diameter (mm)	0.5
Angle between beam line and substrate surface (degree)	45
Substrate scan speed (mm/s)	100

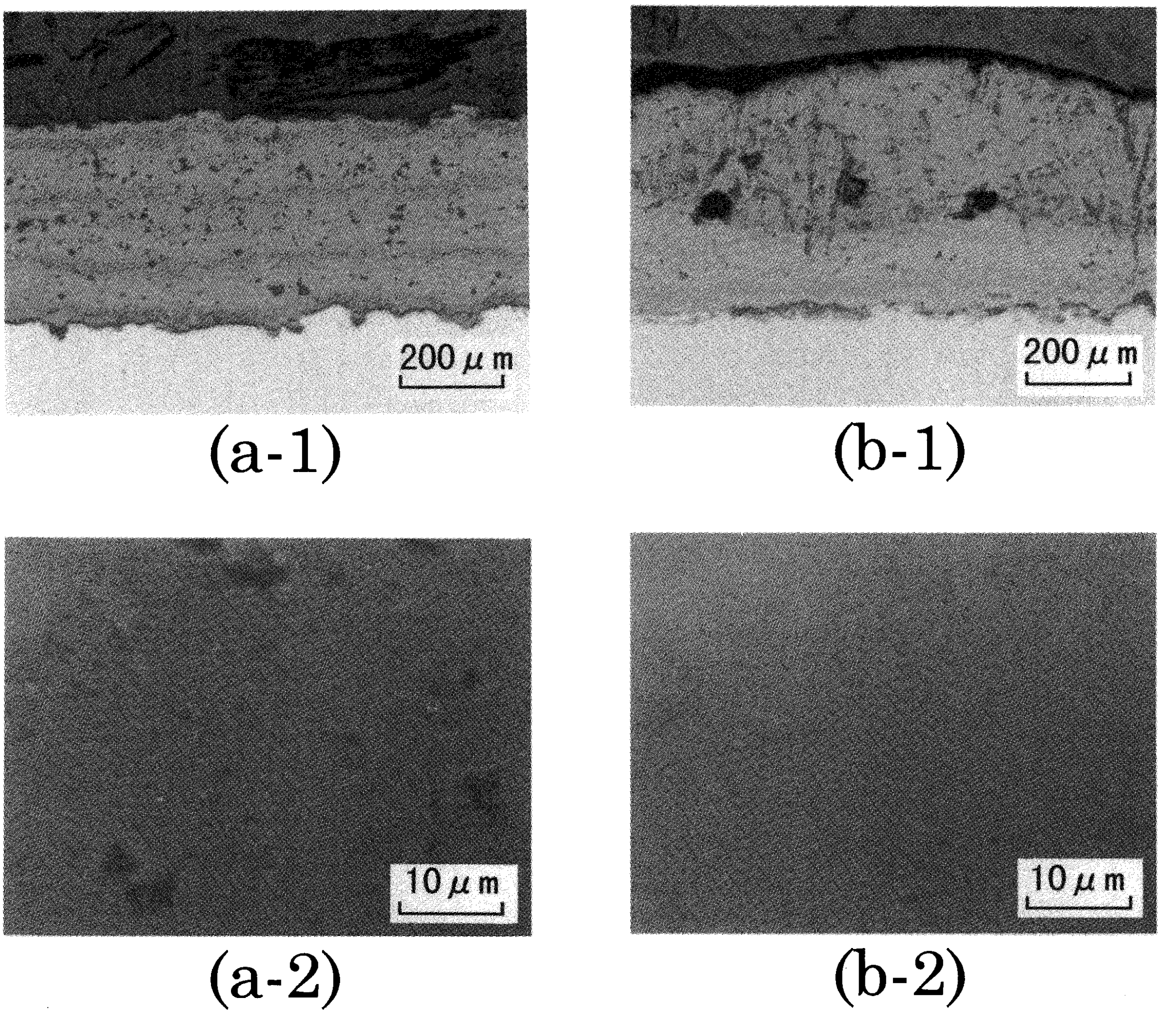

Fig. 3 Cross-sectional views of the titanium oxide coatings. (a-1): as-sprayed coating prepared in air, (a-2):magnification of (a-1), (b-1): laser-treated coating(a-1) in argon at 1.33×10^{4}Pa, (b-2):magnification of (b-1).

These new defects are disadvantages for practical usage of the coating. But, these new defects can be reduced by decreasing the thickness of the fused layer. The laser irradiation method is, therefore, still valuable because the thick modification layer is not needed for the functional coating. In this study, the thick modification layers were prepared for the measurements of oxygen concentration in the modified layer.

3.2 The crystal structure of the surfaces of laser-irradiated coating

XRD results of the titanium oxide coatings before laser irradiation treatment are shown in **Fig. 4**(a) and (b). In air atmospheric spraying, the relative intensity of (110) peaks of the rutile phase decreased and a weak peak of anatase phase appeared as seen in Fig. 4(a) which shows that the directional growth of rutile crystal occurs and that some part of the rutile phase transforms into anatase phase. In low pressure plasma spraying, the directional growth of rutile crystal was more intense than that in air atmosphere spraying and the rutile phase decreased. The magneli phase is suggested by the increase of the base line of XRD pattern in the lower angle region. Ti_3O_5 and Ti_2O_3 phases appeared as shown in Fig. 4(b). These results as a whole show the occurrence of deoxidization. The same tendency for the degree of directional growth and deoxidization enhancement with an increase in the degree of reduction ability of the spraying process was reported in a previous paper[7].

These two as-sprayed coatings were treated by CO_2 laser irradiation in air and argon at 1.33×10^{4}Pa. The XRD results of this experiment are shown in Fig. 4(c), Fig. 4(d), Fig. 4(e), and Fig. 4(f).

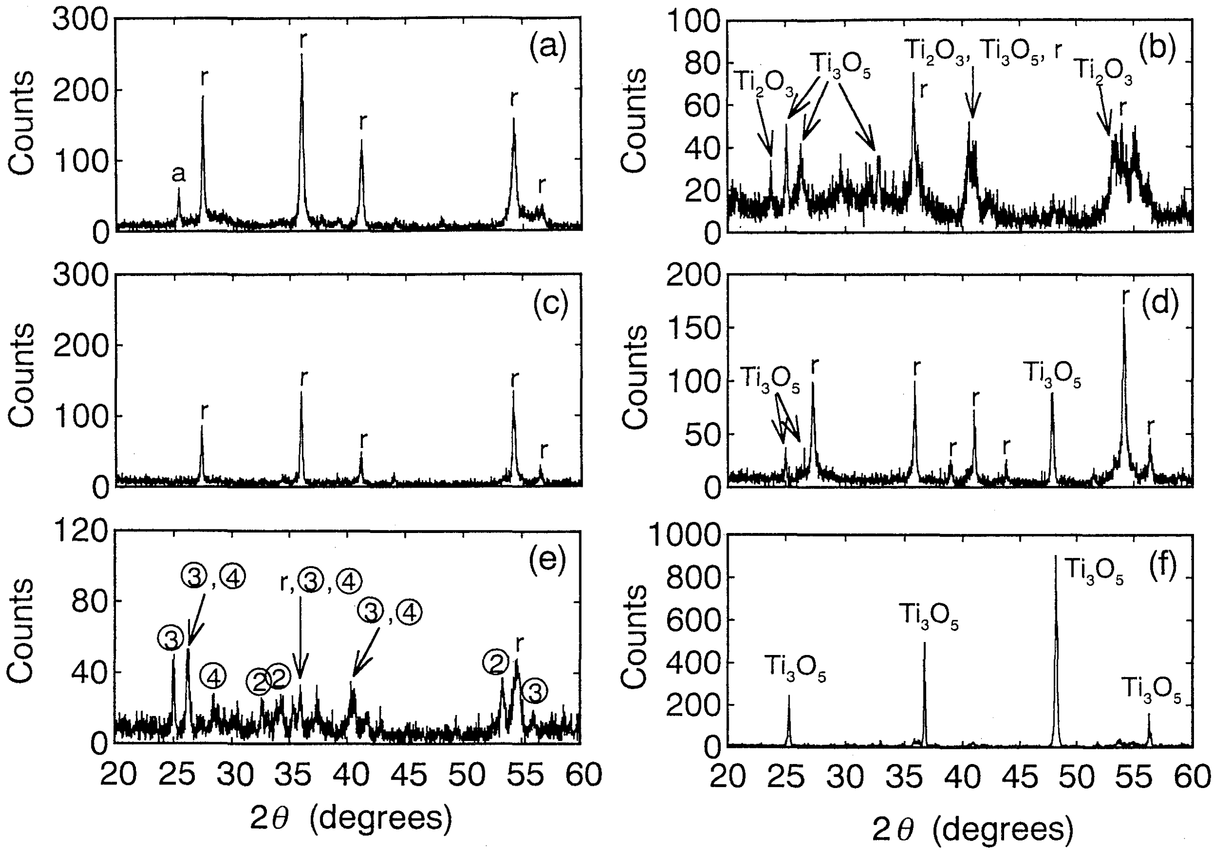

Fig. 4 XRD results of titanium oxide coatings.
(a):as-sprayed coating prepared in air, (b):as-sprayed coating prepared in Ar at 1.33×10^4Pa, (c): laser-treated coating(a) in air, (d): laser-treated coating(b) in air, (e): laser-treated coating(a) in argon at 1.33×10^4Pa, (f): laser-treated coating(b) in argon at 1.33×10^4Pa. 'r', '②', '③' and '④' in the figures denote rutile, Ti_2O_3, Ti_3O_5 and Ti_4O_7, respectively.

In air atmosphere irradiation applied to the slightly deoxidized as-sprayed coating, the change of crystal structure of the coating was not observed, except for the disappearance of anatase phase as shown in Fig. 4(c). In air atmosphere irradiation applied to the highly deoxidized as-sprayed coating, rutile phase became dominant and Ti_3O_5 phase decreased or was directed in crystal structure and Ti_2O_3 phase disappeared as shown in Fig. 4(d), which shows the occurrence of oxidation. These results suggest that the laser irradiation treatment in air atmosphere acts as an oxidation treatment. However, it is shown that the oxidation effect of laser irradiation is limited to the surface layer of the coating in section 3.3.

In argon at 1.33×10^4Pa atmospheric irradiation applied to the slightly deoxidized as-sprayed coating, rutile phase decreased relatively, and the magneli phase and Ti_3O_5 and Ti_2O_3 phases appeared as shown in Fig. 4(e). This crystal structure is similar to that of the highly oxidized as-sprayed coating(see Fig. 4(b)), which shows that the degree of deoxidization in this case is comparable to that of the highly oxidized as-sprayed coating. In argon at 1.33×10^4Pa atmospheric irradiation applied to the highly deoxidized as-sprayed coating, Ti_3O_5 phase became dominant and other phases decreased. These results suggest that the laser irradiation treatment in reductive atmospheres acts as an deoxidization treatment.

3.3 The changes in oxygen concentration of the coatings by laser irradiation

In order to investigate the effect of laser irradiation on the oxygen concentration over the whole of the fused layer of the coating, the change in weight of the fused layer of the coating before and after annealing in air was measured. **Fig. 5** shows the relation between the oxygen loss of titanium oxide coatings and laser irradiation power for different plasma sprayings and laser irradiation atmospheres. 'Oxygen loss' is defined as the change in weight expressed as concentration, regarding the annealed sample to be composed of only TiO_2. The oxygen loss is independent of whether the irradiation atmosphere is air

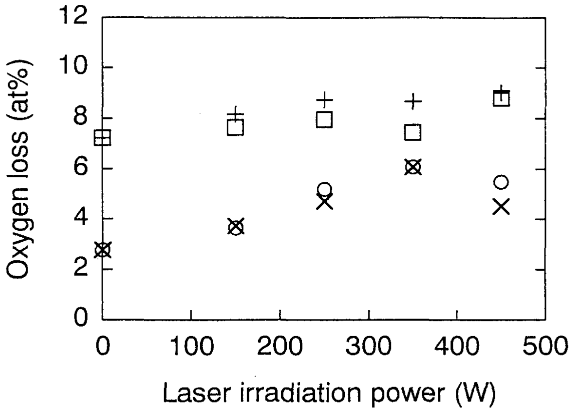

Fig. 5 Relation between oxygen loss of titanium oxide coatings and laser irradiation power for different plasma spraying and laser irradiation atmosphere.
○:coating obtained by plasma spraying in air and laser irradiation in air, ×:coating obtained by plasma spraying in air and laser irradiation in argon at 1.33×10^4Pa, □: coating obtained by plasma spraying in argon at 1.33×10^4Pa and laser irradiation in air, +:coating obtained by plasma spraying in argon at 1.33×10^4Pa and laser irradiation in argon at 1.33×10^4Pa.

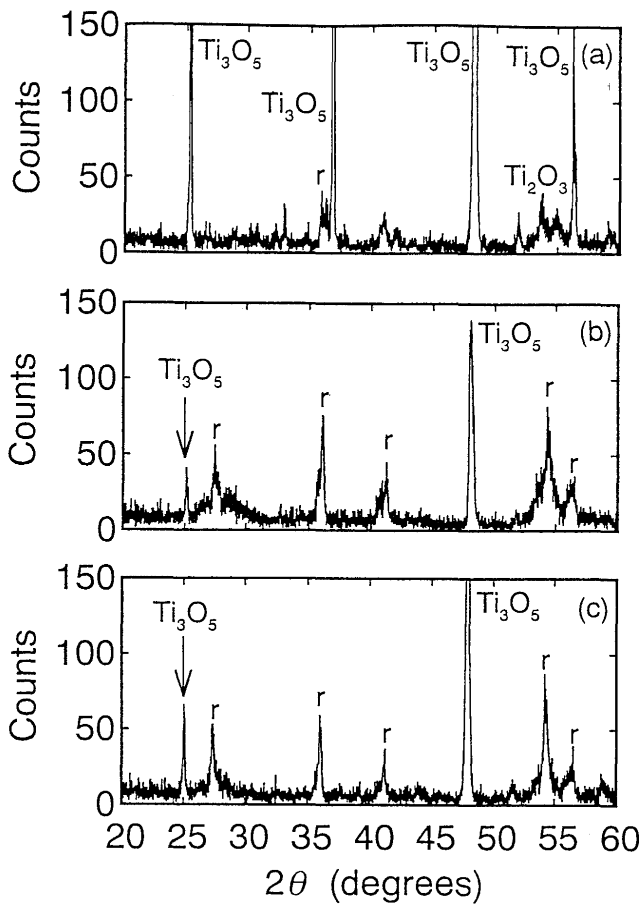

Fig. 7 XRD results of the surfaces of titanium oxide coatings that are an as-sprayed coating and the coatings laser-treated in air at different laser irradiation powers.
(a):before irradiation, (b):irradiation power is 150W, (c):irradiation power is 450W. 'r' in the figure denotes rutile.

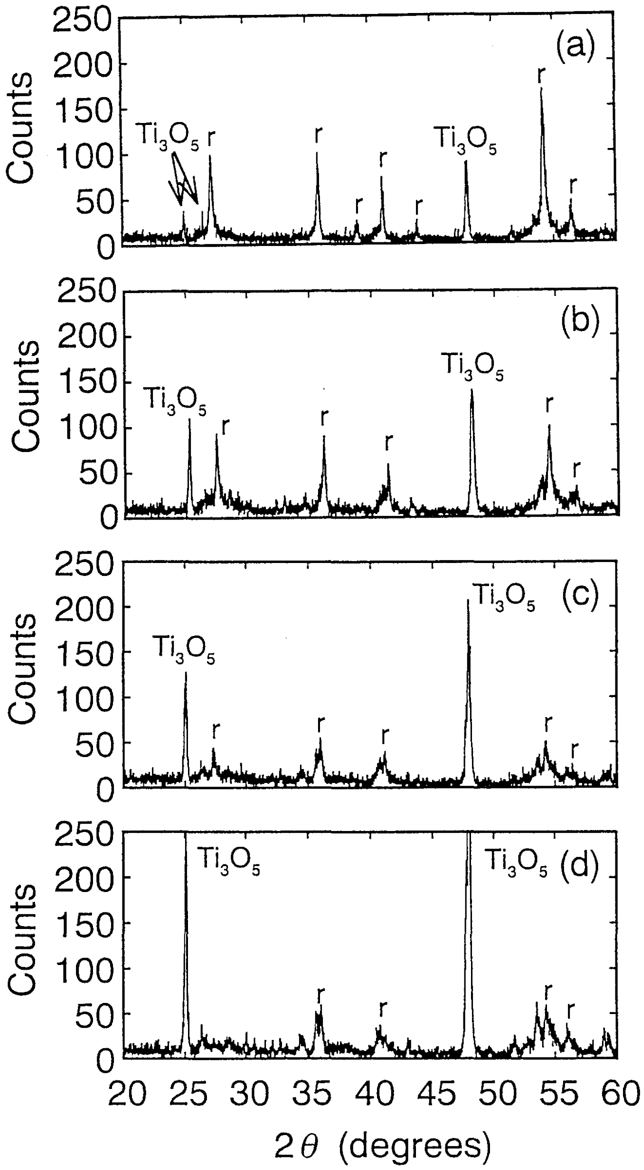

Fig. 6 XRD results of the titanium oxide coating that is laser-treated in air for various distance from the coating surface.
(a):0 μ m, (b):40 μ m, (c):80 μ m, (d):110 μ m. 'r' in the figure denotes rutile.

or argon at 1.33×10^4Pa and increases with an increase of laser irradiation power as shown in Fig. 5. Therefore, the oxidation effect observed when the highly deoxidized as-sprayed coating is laser-irradiated in air atmospheres, as shown in Fig. 4(d), is expected to be limited to the surface layer of the coating.

3.4 The re-oxidation of the surface layer by laser irradiation

XRD results of a titanium oxide coating laser-treated in an air atmosphere at various distances from the coating surface are shown in **Fig. 6**. The relative intensity of rutile peaks decreases with an increase of distance from the coating surface. On the other hand, the relative intensity of Ti_3O_5 peaks increases with an increase of distance from the coating surface. This result shows that the oxygen concentration of the coating laser-irradiated in air atmosphere decreases by gradation in the depth direction from the surface to the inner region. This suggests that the oxidation process by the laser irradiation treatment in air atmosphere is occurring during re-solidification due to the neighboring oxidative environment. **Fig. 7** shows that the degree of oxidation of the surface layer is independent of laser irradiation power. This suggests that the deoxidization is a primary function of the laser irradiation treatment. The oxygen concentration of the coating surface can be controlled continuously, by adjusting the balance between the total deoxidization effect and the surface oxidation effect, through the control of the laser irradiation atmosphere.

4. Conclusions

The modification of plasma sprayed titanium oxide coatings by CO_2 laser irradiation was carried out. XRD and oxygen loss measurements were used to investigate the laser irradiation effect on the crystal structure and oxygen concentration of the titanium oxide coating. The oxygen loss caused by the laser irradiation was found to be independent of whether the irradiation atmosphere is air or argon at 1.33×10^4Pa and to increase with an increase of laser irradiation power. The re-oxidation of the surface layer of the coating was observed when the irradiation atmosphere was air. The oxygen concentration of the coating surface can be controlled continuously by adjusting the balance between the total deoxidization effect and the surface oxidation effect thorough control of the laser irradiation atmosphere.

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