Enhanced Thermal Conductivities of ZrO_2 Pellets Reinforced with Mo Wires or Powder

Joon Hui Kim, Soon H. Hong, Ho Jin Ryu*
Korea Advanced Institute of Science and Technology: 291 Daehak-ro, Yuseong, Daejeon, Republic of Korea 305-701
**corresponding author: hojinryu@kaist.ac.kr*

1. Introduction

Research to improve the low thermal conductivity of UO_2 pellets has been pursued long time. The fabrication of thin tungsten or molybdenum channels at the grain boundaries of UO_2 pellets via sintering WO_3/UO_2 or MoO_3/UO_2 mixture compacts under a reducing atmosphere have been reported [1-3].

Considering the reported results, a promising concept for increasing the thermal conductivity of UO_2 is proposed by employing 2D or 3D networks of thermally conducting phases inside the oxide pellets. But there is not enough systematic results using high thermal conductivity 2D or 3D network structures. Theoretically high porosity metal foams and nanowire networks can be used as the 3D network preforms in the powder processing of UO_2-based composite pellets. ZrO_2 which has a thermal conductivity as low as UO_2 is used for the experiment while its chemical and microstructural evolution might be different from those of UO_2. And since UO_2 pellets are fabricated at high temperatures above 1700℃, the first requirement for the reinforcement network metal should be the high temperature stability. Among the refractory metals, Mo has significantly high thermal conductivity (138 W/mK).

2. Experimental Procedures

Zirconium oxide powder and Molybdenum powder was purchased from Sigma - Aldrich. Mo wire mesh was purchased from Goodfellow (UK). Mo wire's diameter was 70 μm diameter and the aperture of the mesh was 440 μm. Since the particle size of ZrO_2 powder is smaller than Mo mesh diameter, mixing ZrO_2 with Mo mesh was done by conventional mixing with 5 vol % (8.4 wt%) in the composite. Mixing ZrO_2 with Mo powder was done with conventional mixing.

To produce composite pellets, spark plasma (SPS) sintering was used. Spark plasma sintering is very adaptable to be used in high temperature processing and is very fast compared with other conventional sintering processes. Dr. SINTER LAB Model: SPS-515S (Japan) was used for the SPS process. With uniform distribution of Mo mesh in ZrO_2 powder in 13 mm diameter graphite mold, SPS machine loads 50 MPa axial pressure. The SPS process starts at room temperature to the maximum sintering temperature 1700℃ and are held for 10 minutes in 1700℃ in a vacuum of 10^{-3} torr under a pressure of 50 MPa.

The sintered densities of composite pellets were measured using the Archimedes method and scanning electron microscopy (SEM) was used to observe cross sections of polished composite pellets. The chemical interactions of ZrO_2 with Mo mesh and Mo powder were analyzed with energy dispersive X-ray spectroscopy (EDS). The components of composite pellets were analyzed with X-ray diffractometry (XRD). The thermal conductivities of the composite pellets were obtained through measuring the thermal diffusivities, specific heat capacities, and thermal expansion coefficients at room temperature, 500℃, 800℃, and 1100℃. The laser flash method was used to measure the thermal diffusivities; the specific heat capacities of composite pellets were calculated using differential scanning calorimetry (DSC); and the densities of the sintered samples were calculated using the thermal expansion coefficients with measured density in 25℃.

3. Results

According to the z-axis displacement of the SPS press punch on the Mo added ZrO_2 sample compact, Mo-wired ZrO_2 and Mo-powder added ZrO_2 compacts began densification at approximately 970℃ and the densification continued until 1200℃. After 1200℃, thermal expansion dominated the axial displacement of the press punch until 1700℃. Fig. 1 presents the microstructure of the Mo-wired ZrO_2 composite pellet after sintering and Fig. 2 presents the XRD result of the Mo powdered ZrO_2 composite pellet after sintering. The spark plasma sintered Mo-wired ZrO_2 composite pellet is composed of grains with diameters of 20–30 μm as shown in the Fig. 1 and Mo-powder added ZrO_2 composite pellet's XRD shows that Mo and ZrO_2 did not react.

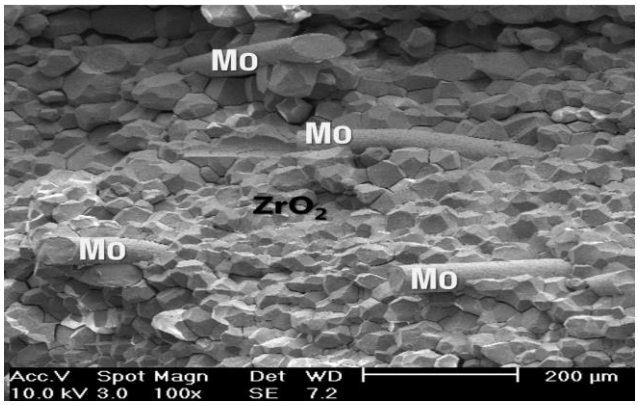

Fig. 1. A SEM image of fractured surface of a Mo wire reinforced ZrO_2 composite pellet

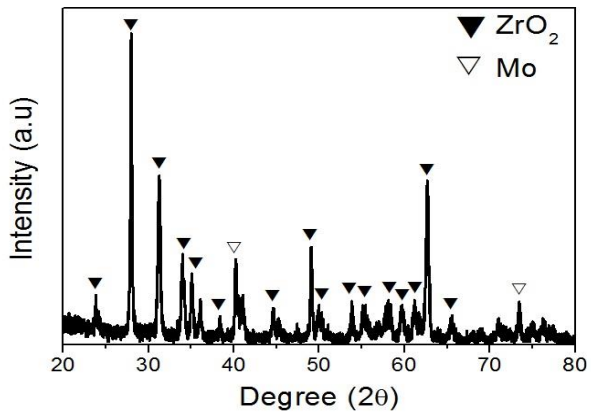

Fig. 2. An XRD image of fractured surface of a Mo powder added ZrO_2 composite pellet

The distribution and volume fraction of the Mo reinforcement is important factors for improving the thermal properties of ZrO_2 composite pellets. In this study, the volume fraction for all Mo reinforcements is fixed as 5vol%. Although uniform distribution of wire-type reinforcement is hard to obtain, the microstructure image with SEM shows uniformly distributed Mo wires in Fig. 1. With a special preform of wire of Mo reinforcement, Mo-wire reinforced ZrO_2 can be fabricated more easily.

The thermal conductivity of the ZrO_2 composite pellets were obtained using the laser flash method that measures the thermal diffusivity of the materials. The measured thermal diffusivity was converted to thermal conductivity using the following equation:

$$k(T) = a(T) \cdot c_p(T) \cdot \rho(T) \qquad (1)$$

where k is the thermal conductivity, a is the thermal diffusivity measured using the laser flash method, c_p is the specific heat measured using differential scanning calorimetry, and ρ is the density at the measuring temperature.

The thermal conductivity of the pure ZrO_2, Mo-wire-mesh added ZrO_2, Mo-powder added ZrO_2, Mo-fiber added ZrO_2, and Mo-rolled-wire-mesh added ZrO_2 composite pellets at 1100℃ were 2.8 W/m-K, 3.0 W/m-K, 3.0 W/m-K, 3.0 W/m-K and 3.5 W/m-K respectively. The thermal conductivity of the Mo reinforcement added ZrO_2 composite pellets except Mo-rolled-wire-mesh added ZrO_2 increased by 7.5%. Thermal conductivity of the Mo-rolled-wire-mesh added ZrO_2 increased by 25% compared with pure ZrO_2. Fig. 3 presents the measured thermal conductivities of ZrO_2 composite pellets at room temperature, 500℃, 800℃, and 1100℃.

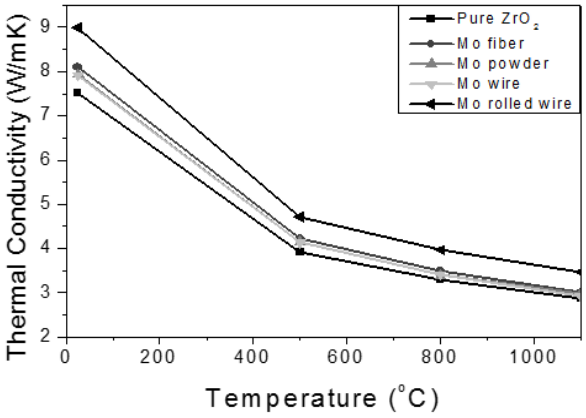

Fig. 3. Thermal conductivities of ZrO_2 composite pellets

On the thermal conductivity of the Mo-added ZrO_2 samples with the same volume fraction of Mo reinforcement, the direction and connectivity of the reinforcement shows significant impact. When the thermal conductivities of ZrO_2 pellets with the stacked Mo wire mesh and the rolled Mo wire mesh, the latter shows higher thermal conductivity because the network of wire mesh enhance the heat transfer from top to bottom of the ZrO_2 composite pellet, while the 2D wire mesh layers are disconnected along the heat transfer axis. The rolled wire mesh reinforcement used in this study is a more similar form to the 3D network reinforcement.

4. Conclusions

In order to increase the thermal conductivity of ZrO_2, which is used for a surrogate material for UO_2 fuel, ZrO_2 composite pellets with the addition of Mo mesh, Mo fiber and Mo powder were fabricated by spark plasma sintering. Thermal conductivity measurement results of composite pellets showed that adding 2D network Mo mesh, 3D network Mo mesh and Mo powder increased thermal conductivity of ZrO_2 composite pellets. But with the same volume percent of Mo, 3D network of Mo mesh showed the best result.

REFERENCES

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