Preparation of nanostructured alumina–titania composite powders by spray drying, heat treatment and plasma treatment

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Ultrafine grained bulk ceramic composites consolidated from nanostructured composite powders by pressure less sintering

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Nanostructured alumina–titania composite powders which are microsized particles composed of nanosized grains were prepared from nano alumina and titania powders with nanodopants (zirconia and ceria) by ball milling, spray drying and heat treating. Then, the as prepared nanostructured composite powders were consolidated into ultrafine grained alumina–titania bulk ceramic composites through powder compacting and pressure less sintering. The addition of nanodopants leads to a finer grain size in the ceramic and improves the densification of bulk ceramic composite. The active mechanisms of nanodopants were discussed in detail.

Keywords: Ultrafine grained ceramic, Nanostructured powders, Powder metallurgy, Pressure less sintering

Introduction

Alumina is utilised in many areas of modern industry due to their unique mechanical, electrical and optical properties and biocompatibility.[1] Al_2O_3–TiO_2 ceramic composite can be a good material for the femoral head of total hip joint replacement as well as many other applications.[2–5]

Ultrafine grained alumina based ceramics demonstrate novel and attractive properties comparing with their coarse grained counterparts (microsized grain ceramics).[6,7] However, it is difficult to get a fully dense ceramic while maintaining an ultrafine grain size. In the preparation of ultrafine grained ceramics from ultrafine powders, when the densities are larger than 90% of theoretical, grain coarsening becomes particularly severe.[8] Therefore, many new consolidation techniques that can accelerate sintering without increasing grain growth have been developed. For example, spark plasma sintering,[9] transformation assisted consolidation[10] and high pressure sintering.[8] However, these advanced approaches for preparing ceramic nanocomposites are often associated with considerable high cost equipments which are not always available in any place all over the world. Therefore, it is significant to prepare ultrafine grained ceramics using conventional powder metallurgy techniques which generally include powder processing, powder compacting and pressure less sintering.

In addition, the efforts having been used to achieve optimisation for preparing ultrafine grained ceramics are coupled with selection of finer starting powders, because finer powder size is preferable for producing ceramics with finer final grain size.[11] With the availability of nanocrystalline powders, a number of studies have been reported on sintering of nanocrystalline powders.[12,13] In the present investigation, nanostructured alumina–titania composite powders which are microsized particles composed of nanosized grains were prepared by doping with small amounts of nanosized zirconia and ceria. Then, the as prepared nanostructured composite powders were consolidated into ultrafine grained bulk composites successfully by pressure less sintering. The effects of nanostructured powders and nanodopants on the densification and microstructures of the ceramic composites were investigated in detail.

Experimental

As received powders were Al_2O_3 (δ and γ phases, 99·9% grade, Degussa Co., Ltd, Germany) with grain size of 20–45 nm and TiO_2 (anatase, 99·9% grade, Nanjing High Technology of Nano Material Co., Ltd, China) with grain size of 20–50 nm. These powders were blended uniformly to produce a powder mixture (labelled as AT) with composition of 87 wt-%Al_2O_3 and 13 wt-%TiO_2 with the addition of binder by wet ball milling. In addition, 7 wt-%ZrO_2 (tetragonal phase, 99·9% grade, Cug-nano Material Manufacture Co., Ltd, Wu Han, China) with grain size of 20–50 nm and 6 wt-%CeO_2 (cubic phase, 99·9% grade, Rare Chem. Co., Ltd, Hui Zhou, Guang Dong, China) with grain size of 20–40 nm were added during mixing for a modified nanostructured powder (labelled as ATD). The mixed powders were then reconstituted to form microsized particles with nanosized grains. The reconstitution process consists of spray drying the slurry of powder mixture and heat treating. Subsequently, the reconstituted powders were compacted into green compacts, after that the green compacts were cool isostatic pressed. At last, the green compacts are pressure less sintered at 1350°C for 1 h in air with the heating rate of 5°C min^{-1}.

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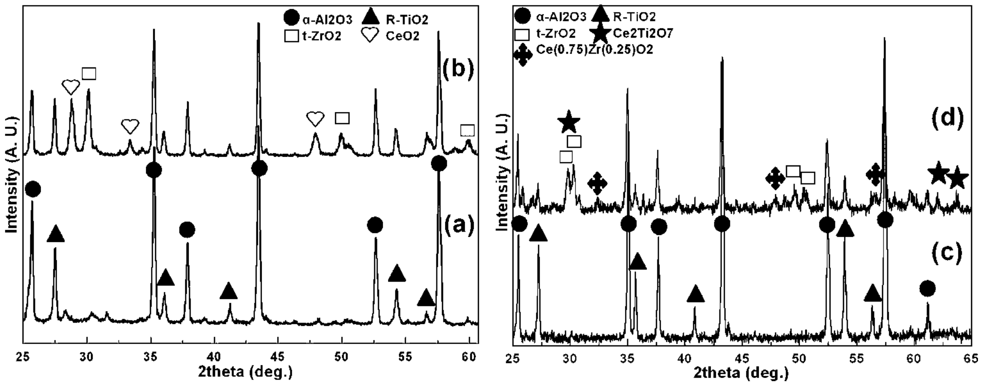


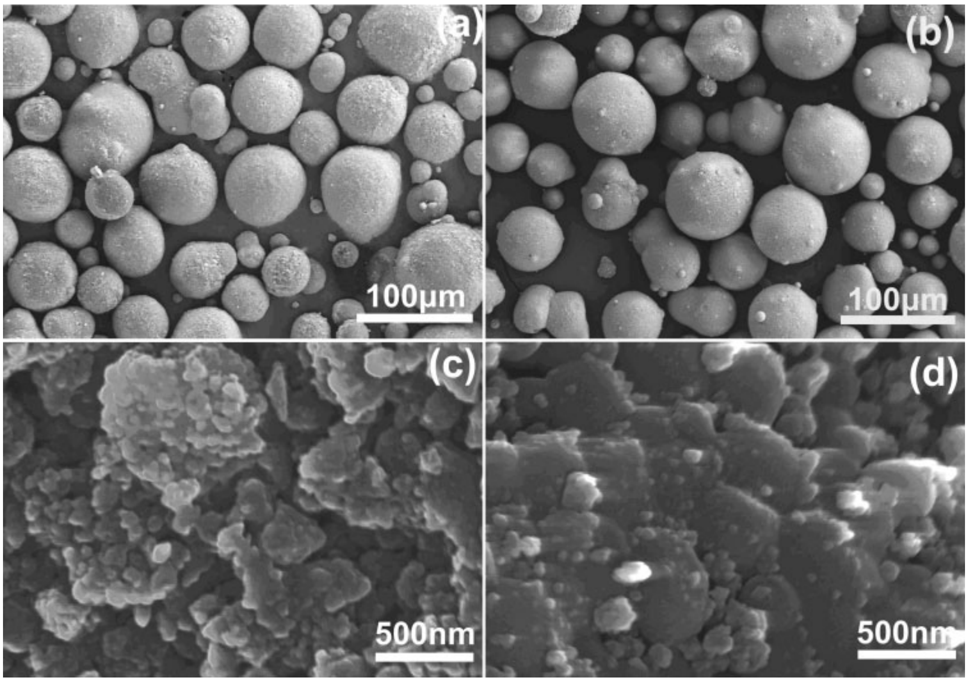
1 X-ray diffraction patterns of *a* nanostructured Al_2O_3–TiO_2 (AT) powders, *b* nanostructured Al_2O_3–TiO_2–ZrO_2–CeO_2 (ATD) powders, *c* bulk ceramic consolidated from AT powders, *d* bulk ceramic consolidated from ATD powders

The density of sintered bodies was determined using the Archimedes method with an immersion medium of distilled water. The phase constitution of reconstituted powders and sintered products was characterised by X-ray diffraction (XRD, D/max-γB, Japan) with Cu K_α radiation. A field emission gun scanning electron microscope (SEM, HITACHI-S570) was employed to characterise the reconstituted powders and the sintered products. The sintered samples were polished and thermally etched at 1200°C for 30 min in air.

Results and discussion

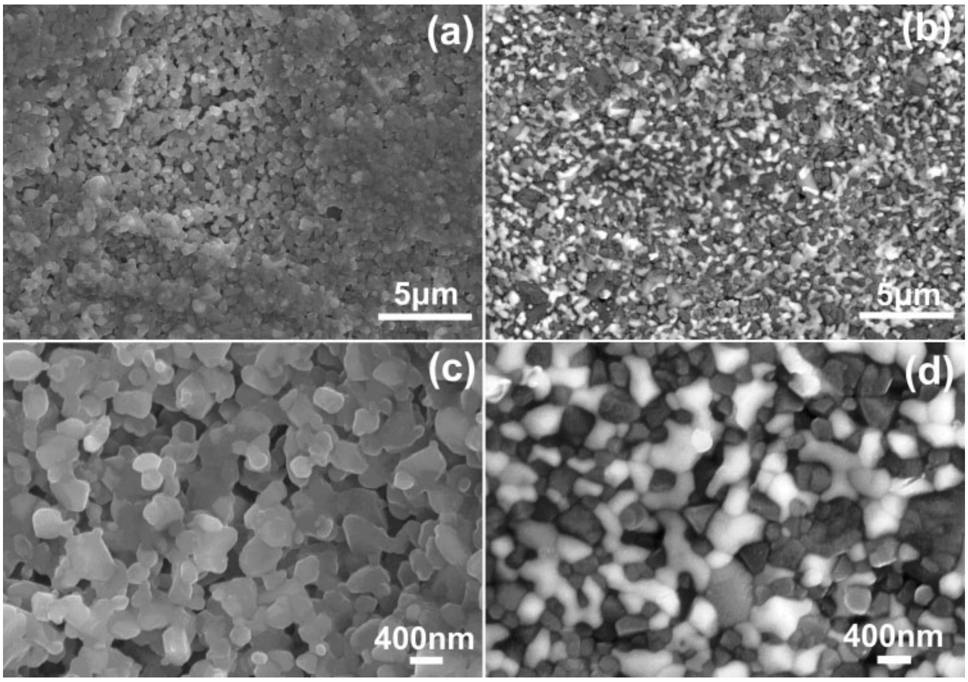
The XRD patterns of nanostructured composite powders are shown in Fig. 1. The metastable phase δ-Al_2O_3, γ-Al_2O_3 and anatase were transformed into stable phase α-Al_2O_3 and rutile, respectively, after appropriate heat treating. The Al_2O_3–TiO_2 (AT) powders consist of α-Al_2O_3 and rutile. The Al_2O_3–TiO_2–ZrO_2–CeO_2 (ATD) powders consist of α-Al_2O_3, rutile, *t*-ZrO_2 and CeO_2 phases. Figure 2 shows the SEM graphs of reconstituted powders. After reconstitution processing, spherical and compact powders had been obtained (Fig. 2*a* and *b*). Each spherical solid particle consists of a great lot of nanosized grains (Fig. 2*c* and *d*).

When AT powders were consolidated at 1350°C for 1 h, the resultant bulk ceramic consisted of α-Al_2O_3 and rutile phases (Fig. 1*c*). The grains of AT had a fast growth rate and the size of some grains grew to approximately 600–800 nm (Fig. 3*c*). In the case where nano ZrO_2 and CeO_2 powders were added to the starting nano Al_2O_3 and TiO_2 powder mixtures (ATD powders), there were some $Ce_{0\cdot75}Zr_{0\cdot25}O_2$ solid solution and $Ce_2Ti_2O_7$ solid solution formed in ATD bulk ceramic. Meanwhile, *t*-ZrO_2 was reserved in ATD because of the presence of CeO_2 and TiO_2.[14] The resultant ATD bulk ceramic consisted of α-Al_2O_3, rutile, *t*-ZrO_2, $Ce_{0\cdot75}Zr_{0\cdot25}O_2$, $Ce_2Ti_2O_7$ (Fig. 1*d*). The microstructure of ATD bulk ceramic is obviously different from that of AT (Fig. 3). A dense ceramic composite (ATD) with a final average grain size $\sim$220 nm was formed. In comparison with the microstructure of ceramic prepared from only nano Al_2O_3 and TiO_2 powder, it can be seen that nanosized ZrO_2 and CeO_2 additives lead to fine



a AT; *b* ATD; *c* high magnification of *a*; *d* high magnification of *b*

2 Scanning electron microscopy graphs of two reconstituted composite powders



a AT; *b* ATD; *c* high magnification of *a*; *d* high magnification of *b*

3 Scanning electron microscopy graphs of thermal etched surface of AT and ATD bulk ceramics

grain size. Scanning electron microscopy observation shows that ATD bulk ceramic is considerably dense comparing with AT. Moreover, the relative density results showed that the relative densities of two ceramics were 80·2 and 92·4% respectively. That means the addition of nanodopants ZrO_2 and CeO_2 improves the densification of bulk ceramic.

The ZrO_2 and CeO_2 nanodopants lead to a finer grain size. One possible reason is that more heterogeneous nucleation sites were formed due to the formation of $Ce_{0\cdot75}Zr_{0\cdot25}O_2$ and $Ce_2Ti_2O_7$ solid solution by the reaction of nano TiO_2, ZrO_2 and CeO_2 during sintering. Another possible reason is that at a certain stage in microstructural development during sintering, the pores at the grain boundary were smaller when ZrO_2 and CeO_2 are present.[15] The pore movement rate M_P during sintering can be described by equation (1)

$$M_P = K\left(\frac{D_S}{r^4}\right) \tag{1}$$

where K is a constant, D_S is the surface diffusion coefficient, and r is the pore radius. The smaller pore radius greatly increased the M_P. A large M_P prevented separation of the pores from the grain boundaries during sintering, and hence eliminated the abnormal grain growth.

The SEM picture (Fig. 3) shows that AT bulk ceramic is porous. After some ZrO_2 and CeO_2 additives are added, the resultant ATD bulk ceramic is considerably dense. The addition of ZrO_2 and CeO_2 nanodopants advances the densification of ceramics, which is consistent with the investigations, by Tsai *et al.*,[16] Harmer *et al.*[15] and Duan *et al.*[8] that density was increased by doping TiO_2, MgO, and ZrO_2 into Al_2O_3. There are four possible reasons for the densification by nanodopants:

(i) nanodopants ZrO_2 and CeO_2 were located between Al_2O_3 and TiO_2 grains and in the grain boundaries of matrix granules. The nanodopants accumulated between matrix granules, making mass transfer of grains accelerate and grain boundary form easily, and eliminating the pores at grain boundaries. As a result, the density of ATD was enhanced

(ii) the formation of the new $Ce_{0\cdot75}Zr_{0\cdot25}O_2$ and $Ce_2Ti_2O_7$ solid solution phases during sintering resulted in more new grain boundaries, and improved the grain boundary diffusion coefficient, thus increasing the densification rate

(iii) Ce^{4+} entered into the crystal lattice of ZrO_2,[17] and oxygen vacancies and substitution atoms brought about high lattice distortion energy, consequently the driving force of sintering was increased. Moreover, the pores wrapped in grains may be eliminated though diffusion of oxygen vacancies

(iv) the ZrO_2 and CeO_2 nanodopants may raise the concentration of interstitial Al ion, increasing the aluminium lattice diffusion coefficient, and improving densification during sintering.[15]

Conclusion

Nanostructured Al_2O_3–TiO_2 composite powders were prepared from nano Al_2O_3 and TiO_2 powders as well as nanodopants (ZrO_2 and CeO_2 powders) by ball milling, spray drying and heat treating. Ultrafine grained Al_2O_3–TiO_2 matrix bulk ceramic composites (with a grain size $\sim$220 nm) were consolidated successfully from the as prepared nanostructured powders by pressure less sintering. The addition of nanodopants leads to a finer grain size in the ceramic and improves the densification of bulk ceramic composite.

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