Preparation of Nanophase Titania Film by Plasma Spraying

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Nanophase titania film was obtained by plasma spraying. The structure of titania film was investigated with transmission electron microscopy (TEM). It was found that the film was composed of grains with mean particle size of 15nm. The crystal structure of nanophase titania film was found to be anatase phase by electron diffraction.

INTRODUCTION

Nanostructured materials have been synthesized and characterized widely by scientists over the world during recent years. A series of methods to synthesize nanostructured materials have been undertaken, such as sol-gel process (1), gas-condensation process (2), DC reactive magnetron sputtering (3), RF magnetron sputtering (4), electrochemical deposition (5) et al.

Titania has been extensively used in fields of photo-catalysis (6), photo-electrical conversion et al(7). Nanophase titania with improved properties has more implications in these fields. In the present work, porous nanophase titania film has been prepared by plasma spraying. Plasma spraying may be a useful method to prepare nanophase film.

EXPERIMENTAL PROCEDURE

Materials. The spraying powders are synthesized through controlled hydrolysis of titanium butoxide in a mixture solution containing both ethanol and water. The powders are obtained through direct precipitation followed with ethanol rinsing, and drying at 60~70°C under the pressure of 3×10^4 Pa for 2 hours. The particle size of the powders is determined with the transmission electron microscopy(TEM).

Processing. The atmosphere plasma spraying process has been used to deposit titania film. Cu net and Cu plate are used as substrates in order to determine the structure of titania film by the transmission electron microscopy. The plasma spraying equipment used in the process is made by Sulzer Metco AG Switzerland.

RESULTS AND DISCUSSION

The transmission electron micrograph of the spraying powders is presented in Fig. 1. The size of aggregates of titanium oxide is distributed in the range of 50~100 nm in diameter. The shape of aggregates is global or ellipsoidal, which is good to feed powders during the process of plasma spraying. The selected area electron diffraction (SAED) pattern is shown in Fig. 2. It can be observed that the powders are in amorphous phase from the SAED pattern. Fig. 3 is the high resolution TEM micrograph of nanophase titania film prepared by plasma spraying. The mean particle size of grains of which the film is composed is about

15 nm. Amorphous phase that distributes among crystalline phase can also be found from the high resolution TEM micrograph in Fig.3. The crystal structure of the nanophase grains is determined by the SAED pattern exhibited in Fig. 4. The interplanar distance calculated from the SAED pattern in fig.4 is presented in table I. Comparing the result of the interplanar distance of this work with that in reference(8), it can be concluded that the crystal structure of the nanophase grains

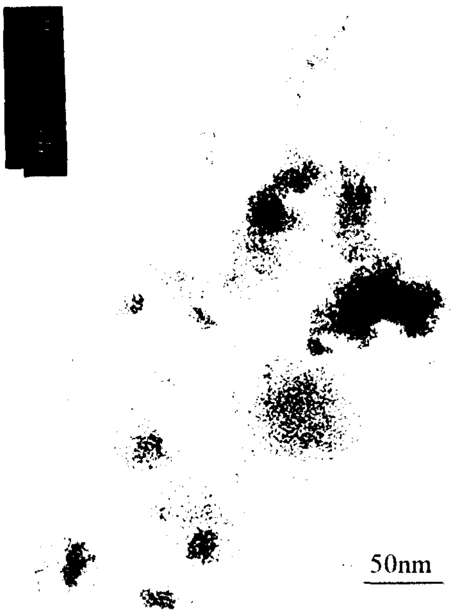

Fig. 1 The TEM micrograph of the titanium oxide powders.

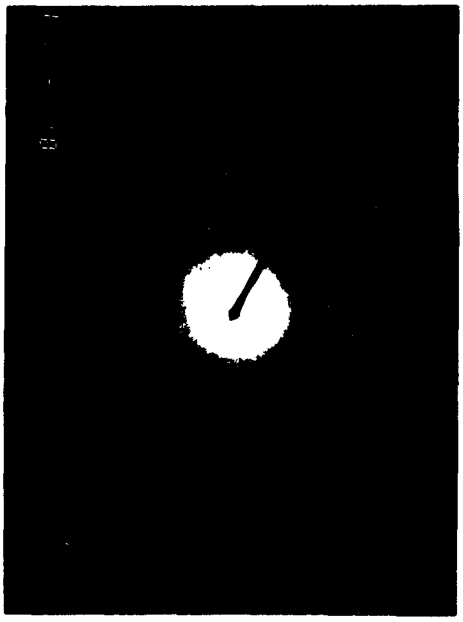

Fig. 2 The SAED pattern of the titanium oxide powders.

Fig. 3 The high resolution TEM micrograph of titania film.

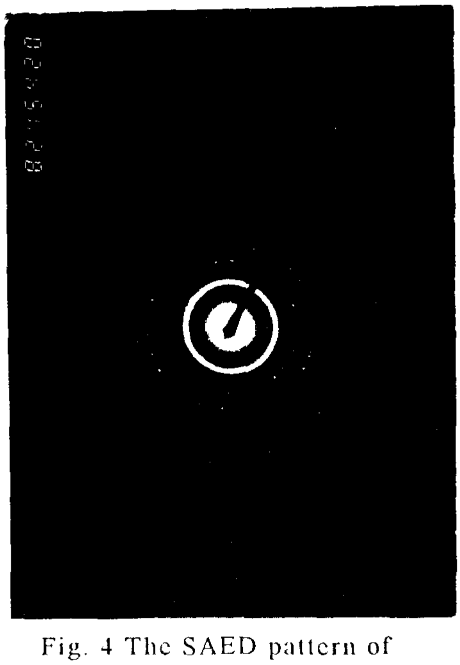

Fig. 4 The SAED pattern of titania film.

in the titania film is in anatase phase state. From fig.4, it can be found that the second, the forth and the sixth diffraction rings are broader than other rings, because these rings are composed of two or three diffraction rings which are located closely. According to the results discussed above, it can be deduced that crystalline cores have been formed and the crystalline grains have grown up during the process of plasma spraying, even though the time when powders are in the plasma flame is very short.

Table I. The interplanar distance of nanophase titania film. The interplanar distance in Å

d_{hkl} (this work)	3.50	2.376	1.894	1.690		1.482	1.350	
d_{hkl} (in ref. 8)	3.52	2.378	1.892	1.6999	1.6665	1.4808	1.3641	1.3378
hkl	101	004	200	105	211	204	116	220

Surface morphology of the film is analyzed by scanning electron microscopy (SEM). The surface morphology of the film is of many features as shown in Fig. 5. The rough surface of the film is composed of small holes and fine particles with a diameter of about 15nm as determined in Fig. 3. However, no microcracks were found in the micrograph of the film. The film of this structure has great specific area and high reactive activity and can be used as electrode in electrochemical cell and can be used as catalyst. Some interesting electrochemical characteristics have been found from the film, and will be reported elsewhere.

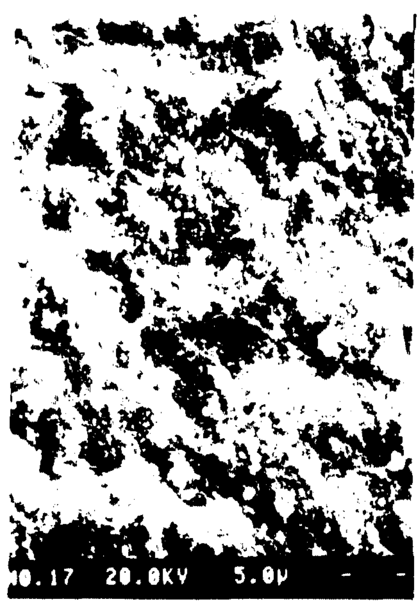

Fig. 5 SEM of the plasma-sprayed titania film

The factors to influence the character of the sprayed film are various. The characters of the spraying powders play an important role in the structure of the sprayed film. The powders used in the spraying process is quite different from the powders ordinarily used in plasma spraying. The powders used in this work has not been calcinated and contain more than 25% weight of ethanol coordinated on the surface of the particle determined by infrared spectroscopy and thermogravimetric analysis. During spraying process, the powders and ethanol coordinated on the particles decompose and evaporate. The decomposition and evaporation of ethanol and the powders could influence the heat transfer between the plasma and the powders. Another characteristic of the powders is its low density, which makes it difficult to inject the powders into the hottest region of the plasma jet. Moreover, the particle size of powders used in this work is smaller than that of ordinary ones by about two orders of magnitude, the Knudsen number (Kn) for the powders should be about 100 where,

$$Kn = \lambda / dp,$$

λ represents for the mean free path of the plasma, and dp represents for the diameter of the particles. In this situation, the mode of heat transfer between the particles and the plasma should be the free molecule flow regime according to Chen (9), and the heat flux of this regime quite different from that of continuum regime. The plasma spraying mechanism of this regime is very complicated, components of atoms, ions, electrons play roles in the total heat flux, and more work should be done to clarify this process of spraying.

CONCLUSION

As a result of this work, nanophase titania film has been produced through plasma spraying with amorphous titanium oxide agglomerates. The mean size of nanophase grains is about 15 nm, and the crystal structure of nanophase grains is anatase phase combined with a little amorphous phase. The film is composed of small holes and fine particles and no microcracks were found in the micrograph of the film. The film of this structure has great specific area. Plasma spraying may be one of the methods to prepare nanophase films.

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