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Simple fabrication process for CeO_2–MgO composite as surrogate for actinide-containing target for use in nuclear fuel

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Abstract

A simple fabrication process for CeO_2–MgO composite as surrogate for actinide-containing target for use in nuclear fuel has been developed. The process is adaptable to present fuel manufacturing technology. The manufactured target has good characteristics, e.g. high density, good appearance, free of reaction phase, etc. In particular, the shape of CeO_2 particles is nearly spherical and their dispersion is homogeneous. Thermal conductivity of the present target can be satisfactorily expressed by using Schulz's equation when CeO_2 spheres are assumed as ideal with no anisotropy. These results indicate that the present simple process gives a composite which is comparable to that fabricated in a complicated process such as an advanced sol–gel supported process.

Keywords: A. Mixing; B. Composites; E. Nuclear applications; Powder metallurgy

1. Introduction

Minor actinides (MAs), such as neptunium (Np), americium (Am) and curium (Cm), are of special concern in nuclear power generation because of their high radioactivity and lasting radiotoxicity. MAs are generated by irradiation of nuclear fuel, which is represented by uranium dioxide (UO_2), in nuclear reactors. Presently, MAs are separated from spent nuclear fuel together with fission products (FPs), which also have high radioactivity. After the separation, they are generally treated as radioactive waste and disposed off deep underground. The MAs can cause a long-term environmental burden owing to their high and lasting radiotoxicity.

Recently, technology for transmutation of MAs to stable and less radiotoxic nuclides by neutron irradiation in a reactor has been pursued in order to reduce the environmental burden and allow effective use of nuclear resources [1,2]. In this technology, MAs are included in a columnar pellet made of sintered ceramics for the irradiation in the reactor, as in normal nuclear fuels. One promising candidate for the MA-containing ceramic form is a composite of MA compound and inert matrix; this is called a ‘‘target’’ and it is schematically shown in Fig. 1 [3]. MA compound is dispersed into the inert matrix as spherical particles having diameters up to about 300 μm. One purpose of making such a structure is to improve thermal properties by combining the MA compound with the inert matrix that has relatively better thermal properties than MA compound. The other purpose is to suppress irradiation damage of the matrix that leads to degradation of thermal properties, as also shown in Fig. 1(a). The irradiation damage is mainly caused by the FP fragments that have a large energy and only a several μm range in the solid. MgO is considered one of the most promising candidates for the inert matrix mainly owing to its high melting temperature and thermal conductivity that can lead to lower operating temperature and large safety margin in the event of an accidental melting of the target [3]. However, these purposes can be achieved when the following conditions for the manufactured target are fulfilled; i.e. homogeneous dispersion and good spherical shape of the MA compound particles. Moreover, the fabrication process should be as simple as possible, since

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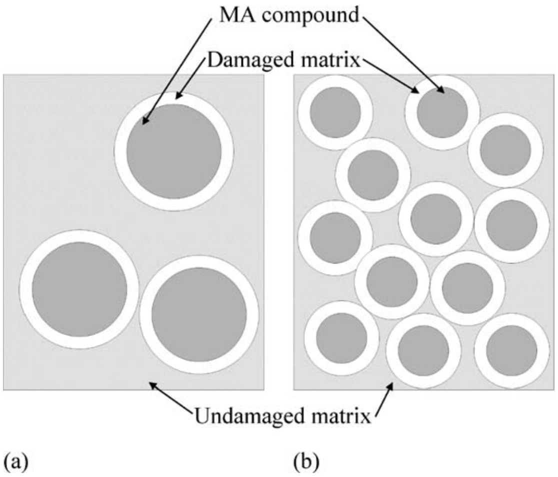

Fig. 1. Schematic view of MA-containing composite target for use in nuclear fuel; (a) target with large MA particle (about φ 300 μm), (b) target with small MA particle.

MAs have to be handled remotely inside an air-tight and shielded apparatus owing to their high radioactivity. For fabrication of the MA-containing target, an advanced method which consists of MA sphere preparation by a sol–gel supported method and powder metallurgy has been proposed [4,5]. Good spherical shape can be obtained by this method, but, the apparatus is complicated which leads to difficulties in maintenance and related technologies have to be optimized and/or established.

In this study, a surrogate target which is a combination of CeO_2 as a substitute for MA compound with MgO as the inert matrix is fabricated by a simple process based on presently used commercial manufacturing technology for nuclear fuel. Cerium is often used as a typical substitution of actinides due to physico-chemical similarity between Ce and actinide elements, especially Pu. The process consists of powder treatment in a rotating milling machine, uni-axial pressing, and finally pressureless sintering in an inert atmosphere. Thermal conductivity of fabricated target is measured and results are discussed from the viewpoint of the validity of the present fabrication process for the MA target.

2. Experimental

Fig. 2 shows the fabrication process for the CeO_2-MgO target. CeO_2 powder (Shinetsu kagaku high-grade, 99.9% purity) and 3 wt.% of PVA binder were put into a plastic bottle and mixed (12 h) with ethanol by mechanical rotation with yttria-stabilized zirconia (YSZ) balls. The mixed slurry of CeO_2 was dried under a reduced pressure atmosphere in a vibration fluid-bed dryer. The dry CeO_2 was then compacted into a columnar pellet by uni-axial pressing (pressure, 30 MPa). The CeO_2 compact was gently crushed in an agate mortar and sieved to obtain spheres. CeO_2 spheres with diameters between 120 and 355 μm were obtained. Pre-

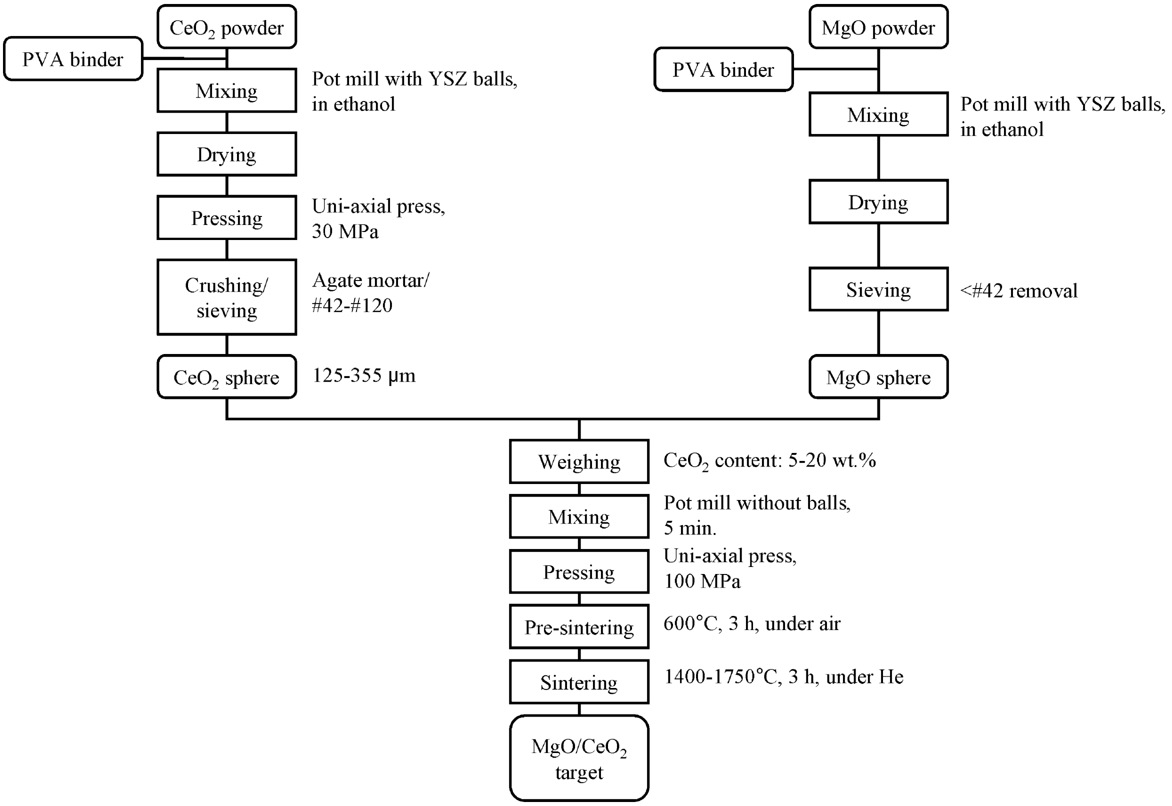

Fig. 2. Fabrication procedure for CeO_2–MgO composite as surrogate for MA-containing target.

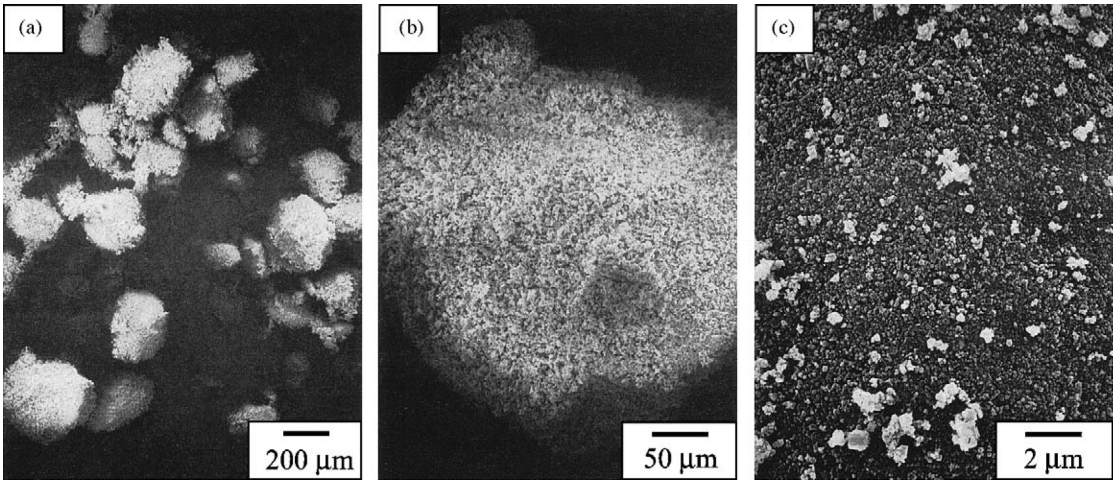

Fig. 3. SEM images of CeO_2 spheres prepared by crushing and sieving of the compact; (a), (b) spheres forming a nearly spherical shape, (c) agglomerate of sub-micron particles.

sintering of the spheres which is usually done in other target fabrication processes [6] was omitted in the present process. This omission could cause a problem that the prepared spheres would be fragile, but, in turn, there was the following advantage: suppression or elimination of crack occurrence which is caused by the difference in densification behaviors between pre-sintered CeO_2 and MgO compact. Consequently, the gap between the sphere and matrix, which causes poor thermal conductivity of the target, could be reduced or closed by the small difference in densification behaviors between them.

To avoid the destruction of prepared spheres, the pre-treatment procedure for MgO powder was added before mixing with CeO_2. MgO powder (Ube materials 1000A, 99.99% purity) was wet-milled in the same way as CeO_2 powder. MgO slurry was then spray-dried by a rotating disk atomizer (4000–5000 rpm) to make micro spheres having a diameter of about 50 μm. This procedure was added so as to enhance the homogeneous mixing of CeO_2 and MgO within a short mixing time, which aims at avoiding destruction of CeO_2 spheres. Pre-determined amounts of CeO_2 and MgO spheres were weighed and mixed for only 5 min in the rotating milling machine. Content of CeO_2 was adjusted to 5, 10 and 20 wt.%. The mixed spheres were compacted into a columnar pellet (diameter, 6 mm) by uni-axial pressing (pressure,100 MPa). The compacts were then pre-sintered under air at 600 °C for 3 h to remove the organic PVA binder. Finally, sintering was carried out in He atmosphere for 3 h at pre-determined temperatures which ranged from 1400 to 1750 °C.

The sintered pellets were subjected to a series of examinations to characterize the target. An X-ray diffraction meter (Rigaku model RINT-2000) was used for the structural analysis with Cu Kα radiation. Visual inspection, SEM (Hitachi model S-800) and EDS (Philips model PV-9900) analyses were made regarding the shape and dispersion homogeneity of the CeO_2 spheres. Thermal conductivity was calculated from specific heat and thermal diffusivity. Thermal diffusivity was measured by the laser-flash method at ambient temperature (Kyoto-denshi model LFA-501).

3. Results and discussion

Fig. 3 shows SEM images of CeO_2 spheres prepared by crushing and sieving of the CeO_2 compact. Spheres form a nearly spherical shape (Fig. 3a and b) and they consist of an agglomerate of sub-micron particles (Fig. 3c). Density of the sintered CeO_2–MgO target as a function of sintering temperature is shown in Fig. 4. The densities increase with temperature until about 1600 °C, then saturate above this temperature. From this result, appropriate sintering temperature and time for acquiring dense pellets are decided to be 1700 °C and 3 h, respectively.

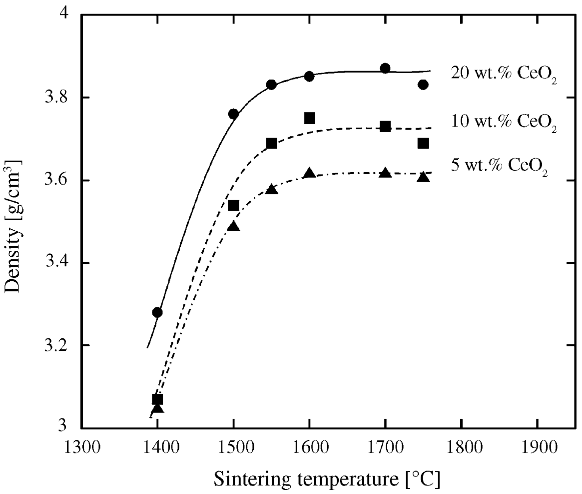

Fig. 4. Increasing tendency of the CeO_2–MgO target density as a function of sintering temperature.

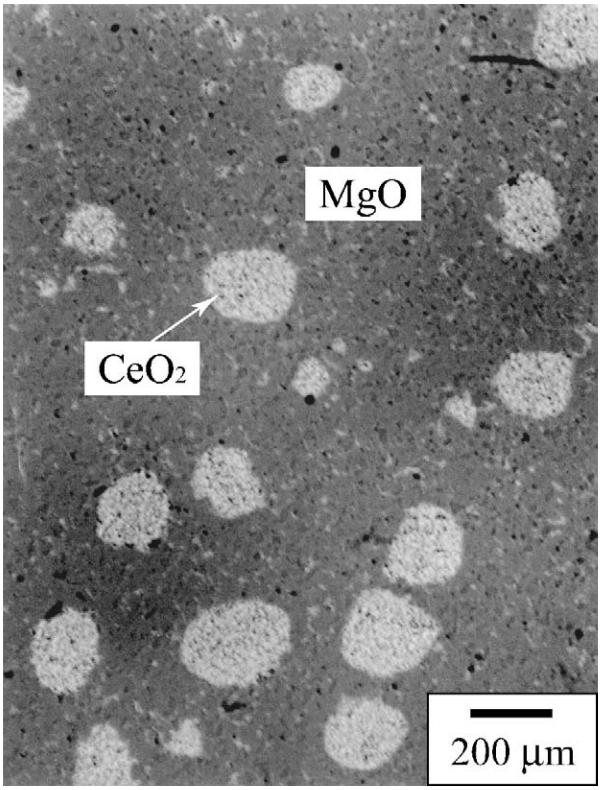

Fig. 5. Dispersion aspect of CeO_2 spheres into MgO matrix (20 wt.% CeO_2–MgO).

XRD results of the sintered target show peaks for only CeO_2 and MgO, and no other peaks derived from a reaction phase between the two components are observed, which indicates that the target is composed of a two-phase mixture as expected. Fig. 5 shows an optical microscopic image of the target cross section. Shape of CeO_2 particles is elliptic rather than spherical. Nevertheless, dispersion of CeO_2 spheres into MgO matrix is homogeneous and hardly any fragmented CeO_2 particles can be seen, although the mixing time of CeO_2 and MgO is only 5 min. In addition, hardly any cracks and gaps between CeO_2 spheres and MgO can be seen. This is achieved by the addition of the spray-dry treatment procedure for MgO powder.

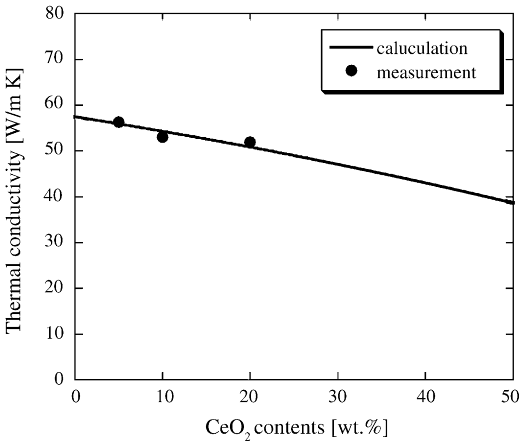

Fig. 6. Thermal conductivity of CeO_2–MgO target as a function of CeO_2 content.

Fig. 6 shows thermal conductivity of the CeO_2–MgO target as a function of CeO_2 content at ambient temperature. Calculated thermal conductivities obtained by using Schulz's method [7] are also shown there, as obtained by the following equations.

$$
\begin{aligned}
1-c_{\mathrm{D}}^{V} &= \left(\frac{\lambda_{\mathrm{M}}}{\lambda}\right)^{m}\frac{\lambda_{\mathrm{D}}-\lambda}{\lambda_{\mathrm{D}}-\lambda_{\mathrm{M}}}\left(\frac{\lambda+n\lambda_{\mathrm{D}}}{\lambda_{\mathrm{M}}+n\lambda_{\mathrm{D}}}\right)^{q}\\
m &= \frac{F(1-2F)}{1-(1-F)\cos^2\alpha-2F(1-\cos^2\alpha)};\\
n &= \frac{1-(1-F)\cos^2\alpha-2F(1-\cos^2\alpha)}{2F(1-\cos^2\alpha)+(1-F)\cos^2\alpha};\\
q &= \frac{F(1-2F)}{1-(1-F)\cos^2\alpha-2F(1-\cos^2\alpha)}\\
&\quad+\frac{(1-F)2F}{2F(1-\cos^2\alpha)+(1-F)\cos^2\alpha}-1
\end{aligned}
\tag{1}
$$

Here, λ, λ_{M} and λ_{D} are thermal conductivities of the composite (CeO_2–MgO), the matrix (MgO; 57 W/m K) and dispersed phase (CeO_2; 12 W/m K [8]), F and $\cos^2\alpha$ are shape and orientation factors for the dispersed sphere, and c_{D}^{V} is the volume fraction of dispersed spheres.

Experimentally determined thermal conductivities are corrected to those at theoretical densities for comparison. These corrections are made by using the following relationship when the pore shape is assumed as an ideal sphere.

$$\lambda_{\mathrm{D}}=\lambda_{\mathrm{P}}(1-P)^{-3/2} \tag{2}$$

Here, λ_{D} and λ_{P} are thermal conductivities of the dense material and the porous material, respectively, and P is porosity. Porosity is defined as $1-D_{\mathrm{R}}$, where D_{R} is the density of the target relative to the theoretical one. D_{R} is calculated by using the following equation.

$$D_{\mathrm{R}}=\frac{\rho_{\mathrm{C}}}{\rho_{\mathrm{M}}c_{\mathrm{M}}^{\mathrm{W}}+\rho_{\mathrm{D}}c_{\mathrm{D}}^{\mathrm{W}}} \tag{3}$$

Here, ρ_{C} is measured density of the composite (CeO_2–MgO), ρ_{M} and ρ_{D} are the theoretical densities of the matrix (MgO; 3.59 g/cm^3) and dispersed phase (CeO_2; 7.25 g/cm^3), respectively. $c_{\mathrm{M}}^{\mathrm{W}}$ and $c_{\mathrm{D}}^{\mathrm{W}}$ are weight fractions of the matrix (MgO) and dispersed phase (CeO_2), respectively. As can be seen in Eq. (3), it is assumed that relative densities to the theoretical one of MgO and CeO_2 are identical, and there are only two phases, MgO and CeO_2.

The thermal conductivities corrected to the theoretical densities are about 56, 53 and 52 W/m K for 5, 10 and 20 wt.% of CeO_2 content targets, respectively. It is seen that the thermal conductivity of target decreases with increase of CeO_2 content. Concerning the calculated and experimental values, agreement between them is good when the shape of

CeO_2 particles is assumed as ideal spheres ($F = 1/3$) and orientation of the spheres is isotropic ($\cos^2 \alpha = 1/3$), as shown in Fig. 6. This agreement implies that thermal conductivity of the present target is expected to be comparable with that of target fabricated by the sol–gel supported method, which can make almost ideal spheres. Thus the present fabrication process is valid in this aspect although it is simpler than the sol–gel supported one.

4. Conclusion

A simple process for the fabrication of CeO_2–MgO composite as surrogate for MA-containing target for the use in nuclear fuel was established. The process would be adaptable to present commercial manufacturing technology for the nuclear fuel. The fabricated target had good characteristics, e.g. high density, good appearance, free of reaction phase, etc. In particular, the shape of CeO_2 particles was nearly spherical and dispersion of the spheres was homogeneous. In addition, thermal conductivity of the present target could be expressed well by using Schulz's equation when CeO_2 spheres were assumed as ideal with no anisotropy. These results indicated that the present simple process gave target which was comparable to that of the more complicated, advanced sol–gel supported process.

Acknowledgements

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