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Short communication

Rapid consolidation of a nanostructured Mo-reinforced ZrO_2 composite

In-Jin Shon

Division of Advanced Materials Engineering, The Center for Hydrogen Fuel Research, Chonbuk National University, 664-14 Deokjin-dong 1-ga, Deokjin-gu, Jeonju, Jeonbuk 561-756, Republic of Korea

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ABSTRACT

MoO_3 and Zr powders at a molar ratio of 1:1.5 were milled using a high-energy ball mill. The mixture powders produced Mo and ZrO_2 powders through a solid replacement reaction ($MoO_3 + 1.5Zr \rightarrow Mo + 1.5\ ZrO_2$). The synthesized powders were consolidated via pulsed current activated sintering (PCAS) within 2 min. The mechanical properties (hardness and fracture toughness) and microstructure were then evaluated. Both the hardness and fracture toughness of the Mo-1.5 ZrO_2 composite were higher than those of monolithic ZrO_2.

1. Introduction

ZrO_2 is considered as a candidate material for use as the matrix of inert matrix fuels in nuclear power plants due to its high melting point, resistance to irradiation and excellent chemical stability. However, pure ZrO_2 has limitations in its low thermal conductivity and inadequate fracture toughness at room temperature. These problems can be addressed by adding a reinforcement with a high thermal conductivity and by fabricating nanostructured composites with improved thermal conductivity and fracture toughness [1,2]. Specifically, Mo has a high thermal conductivity and melting point. Hence, the physical properties of a microstructure consisting of Mo and ZrO_2 may be suitable for use as structural material in nuclear power plants.

Nanostructured materials can be produced with improved mechanical properties (hardness and fracture toughness) [3,4]. Nanopowders have been fabricated using several methods including wire explosion, co-precipitation and high-energy ball milling. Nevertheless, the grain size in sintered materials becomes much larger than that in the raw powders due to rapid grain growth during conventional with high temperatures for long periods of time. Therefore, preventing the grain growth during sintering is important to produce the desired nanomaterials. In this respect, pulsed current activated sintering (PCAS) completes consolidation completed within a short period of time at a low temperature, so it can be used to achieve this goal [5,6].

In this study, Mo and ZrO_2 nanopowders were fabricated using high-energy ball milling, and the nanostructured Mo-ZrO_2 composite was then made via PCAS. The mechanical properties and microstructure were then evaluated.

2. Experimental procedures

MoO_3 and Zr powders at a molar ratio of 1:1.5 were mixed for 10 h under an argon atmosphere using a high-energy ball mill (a Pulverisette-5 planetary mill). WC-7% Co hard materials with 10 mm in diameter were used as balls.

The milled powder was placed in a graphite die and was sealed with upper and lower graphite punches. The schematics of the rapid sintering (pulsed current activated sintering) equipment are shown in Ref. [7]. 80 MPa of uniaxial pressure and 2000A of pulsed current were applied to the powder under a 20 Pa vacuum. The power was maintained at 1200 °C and was then turned off without a holding time. At the end of the process, the sample was allowed to cool to room temperature.

The grain sizes of the ZrO_2 and Mo were calculated by Suryanarayana and Grant Norton's equation [8]. After evaluating the volume of the sintered specimen using Archimedes' method, the relative density of the specimen was calculated. The microstructure and phase information of the Mo-ZrO_2 composite were observed via Fe-SEM and X-ray diffraction (XRD). The Vickers hardness and fracture toughness of the sintered samples were calculated, using the indent and crack length on a specimen at a load of 20 kg_f.

E-mail address: ijshon@chonbuk.ac.kr.

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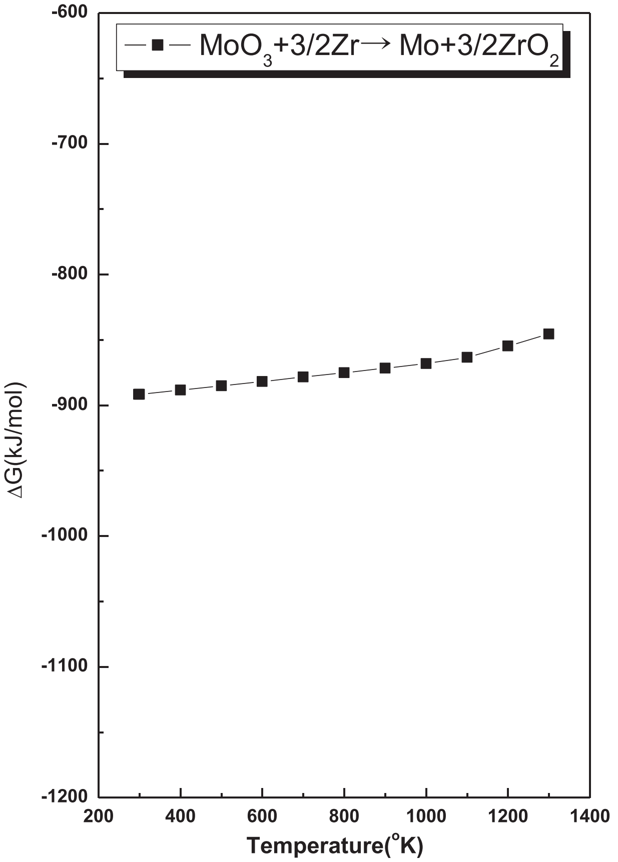

Fig. 1. The Gibbs free energy variation with temperature by interaction of MoO_3 with 1.5 Zr.

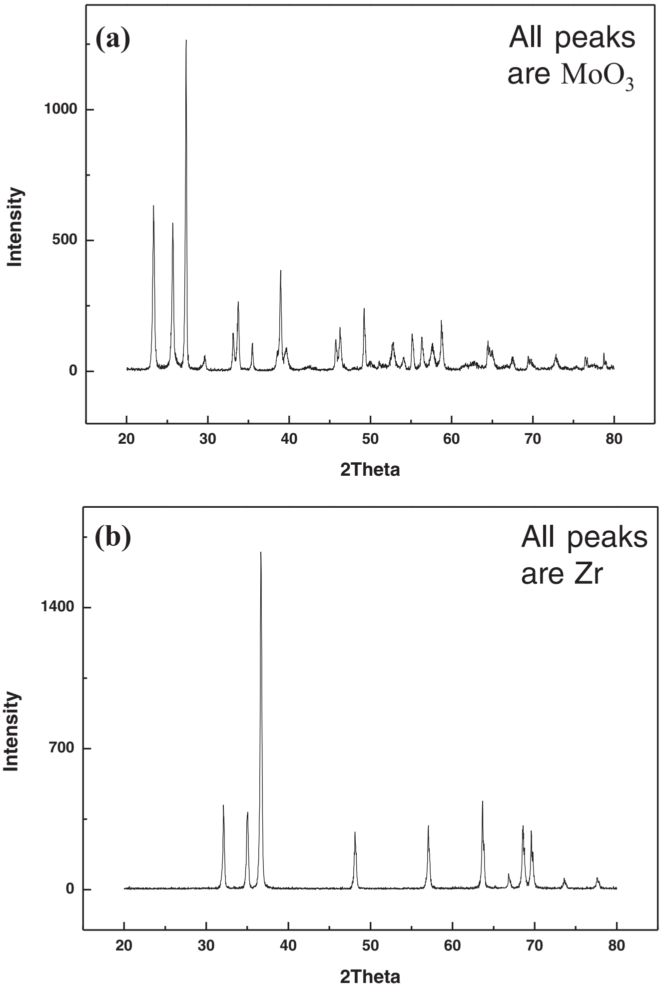

Fig. 2. XRD patterns of raw materials: (a)Molybdenum trioxide, (b) Zirconium.

3. Results and discussion

The interaction between MoO_3 and Zr, i.e.:

$$MoO_3 + 1.5\ Zr \rightarrow Mo + 1.5\ ZrO_2 \qquad (1)$$

is thermodynamically feasible, as shown in Fig. 1.

Fig. 2 indicates the XRD patterns of the raw powders. In Fig. 2(a) and (b), only MoO_3 and Zr peaks were detected, respectively. FE-SEM images of molybdenum trioxide and zirconium powders are shown in Fig. 3. The powders have an irregular shape. Fig. 4 shows the XRD pattern of the milled powders. Individual Mo and ZrO_2 peaks were detected after milling, which indicates that reaction (1) occurred during the high energy ball milling. The full width at half-maximum (FWHM) of the diffraction peak in Fig. 4 is more broad due to the refinement of the powders and strains. Recently, the direct reduction of several metal oxides with zirconium has been achieved during high-energy ball milling [9,10]. The synthesis can be explained by the kinetic point. A high-energy ball milling treatment allows the control of the powder microstructure, indeed, high-energy ball milling produces finer crystallites, more strain, and defects. The synthesis of high-energy mechanically milled powder is therefore faster than that of unmilled powder due to the increased reactivity, internal and surface energies, surface area, and diffusion routes (contact points of powders) for atomic diffusion of the high-energy milled powder, and they contribute to its so-called mechanical activation [11–13].

Fig. 5 shows the plot of B_r cosθ versus sinθ to calculate the grain size of the Mo and ZrO_2. The grain sizes of these were 15 and 24 nm, respectively. FE-SEM and EDS analyses of the milled powders are shown in Fig. 6. The mixture powders consist of very fine particles and have some agglomeration. In EDS, only Mo, Zr and O peaks were detected.

Fig. 7. shows variations in the temperature and shrinkage displacement with the heating time during pulse current activated sintering of the MoO3 + 3/2Zr powder milled via high energy ball milling for 10 h. The milled powder was sintered using PCAS at 1200 °C within two minutes. As the pulsed current was applied to the powder and die, thermal expansion appears at up to 5 s of heating time, and the shrinkage displacement abruptly increases above that of the heating time. The variation in the shrinkage is nearly constant at above 1180 °C, which indicates that the sample with a nearly full density was achieved at that temperature.

Fig. 8 shows the X-ray diffraction pattern of the specimen sintered to 1200 °C in which only Mo and ZrO_2 peaks are detected. The plot of B_r cosθ versus sinθ used to evaluate the grain sizes of Mo and ZrO_2 is shown in Fig. 9. The average grain sizes of Mo and ZrO_2 in the sintered composite are 72 and 44 nm, respectively, as obtained using X-ray data in Fig. 8. FE-SEM images and X-ray mappings of the specimen sintered