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Preparation and Characterization of Nano-modification TiB_2 Ceramic Particle and Its Reinforced Epoxy Composite coating

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Abstract: Using tetrabutyl titanate as the raw materials, the surface of TiB_2 powders was coated with TiO_2 nanoparticles prepared by the peptization and reflux method at low temperature. The surface morphology, the phase composition of coating layers and specific surface area of composite particles were characterized by SEM, XRD and BET, respectively. The results show that the TiO_2 nanoparticles are coated on the surface of powders uniformly and discretely and the main phase of coating layers is anatase. The surface of TiB_2 powders is rougher after nano-modification and the value of specific surface area of the composite particles is elevated by over 35 times compared with that before coating. Wear-resistant composite coatings are prepared by adding coated TiB_2 powders to epoxy resins. The abrasive loss of composite coatings decreases to 50% of the coatings filled with uncoated TiB_2 powders. Finally, the wear properties, worn surface morphologies and antiwear mechanisms of wear-resistance coatings were analyzed.

Key words: nano-modification; composite particles; composite coatings; wear-resistance

Fiber-reinforced composites are being increasingly used in modern industry because they have high specific strength and modulus, outstanding fatigue properties and fracture toughness, low friction coefficient and good thermal, corrosion and electrical resistance properties[1]. This combination of properties, especially their high strength/stiffness to weight ratio, makes them very attractive for transport applications[2]. Hence, there is a tremendous advantage in minimizing equipment weight and because of their low sliding friction coefficient, they are widely used to manufacture sliding parts, such as chutes in mining, chemical and agricultural equipments[3]. Particularly, they are commonly used as antifriction coatings.

However, in general, fiber-reinforced composites have poor abrasive wear resistance, which restrict their applications[4]. Therefore, more and more attention has been paid to abrasive wear property. In order to overcome the disadvantages of poor wear resistance, many researchers have tried to improve this property by introducing various inorganic particle reinforcing agents and fillers. When fiber-reinforced composites are reinforced by particulate reinforcement, the abrasive wear resistance can be greatly improved[5-10]. Meanwhile, TiB_2 powders have become promising fillers owing to high hardness, low density, high corrosion resistance and good thermal shock resistance[11].

In this work, TiB_2/TiO_2 composite particles in acidic abundant aqueous solution were prepared by the peptization and reflux method at low temperature (80 ℃) using tetrabutyl titanate as the raw materials[12]. TiO_2 nanoparticles were deposited on the surfaces of TiB_2 powders pretreated with phytic acid (PA) solution of various concentrations forming composite particles with core/shell structure which was helpful for increasing the specific surface areas of fillers and the wear-resistance properties of composite coating[13]. The as-prepared samples were characterized by SEM, XRD, Raman and BET. The effects of PA concentration on the micro-morphologies and microstructures of the TiB_2/TiO_2 composite particles were studied. The wear-resistance properties of polymer matrix coatings filled with TiB_2/TiO_2 composite particles were also investigated. The worn surface morphologies of the specimen were analyzed by scanning electron microscopy (SEM). Our results provided a new method to design the wear-resistant coatings by filling in the as-prepared composite particles.

1 Experiment

TiB_2 powders were produced by combustion system in

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ultra-high gravity field[13]. Initially, the TiB_2 powders were washed with acetone and dried in an electric vacuum drying chamber. Then TiB_2 powders were dipped in 0.6 mol/L H_2SO_4 solution for 15 min to remove the oxide layers, and rinsed with distilled water and ethanol for 5 times separately, and finally dried in vacuum at 60 ℃. $Ti(OBu)_4$ (chemical grade) was used as raw materials for the synthesis of TiO_2 nanoparticles. In a typical process, 10 mL $Ti(OBu)_4$ was mixed with 100 mL absolute ethanol (analytical grade) and 2 mL acetyleactone (ACAC, analytical grade). Then 24 mL H_2O was added to the solution with a strong stirring to form a white precipitate. A limpid yellow ethanol-based TiO_2 sol was formed by dropwise addition of hydrochloric acid into the precipitate. TiB_2 powders (20 g) along with 50 mL absolute ethanol were poured into a three-necked flask with a stirring device. Thereafter, the prepared TiO_2 sol was added into the flask, and the mixture was heated and refluxed with stirring at a constant rate for 40 min. Finally, TiB_2 powders were filtered, washed with distilled water and ethanol, and dried in drying chamber to obtain the resulting composites of TiO_2 nanoparticles and TiB_2 powders. Blank experiments were carried out in similar procedures but only TiO_2 sol was heated and refluxed without any TiB_2 powders. The resulting TiO_2 powders were also washed with distilled water and anhydrous ethanol.

The morphology and microstructure were analyzed by scanning electron microscopy (SEM, EM-30 Plus, Coxem, Korea). The phase composition was identified by X-ray diffraction (XRD, TD-3700X, Tongda, China) and Raman spectroscopy (M4000, Yingan, China), and the specific surface area was determined by Brunauer-Emmett-Teller (BET, 3H-2000A, Beishide, China). Wear-resistance testing was carried out on an abrasion machine (MVF-2A, Hengxu, China) under the Chinese national standards of GB 1768-79.

2 Results and Discussion

2.1 SEM analysis

Fig.1a shows the SEM image of uncoated TiB_2 powders. As can be seen, the uncoated TiB_2 powders are fragmented powders with an irregular shape and a large size range from several micrometers to approximate 120 μm. The surface of the uncoated TiB_2 powders is smooth, as shown in Fig.1a. Fig.1b of the nano-modified TiB_2 powders shows that the TiB_2 powders are compactly coated with about 10 nm TiO_2 particles, forming a core-shell structure. It is clear that the TiB_2 particles are coated with approximately spherical powders of 10 nm in diameter.

2.2 XRD and Raman analysis

In order to confirm the crystal of TiO_2 on the surface of composites, blank experiments without TiB_2 powders were carried out. The crystalline phase of TiO_2 is mainly determined by the conditions of sol-gel synthesis, such as the Ti/H_2O molar ratio, pH value, and refluxing time. Similarly, under the sol-gel synthesis conditions, it is reasonable to speculate that the TiO_2 particles prepared in the blank experiment have the same crystalline phase as those on the surface of TiB_2 powders. Fig.2 shows the XRD pattern of the TiO_2 particles obtained from the experiment. As shown in Fig.2, the TiO_2 particles possess distinct diffraction peaks with characteristic of anatase (major peaks at 2θ=25°, 37°, 48°, 54° and 61°), indicating that the TiO_2 particles are predominantly of anatase crystal phase. The relatively wide XRD peaks indicate that the anatase phase has very fine titania grains. The very low and wide signal from 20° to 30° indicates that the size of titania is no more than 10 nm. Relatively high background intensities observed at low 2θ values in the XRD analysis show the presence of anamorphous phase of TiO_2.

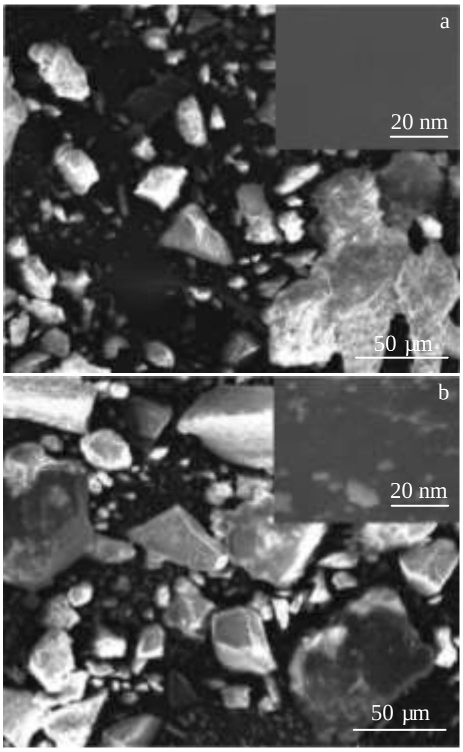

Fig.1 SEM images of TiB_2 powders: (a) uncoated with TiO_2 and (b) coated with TiO_2

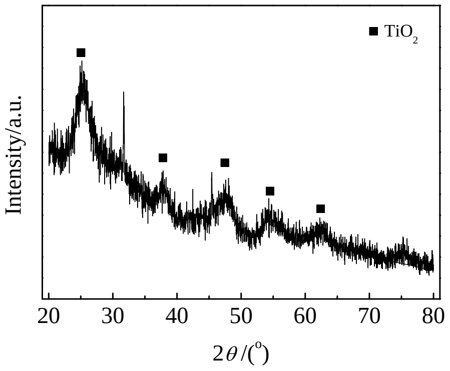

Fig.2 XRD pattern of the nano-TiO_2

Raman spectroscopy, which is known to be more sensitive to short-range-order than XRD was used to characterize the microstructure of the TiO_2 particles, and the result is shown in Fig.3. The typical peaks appearing at 154, 405, 514 and 638 cm^{-1} stand for Raman oscillating mode E_g (154, 638 cm^{-1}), B_{1g} (405 cm^{-1}) and A_{1g} (514 cm^{-1}) of anatase, respectively. The results show that the microstructure of TiO_2 nanoparticles are mainly anatase. The broadened Raman peaks may be recognized as very small TiO_2 particle sizes. The results are in agreement with the XRD analysis and SEM observation of the blank sample. It is reasonable to assume that the structure of TiO_2 mainly depends on the composition of the sol. The nano-TiO_2 particles coated on the surface of TiB_2 powders can be regarded as anatase.

2.3 Specific surface area analysis

The specific surface area of the as-prepared composite coating samples was determined by BET method. The results show that the specific surface areas of TiB_2 and TiB_2/TiO_2 are 0.2438 m^2/g and 8.5125 m^2/g, respectively. The specific surface areas of TiB_2/TiO_2 is 35 times higher than that of the uncoated TiB_2 powders. The network structure on the surface of TiO_2 particles is helpful to improve the specific surface area of composite particles. Some literatures have explained that large surface areas can increase the contact area between composite powders and epoxy resin matrix, thus enhancing the adhesion between them. Therefore, it is difficult to strip the powder from the composite coating. The results show that the wear resistance of the composite coating is improved when the coated TiB_2 powder is filled in the epoxy resin matrix.

2.4 Wear-resistance properties analysis

The abrasion resistance was evaluated by mass loss obtained by wear test of composite coating. Lower mass loss means better wear resistance. The values of abrasive loss and average wear width of coatings filled with TiB_2 and TiB_2/TiO_2 are shown in Table 1. Composite coatings consisting of composite particles and epoxy resin possess lower mass loss, which means that the coating abrasion resistance is improved. The main reason is that composite particles have a better interfacial action with the epoxy resin matrix. As a result, litter wreckages is peeled off from the composite coatings when suffered to friction. At the same time, the nano-TiO_2 particles coated on the surface of TiB_2 powder can be used as an effective antifriction material. Therefore, the synergistic effects of nano-TiO_2 particles and rough surface TiB_2 powders improve the wear resistance of composite coatings. In other words, the high abrasive masslessness is the result of the interaction of the TiO_2 sphere effect and the surface roughness.

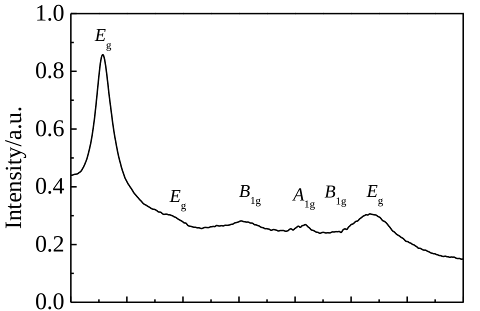

Fig.3 Raman spectrum of nano-TiO_2

Table 1 Wear-resistance properties of coatings filled with TiB_2 and TiB_2/TiO_2

Samples	Abrasive loss/mg	Average wear width/mm
Coatings filled with TiB_2	18.1	1.21
Coatings filled with TiB_2/TiO_2	9.2	2.38

The worn surface morphologies of the composite coatings were observed by scanning electron microscopy, and typical wear morphologies are characterized, as shown in Fig.4. In Fig.4, there are a large number of deep and wide furrows at no TiB_2 particle area. However, the furrows are not only shallow and narrow but also discontinuous at TiB_2 particles existing area and TiB_2 particles protrude from the worn surface. This fact indicates that TiB_2 particles can prevent the grinding of the abrasive and facilitate the wear resistance of the composite coating.

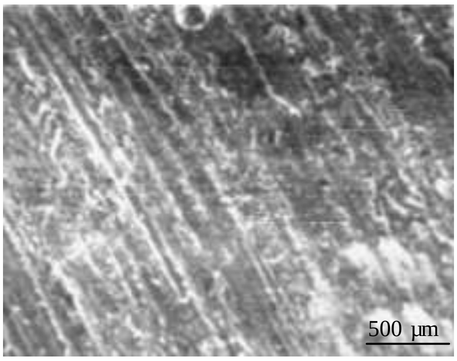

Fig.4 Typical worn morphology of the composite coating

3 Conclusions

1) Using tetrabutyl titanate as the main raw materials, the TiB_2/TiO_2 composite particles can be prepared at low temperature in acidic abundant aqueous solution.

2) TiB_2 powders are coated by TiO_2 of about 10 nm in size. The as-prepared titania mainly contain fine anatase nanocrystals. The specific surface area of coated TiB_2 powders is 35 times greater than that of the uncoated TiB_2 powders.

3) Compared to the uncoated TiB_2 powders as fillers, the abrasive loss of composite coatings with the coated TiB_2 powders decreases by 50% when the composite particles are filled in wear-resistant coatings based on epoxy resins.

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TiB_2陶瓷粉末纳米化改性及其增强环氧复合涂层的制备与表征

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摘　要：低温条件下，以钛酸丁酯为原料，采用胶溶-回流方法在 TiB_2粉体表面包覆纳米 TiO_2颗粒。通过 SEM、XRD、BET 等分析检测方法对复合颗粒的表观形貌、包覆层相成分、比表面积等进行表征。结果显示，纳米 TiO_2颗粒均匀离散地包覆在 TiB_2粉体表面，包覆层主要为锐钛矿型相，TiB_2粉体纳米化改性后复合颗粒的表面粗糙度显著增加，比表面积较包覆前提高 35 倍以上。将包覆后的 TiB_2粉体引入环氧树脂制备耐磨复合涂层，测得其磨损失重仅为包覆前复合耐磨涂层的 50%，其耐磨性显著提高，并初步分析了复合耐磨涂层的摩擦磨损性能、磨损形貌及耐磨机理。

关键词：纳米化改性；复合颗粒；复合涂层；耐摩擦磨损

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