

Fabrication of nano-sized oxide composite coatings and photo-electric conversion/electron storage characteristics

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Abstract

Titanium dioxide TiO₂ can be used as a photo-anode to give generated electrons to the metal substrate under illumination. The transition metal oxide such as iron oxide Fe₂O₃ can be used to store electrons generated by the photo-electric conversion function of TiO₂ under the illuminated situation while the electrons are discharged from the transition metal oxide to the metal substrate in the dark. In this paper, coatings of nano-sized composite of TiO₂ and Fe₂O₃ were fabricated by the Warm Spray process, in which the feedstock powder is accelerated by a supersonic gas jet with speed above 1.0 km s⁻¹ and temperature between 800 and 2500 K, and then impacted onto the target substrate continuously to form coatings. The coatings of TiO₂ and Fe₂O₃ nano-composite fabricated by Warm Spray showed no thermal deterioration such as phase transformation and particle growth of the feedstock during the spray process. The coatings fabricated by the Warm Spray had larger photo-current and the electron charge/discharge capacity than that by a conventional HVOF process. In addition, these characteristics were improved by decreasing the primary particle size of TiO₂ and Fe₂O₃.

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1. Introduction

Strong attention has been attracted in recent years to various systems to convert light into electricity from the viewpoint of effective use of the clean solar energy. One issue of such system to be considered is how to guarantee the supply of electricity in the dark situation. One obvious solution is to provide connection with an outside electron storage system such as batteries, but the overall system tends to become large. One of the methods to solve this problem is to mount the photo-electric conversion function and the electron storage function onto one device. Such approach is expected to be effective for applications such as photo-cathodic corrosion protection and solar secondary battery. For instance, the principle of the full-time photo cathodic protection is based on the combination of photo-electrochemical function and electron charge/discharge

function. [1,2] During daytime, the photo-electrochemical function makes the electrode potential less noble, exerting cathodic protection of the metal substrate and charge electrons into the storage. During night time, electrons in the storage are discharged to the substrate, enabling to sustain the cathodic protection function. Titanium dioxide TiO₂ is well known as a material with the photo-electrochemical function, e.g. photo-catalyst. The transition metal oxides such as Fe₂O₃, WO₃ and SnO₂ can be proposed as the electron storage material.

Regarding TiO₂, it was reported that the photo-catalytic function could be improved by nano-size effect because of decrease in probability of recombination of electrons and holes once generated by irradiation [3]. The use of nano-sized TiO₂ is expected effective to improve photo-electrochemical function also in this study. Moreover, reaction rates of charge/discharge can be increased by reducing the particle size of transition metal oxide because the electron and the proton are transferred by the electrochemical reactions and therefore larger surface area takes advantage of transferring protons at the interface between the electrolyte and the transition metal oxide.

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Table 1
Combination of TiO₂ and Fe₂O₃ in feedstock

Mixture notation	TiO ₂		Fe ₂ O ₃	
	Product name	Nominal particle size/nm	Product name	Nominal particle size/nm
LCP	ST41	200	SEW	800
SCP	ST21	20	FH04	80

For industrial development concerning deposition of TiO₂, solution-based processes such as application of painting technology as well as electro-deposition have been used [4–6]. There, however, still are problems of remaining of binders, inevitable post heat treatment, low adhesion and cohesion of the coatings, even taking into account the merits of these methods such as the capability of high-speed deposition to a large surface area. As a dry process, although conventional thermal spray technology has been applied to deposit TiO₂, thermal deterioration of TiO₂ such as phase transformation and particle growth could not be controlled completely [7,8].

In this paper, coatings of TiO₂ and Fe₂O₃ composites with nano particle size were fabricated by Warm Spray, which is one of the supersonic solid impact deposition processes investigated actively in recent years [9]. Since it is possible to control the maximum temperature of the particles and the processing time is very short in the order of ms in Warm Spray, it is expected to attain deposition of the composite oxides without significant thermal deterioration, for instance, phase transformation of TiO₂ from anatase to rutile and particle's growth or melt.

In this research, the photo-electrochemical function of the TiO₂-Fe₂O₃ nano-composite coatings and their charge/discharge characteristic were investigated in addition to the characterisation of the microscopic structure and of the crystallographic phase.

2. Experimental

2.1. Preparation of feedstock powder

The feedstock powder for Warm Spray was prepared through the spray-dry method. In this research, powders of TiO₂ (anatase phase, Ishihara Sangyo Kaisha) and Fe₂O₃ (hematite phase, JFE Chemical Corporation) with mixture ratio of 50:50 (mass%) were put into a plastic pot. The combination of TiO₂-Fe₂O₃ in different primary particle size is listed in Table 1. Notations of LCP and SCP will be used for the composite powders made of mixture of 200 nm TiO₂ with 800 nm Fe₂O₃ and that by 20 nm TiO₂ with 80 nm Fe₂O₃ respectively throughout this paper. Water, poly-vinyl alcohol solution (10 mass%), zirconia ball (10 mm diameter) and a slight amount of surfactant reagent were added into the pot. After closed, the pot was rotated to stir the mixture for 24 h with a ball-milling apparatus to prepare a slurry. The slurry was supplied at an approximate speed of 20 cm³ min⁻¹ into the spray-dry chamber and dropped onto the atomizer disk rotating at 1.5 × 10⁴ rev min⁻¹. The atomized droplets were sprayed in the chamber, into which air was blown to dry them; the gas temperature at the inlet and outlet was 423 K and 358 K,

respectively. The spray-dried powder was sieved to 25–90 μm in particle size as a feedstock for subsequent coating fabrication.

2.2. Fabrication of coatings

Coatings of the TiO₂ and Fe₂O₃ nano-composites were fabricated by Warm Spray. In the process, the feedstock powder is supplied into a supersonic jet with velocity above 1.0 km s⁻¹ and the temperature controlled between 800 and 2500 K. Such a gas jet is generated by introduction of nitrogen gas as a cooling media into the combustion flame generated from kerosene and oxygen. The powder particles become heated and accelerated during flight in the gas, and then are impacted and deposited to the target substrate continuously to form the coatings. Spray parameters of Warm Spray are listed in Table 2. The substrate material for spraying was 316 L stainless steel with the dimensions of 50 × 100 × 5 mm. The substrate was blasted with alumina grit and degreased with supersonic in acetone. For comparison, additional coatings were prepared with conventional high-velocity oxy-fuel (HVOF) spraying. The spray condition for HVOF is also listed in Table 2.

2.3. Evaluation of coatings

The coated specimens were cut into small pieces of 20 mm square for subsequent evaluation.

The crystallographic phase of the specimens was identified by the X-ray diffraction (XRD) method (Rigaku, RINT-2500) and the microscopic structure was observed by a scanning electron microscope (SEM, JEOL, Model 6500).

The electrochemical characteristics were evaluated by the following techniques. The electrochemical cell had a rectangular parallelepiped with two open windows. One window with the area of 1.23 cm² was covered with the coated surface of the specimens, which contacted the electrolyte. The electric signal as of the sample electrode was taken out from the back side of the coated specimens. Another window was set opposite to the coated surface and the transparent quartz glass was put in to the window frame for introduction of the UV light to the sample surface. A Pt spiral and Ag/AgCl/saturated KCl were used for the counter and the reference electrodes, respectively. The phosphate buffer solution (pH6.0) was used for the electrolyte. The mercury lamp (500 W, Ushio Inc., USH-500D) was a source of UV irradiation. Photo-current was measured by the dynamic potential polarization up to 1.5 V from the corrosion potential at a scan rate of

Table 2
Spray condition

		Warm spray	HVOF
N ₂ flow rate	m ³ min ⁻¹	1.0	-
O ₂ flow rate	m ³ min ⁻¹	0.64	0.81
Fuel (kerosene)	dm ³ min ⁻¹	0.33	0.32
Powder feed rate	g min ⁻¹		40
Spray distance	mm	100	380
Barrel length	mm	204	102
Pass number	-		1
Pitch width	mm		4
Gun traversing speed	m s ⁻¹		0.7

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