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Rapid synthesis and consolidation of a nanostructured 3Ti-Al_2O_3 composite by HFIHS for biomedical application

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Nanopowders of TiO and Al were fabricated using high energy ball milling. Dense nanostuctured 3Ti-Al_2O_3 composite was simultaneously synthesized and consolidated by high frequency induction heated combustion synthesis method within 2 min in one step from mechanically activated powders of 3 TiO and 2 Al. Highly dense 3Ti-Al_2O_3 with relative density of up to 99.5% was produced under simultaneous application of a 80 MPa pressure and the induced current. The average hardness and fracture toughness values of the composite were 1445 kg/mm^2 and 7.2 MPa · m$^{1/2}$, respectively.

Key words: Synthesis, Composite materials, Nanomaterials, Mechanical properties, Sintering.

Introduction

Al_2O_3 ceramic have been found to be promising alternative materials for total hip arthroplasty (THA) and total knee arthroplasty (TKA) since 1970s. The advantages of the Al_2O_3 ceramic in orthopaedic bearings are the reduction or possible elimination of polyethylene wear particles from the periprosthetic space, their excellent hardness and biocompatibility. However, pure Al_2O_3 does not satisfy the mechanical properties for total hip and knee arthroplasty due to its low fracture toughness. To cope with this problem, we fabricated a nanostructured metal-ceramic composite adding Ti to improve the fracture toughness of Al_2O_3. Ti has a density of 4.54 g cm^{-3}, a Young's modulus of 116 GPa and good fracture toughness and biocompatibility. In addition, as titanium and alumina have a similar coefficient of thermal expansion, these cermets will have a better performance than other materials [1]. Therefore, the metal matrix composites are recognized as candidates for aerospace, automotive, bio-materials and defense applications. Traditionally, discontinuously reinforced metal matrix composites have been produced by several processing routes such as powder metallurgy, spray deposition, mechanical alloying, various casting techniques and SHS(self-propagating high temperature synthesis). One of all these techniques, high energy ball milling and mechanical alloying of powder mixtures, were reported to be efficient techniques for the preparation of nano-crystalline metals and alloys, which is a combination of mechanical milling and chemical reactions [2, 3]. Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties. As nanomaterials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, more attention has been paid for the application of nanomaterials [4,5]. In recent days, nanocrystalline powders have been developed by the thermochemical and thermomechanical process named as the spray conversion process (SCP), co-precipitation and high energy milling [6-8]. However, the grain size in sintered materials becomes much larger than that in pre-sintered powders due to a fast grain growth during conventional sintering process. So, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the high frequency induction heated sintering method which can make dense materials within 2 min, has been shown to be effective in achieving this goal [9-11].

The purpose of this work is to produce dense nanocrystalline 3Ti-Al_2O_3 composite within 2 min in one-step from mixtures of mechanically activated 3 TiO and 2 Al powders by using this induced current activated sintering method and to evaluate its mechanical properties and grain size.

Experimental Procedures

Powders of 99.5% TiO (< 5 μm mesh, Alfa company) and 99.5% pure Al (−325 mesh, Alfa company) were used as a starting materials. 3 TiO_2 and 2 Al powder mixtures were first milled in a high-energy ball mill, Pulverisette-5 planetary mill with 250 rpm and for 10 hrs. Tungsten carbide balls (9 mm in diameter) were used in a sealed cylindrical stainless

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steel vial under argon atmosphere. The weight ratio of ball-to-powder was 30 : 1. The grain sizes were calculated by Suryanarayana and Grant Norton's formula [12],

After milling, the mixed powders were placed in a graphite die (outside diameter, 35 mm; inside diameter, 10 mm; height, 40 mm) and then introduced into the high frequency induction heated combustion system made by Eltek in South Korea shown schematically in Ref. [9-11]. The four major stages in the synthesis are as follows. The system was evacuated (stage 1). And a uniaxial pressure of 80 MPa was applied (stage 2). An induced current was then activated and maintained until densification was attained as indicated by a linear gauge measuring the shrinkage of the sample (stage 3). Temperature was measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the sample was cooled to room temperature (stage 4).

The relative densities of the sintered sample were measured by the Archimedes method. Microstructural information was obtained from product samples which were polished and etched using a solution of HF (10 vol.%), HNO_3 (20 vol.%) and H_2O (70 vol.%) for 5 s at room temperature. Compositional and micro structural analyses of the products were made through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured by performing indentations at load of 20 kg and a dwell time of 15 s on the sintered samples.

Results and Discussion

The interaction between 3 TiO and 2 Al, i.e.

$$3\ TiO + 2\ Al \rightarrow 3\ Ti + Al_2O_3 \quad (1)$$

is thermodynamically feasible as shown in Fig. 1.

XRD patterns of raw materials and milled powder is shown in Fig. 2. In Fig. 2(c), reactant TiO and Al peaks were detected and product peaks of Ti and Al_2O_3 were not observed. From the results, synthesis does not occur during the high energy ball milling. The full width at half-maximum of the diffraction peak in milled powder is wider than that of raw powder due to strain and refinement of grain size. The average grain sizes of TiO and Al measured by Suryanarayana and Grant Norton's formula [12] were about 14 nm and 33 nm, respectively.

The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the processing of 3 TiO and 2 Al system are shown Fig. 3. As the induced current was applied the specimen showed the shrinkage displacement was nearly constant up to heating time of 10s but then abruptly increased. And the shrinkage displacement gradually increased with temperature up to about 1230 °C. Fig. 4 shows X-ray diffraction result of a

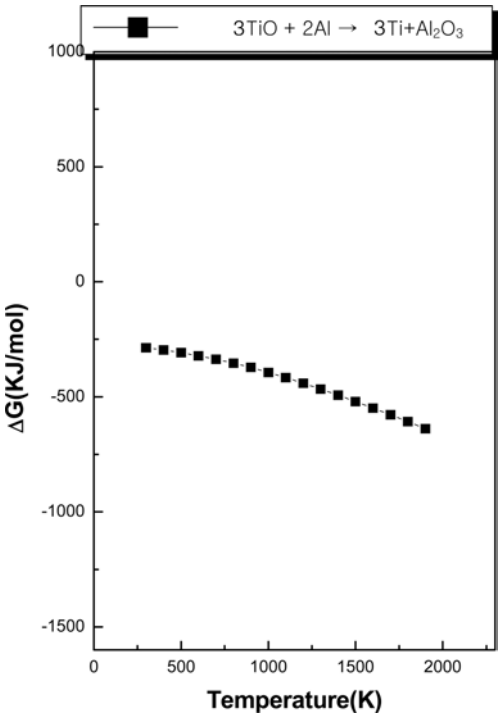

Fig. 1. Temperature dependence of the Gibbs free energy change for the interaction between titanium oxide and aluminum.

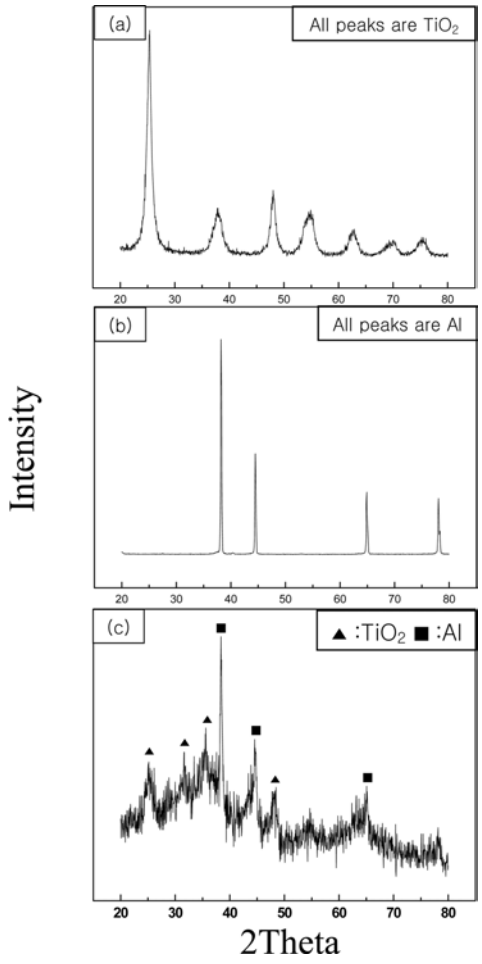

Fig. 2. XRD patterns of raw materials and mechanically milled powder: (a) TiO, (b) Al and (c) mechanically milled 3TiO-2Al .

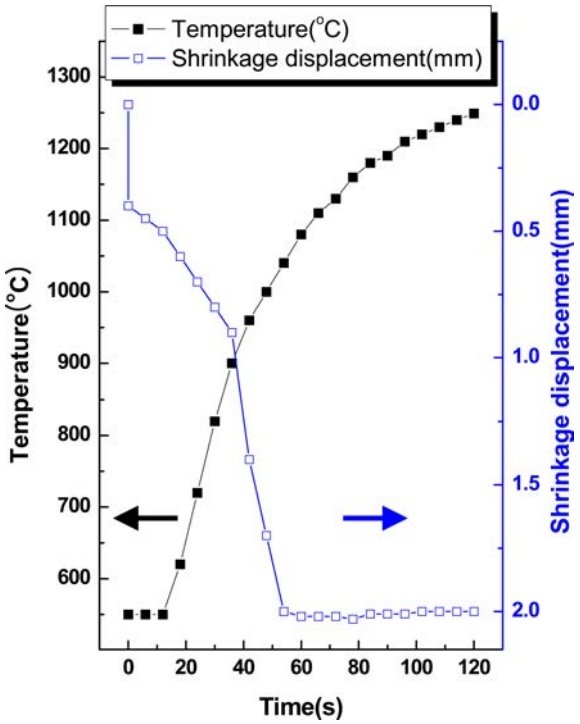

Fig. 3. Variations of temperature and shrinkage displacement with heating time during high frequency induction heated combustion of 3TiO- 2Al system.

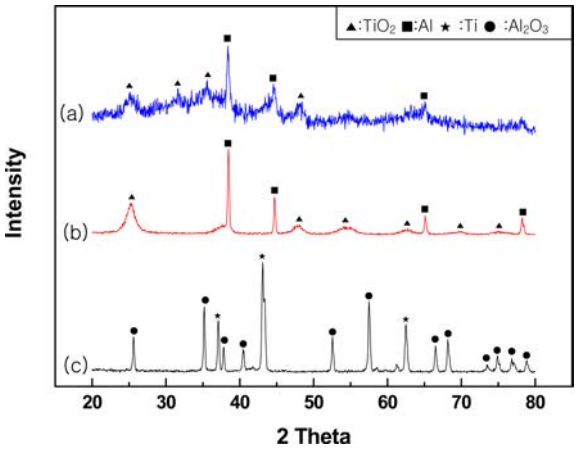

Fig. 4. XRD pattern of the 3Ti-Al_2O_3 composite sintered by HFIHS.

specimen heated to 1230 ºC. The figure exhibit only peaks pertaining to the Ti and Al_2O_3. From the result, simultaneous synthesis and densification occurs during the heating under the 80 MPa pressure. FE-SEM image of an etched surface of the samples heated to 1230 ºC under a pressure of 80 MPa is shown in Fig. 5. A complete reaction between these elements (3 TiO and 2 Al) has taken place under these conditions. These conclusions were supported by X-ray diffraction analyses with peaks of the product phase, Ti and Al_2O_3 phase, as indicated in Fig. 4. The microstructure consists of nanophases. The corresponding relative density is about 99.5%. The structure parameters, i.e. the average grain sizes of Ti and Al_2O_3 are obtained from by

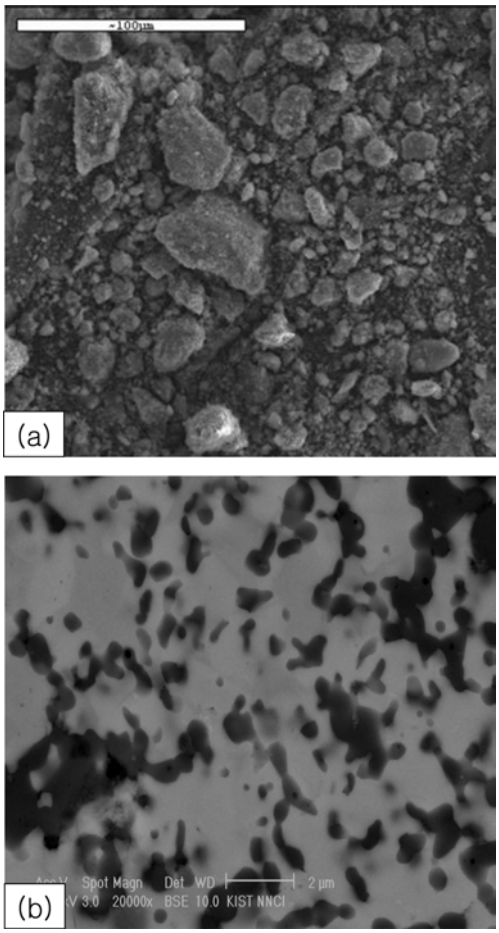

Fig. 5. FE-SEM of the 3Ti-Al_2O_3 composite sintered by HFIHS.

Suryanarayana and Grant Norton's formula [12], were 76 nm and 48 nm, respectively The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density as a result of molar volume change associated with the formation of Ti and Al_2O_3 from 3 TiO and 2 Al reactant and the consolidation of the product.

Vickers hardness measurements were made on polished sections of the 3 Ti-Al_2O_3 composite using a 20 kg_f load and 15 s dwell time. The calculated hardness value of 3 Ti-Al_2O_3 composite was 1445 Kg/mm^2. This value represents an average of five measurements. The length of these cracks permits an estimation of the fracture toughness of the material. From the length of these cracks, fracture toughness values can be determined using two expressions. The first expression, proposed by Anstis *et al*. [13] is

$$K_{IC} = 0.016\ (E/H)^{1/2} \cdot P/C^{3/2} \quad (2)$$

where E is Young's modulus, H the indentation hardness, P the indentation load, and C the trace length of the crack measured from the center of the indentation. The modulus was estimated by the rule mixtures for the 0.45 volume fraction of Al_2O_3 and the

0.55 volume fraction of Ti using $E(Al_2O_3)$ = 336 GPa [14] and E(Ti) = 116 Gpa [15]. The second expression, proposed by Niihara et al. [16] is

$$K_{IC} = 0.023\ (c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (3)$$

where c is the trace length of the crack measured from the center of the indentation, a the half of average length of two indent diagonals, and H_v the hardness.

As in the case of hardness values, the toughness values were derived from the average of five measurements. The toughness values obtained by the two methods of calculation are 7.2 and 6.8 MPa · $m^{1/2}$, respectively. The hardness and fracture toughness of Al_2O_3 with grain size of 4.5 μm are reported as 1800 kg/mm^2 and 4 MPa · $m^{1/2}$, respectively [2]. The hardness of 3Ti-Al_2O_3 composite is lower than that of monolithic Al_2O_3 but the fracture toughness is higher than the value of Al_2O_3 due to addition of ductile Ti. 3Ti-Al_2O_3 composite may used for alternative materials for total hip arthroplasty (THA) and total knee arthroplasty (TKA) due to an enhanced fracture toughness.

Conclusions

Using the high frequency induction heated combustion method, the simultaneous synthesis and densification of nanostructured 3 Ti-Al_2O_3 composite was accomplished from mechanically activated powders of 3 TiO and 2 Al. Complete synthesis and densification can be achieved in one step within duration of 2 min. The relative density of the composite was 99.5% for the applied pressure of 80 MPa and the induced current. The average grain sizes of Ti and Al_2O_3 prepared by high frequency induction heated combustion method were about 76 nm and 48, respectively. The average hardness and fracture toughness values obtained were 1445 kg/mm^2 and 7.2 MPa · $m^{1/2}$, respectively.

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