Surface Modification of TiO_2-ZrO_2 Layers with Direct Diode Laser†

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Abstract

Laser cladding technology has been used for erosion resistance, heat resistance and corrosion resistance. In the new solid cold spray process, the coating is formed by high-velocity particles impacting with the substrate to be coated. These particles bond mechanically with the substrate by way of plastic deformation only. Solid cold sprayed coatings have defects such as connected pores and poorly bonded lamellae which damage coating properties. In this research, a direct diode laser was utilized for laser treatments of cold sprayed composite coatings. The influence of laser power and scan speed, on the properties of the laser-treated layers was investigated. The laser treatment is the present subject of research in order to obtain denser coatings with good adhesion to the substrate. Therefore laser technology in combination with solid cold spraying broadens the area of applications for cold sprayed coatings.

KEY WORDS: (Direct diode laser)(Solid cold spay)(TiO_2-ZrO_2 coating)(Wear resistance)

1. Introduction

The cold spray process is a fairly recent process that shows promise as a complement to such well-established techniques as plasma spraying[1] and high velocity oxy-fuel spraying[2]. In the cold spray process[3], the coating is formed by high-velocity particles impacting with the substrate to be coated. The particles are accelerated by a jet of compressed air whose temperature is always lower than the melting temperature of the material being sprayed, and the coating is formed by particles in the solid state. These particles bond mechanically with the substrate by way of plastic deformation only[4]. Solid cold sprayed coatings have defects such as connected pores and poorly bonded lamellae which damage coating properties. In this research, a direct diode laser was utilized for laser treatments of cold sprayed Zn-base composite coatings. The sprayed powders were Zn-Fe composite powder, ZrO_2 nanopowder, anatase TiO_2 nanopowder and WC-Co powder. The influence of the two most important laser-related variables, namely laser power and scan speed, on the properties of the laser-treated layers was investigated. Laser treatment is the present subject of research in order to obtain denser coatings with good adhesion to the substrate. Therefore laser technology in combination with solid cold spraying broadens the area of applications for cold sprayed coatings. The laser treated TiO_2-ZrO_2-WC-Co composite coatings showed high values of hardness from 1280 to 1490 VHN_{50}.

2. Experimental procedure

2.1 Solid cold spraying method and materials

For this experiment, the spraying conditions were compressed air jet pressure: 4~6 kg/cm^2, and spraying distance: 50~130mm. The sprayed powders were Zn-Fe composite powder, ZrO_2 nanopowder, anatase TiO_2 nanopowder and WC-12%Co powder. The SEM images of powder are shown in **Fig.1**. Zn-Fe alloy powder and ceramic powder were mechanically mixed with different ceramic content.

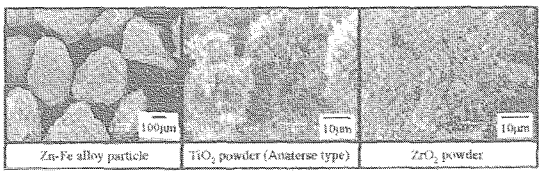

Fig.1 SEM micrographs of powder

Table 1 Zn-Fe composite powder

Composition (mass%)		Particle size distribution (%)				
Fe	Zn	>500 μm	~300 μm	~250 μm	~180 μm	<180 μm
Bal.	39.8	9.5	56.7	21.9	11.5	0.4

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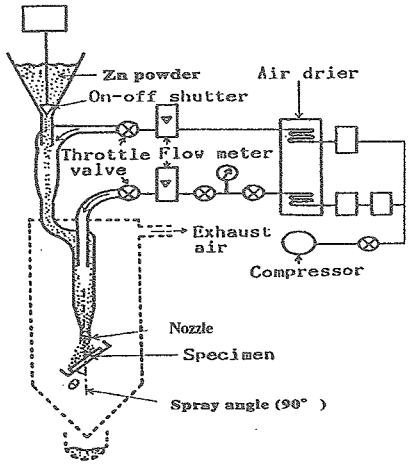

Fig.2 Schematic diagram of solid cold spray apparatus

The composition of the Zn-Fe spraying powder used in this study is shown in **Table 1**. Zn-Fe spraying powder has a hard core of Fe surrounded by the Zn layer. The base materials for the cold spraying were mild steel (SS400) and copper, which were polished before spraying. The substrates were 2mm thick steel (60×50mm), which was mechanically and chemically cleaned and then polished. The structure of the coating was examined by X-ray diffraction analysis. The microstructure of the cold sprayed coating was examined by scanning electron microscopy (SEM) and electron probe micro-analyzer (EPMA). The solid cold spray apparatus is illustrated in **Fig.2**. The mechanical properties of these coatings were evaluated by standard microhardness testing.

2.2 Laser irradiation to solid cold sprayed coating

Figure 3 shows a schematic drawing of the experimental apparatus. The copper plate was used as the substrate. The scan speed was varied between 2mm/sec and 16mm/sec. The laser beam power was varied between 100W and 200 W. The laser beam was focused on the surface of sprayed coating. Two laser irradiation patterns were used and are shown in **Fig.3.**

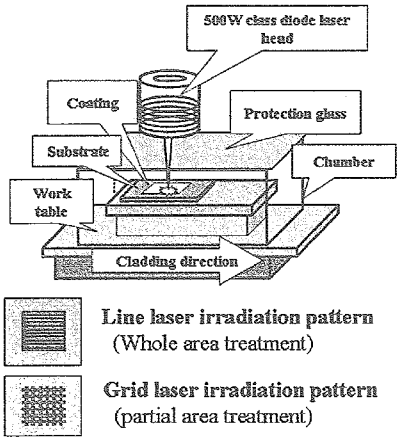

Fig.3 Schematic diagram of 500W class diode laser irradiation apparatus and irradiation pattern

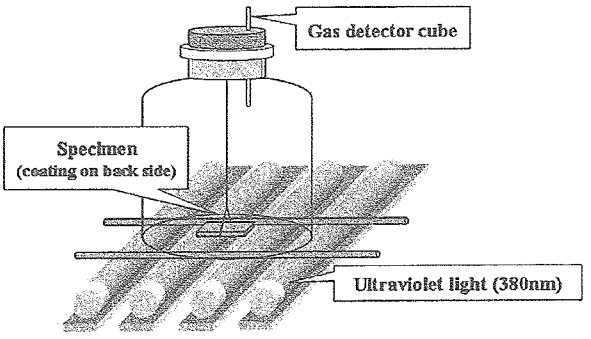

Fig.4 Schematic diagram of acetaldehyde gas decomposition test apparatus

2.3 Evaluation of photo-catalytic property of the coating

Acetaldehyde gas decomposition tests were carried out to evaluate the photo-catalytic property of the coating. The volume of the container was 2.1L. After the container was filled with acetaldehyde gas to 100 ppm, the ultraviolet lamps with a 360 nm wavelength were switched on. The experimental set-up is illustrated in **Fig.4**. The concentration of acetaldehyde gas was measured with a gas detector after a certain time interval.

3. Results and Discussion

3.1 Microstructure and properties of solid cold sprayed coatings

The results of SEM and EPMA images of the surface of solid cold sprayed TiO_2-Zn composite coating are shown in **Fig.5**. These images indicate that the surface of cold sprayed coatings consisted of mainly TiO_2, with small amount of Zn-Fe alloy dispersed particles. These specific properties determine the deformation share in the substrate and particle, as well as the degree of mechanical clamping and/or toothing, respectively, of coating and substrate. **Figure 6** shows the surface of a laser-irradiated coating made at different laser powers, which mainly influenced remelting of particles. An increase in laser power improves surface roughness. The laser treated TiO_2-Zn coatings exhibit a high density and high bond strength.

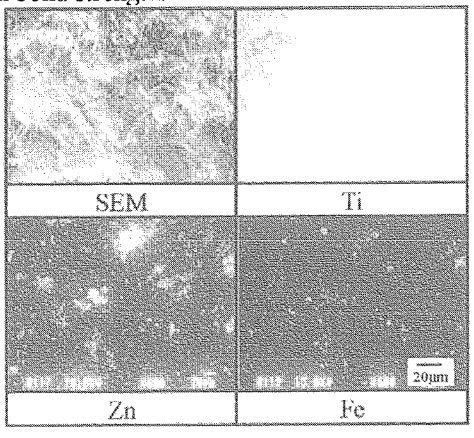

Fig.5 EPMA analysis of TiO_2-Zn sprayed coating (Composition rate,1:40)

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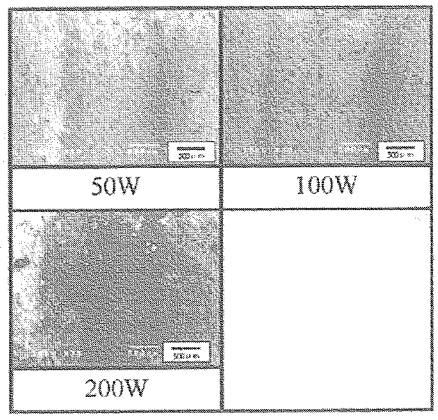

Fig.6 SEM images of TiO_2-Zn coating at different laser power (Scan speed of 8mm/sec)

3.2 Photo-catalytic properties of laser treated TiO_2-Zn coatings

In order to characterize the photo-catalytic property of the coating, decomposition tests of acetaldehyde gas were carried out. **Figure 7** shows the results of acetaldehyde gas decomposition tests. This experiment was performed using cold spray TiO_2-Zn coatings and laser treated TiO_2-TiO_2-Zn coating. The photo-catalytic properties of the grid laser treated TiO_2-Zn coating were excellent, being equivalent to those of cold spray coatings. The characteristic decay time of line laser treated TiO_2-Zn coatings was worse than coatings without laser treatment. It is revealed that phase composition of the TiO_2-Zn composite coating is similar to that of starting powders. **Figure 8** shows the XRD patterns of the line laser treated TiO_2-Zn composite coatings and grid laser treated TiO_2-Zn composite coatings. The anatase phases of TiO_2 remained in the grid laser treated coatings, and part of the anatase phases of TiO_2 has transformed into rutile phases by laser treatment.

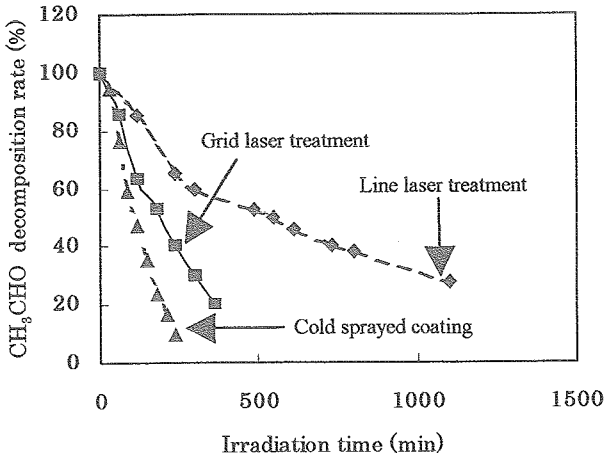

Fig.7 Decay characteristics of acetaldehyde concentration with TiO_2-Zn coatings

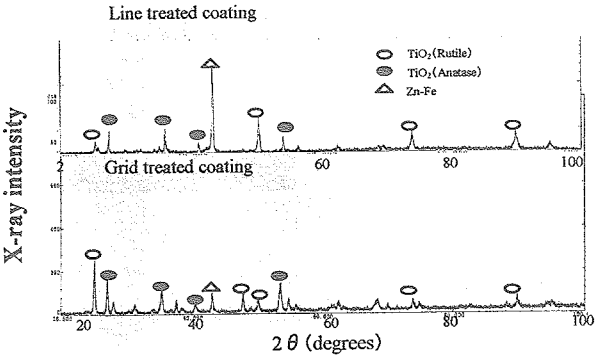

Fig. 8 XRD pattern of laser treated TiO_2-Zn coatings

3.3 Properties of laser treated TiO_2-ZrO_2-WC-Co coatings

The results of SEM images of the surface of as sprayed coatings and laser-treated TiO_2-ZrO_2-WC-Co coatings are shown in **Fig.9**. The laser treated TiO_2-ZrO_2-WC-Co coatings became denser and smoother than those of cold spraying. **Figure 10** shows SEM and EPMA images of the cross section of TiO_2-ZrO_2-WC-Co coatings after laser treatment at a power of 150W and a scan-speed of 8 mm/sec. WC, Co and Zr were distributed uniformly. A diffusion zone at the interface is seen after laser treatments. The uniformly sealed depth of layer was obtained over the whole area of the sample treated by the diode laser.

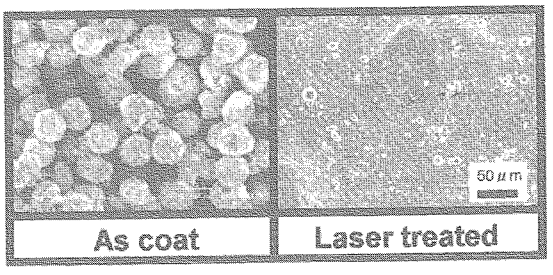

Fig.9 SEM images of as coat and laser treated TiO_2-ZrO_2-WC-Co coating

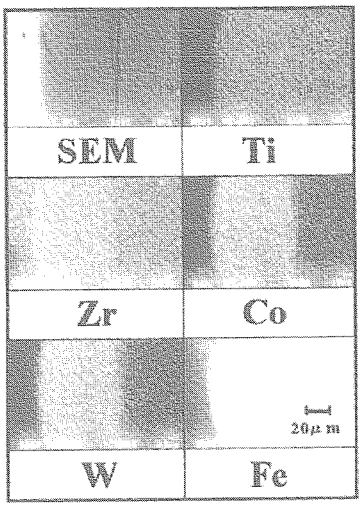

Fig.10 EPMA analysis of laser treated TiO_2-ZrO_2-WC-Co layer

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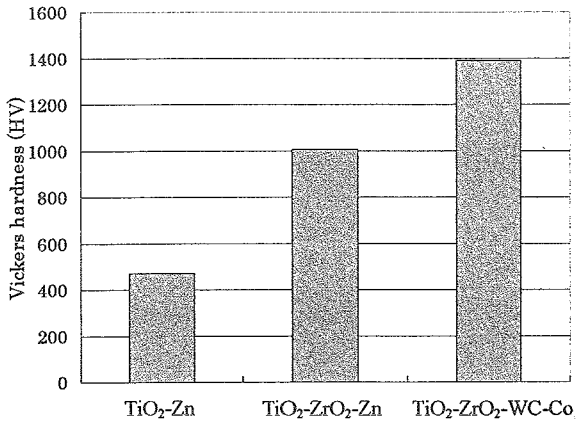

Fig.11 Microhardness results of laser treated solid cold sprayed composite coatings.

The average microhardnesses of the laser treated coatings are presented in **Fig.11**. Laser treated TiO_2-ZrO_2-WC-Co coatings have very high microhardness values. It is seen that the Vickers hardness of all the TiO_2-ZrO_2-Zn coatings increases compared with the TiO_2-Zn coatings without ZrO_2 powder. The Vickers hardness of the laser treated TiO_2-ZrO_2-WC-Co coatings increased with the content of WC. Very high microhardness values in the range of 1280~1490 HV were measured in the specimens.

4. Conclusions

The results are summarized as follows.

(1) The laser treated TiO_2-Zn composite coatings exhibit a high density and high bond strength. The photocatalytic properties of the grid laser treated TiO_2-Zn composite coatings were excellent, being equivalent to those of cold spray TiO_2-Zn composite coatings.

(2) The laser treated TiO_2-ZrO_2-WC-Co coatings showed high microhardness values from 1280 to 1490 VHN_{50}. The laser treatment was found to improve the particle bond strength and density at the optimum conditions of the laser power and scan speed.

(3) The Vickers hardness of the laser treated TiO_2-ZrO_2-Zn composite coatings increased with the ZrO_2 content.

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