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Ti-based nanocoatings on Al_2O_3 powders

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Abstract

Ti-based nanocoatings on ceramic powders were successfully fabricated by heterogeneous precipitation method. Commercial Al_2O_3 (average particle size of 0.5 μm), titanium tetrabutoxide ($Ti(C_4H_9O)_4$) and urea ($CO(NH_2)_2$) have been used as starting materials. Selecting appropriate precipitation conditions, both the thickness and the uniformity of Ti-based nanocoatings were adjusted. With a molar ratio $TiO_2/Al_2O_3 = 0.05$ and the use of urea in excess, a homogeneous nanocoating of ~20 nm on the alumina powder surface was attained. FTIR spectra indicated the formation of the TiO_2-based nanocoating onto Al_2O_3 particles and TEM examinations showed that the amorphous coating layer crystallized to <10 nm TiO_2 particles upon calcination at 500 °C.

Keywords: Heterogeneous precipitation; Nanocoatings

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1. Introduction

In recent years, coating processes with nanoparticles have been investigated for the development of nanostructured materials [1]. Inorganic coated polymer (core-shell) capsules and hollow spheres have attracted increasing interest because of their applications in catalysis, low dielectric constant materials, acoustic insulation, and photonic crystal [2,3]. Coated powders as a technology shows impacts on a great variety of products [4,5]. In the ceramic field, the particle-coating technology was initially related to surface modification that improves the sintering behaviour and results in phase uniformity and improved performance properties.

Meanwhile the processing of monodispersed nanopowders has been successfully adopted; however, the methods to obtain nanocoatings are not well developed up to now. Several methods have been introduced to prepare the coated powders, such as coprecipitation [6], heterogeneous precipitation [4], sol–gel [7], homogeneous precipitation [8], hydrothermal synthesis [9], inverse microemulsion [10], emulsion evaporation [11] and spray drying [12].

Titania nanopowders have a wide spectrum of applications. Typically, titania nanoparticles are used as pigments, raw material in electronic and structural ceramics, sensors, membranes [13,14], and catalyst supports [15]. TiO_2 powders and nanopowders are usually prepared by wet precipitation from $TiO(SO_4)$, $Ti(SO_4)_2$ or $TiCl_4$. However, the counter anions of the starting titanium salts may remain in the final product and thus deteriorate the powder purity [16]. To avoid counter anion contamination, titanium alkoxides as $Ti(C_3H_7O)_4$ or $Ti(C_4H_9O)_4$ can be used as starting materials [17].

In the present study, Ti-based nanocoatings on alumina powders were produced by heterogeneous precipitation, which is the most promising method due both to the relative low cost of the reactants and to an easily controlled processing.

2. Experimental procedure

Titania-nanocoated alumina powders were fabricated by heterogeneous precipitation method using the following precursors: commercial Al_2O_3 (SASOL) with an average particle size of 0.5 μm, titanium tetrabutoxide $Ti(C_4H_9O)_4$ (Aldrich Chemical, USA) and urea $(NH_2)_2CO$ (Aldrich, 98%). In the first step, the $Ti(C_4H_9O)_4$ was dissolved in HNO_3 6 M (pH 0.5). This solution was added drop wise to a previously prepared alumina suspension in an aqueous medium containing urea in excess. The final molar ratio achieved was $TiO_2/Al_2O_3 = 0.05$. The suspension was buffered to pH 8, by using NH_4OH 12 M. The solutions hence prepared were stirred continuously with a magnetic stirrer at 80 °C for 48 h. The

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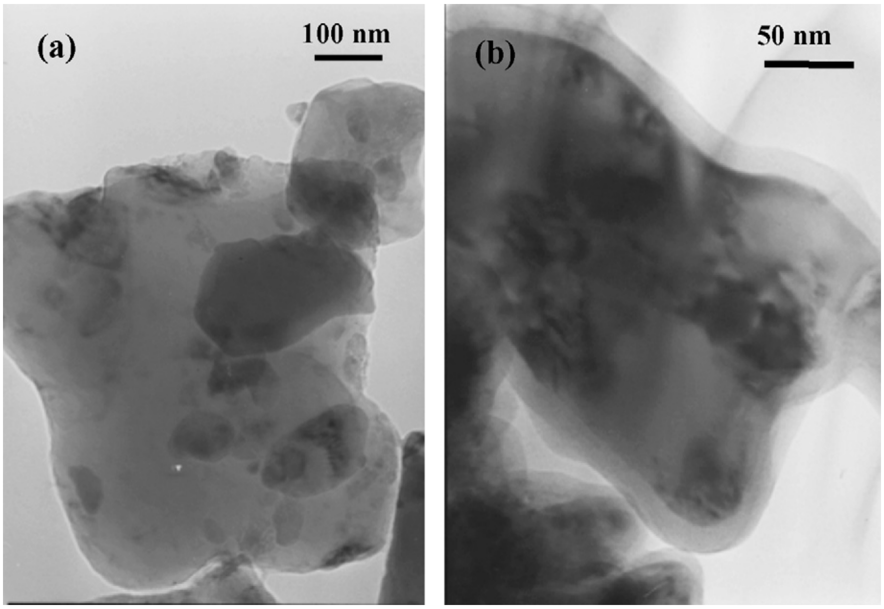

Fig. 1. TEM images of (a) Al_2O_3 particles as received and (b) nanocoated (as-precipitated) Al_2O_3 particles.

water level was kept constant. The reactions occurred are shown in the following equations:

$$(NH_2)_2CO + 2H_2O + H^+ \rightarrow 2NH_4{}^+ + HCO_3{}^- \qquad (1)$$

$$TiO^{2+} + 2HCO_3{}^- \rightarrow TiO_2{\cdot}H_2O(\downarrow) + CO_2(\uparrow) \qquad (2)$$

The resulting powders were filtered and washed with distilled water and acetone until no $NO_3{}^-$ was present. The washed precipitates were dried at 60 °C in an oven. To analyze the coating morphology transmission electron microscopy (TEM) was used. The structural development of the coating was studied by Fourier transform infrared spectroscopy (FTIR). Differential thermal analysis and thermogravimetry (DTA–TG) were used to trace off the thermal behaviour of the resulting powder. In DTA–TG essays, the sample was heated under flowing air up to 1000 °C using a ramp rate of 2 °C/min.

3. Results and discussion

The heterogeneous precipitation method involves the hydrolysis and interaction of the soluble Ti precursor with the surface of the Al_2O_3 particles. If the precursor is allowed to hydrolyse and condense only to the extent of forming clusters then a smooth coating will be formed on the surface of the ceramic powder. If the precursor is allowed to hydrolyse and condense till colloidal size then a rough coating and agglomerates of nanoparticles will result.

Fig. 1a shows the TEM image of the commercial alumina as received and corresponds to a dense alumina particle with a particle size of ~0.5 μm. The morphology of the particles was clearly irregular and showed the characteristic roughness. The Al_2O_3 particles appeared to be slightly decorated with dislocations in the areas where the surface roughness is more pronounced. A TEM image of the nanocoated Al_2O_3 powders

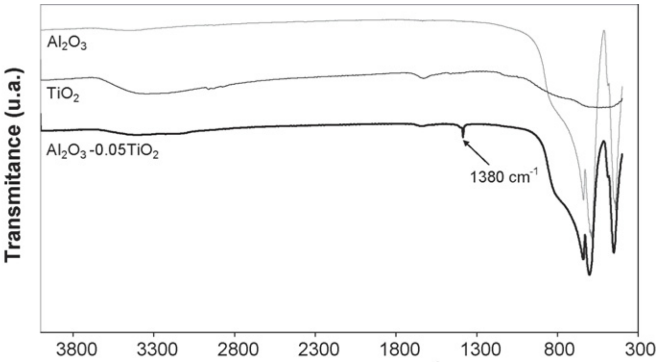

Fig. 2. FTIR spectra of Al_2O_3–TiO_2 nanocoated particles. FTIR spectra of Al_2O_3 and TiO_2 are shown for comparison.

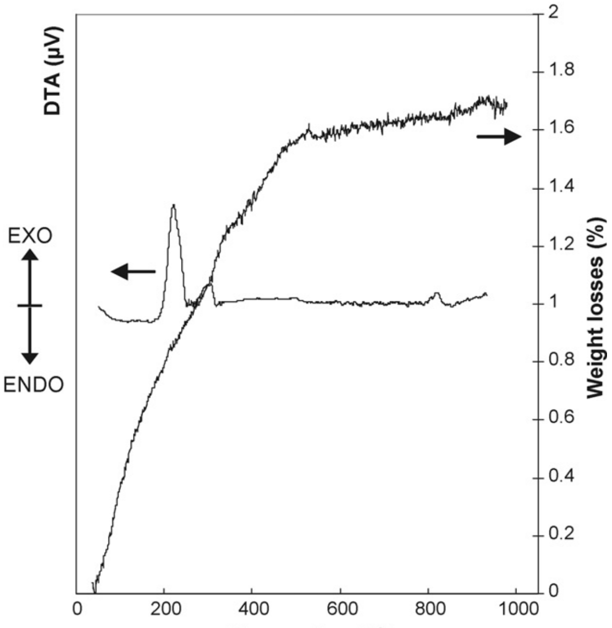

Fig. 3. DTA and TG curves of the TiO_2-coated (as-precipitated) Al_2O_3 powders.

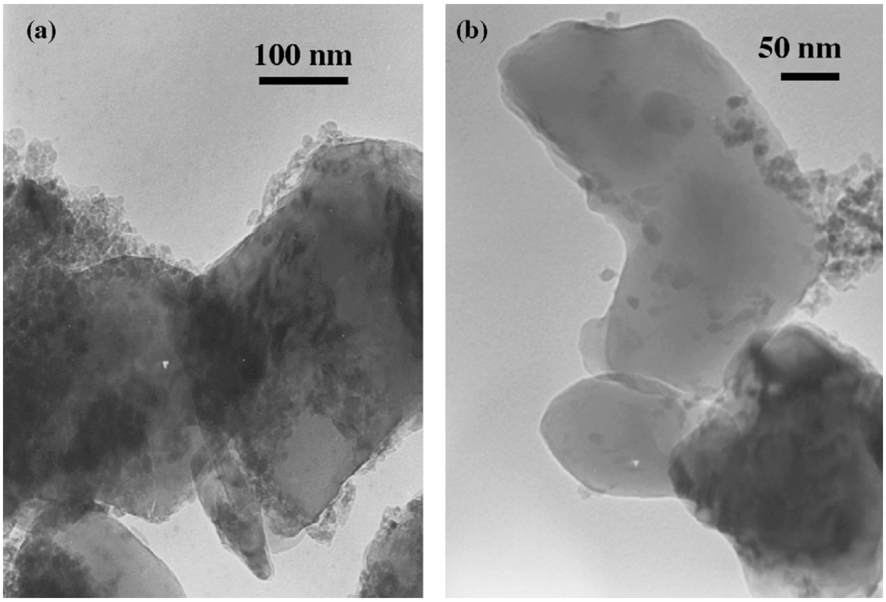

Fig. 4. TEM images of Ti-nanocoated Al_2O_3 particles: (a) calcined at 280 °C and (b) calcined at 500 °C.

obtained is shown in Fig. 1b. There is a uniform coating on the surface of the Al_2O_3 particles. The thickness of the titania-based layer is ~20 nm.

The FTIR spectra of Al_2O_3 powder, Ti-precursor ($Ti(C_4H_9O)_4$) precipitated in basic media and thermally treated at 500 °C to obtain TiO_2 and Ti-nanocoated alumina powders treated at 500 °C are shown in Fig. 2. The bands under 800 cm^{-1} are characteristic of Al_2O_3 powders, whereas the bands at 2970 cm^{-1}, 1640 cm^{-1}, 1100 cm^{-1} as well as the broad band under 780 cm^{-1} are characteristic of TiO_2. However, in the FTIR spectra of Ti-nanocoated Al_2O_3, the band showed at 1380 cm^{-1} was not present in the in the Al_2O_3 nor TiO_2 indicating the formation of a bonding between Al_2O_3 and TiO_2-nanocoating.

DTA–TG curves of the Ti-nanocoated alumina powders are shown in Fig. 3. The DTA curve shows a first broad endothermic peak in the range of 100–200 °C associated with a weight loss of 1 wt.% according with TG curve. These losses are related to the evaporation of physically adsorbed water. The second exothermic peak around 230 °C can be related to the elimination of water of hydration of $TiO_2{\cdot}H_2O$ coating with an additional weight loss of ~0.2 wt.% and the crystallization of tetragonal anatase phase of TiO_2 [17]. At 830 °C an exothermic peak indicates the anatase to rutile transformation. Weight losses continued up to ~500 °C, associated to a very small exothermic peak in this temperature range, probably due to the burning of residual organic species from the reactants used during coprecipitation.

The TEM images of the coated Al_2O_3 powders calcined at 280 °C (heating 2 °C/min, no residence time, air quenching) are shown in Fig. 4a. The nanocoating decomposed to produce Ti-based nanoparticles upon calcination. The amorphous precipitate $TiO_2{\cdot}H_2O$ transforms at ~230 °C to anatase giving up worm like structures on some parts of the alumina particles. The areas where the coating was removed showed absence of surface dislocations indicating that the nanocoating could be easily released only in those zones with lower amount of defects. The powder thermally treated at 500 °C (heating 2 °C/min, no residence time, air quenching) is shown in Fig. 4b. This thermal treatment reached a mass loss of ~1.5 wt.% which is approximately the weight loss registered at 550 °C in the DTA–TG run. As it can be seen, agglomerated nanoparticles spherical in shape (TiO_2) with an average size of ~8 nm were formed. The surface diffusion promoted the mass transport and the formed nanoparticles were concentrated in some areas of the alumina powders. This behaviour was favoured by the wrapping of the nanocoating when the first chemical species were removed. In addition to this, some areas still show the nanocoating. This fact points to a certain relationship between Al_2O_3 surface dislocations and strong bonding of the nanocoating.

4. Conclusions

Ti-based nanocoatings on alumina were prepared by controlling the heterogeneous precipitation in the presence of urea of a soluble titanium precursor. A commercial alumina powder with an average size of 0.5 μm was used. The Ti-nanocoating obtained was smooth with a thickness of ~20 nm. Upon calcinations at 500 °C spherical discrete TiO_2 nanoparticles of ~8 nm were formed along with some remaining rests of the nanocoating. The dislocations present in the Al_2O_3 particles seemed to play an important role in the decomposition and the formation of the nanocoating.

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