Mechanochemical Synthesis and Rapid Consolidation of Nanocrystalline Al2O3–2.25Co Composite by High-Frequency Induction Heating and Its Mechanical Properties

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This study focused on synthesizing nanopowders of Co and Al2O3 from Co3O4 and Al powders and fabricating nanocrystalline Al2O3 reinforced Co composite to improve its mechanical properties. Nanopowders of Co and Al2O3 were synthesized from Co3O4 and Al by high-energy ball milling. A highly dense nanostructured 2.25Co–Al2O3 composite was consolidated by high-frequency induction heated sintering method within 3 min from the mechanically synthesized powders (2.25Co–Al2O3) under the 80 MPa pressure. The advantage of this process is that it allows for very quick densification to near theoretical density and prohibits grain growth in nanostructured materials. The grain sizes of Co and Al2O3 in the composite were calculated. And the average hardness and fracture toughness values of nanostuctured Co–Al2O3 composite were investigated. [doi:10.2320/matertrans.M2013008]

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1. Introduction

Metal-Ceramic composite has the advantage of high specific modulus, good strength-to-weight ratio, high fatigue strength, good temperature stability, high wear resistance, etc. In addition, metal matrix composites combine metallic properties (ductility and toughness) with ceramic characteristics (high hardness and modulus).

Generally, ceramics are difficult to bond to metals due to their differing physical, chemical, electrical and mechanical properties. However, using high energy ball milling method, Co and Al2O3 powders were synthesized from Co3O4 and Al. Therefore, mechanical properties of Metal-Ceramic composite will be improved both by combining properties of metal and ceramic and by making a good bonding at interface of metal and ceramic from the reaction of solid state replacement.

In these days, 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. 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. 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. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 500 nm or larger during the conventional sintering. 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 3 min, has been shown to be effective in achieving this goal.

The purpose of this work is to produce nanopowders of Co, Al2O3 and dense nanocrystalline 2.25Co–Al2O3 composite within 3 min from mechanically synthesized powders (2.25Co–Al2O3) using this high-frequency induction heated sintering method and to evaluate its grain size and mechanical properties (hardness and fracture toughness).

2. Experimental Procedures

Co3O4 (99+% , <5 µm, ALDRICH) and Al (99%, 38 µm, CERAC) powders were used to synthesize Co and Al2O3 as raw materials. These starting powders were mixed with WC ball under Ar gas atmosphere by high energy ball milling method for 10 h and the weight ratio of ball-to-powders was 30:1.

The milled powders were inserted in a graphite die (outside diameter, 35 mm; inside diameter, 10.5 mm; height, 40 mm) and then introduced into the high frequency induction heated sintering system made by Eltek in South Korea shown schematically in Refs. The four major stages in the sintering are as follows. The system was evacuated (stage 1) and a uniaxial pressure of 80 MPa was applied (stage 2). A induced current was then activated and maintained to 1000°C 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. Temperature was measured by a pyrometer focused on the surface of the graphite die.

The apparent densities of the sintered sample were measured by the Archimedes method and the relative densities were calculated from dividing apparent density by theoretical density. The theoretical density of the 2.25Co–Al2O3 composite were calculated from multiplying the vol% with...
of Co by the density of Co and the vol% of Al$_2$O$_3$ by the density of Al$_2$O$_3$. Compositional and micro structural analyses of the products which were polished were made through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). The atom arrays of the composite prepared by focused ion beam were investigated by HRTEM accelerated with 200 kV. Vickers hardness was measured by performing indentations at load of 10 kgf and a dwell time of 15 s on the sintered samples.

The Grain size was calculated by Suryanarayana and Grant Norton’s formula,$^\text{11}$

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

where $B_s$ is the full width at half-maximum (FWHM) of the diffraction peak after instrumental correction; $B_{\text{crystalline}}$ and $B_{\text{strain}}$ are FWHM caused by small grain size and internal stress, respectively; $k$ is constant (with a value of 0.9); $\lambda$ is wavelength of the X-ray radiation; $L$ and $\eta$ are grain size and internal strain, respectively; and $\theta$ is the Bragg angle. The parameters $B_s$, $B_{\text{crystalline}}$, and $B_{\text{strain}}$ follow Cauchy’s form with the relationship: 

$$B_s = B_{\text{crystalline}} + B_{\text{strain}}$$

where $B_s$, $B_{\text{crystalline}}$, and $B_{\text{strain}}$ are FWHM of the broadened Bragg peaks and the standard sample’s Bragg peaks, respectively.

3. Results and Discussion

The interaction between 3 Co$_3$O$_4$ and 8 Al, i.e.,

$$3\text{Co}_3\text{O}_4 + 8\text{Al} \rightarrow 9\text{Co} + 4\text{Al}_2\text{O}_3$$  \hspace{1cm} (2)

is thermodynamically feasible.$^{12-15}$

Figure 1 shows XRD patterns of staring materials and powders milled by high energy ball milling for 10 h. We can find Co and Al$_2$O$_3$ peaks in the XRD pattern (C) in Fig. 1 that indicate that Co and Al$_2$O$_3$ were synthesized during high energy ball milling from Co$_3$O$_4$ and Al powders. The average grain size of Al$_2$O$_3$ measured by C. Suryanarayana and M. Grant Norton’s formula was about 33 nm. SEM image and X-ray mapping of milled powders are shown in Fig. 2. In these mapping images such as (a) oxygen, (b) aluminum, and (c) cobalt, Al and O are detected at the same position and mapping images of Al and O are different from that of Co. Therefore, we can consider that Co and Al$_2$O$_3$ synthesized from Co$_3$O$_4$ and Al during the ball milling, as well.

A variation of shrinkage displacement and temperature with heating time during densification of 2.25Co–Al$_2$O$_3$ composite is shown in Fig. 3. The application of the induced current resulted in shrinkage due to consolidation. As the induced current was applied, shrinkage displacement slowly increased up to 700°C and then abruptly increased above the temperature. The longer the induced current was applied, the more the specimens shrunk. Figure 4 shows XRD patterns of the high-energy ball milled powder heated to 1000°C. Co and Al$_2$O$_3$ peaks are detected. The structure parameters, i.e., the average grain sizes of Co and Al$_2$O$_3$ in composite sintered from high energy ball milled powder obtained from X-ray data in Fig. 4 by Suryanarayana and Grant Norton’s formula, are 147 and 79 nm, respectively. And the relative density of the 2.25Co–Al$_2$O$_3$ composites was about 96%. Its BSE image of 2.25Co–Al$_2$O$_3$ composite sintered at 1000°C from high energy ball milled powders is shown in Fig. 5. In this image, dark regions are Al$_2$O$_3$ and bright regions are Co due to mass contrast. Figure 6 shows high-resolution TEM image of 2.25Co–Al$_2$O$_3$ composite. We can find that microstructure consists of nanograins.

Vickers hardness measurements were made on polished sections of the 2.25Co–Al$_2$O$_3$ composite using a 10 kgf load and 15 s dwell time. The calculated hardness value of 2.25Co–Al$_2$O$_3$ composite was 7.9 GPa. This value represents an average of five measurements. Typically, one to three additional cracks were observed to propagate from the indentation corner. 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 used by Anstis et al.$^{16}$ which is

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

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 Young’s
modulus of the 2.25Co–Al2O3 composite has not reported. So, in order to calculate the Young’s modulus of the 2.25Co–Al2O3 composite, it was estimated by the rule mixtures for the 0.63 volume fraction of Al2O3 and the 0.37 volume fraction of Co using $E(\text{Al}_2\text{O}_3) = 336$ GPa$^6$ and $E(\text{Co}) = 209$ GPa.$^{17}$ As in the case of hardness values, the toughness values were calculated from the average of five measurements. The average toughness values of 2.25Co–Al2O3 were 5.5 MPa·m$^{1/2}$. Indentations with large enough loads produced median cracks around the indent. The hardness and fracture toughness of Al2O3 with grain size of 4.5 µm are reported as 17.7 GPa and 4 MPa·m$^{1/2}$, respectively.$^{18}$ The hardness of 2.25Co–Al2O3 composite is lower than that of monolithic Al2O3 but the fracture toughness is higher than the value of Al2O3 due to addition of ductile Co.
4. Conclusions

Nanopowders of Co and Al\textsubscript{2}O\textsubscript{3} were synthesized from Co\textsubscript{3}O\textsubscript{4} and Al by high-energy ball milling. Using the high frequency induction heated sintering method, the densification of nanostructured 2.25Co–Al\textsubscript{2}O\textsubscript{3} composite (volume fraction of Al\textsubscript{2}O\textsubscript{3}: 0.63, volume fraction of Co: 0.37) was accomplished from mechanically alloyed powders of Co and Al\textsubscript{2}O\textsubscript{3}. Nearly full densification can be achieved within duration of 3 min. The relative density of the composite was 96\% for the applied pressure of 80 MPa and the induced current. The average grain sizes of Co and Al\textsubscript{2}O\textsubscript{3} prepared by high frequency induction heated sintering method were about 147 and 79 nm, respectively. The average hardness and fracture toughness values obtained were 7.9 GPa and 5.5 MPa·m\textsuperscript{1/2}, respectively.

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