ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 27, No. 4. 2021

Preparation of Copper Oxide/TiO_2 Composite Films by Mechanical Ball Milling and Investigated Photocatalytic Activity

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crossref http://dx.doi.org/10.5755/j02.ms.24735

Received 28 November 2019; accepted 24 February 2020

The Cu/Ti composite coatings were prepared by the mechanical ball milling, the CuO/TiO_2 and Cu_2O/TiO_2 composite photocatalytic films were obtained by the subsequent oxidation process. The microstructure of the composite films was analyzed by X-ray Diffraction (XRD） and scanning electron microscope (SEM). The photocatalytic activity was evaluated, the effects of ball milling time on the formation of the Cu/Ti coatings were investigated, and the effects of the oxidation temperature and oxidation atmosphere on microstructure and photocatalytic activity of the films were studied. The results illustrate that the ball milling time has significant effects on the formation of the coatings and the coatings are continuous and compact by ball milling for 15 h. The photocatalytic activity of the CuO/TiO_2 composite films is increased first and then decreased with the oxidation temperature increases, and the photocatalytic activity is the best at 500 °C. The CuO/TiO_2 composite films are obtained by the oxidation of Cu/Ti coatings at 500 °C for 15 h in the air, while the Cu_2O/TiO_2 composite films are oxidized in carbon atmosphere. Photocatalysis efficiency of the films is obviously enhanced with the help of the p-n junction heterostructure in the Cu_2O/TiO_2 composite films.

Keywords: mechanical ball milling, photocatalytic activity, composite films, oxidation temperature, oxidation atmosphere.

1. INTRODUCTION

Mechanical ball milling is a new type of film-forming method. During the mechanical ball milling process, the film-forming material which is among the grinding balls, and between the grinding balls and the inner wall of the grinding tank is repeatedly collided, rubbed and extruded, resulting in the plastic deformation, cold-welded and deposition on the surface of the grinding ball to form a film or coating [1, 2].

As well known, when the p-type and n-type semiconductor are tightly bonded by a certain way, an inner electric field will be constructed at the bonding interface, and then the photocatalytic characteristic will be improved by the structure [3 – 6]. Lu Yun and others prepared Ti/Ni coatings by the mechanical ball milling and the NiO/TiO_2 composite photocatalytic films were obtained by subsequent oxidation process. They found that the photocatalytic performance was improved significantly by the P-N junction heterostructure, which was formed inside the films [7]. Meng Long and others successfully prepared Cu_2O and TiO_2 junction heterostructure nanotubes by square wave voltammetry electrochemical deposition method. They found that the photocatalytic performance was enhanced effectively by the structure [8]. But the preparation of copper oxide/TiO_2 composite films by mechanical ball milling and the investigation of photocatalytic activity, they did not discuss deeply.

In this paper, the Cu/Ti composite coatings were prepared on the surface of ZrO_2 balls by the mechanical ball milling, the CuO/TiO_2 and Cu_2O/TiO_2 composite photocatalytic films were obtained by the subsequent oxidation process. The effects of ball milling time on the formation of Cu/Ti coatings were investigated. The effects of oxidation temperature and oxidation atmosphere on the microstructure and photocatalytic properties of the composite films were researched.

2. EXPERIMENTAL DETAILS

The powders, Ti powders (with the 99.5 % purity and an average diameter of 38 μm) and Cu powders (with the 99.5 % purity and average diameter of 75 μm) were poured into a grinding plot, which the weight ratio was maintained at 3:1. ZrO_2 balls with an average diameter of 1mm were used as substrates, and the ball-to-powder weight ratio was maintained at 2.5:1. A planetary ball mill was used to perform the mechanical coating operation, and carried out with a rotation speed of 300 rpm for 5 h, 10 h, 15 h, 20 h and 25 h to obtain the different Cu/Ti coatings. The Cu/Ti coatings were oxidized in the air at 400 °C, 450 °C, 500 °C, 550 °C and 600 °C for 15 h to prepared CuO/TiO_2 composite films. In addition, the Cu/Ti coatings which were buried in graphite powder and then placed in the air were oxidized at 500 °C for 15 h to prepare Cu_2O/TiO_2 composite films.

Each group of samples with 10 mg was poured into the 20 mL methyl orange solution (with the concentration of 10 mg/L), and then under the ultraviolet irradiation for 24 h. The spectrophotometer was used to measure the rate

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of concentration change of the methyl orange solution, the measured wavelength was set as 464 nm, which is near the peak of absorption spectrum of the methyl orange solution. To ensure identical initial condition, the samples were pre-adsorbed by the methyl orange solution in the dark for 12 h. And a control group was provided to eliminate the experimental error caused by the spontaneous decomposition of methyl orange solution under the ultraviolet irradiation.

The surface characteristics of the films were studied by the optical microscope. The phase composition was analyzed by XRD (DMAX2500) with Cu-Kα radiation. The microstructures of the surface and cross-section of the films were observed by the SEM (S-3400, secondary electron mode).

3. RESULTS AND DISCUSSION

3.1. Effects of the ball milling time on the formation of Cu/Ti coatings

Fig. 1 shows the appearance of the Cu/Ti coatings which are prepared at different ball milling time. The surface of the substrate is covered by the discontinuous coatings when the ball milling time is shorter (Fig. 1 a, b). The continuous and smooth Cu/Ti coatings are formed by ball milling for 15 h at Fig. 1 c. The Cu/Ti coatings become discontinuous again and have sharp corners with the ball milling time increases (Fig. 1 d, e). So the Cu/Ti coatings are continuous and smooth when the ball milling time is 15 h.

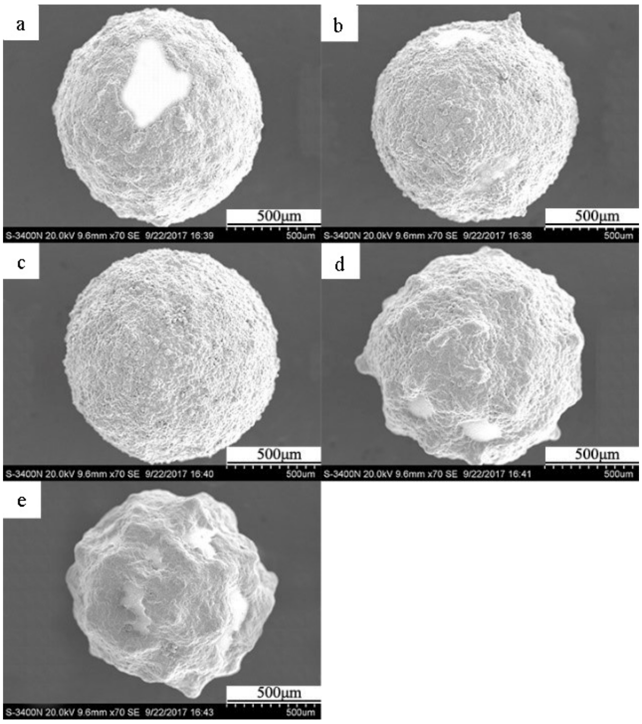

Fig. 1. SEM micrographs of the samples with different milling time: a – 5 h; b – 10 h; c – 15 h; d – 20 h; e – 25 h

Fig. 2 shows the microscopic morphology of the Cu/Ti samples surface at different ball milling time. The particles on the surface of substrate are flat and small when the ball milling time is shorter (Fig. 2 a). The particles on the surface of the coatings become round and the size gradually increases with the ball milling time increases (Fig. 2 b – d). Eventually, the particles of the coatings are separated from each other (Fig. 2 e). The coatings are the densest only when ball milling for 15 h was applied.

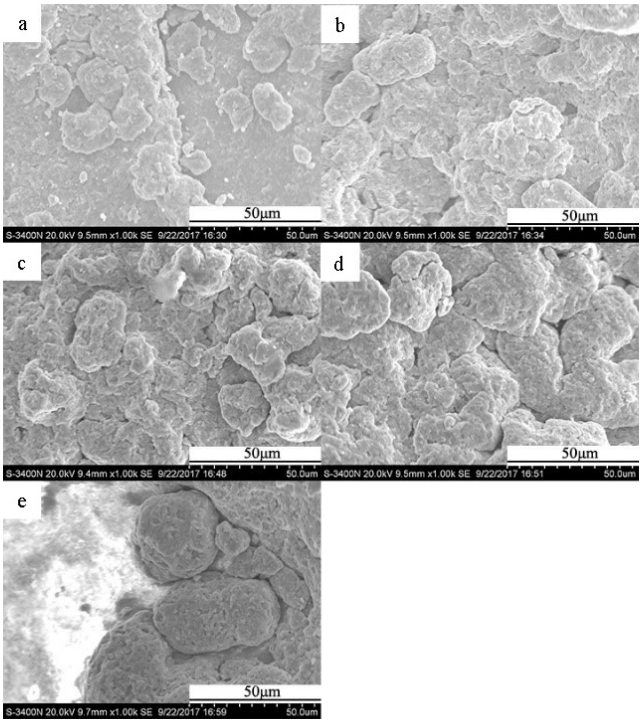

Fig. 2. SEM micrographs of the coatings with different milling time: a – 5 h; b – 10 h; c – 15 h; d – 20 h; e – 25 h

In the initial stage of mechanical ball milling, the metal particles have an excellent plasticity. When the metal particles which are among the grinding balls, between the grinding balls and the grinding tank wall are continuously pressed and collided, they are pressed into the pits on the surface of the substrate, and then they are captured by the grinding balls. Thereafter, the free metal particles in the grinding tank are cold-welded with the metal particles in the pits on the surface of the substrate under the impact of the grinding balls. As the metal particles are deposited gradually, the metal particles on the surface of the substrate are bonded with each other to form the partially continuous coatings (Fig. 1 a, b). Fig. 2 a and b shows that the particles on the surface of the coatings become flat after being subjected to strong extrusion deformation, because at this time, the coatings are thin and the absorbed energy by a single collision per unit volume is large. Thus, the coatings show partially continuous and the whole display discontinuous.

The metal particles deposited on the surface of the substrate are increased and the localized coatings are bonded together to form continuous coatings with the ball milling time is prolonged to 15 h, as shown in Fig. 1 c. Meanwhile, the metal particles are cold-welded to each other to form large size particles and then they deposited on the surface of the coatings. At this time, the coatings are thicker and the absorption kinetic energy per unit volume is lower, so the surface of the coatings has a low degree of deformation and the particles are rounded and coarse shape, as shown in Fig. 2 c.

With the mechanical ball milling continues, the metal coatings are work-hardened under the repeated impact force and they become brittle gradually. In addition, the coatings are thickened gradually and accumulated internal stress, and the coatings will peel off when the stress is more than the coated force of the coatings on the substrate, as shown in Fig. 1 d, e. Under the strongly plastic deformation, the internal dislocation density of the metal particles on the surface of the coatings is gradually increased, and the metal particles become hard and brittle. Meanwhile the effect of cold-weld among the particles is gradually decreased, and the metal particles separate from each other under the impact of the grinding balls, as shown in Fig. 2 d, e.

3.2. Effects of sintering temperature on microstructure and photocatalytic performance of the composite films

Fig. 3 shows the cross-section morphology of the as-oxidized Cu/Ti samples, which are oxidized at 400 °C, 450 °C, 500 °C, 550 °C and 600 °C for 15 h in the air after ball milling for 15 h. There exist red blocks in the bright white section shown by the rectangular box. A gray phase is formed around the red phase and then is thickened gradually with the oxidation temperature increases. Fig. 3 e shows that the outermost layer of the films is covered with a layer of gray material, which is about 5 μm when the oxidation temperature is 600 °C.

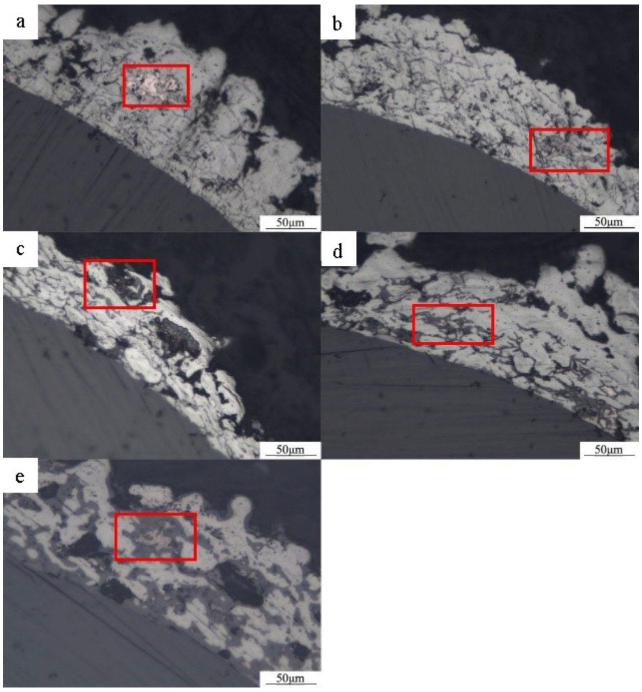

Fig. 3. Optical micrographs of the cross-section of the as-oxidized samples with the temperature of: a – 400 °C; b – 450 °C; c – 500 °C; d – 550 °C; e – 600 °C

It is known that whether it was easy or not to apply the abrasive to the surface of the grinding ball depends on the electronegativity of the material in the initial stage of mechanical coating, the lower the electronegativity of the material is, the easier the film formation is [9]. Although the Cu metal has good plasticity, strong cold-welded ability, it is difficult to bond with the substrate because of the high electronegativity. Therefore, during the mechanical ball milling process, the Cu particles are wrapped by the large-sized Ti particles and then they are cold-welded to the surface of the substrate to form a red sheet, as shown in Fig. 3. The oxygen in the air enters the interior of the coatings through the gap of the composite coatings and cause the metal around the gap to be oxidized during the oxidation process. The oxidation of the coating is gradually intensified as the oxidation temperature increases [10].

Fig. 4 shows the XRD pattern of the as-oxidized sample, which is obtained in the air at 500 °C. The Ti and rutile TiO_2 diffraction peaks with high intensity, the CuO diffraction peaks with the lower intensity appear and the ZrO_2 diffraction peaks was not detected. It means that the CuO/TiO_2 composite films are successfully prepared and the composite films are continuous and compact. The rutile phase TiO_2 was detected in the films, while the anatase phase TiO_2 was not detected, it indicates that the outer Ti film was converted into a thermodynamically stable phase after oxidation and sintering at 500 °C. A small amount of CuO phase appeared in the spectrum, while the Cu_2O and Cu phases done not, which indicates that the outer Cu particles were all oxidized to CuO.

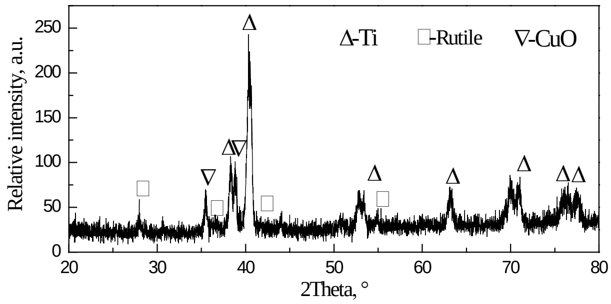

Fig. 4. XRD pattern of the composite films oxidized in the air at 500 °C

Fig. 5 shows that the degradation rate of methyl orange solution by the samples, which were prepared at different temperatures.

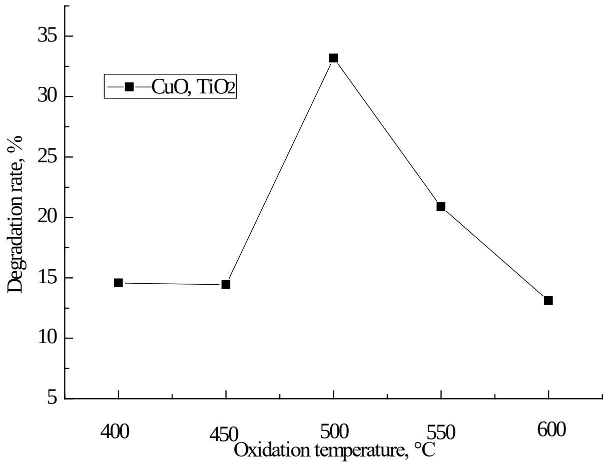

Fig. 5. Dependence of the oxidation temperature on the degradation rate of methyl orange solutions

The degradation rate of methyl orange solution increases first and then decreases with the oxidation temperature increases. The degradation rate of methyl orange solution reaches a peak of 33 %, of which the oxidation temperature is 500 °C. The research has shown that the composite structure of Ti and TiO_2 can enhance the photocatalytic activity of the composite films [7]. The oxidation of Ti coating is intensified, which caused the content of Ti in the film gradually decreases and TiO_2 gradually increases with the oxidation temperature increases. The ratio of Ti and TiO_2 makes the composite films have the best photocatalytic activity when the oxidation temperature is 500 °C.

3.3. Effects of sintering environment on the microstructure and photocatalytic performance of the composite films

Fig. 6 shows the XRD pattern of the as-oxidized sample, which is oxidized in carbon atmosphere at 500 °C. The Ti and rutile TiO_2 diffraction peaks with high intensity and the Cu_2O diffraction peaks as the lower intensity appears, it indicates that the Cu_2O/TiO_2 composite films are successfully prepared. It is known that the oxide-sintered of Ti coating in the carbon powder environment can effectively reduce the oxygen concentration on the coating surface [11]. It can be inferred that the Cu particles on the surface of the coatings are not sufficiently oxidized due to the scarcity of oxygen molecules, thereby generated Cu_2O during the oxidation of the samples in carbon atmosphere.

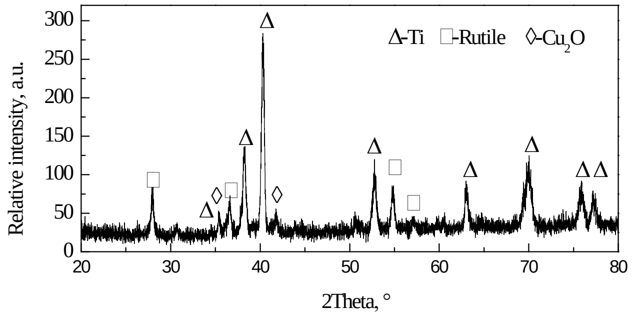

Fig. 6. XRD pattern of the composite films oxidized in carbon atmosphere at 500 °C

Fig. 7 illustrates the dependence of the 24 hour's degradation rates of methyl orange solution on the Cu/Ti coatings samples which were oxidized at 500 °C for 15 h in the air and carbon atmosphere.

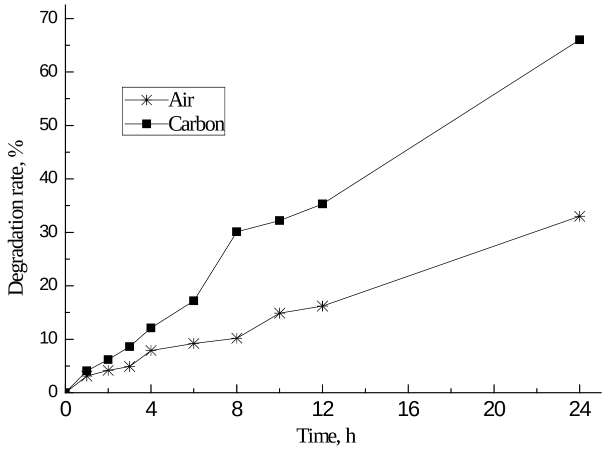

Fig. 7. Dependence of the 24 hour's degradation rates of methyl orange solution on the samples are oxidized in the air and carbon atmosphere

It is shown that the degradation rate of the methyl orange solution by the sample, which was prepared in carbon atmosphere, is higher than in the air within 0 to 24 h, and it finally reaches a peak of 66.01 %. From the foregoing analysis, it is known that the surface of the sample, which is oxidized in carbon atmosphere, has the Cu_2O/TiO_2 composite structure. It is known that Ti and Cu are tightly bonded by cold-welding during the mechanical ball milling process. After the subsequent oxidation process, the grains at the interface between Cu_2O and TiO_2 in the composite film are tightly bonded to form a p-n junction heterostructure, which constructs a built-in electric field effectively. The electron and hole pairs, which are generated by the excitation, are effectively separated under the action of the electric field, and then the ultraviolet photocatalytic efficiency of the composite films is remarkably improved. The research results are consistent with other works [5, 7].

4. CONCLUSIONS

1. The ball milling time has significant effects on the formation of the coating. It is formed as a continuous coating with the ball milling time increase. However, the long-term ball milling time causes the internal dislocation density and internal stress of the coating to increase, therefore, the coating falls off and forms sharp corners. The coating is continuous and dense only when the ball milling time is 15 h.
2. The photocatalytic activity of the CuO/TiO_2 composite films is increased first and then decreased with the oxidation temperature increase, and the sample has the best photocatalytic activity at 500 °C.
3. The phase composition of the coatings is affected by the different oxidation atmosphere. The CuO/TiO_2 composite films are obtained by the oxidation of Cu/Ti coatings at 500 °C for 15 h in the air, while the Cu_2O/TiO_2 composite films are oxidized in carbon atmosphere.
4. The photocatalytic activity of the sample which is oxidized in carbon atmosphere is better than in the air with the help of the p-n junction heterostructure in the Cu_2O/TiO_2 composite films.

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