

Properties and rapid sintering of nanostructured CoAl-Al₂O₃ composite for prosthetic joint replacements

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Even though Al₂O₃ material having high hardness reduces wear debris materials, it cannot satisfy the properties of prosthetic hip or knee joint replacements because of its low fracture toughness. Thus, bearing materials in prosthetic hip or knee joint replacements basically require high hardness and high fracture toughness. To improve their mechanical properties (hardness and fracture toughness), the approach commonly utilized has been the addition of a second phase to form a composite and produce nanostructured materials. The nanopowders of CoAl and Al₂O₃ were synthesized from Co₃O₄ and Al powders by high energy ball milling. The nanostructured 2.25CoAl-Al₂O₃ composite from the milled powder was densified within a short time by the high frequency induction heated sintering. The mechanical properties of the nanostructured 2.25CoAl-Al₂O₃ were higher than those of monolithic CoAl and Al₂O₃, respectively. And the composite was evaluated as excellent biocompatibility.

Key words: Composite, Nanostructure, Mechanical properties, Sintering, Powder processing.

Introduction

The most commonly used bearing couple in prosthetic hip or knee joint replacements consist of a cobalt-chrome (CoCr) metal alloy articulating against ultrahigh-molecular-weight polyethylene [1]. However, the CoCr metal alloy generates wear debris in prosthetic hip and knee bearing due to its low hardness. These wear debris have a negative role in producing tissue inflammation adjacent to the bearing. Therefore, alumina and zirconia ceramics have been used as alternatives to cobalt-chrome (CoCr) in total hip arthroplasty and total knee arthroplasty since the 1970s [2, 3]. However, even though ceramic materials having high hardness reduces wear debris materials, they cannot satisfy the properties of prosthetic hip or knee joint replacements because of its low fracture toughness. Thus, bearing materials in prosthetic hip or knee joint replacements basically require high hardness and high fracture toughness.

To improve their mechanical properties (hardness and fracture toughness), the approach commonly utilized has been the addition of a second phase to form a composite [4, 5] and produce nanostructured materials [6, 7]. The attractive physical and mechanical properties that can be obtained with cermets, such as high specific modulus, strength, and thermal stability, have been documented extensively [8-11]. Nanomaterials have

received a good deal of attention recently as they possess high strength, high hardness, excellent ductility and toughness [12, 13]. 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 [14-16]. 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 [17-19].

The purpose of this study is to produce the mechanical synthesis of nanopowders of CoAl and Al₂O₃ from Co₃O₄ and Al powders and dense nanocrystalline CoAl-Al₂O₃ composites within two minutes by using this high frequency induction heated sintering method and to evaluate their mechanical properties and biocompatibility.

Experimental Procedure

Powders of 99.5 % pure Co₃O₄ (Sigma Aldrich, Inc.) and 99.5 % pure Al (-325 mesh, Alfa Aesar, Inc.) were used as raw materials. The shape and size of the raw powders are irregular, respectively, as shown Fig. 1.

3/4Co₃O₄ and 17/4Al powders were mixed by a high-energy ball mill, a Pulverisette-5 planetary mill at 250 rpm and for 10 hrs. Tungsten carbide balls (10 mm in

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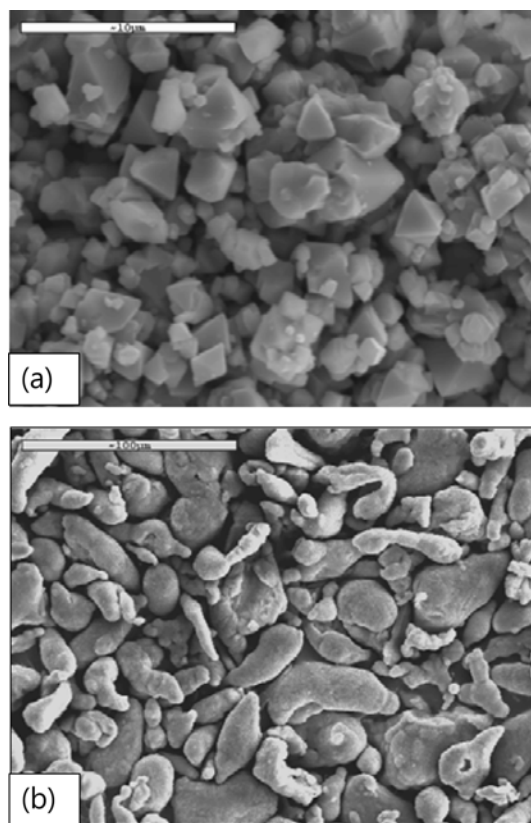


Fig. 1. FE-SEM image of raw materials: (a) Co_3O_4 and (b) Al powders.

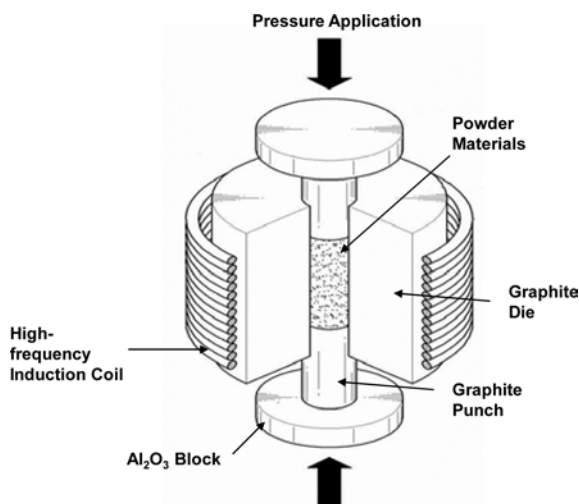


Fig. 2. Schematic diagram of apparatus for high frequency induction heated sintering.

diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of ball-to-powder was 30 : 1.

Placed in a graphite die (45 mm in outside diameter, 20 mm in inside diameter, 40 mm in height), the milled powder was sealed by upper and lower graphite punches. The high frequency induction heating sintering system made by Eltek in South Korea is shown schematically in

Fig. 2. The four major stages in the sintering are as follows. The system was evacuated (stage 1), and a mechanically uniaxial pressure of 80 MPa was applied (stage 2). An induced current was then activated, and maintained to 1500 °C with heating rate of 1000 °C/min, and then turned off, without holding time (stage 3). The temperatures were measured, using 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 process was carried out under a vacuum of 5.33 Pa.

The grain sizes of CoAl and Al_2O_3 were calculated by Suryanarayana and Grant Norton's formula [20]:

$$B_r(B_{\text{crystalline}} + B_{\text{strain}})\cos\theta = k\lambda / L + \eta\sin\theta \quad (1)$$

where, B_r is the full width at half-maximum (FWHM) of the diffraction peak, after instrumental correction; $B_{\text{crystalline}}$ and B_{strain} are the FWHM caused by small grain size and internal stress, respectively; k is a constant (with a value of 0.9); λ is the wavelength of X-ray radiation; L and η are the grain size and internal strain, respectively; and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship: $B = B_r + B_s$, where B and B_s are the FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.

The relative densities of the sintered sample were measured by Archimedes' method. Microstructural information was obtained from the 2.25CoAl- Al_2O_3 composite, which was polished. Compositional and microstructural 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 a load of 20 kg_f and a dwell time of 15 sec, on the sintered samples.

A cytotoxicity test using the fibroblast cell was conducted. The fibroblasts were proliferated in Dulbecco's Modified Eagle's Medium (DMEM) with 10% fetal bovine serum (FBS) at 37 ± 1 °C, and the concentration of CO_2 was $5 \pm 0.5\%$. After enough growth, the fibroblasts were seeded at a density of 710^3 cells per well, into 96 well cell culture plates. They were cultured for 1, 3, and 7 days, respectively, with 100 µl of media ionized from the 2.25CoAl- Al_2O_3 composite. The cells were treated using CCK-8 solution for 24 hrs. The absorbance of 2.25CoAl- Al_2O_3 composite was measured, using a microplate reader, at 570 nm.

Results and Discussion

The X-ray diffraction patterns of raw powders and mechanically high energy ball- milled powders are shown in Fig. 3. In Fig. 3(c), the peaks of Al_2O_3 and CoAl were detected and there are no other peaks such as Fe or WC which is possible to happen during the

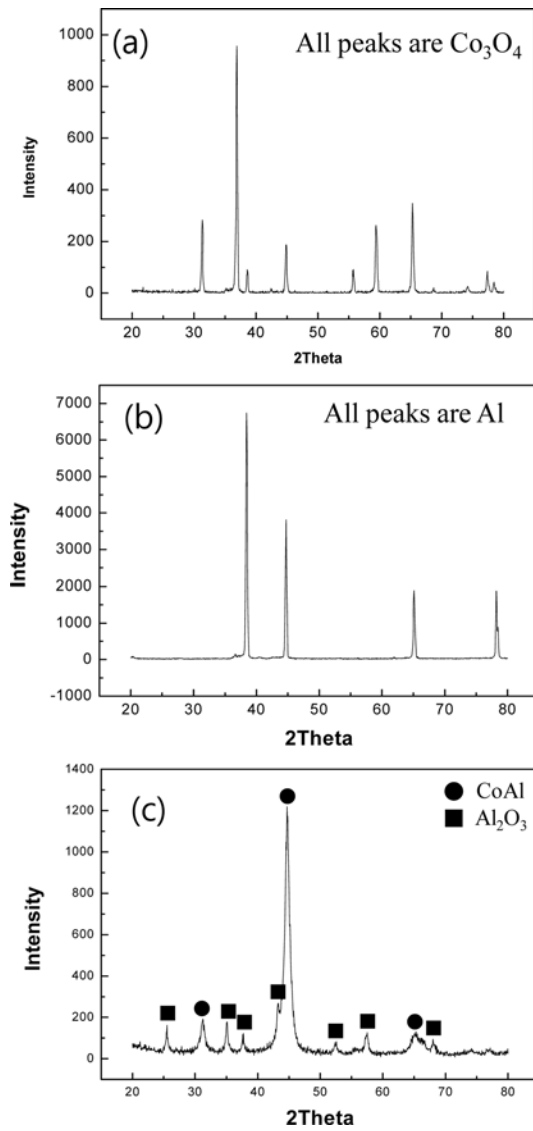


Fig. 3. XRD pattern of raw materials and milled powder: (a) Co₃O₄, (b) Al, and (c) mechanically milled powder

milling process. The powders milled from the high energy ball milling method were synthesized through milling processes. Fig. 4 shows that the interaction between $3/4\text{Co}_3\text{O}_4$ and $17/4\text{Al}$ is feasible.



Fig. 5 shows plots of $B_r(B_{\text{crystalline}} + B_{\text{strain}})\cos\theta$ versus $\sin\theta$ for CoAl and Al₂O₃ in milled powders, respectively. The average grain sizes of CoAl and Al₂O₃ measured by Suryanarayana and Norton's formula [20] was 58 and 14 nm, respectively.

A variation of shrinkage displacement and temperature with heating time during densification of 2.25CoAl-Al₂O₃ composite is shown in Fig. 6. The application of the induced current resulted in shrinkage due to consolidation and synthesis. As the induced current was applied, shrinkage displacement continuously increased

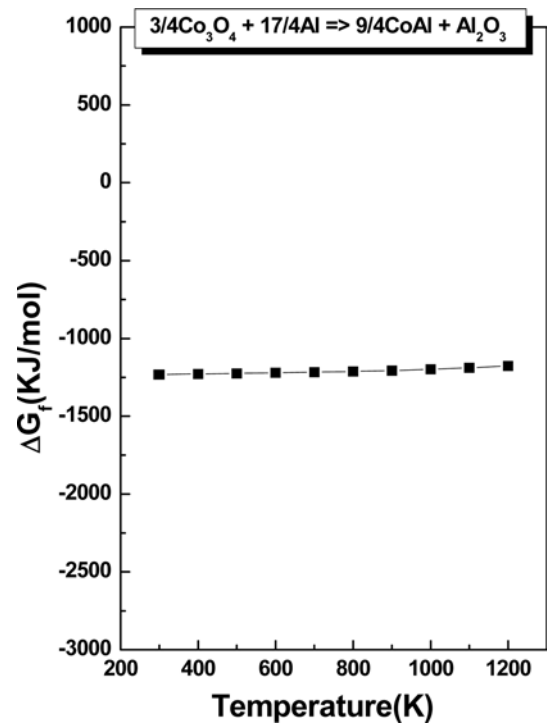


Fig. 4. Temperature dependence of the Gibbs free energy.

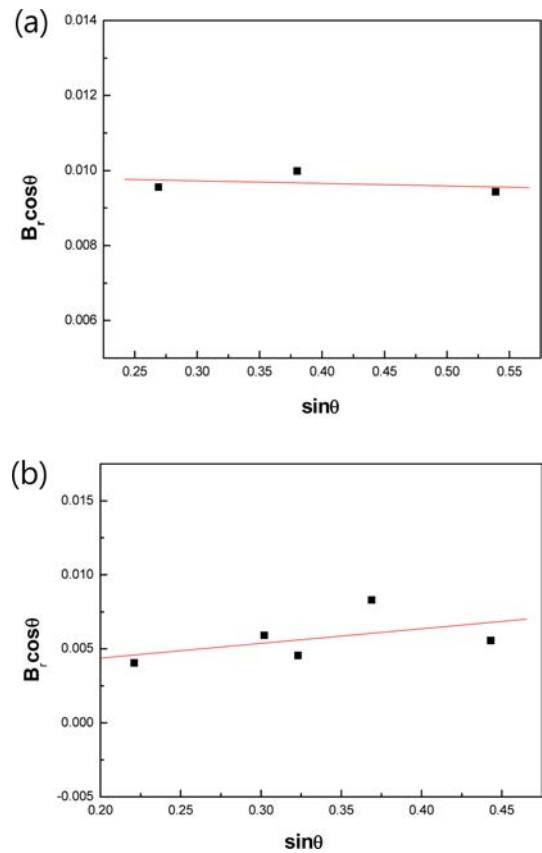


Fig. 5. Plot of $B_r(B_{\text{crystalline}} + B_{\text{strain}})\cos\theta$ versus $\sin\theta$ for (a) CoAl and (b) Al₂O₃ in milled powders.

up to 1500 °C.

Fig. 7 shows XRD patterns of 2.25CoAl-Al₂O₃

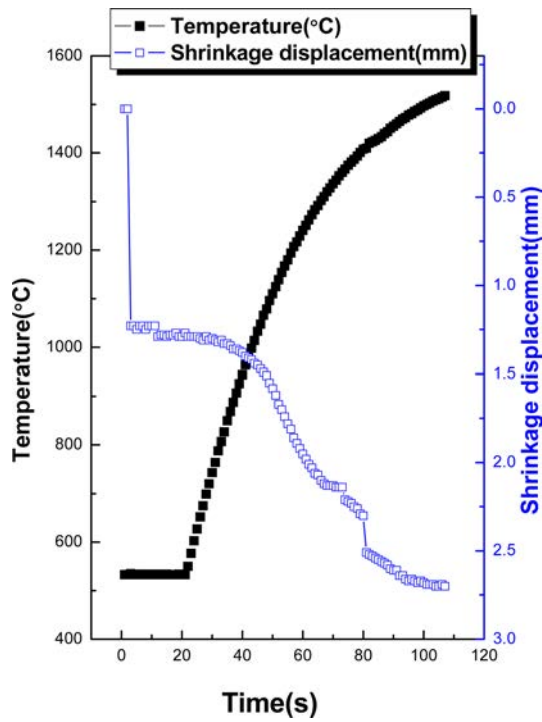


Fig. 6. Variations of temperature and shrinkage with heating time during the high frequency induction heated sintering of 2.25CoAl- Al_2O_3 powder milled by high energy ball milling for 10 hrs.

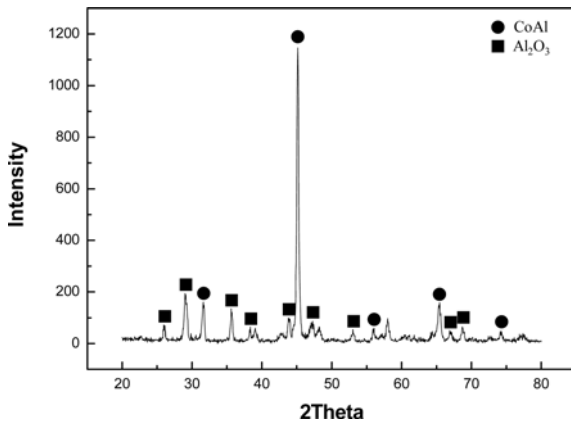


Fig. 7. XRD patterns of 2.25CoAl- Al_2O_3 composite sintered to 1500 °C.

composite heated to 1500 °C, in which only CoAl and Al_2O_3 peaks are detected. Fig. 8 indicates a plot of $B_r \cos \theta$ versus $\sin \theta$ to calculate the grain size of CoAl and Al_2O_3 . The structural parameters, i.e. the average grain sizes of CoAl and Al_2O_3 in composite heated to 1500 °C, are 53 and 51 nm, which were obtained from the X-ray data in Fig. 7 by Suryanarayana and Grant Norton's formula. The relative density of the 2.25CoAl- Al_2O_3 composite was 98%. It is considered that the reasons for the high density of the composite obtained at low temperature are as follows. Firstly, the application of pressure during initial stage sintering adds another term to the surface energy driving force, such that the total driving force, F_D , [21]

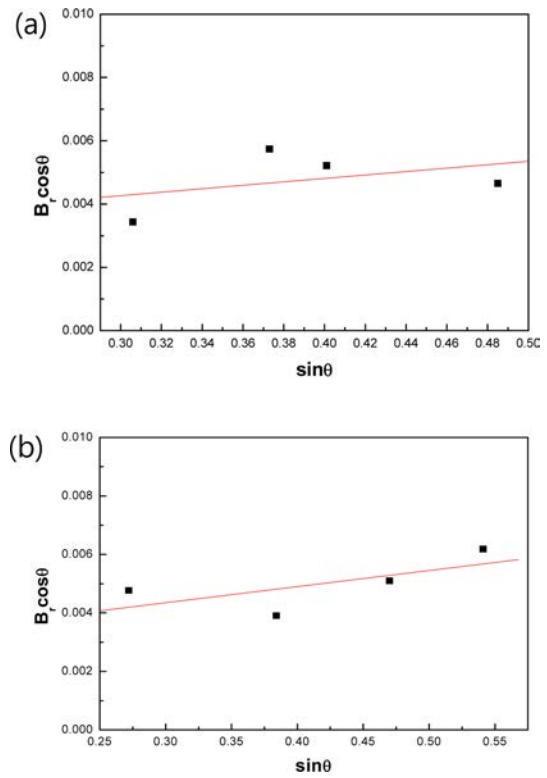


Fig. 8. Plot of $B_r(B_{\text{crystalline}} + B_{\text{strain}})\cos \theta$ versus $\sin \theta$ for (a) CoAl and (b) Al_2O_3 in 2.25CoAl- Al_2O_3 composite heated to 1500 °C.

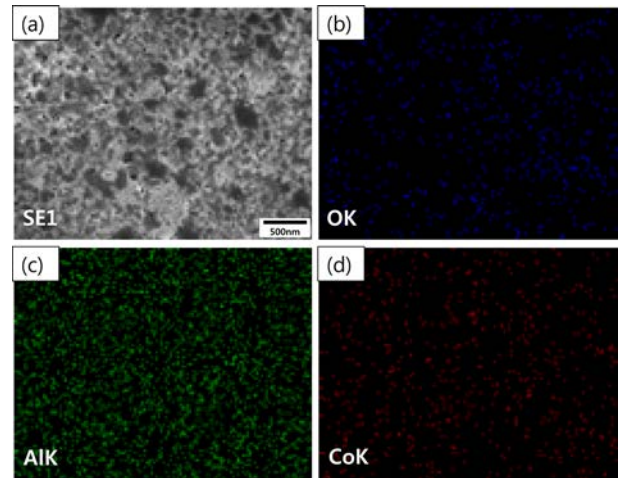


Fig. 9. SEM image and X-ray mapping analysis of 2.25CoAl- Al_2O_3 composite heated to 1500 °C: (a) SEM image and elemental mapping of (b) O, (c) Al and (d) Co.

$$F_D = \gamma + (P_a r / \pi) \quad (3)$$

where, γ is the surface energy, P_a is the applied pressure, and r is the radius of the particle. The effect of pressure on the densification of TiO_2 during high-frequency induction heated sintering was investigated by Shon et al. [22]. A significant increase in the relative density was observed, as the pressure was increased from about 60 to 100 MPa, for sintering at 800 °C. Secondly, the role of the current in sintering and or synthesis has been the focus of several attempts aimed

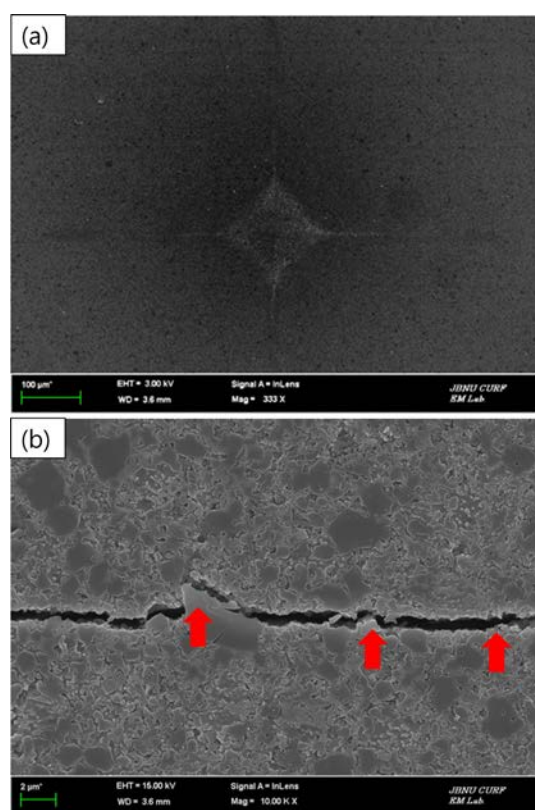


Fig. 10. (a) Vickers hardness indentation and (b) median crack propagating in 2.25CoAl-Al₂O₃ composite heated to 1500 °C.

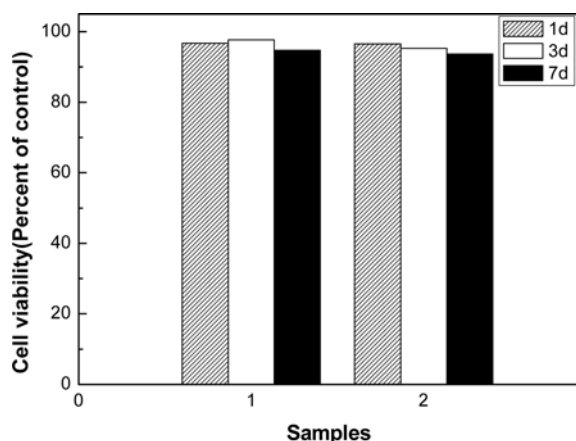


Fig. 11. Measurement of cell viability in (1) Ti and (2) 2.25CoAl-Al₂O₃ composite using CCK-8 solution, on 1, 3, and 7 days.

at providing an explanation of the observed enhancement of sintering, and the improved characteristics of the products. The role played by the current has been variously interpreted, the effect being explained in terms of the fast heating rate due to Joule heating, the presence of plasma in pores separating powder particles, and the intrinsic contribution of the current to mass transport [23-26].

Fig. 9 shows the SEM image of the sample heated to 1500 °C and X-ray mappings. Fig. 9(a) has several different phases and to compare CoAl phases with

Al₂O₃ phases, the X-ray mappings of Co, Al and O were conducted. With the Fig. 9(b-d), CoAl and Al₂O₃ phases were surely divided as well as fine Al₂O₃ grains existed in CoAl phases from Fig. 9(c) and (d). Dark phase and bright phase in Fig. 9(a) are Al₂O₃ and CoAl due to mass contrast.

Vickers hardness measurements were made on polished sections of the 2.25CoAl-Al₂O₃ composite using a 20 kg_f load and 15 sec dwell time. The calculated hardness value of 2.25CoAl-Al₂O₃ composite sintered from high energy ball milled powder was 1030 kg/mm². This value represents an average of five measurements. Hohls et al. reported the hardness of CoAl was about 500 kg/mm² [27]. The hardness of the composite in this study is higher than that of monolithic CoAl due to the addition of hard Al₂O₃.

The lengths of these cracks permit estimation of the fracture toughness of the materials by means of the expression [28]:

$$K_{IC} = 0.023(c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (4)$$

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

As in the case of hardness values, the toughness values were derived from the average of five measurements. The toughness of 2.25CoAl-Al₂O₃ composite obtained by this method of calculation is 6.5 MPa · m^{1/2}. Typically, one to three additional cracks were observed to propagate from the indentation corners as shown in Fig. 10(a).

The fracture toughness of Al₂O₃ with a grain size of 4.5 μm is reported as 4 MPa · m^{1/2} [1]. The fracture toughness of the 2.25CoAl-Al₂O₃ composite is higher than that of monolithic Al₂O₃. A crack propagated in a deflective manner (↑) in Fig. 10(b). The enhanced fracture toughness of 2.25CoAl-Al₂O₃ composite is believed that CoAl and Al₂O₃ in the composite may deter the propagation of cracks and CoAl and Al₂O₃ have nanostructure phases.

Fig. 11 shows the cell viability of 2.25CoAl-Al₂O₃ composite, which is measured by the CCK-8 assay. The CCK-8 assay is one of the most convenient methods that use highly water-soluble tetrazolium salt. By adding tetrazolium to media, we can quantify cell viability, as tetrazolium would change specific color, reacted by the dehydrogenase of mitochondria. The value of the cell viability regarding the 2.25CoAl-Al₂O₃ composite was of similar value compared to that of Ti, which is widely known to be used for *in vivo* materials.

Conclusions

The nanopowders of CoAl and Al₂O₃ were synthesized from Co₃O₄ and Al powders by high energy ball milling.

By using HFIHS, the nanostructured 2.25CoAl-Al₂O₃ composite was fabricated from the milled powder. The relative density of the composite was 98% and the average grain sizes of CoAl and Al₂O₃ in composite sintered to 1500 °C are 53 and 51 nm, respectively. The hardness and fracture toughness of the composite were 1030 kg/mm², 6.5 MPa·m^{1/2}, respectively. The fracture toughness of the 2.25CoAl-Al₂O₃ composite is higher than that of monolithic Al₂O₃. The enhanced fracture toughness of 2.25CoAl-Al₂O₃ composite is believed that CoAl and Al₂O₃ in the composite may deter the propagation of cracks and CoAl and Al₂O₃ have nanostructure phases. The cell viability portion of the composite was higher than 90%, which means little of the toxicity.

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