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Titanium dioxide–nickel oxide composite coatings: Preparation by mechanical coating/thermal oxidation and photocatalytic activity

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ABSTRACT

Photocatalytic TiO_2–NiO composite coatings were prepared by the mechanical coating technique and subsequent heat oxidation. The preparation process is examined in detail. The prepared coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The results showed that Ni particles were mainly located at the inner layer of these composite coatings if prepared by 1-step MCT, whereas the Ni particles adhered to the surfaces of the Ti–Ni composite coatings if prepared by 2-step MCT. At oxidation temperatures of 973 and 1073 K, the Ti coatings were partly oxidized to rutile TiO_2 and a Ti–TiO_2–NiO composite microstructure was formed. When the oxidation temperature was further increased to 1173 and 1273 K, the Ti coatings were oxidized to rutile TiO_2 and a TiO_2–NiO composite microstructure was obtained. The photocatalytic activity of these composite coatings was evaluated by the degradation of a methylene-blue (MB) solution under UV irradiation. The results showed that the sample prepared by 2-step MCT and subsequent heat oxidation at 1073 K had the highest photocatalytic activity, i.e., more than 200 nmol L^{-1} h^{-1}. The improvement in the photocatalytic activity could be attributed to the efficiency increase in charge separation, which may result from the formation of the TiO_2–Ti composite microstructure and TiO_2–NiO p–n heterojunctions.

1. Introduction

Ball milling has found a new application in terms of mechanical coating, based on the principle of contamination phenomenon [1]. This involves making effective use of the friction and impact forces in order to form coatings or films on a grinding medium (a substrate in the present case). As a new film- and coating-preparation method, mechanical coating technique (MCT) has been used to prepare a variety of advanced materials, including metal coatings [2–4], alloy coatings [5], solid-solution coatings [6], and photocatalytic films [7–9].

In particular, the preparation of photocatalytic coatings by MCT has attracted increasing attention. The detailed procedure is as follows. Ti powder particles are first coated

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on Al_2O_3 balls by MCT to form continuous Ti coatings. Subsequently, the Ti coatings are oxidized at elevated temperatures to form TiO_2 coatings [8] or TiO_2/Ti composite coatings [7,9]. These coatings show a relatively high photocatalytic activity. To increase the photocatalytic activity of the TiO_2 coatings, the TiO_2/Ti composite microstructure is produced since it can decrease the recombination rate of electron–hole pairs [10–13].

In addition to the above method of doping TiO_2 with a metal, an alternative is to couple TiO_2 with other semiconductors [14–16]. It is generally known that TiO_2 and NiO are n-type and p-type semiconductors, respectively. When TiO_2 couples with NiO, a p–n junction may be formed. It is believed that an inner electric field will emerge at the interface. At equilibrium, the electric field induces a negative charge in the NiO region, whereas the TiO_2 region has a positive charge. The photogenerated electron–hole pairs at the surface of TiO_2 will be separated by the inner electric field. The holes move to the negative and the electrons flow to the positive region of the electric field. As a result, the recombination rate of electron–hole pairs is decreased and the photocatalytic activity is enhanced [17].

In this work, p–n heterojunctions of photocatalytic TiO_2–NiO films were prepared by MCT and subsequent heat oxidation. The microstructural evolution of the metal coatings during heat oxidation was examined. The photocatalytic activity of these coatings was also evaluated.

2. Experimental

2.1. Source materials and experimental installation

Metal powders and ceramic balls were used as coating and substrate material, respectively. The metal powders included Ti (titanium) and Ni (nickel). The relevant parameters of the source materials are listed in Table 1. A planetary ball mill (type: P5/4, Fritsch, Germany) was employed to perform the mechanical coating operation.

2.2. Preparation of metal coatings by MCT

There are two methods to prepare Ti–Ni metal coatings, either by 1-step or by 2-step MCT. The detailed procedure of the 1-step MCT preparation is as follows. 60 g of Al_2O_3 balls and 40 g of Ti and Ni powder were charged into a bowl made of alumina with a volume of 250 ml (Φ75 mm × 70 mm). The percentage of Ni powder was 0, 1, 5, and 10 vol% of the totally filled powder. The mechanical coating operation was carried out for 10 h. A 10-min milling operation was followed by a 2-min cooling interval. The cooling interval was introduced to decrease any temperature effect on the mechanical coating operation and to ensure that the mechanical coating was performed at relatively low temperature. The rotation speed was set at 480 rpm.

Table 1
Parameters of the source materials for the fabrication of metal coatings by MCT.

Source materials	Average diameter (mm)	Purity (wt%)	Manufacturer
Metal powder			
Ti	0.030	99.1	Osaka Titanium Technology
Ni	0.005	99.8	Fukuda Metal Foil & Powder
Ceramic substrate			
Al_2O_3 balls	1.0	93.0	Nikkato Corporation

The other method is a 2-step MCT in which first Ti coatings were prepared and, then, Ni powder was deposited onto the Ti coatings. The detailed procedure is as follows. 40 g of Ti powder and 60 g of Al_2O_3 balls were charged into the bowl. Then, the mechanical coating operation was carried out for 10 h at the rotation speed of 480 rpm. After this operation, Ti coatings on Al_2O_3 balls were obtained. In the second step, 15 g of Ti-coated Al_2O_3 balls and 30 g Ni powder were charged into the bowl. Then, the mechanical coating operation was performed again at 480 rpm for 1, 5 and 10 h.

The samples prepared by 1-step or 2-step MCT were then heated to elevated temperatures. Heat oxidation was performed using an electric furnace in air atmosphere at temperatures of 973, 1073, 1173, and 1273 K. The samples were held at elevated temperature for 10 h and then cooled in the furnace.

The prepared samples were labeled as follows. "M10-Ti" is the sample prepared with Ti powder by MCT at 480 rpm for 10 h. "Ti–*x*% Ni" indicates the samples prepared by 1-step MCT with mixed Ti and Ni powder with *x* being the volume fraction of Ni. "2SMy" are the samples prepared by 2-step MCT with *y* indicating the MCT time for the coating of the Ni powder. "Ti–*x*% Ni–*h* K–*t* h" are the final oxidized products of the Ti–*x*%Ni samples, heat oxidation at the elevated temperature *h* K for a period of *t* h. Likewise, "2SM*y*–*h* K–*t* h" are the oxidized products of the 2SM*y* samples after they were subjected to the elevated temperature *h* K for *t* h.

2.3. Characterization of these coatings

Before the characterization of the samples, they were treated by ultrasonic cleaning (frequency: 28 kHz) in acetone to remove any substances that did not strongly adhere to the surfaces of the Al_2O_3 balls. An XRD analyzer (JDX-3530, JEOL, Japan) with Cu-Kα radiation at 30 kV and 20 mA was used to determine the compositions and crystal structures. The surface morphologies and cross-sectional microstructures of the samples were observed by SEM (JSM-5300, JEOL, Japan). The elemental distribution was examined using an energy dispersive spectrometer (EDS) being part of SEM.

2.4. Evaluation of the photocatalytic activity

Methylene-blue (MB) is a common organic dye that is frequently used as target degradation product to evaluate the photocatalytic activity of TiO_2. The photocatalytic activity of the samples was evaluated by measuring the degradation of MB solution at room temperature. After ultrasonic cleaning, the samples were spread uniformly on the bottom of a cylindrical cell (Φ20 mm × 50 mm). To