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

Yun Lu a,⁎, Liang Hao b,⁎, Kou Matsuzaka a, Hiroyuki Yoshida c, Hiroshi Asanuma a, Jinxiang Chen d, Fusheng Pan e

a Graduate School & Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan
b College of Mechanical Engineering, Tianjin University of Science and Technology, No. 1038, Dagu Nantu, Hexi District, Tianjin 300222, PR China
c Chiba Industrial Technology Research Institute, 6-13-1, Tendai, Inage-ku, Chiba-shi, Chiba 263-0016, Japan
d School of Civil Engineering, Southeast University, No. 2, Sipailou, Nanjing 210096, China
e College of Materials Science & Engineering, Chongqing University, No. 174, Shazhengjie, Shapingba, Chongqing 400044, China

ARTICLE INFO

Keywords:
Mechanical coating technique
Heat oxidation
Composite coatings
Photocatalytic activity

ABSTRACT

Photocatalytic TiO2–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 TiO2 and a TiO2–NiO composite microstructure was formed. When the oxidation temperature was further increased to 1173 and 1273 K, the Ti coatings were oxidized to rutile TiO2 and a TiO2–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 TiO2–Ti composite microstructure and TiO2–NiO p–n heterojunctions.

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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...
on Al₂O₃ balls by MCT to form continuous Ti coatings. Subsequently, the Ti coatings are oxidized at elevated temperatures to form TiO₂ coatings [8] or TiO₂/Ti composite coatings [7,9]. These coatings show a relatively high photocatalytic activity. To increase the photocatalytic activity of the TiO₂ coatings, the TiO₂/Ti composite micro-structure is produced since it can decrease the recombination rate of electron–hole pairs [10–13].

In addition to the above method of doping TiO₂ with a metal, an alternative is to couple TiO₂ with other semiconductors [14–16]. It is generally known that TiO₂ and NiO are n-type and p-type semiconductors, respectively. When TiO₂ 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 TiO₂ region has a positive charge. The photogenerated electron–hole pairs at the surface of TiO₂ 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 TiO₂–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 Al₂O₃ balls and 40 g of Ti and Ni powder were charged into a bowl made of alumina with a volume of 250 ml (Ø75 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.

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 Al₂O₃ 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 Al₂O₃ balls were obtained. In the second step, 15 g of Ti-coated Al₂O₃ 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. “2SMx” 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, “2SMx–h K–t h” are the oxidized products of the 2SMx 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 Al₂O₃ 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 TiO₂. 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 (Ø20 mm × 50 mm). To
ensure identical initial conditions for all investigated samples, the MB solution (3 ml, 20 \( \mu \text{mol L}^{-1} \)) was pre-adsorbed onto the samples before evaluating their photocatalytic activity. The cell containing the samples and the MB solution were kept in the dark for 12 h to allow for adsorption. The samples were then spread uniformly on the bottom of the cell again, and the MB solution (7 ml, 10 \( \mu \text{mol L}^{-1} \)) was poured into it. The photocatalytic activity of each sample was evaluated under ultraviolet (UV) light (wavelength < 400 nm) with an intensity of 1 mW cm\(^{-2}\) for 24 h. These conditions correspond to the Japanese Industrial Standard (JIS R 1703-2). The absorbance of the MB solution was measured by a colorimeter (Sanshin Industrial Co., Ltd., Japan) under visible light irradiation at a wavelength of 660 nm, which is near the absorption maximum (664 nm) of MB. The gradient \( k \) (nmol L\(^{-1}\) h\(^{-1}\)) of the MB concentration versus irradiation time was calculated by the least squares method for a period of 1–12 h and was used as the degradation-rate constants. From its unit, we can see that \( k \) indicates the variation in MB concentration per unit time or the variation in MB amount per unit volume and per unit time. We used the degradation-rate constants as the evaluation standard of the photocatalytic activity. The greater the gradient (larger degradation-rate constant \( k \)), the quicker is MB degradation, and higher is the photocatalytic activity.

3. Results and discussion

3.1. Preparation of Ti–Ni composite coatings

Fig. 1 shows the XRD patterns of Ti–Ni-coated Al\(_2\)O\(_3\) balls prepared by MCT. It can be seen that only the diffraction peaks of Ti are detected for the M10-Ti sample. This means that continuous Ti coatings were formed on the surfaces of the Al\(_2\)O\(_3\) balls. For the Ti–5% Ni and Ti–10% Ni samples, diffraction peaks of alumina, Ti, and Ni were found (Fig. 1a). This shows that the Al\(_2\)O\(_3\) balls were coated by Ti and Ni. However, the diffraction peaks of Ni could hardly be detected for the Ti–1% Ni sample, indicating that the content of Ni in the coatings is rather small or even zero. As for the samples prepared by 2-step MCT (Fig. 1b), the diffraction peaks of Ti and Ni could be found while those of alumina were not detected. This implies that the Ti–Ni coatings were uniform and covered the entire surface of the Al\(_2\)O\(_3\) balls. In addition, the diffraction peaks of Ni were quite strong, indicating a rather high Ni content.

The surface SEM images of the Ti–Ni-coated Al\(_2\)O\(_3\) balls prepared by MCT are presented in Fig. 2. The EDS results (not shown) have proved that the dark and light gray areas correspond to Ni and Ti particles, respectively. For 1-step MCT (Fig. 2a–d), few Ni particles are observed at the surface of the Ti–Ni coatings, implying that the Ni content is rather low. In addition, the Ti–Ni coatings become discontinuous on increasing the Ni content. In contrast, the Ti–Ni coatings prepared by 2-step MCT are continuous and the Ni content in the coatings is greater than that of coating prepared by 1-step MCT (Fig. 2e–f).

The cross-sectional SEM images of the Ti–Ni-coated Al\(_2\)O\(_3\) balls prepared by MCT are presented in Fig. 3. As pointed out above, the dark and light gray areas correspond to Ni and Ti particles, respectively. For the samples prepared by 1-step MCT, the Ni particles are located at the inner layer of the Ti–Ni coatings (Fig. 3b–d). On the other hand, in case of the samples prepared by 2-step MCT, Ni particles are found at the surface of the Ti coatings (Fig. 3e–f). On the basis of these results, Ti–Ni composite coatings prepared by either 1-step or 2-step MCT can be distinguished.

3.2. Preparation of TiO\(_2\)–NiO composite coatings

After MCT, heat oxidation was also performed for all samples. Fig. 4 shows the XRD patterns of the Ti–Ni-coated Al\(_2\)O\(_3\) balls prepared by 1-step MCT after heat oxidation at elevated temperatures. The diffractograms of the Ti–1% Ni and Ti–5% Ni samples are presented in Fig. 4a and b, respectively. For the Ti–1% Ni samples (Fig. 4a), only the diffraction peaks of rutile TiO\(_2\) are detected, irrespective of the oxidation conditions. For the oxidized Ti–5% Ni samples (Fig. 4b), in addition to rutile TiO\(_2\), the diffraction peaks of Al\(_2\)O\(_3\), NiO, and Ni\(_2\)O\(_3\) are also found. This means that the coated Ni was oxidized to form NiO and Ni\(_2\)O\(_3\). In

**Fig. 1.** XRD patterns of Ti–Ni-coated Al\(_2\)O\(_3\) balls prepared by (a) 1-step MCT and (b) 2-step MCT.
summary, TiO$_2$–NiO–Ni$_2$O$_3$ composite coatings could be prepared by 1-step MCT and subsequent heat oxidation.

The cross-sectional SEM images of the Ti–1% Ni samples after heat oxidation are shown in Fig. 5. It can be seen that the thickness of TiO$_2$ coating increased with oxidation temperature. At oxidation temperatures of 1173 and 1273 K, the Ti coatings were totally oxidized to form TiO$_2$ coatings (Fig. 5c and d). Fig. 6 shows the cross-sectional SEM images of the Ti–5% Ni samples after heat oxidation. Since the content of Ni in the coatings is rather low, NiO and Ni$_2$O$_3$ cannot be found in the corresponding SEM images. The evolution of the coatings during heat oxidation shows a pattern similar to that shown in Fig. 5. However, it should be noted that the thickness of the coatings is less than that in the case of the Ti–1% Ni samples. This may be related to the poor wettability of Ni at low temperatures, compared to that of Ti.

The oxidation evolution of Ti–Ni-coated Al$_2$O$_3$ prepared by 2-step MCT was also examined. Fig. 7 shows the corresponding XRD patterns of these samples after heat oxidation. If oxidized at 973 K, rutile TiO$_2$ and NiO were found. With an increase in the oxidation temperature to
1073 K, diffraction peaks of Ti$_2$O$_3$ were detected, which means that Ti was further oxidized to form Ti$_2$O$_3$. However, when oxidation temperature was further increased to 1173 K and 1273 K, only the diffraction peaks of rutile TiO$_2$ were found. Those of NiO and Ti$_2$O$_3$ are hardly found, which means that the amounts of NiO and Ti$_2$O$_3$ were rather small or even zero, which is probably because of falling away of NiO on the surface during the oxidation process at higher temperatures.

The cross-sectional SEM images of Ti–Ni-coated Al$_2$O$_3$ prepared by 2-step MCT after heat oxidation are given in Fig. 8. When oxidized at 973 K, TiO$_2$ and NiO were formed at the surface of the Ti coatings (Fig. 8a) and, therefore, TiO$_2$–NiO–Ti composite coatings were prepared. With an increase in the oxidation temperature to 1073 K, the thickness of TiO$_2$ increased. When the oxidation temperature was further increased to 1173 K and 1273 K, the Ti coatings were totally oxidized to TiO$_2$. The results were consistent with those presented in Fig. 7.

### 3.3. Photocatalytic activity of the composite coatings

After preparation of the TiO$_2$–NiO composite coatings, their photocatalytic activity was evaluated. Figs. 9 and 10 show the MB degradation under the action of the prepared coatings under irradiation with UV light. For the different
samples, the concentration of MB in the solution decreased at different rates. In other words, all samples showed photocatalytic activity. For the samples prepared by 1-step MCT and subsequent heat oxidation (Fig. 9), the MB solution with Ti–1% Ni–1073 K–10 h degraded to the largest extent. For the samples prepared by 2-step MCT and subsequent heat oxidation (Fig. 10), the MB solution containing the 2SM1–1073 K–10 h sample degraded the most. The MB solution with samples oxidized at 1073 K showed a larger extent of degradation than the samples with the same composition but different oxidation temperatures.

Fig. 11 shows the degradation-rate constants k of MB solution containing different samples. From the figure, it can be seen that the photocatalytic activity first increased and then decreased on increasing the oxidation temperature. The samples with a given composition oxidized at 1073 K showed a higher photocatalytic activity. Among all samples, 2SM1–1073 K–10 h showed the highest photocatalytic activity.

The relationship between composition, microstructure, and photocatalytic activity of the coatings is discussed as follows. The M10–Ti–h K–t h samples have been discussed in our previously published work [9]. The M10–Ti–1073 K–t h samples show the highest photocatalytic activity compared to the other M10–Ti–h K–t h samples for the same oxidation time, in agreement with the result shown in Fig. 11. From the published work [9], it can be concluded that the photocatalytic activity of the M10–Ti–h K–t h samples is determined by the specific area, crystallinity, and crystallite size of rutile TiO2. Since these microstructural parameters of the M10–Ti–1073 K–t h samples reached a proper balance, they showed the highest photocatalytic activity.

It is also found that the samples oxidized at 1073 K for 10 h showed the highest photocatalytic activity in the present work (Fig. 11). There is another reason for this high photocatalytic activity, namely, the formation of TiO2/Ti composite coatings, as shown in Figs. 5, 6 and 8. The enhanced photocatalytic activity can be explained by the increased efficiency in charge separation [18,19]. If TiO2 is in contact with a metal with a higher work function, photogenerated electrons in the conduction band of TiO2 may be transferred to the metal. This process can decrease the recombination rate of electron–hole pairs in TiO2, thereby improving the photocatalytic activity [9].
As described in Section 1, the aim of the present work is to prepare p–n heterojunctions. Another possible reason is the formation of TiO$_2$/NiO composite microstructure, in fact, p–n heterojunction. From Fig. 11, it can be seen that the samples with TiO$_2$/NiO showed a higher photocatalytic activity than M10–Ti–h K–t h samples at oxidation temperatures of 973, 1073, and 1173 K. In this work, it is assumed that a p–n heterojunction may be formed, along with a corresponding inner electric field at the interface of TiO$_2$ and NiO. At equilibrium, the NiO region has a negative charge while the TiO$_2$ region has a positive charge. The 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 field component. As a result, the recombination of photogenerated electron–hole pairs is decreased and, thereby, the photocatalytic activity is enhanced [17].

4. Conclusions

Photocatalytic Ti–TiO$_2$–NiO composite coatings were prepared by the mechanical coating technique (MCT) and subsequent heat oxidation. The Ni particles in the Ti–Ni composite coatings prepared by 1-step and 2-step MCT were located at the inner and the surface layer, respectively. If the oxidation temperature was not higher than 1073 K, a Ti–TiO$_2$–NiO composite microstructure was formed. With the further increase in the oxidation temperature to 1173 and 1273 K, the
Ti coatings were totally oxidized to TiO$_2$ and a TiO$_2$–NiO composite microstructure was obtained. The sample prepared by 2-step MCT and subsequent heat oxidation at 1073 K showed the highest photocatalytic activity above 200 nmol L$^{-1}$ h$^{-1}$. The improvement in the photocatalytic activity could be attributed to the efficiency increase in charge separation, which should result from the formation of the TiO$_2$–Ti composite microstructure and a TiO$_2$–NiO p–n heterojunction.

References