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An investigation of the thermal conductivity of Cs_2MoO_4

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Abstract

The thermal diffusivity of 82.6% TD and 89.3% TD Cs_2MoO_4 was measured by the laser flash method and the thermal conductivity was calculated. The thermal conductivity of these Cs_2MoO_4 ranged from 0.3 to 0.5 W m^{-1} K^{-1}. The density dependence of the thermal conductivity was correlated based on the experimental values of these two densities and on the 94.3% TD specimen from the preceding study. The correlation of the thermal conductivity of Cs_2MoO_4 is $k = (1.0 - 1.848 \times P)/(1.0 - 1.848 \times P_{ref}) \times k_{ref}$, where $k_{ref} = 132.56/T + 0.03 + 3.2 \times 10^{-10} \times T^3$, $P_{ref} = 1.0 - 0.943 = 0.057$ and k and k_{ref} are the thermal conductivities (W m^{-1} K^{-1}) of Cs_2MoO_4 with the porosities P and P_{ref}, respectively, where P_{ref} is the porosity for the 94.3% TD Cs_2MoO_4. T is the temperature (K). This correlation is applicable for 82.6 to 94.3% TD Cs_2MoO_4 from 873 to 1023 K. © 1997 Elsevier Science B.V.

1. Introduction

Solid fission products (FP) and/or their chemical compounds have been observed in the fuel-cladding gap of mixed oxide fast reactor fuels at high burnup [1]. In order to understand the fuel performance at high burnup, it is necessary to have knowledge of the thermal properties of solid FPs and their compounds.

Cesium molybdate (Cs_2MoO_4) is considered to be one of the typical FP compounds in the fuel-cladding gap at high burnup. The thermal conductivity of 94.3% TD Cs_2MoO_4 from room temperature (RT) to 1073 K was previously reported by the present authors [2]. In the study, the temperature dependence of the thermal conductivity was mainly discussed and it was considered that the thermal conductivity might be affected by the phase transition from an orthorhombic to a hexagonal structure at 845 K [3,4].

The density of FP compounds in the fuel-cladding gap may be various. Therefore, the study of the thermal conductivity of Cs_2MoO_4 was continued to determine its density dependence.

In the present paper, both the thermal conductivities of 82.6 and 89.3% TD Cs_2MoO_4 from 873 to 1023 K and its density dependence are discussed.

2. Experimental

Two samples of Cs_2MoO_4 were prepared and used for determining the thermal conductivity. The preparation and measurement methods were identical to those used in the preceding study on the 94.3% TD Cs_2MoO_4 [2]. The sample disks were prepared from powder of Cs_2MoO_4 (99.9% purity) supplied by Soekawa Chemical Co. The disks were sintered in an argon atmosphere. The sintered disks are described as follows:

(1) 3.90 g/cm^3 (89.3% TD) and 9.8 mm diameter by 1.7 mm thick.

(2) 3.60 g/cm^3 (82.6% TD) and 9.8 mm diameter by 1.8 mm thick.

The results of the X-ray diffraction analysis (XRD) for the sintered samples of Cs_2MoO_4 indicated no change in the diffraction pattern by sintering.

The thermal diffusivity of each sintered sample was measured using the laser flash method, from 873 to 1023 K, in a vacuum at a pressure of $\sim 10^{-2}$ Pa. The samples were coated with graphite since Cs_2MoO_4 is transparent to the laser beam. The measurement was performed twice at each temperature and the average value was used as the measured value.

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The thermal conductivity (k) was calculated using the thermal diffusivity (α) obtained in this study by using the relation

$$k = \alpha C_p \rho. \quad (1)$$

The values of the specific heat capacity (C_p) were obtained from Refs. [3,4] and the densities (ρ) were those of test samples.

The uncertainty in the diffusivity data was estimated to be about 7% and the uncertainty in the thermal conductivity was considered to be nearly equal as described in the preceding study [2].

3. Results and discussion

3.1. Thermal diffusivity

The thermal diffusivities are plotted in Fig. 1. It can be seen that the thermal diffusivity increases with temperature from 873 to 1023 K. The temperature dependence of thermal diffusivity for both densities are similar.

The results of the XRD on each of the two samples showed that there was no change in diffraction pattern during measurement. Metallographical examinations using a scanning electron microscope (SEM) were also performed and no substantial structural changes such as cracking were observed.

3.2. Thermal conductivity

The thermal conductivities calculated from the thermal diffusivities are plotted in Fig. 2, including the data of 94.3% TD Cs_2MoO_4 from the preceding study [2].

Fig. 2 shows that the thermal conductivity increases with temperature in the range of measurements for all densities and that it is higher for the higher density specimen. Note that the thermal conductivity has a similar temperature dependence for all three densities.

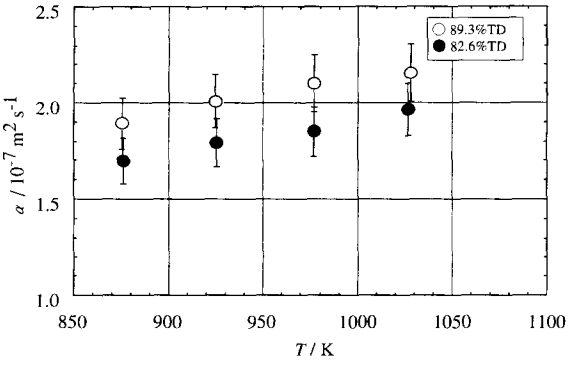

Fig. 1. Temperature (T) dependence of thermal diffusivities (α) of 82.6 and 89.3% TD Cs_2MoO_4.

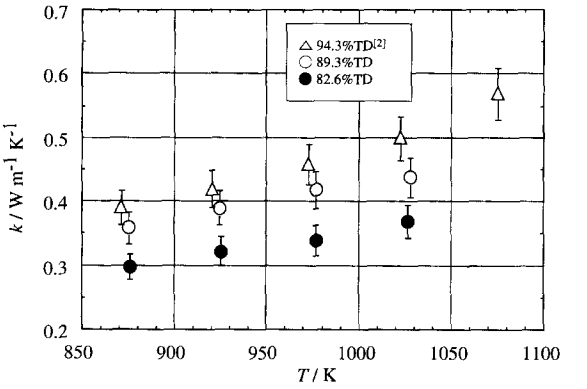

Fig. 2. Temperature (T) dependence of thermal conductivities (k) of 82.6, 89.3 and 94.3% TD Cs_2MoO_4.

3.3. Effect of porosity on thermal conductivity

The effect of porosity on thermal conductivity is shown in Fig. 3. The data are grouped into four temperatures, 873, 923, 973 and 1023 K.

The figure shows that the thermal conductivity of Cs_2MoO_4 seems to decrease linearly with increasing porosity at each temperature.

The effect of porosity on thermal conductivity is sometimes expressed as a simple correlation with linear porosity dependence as follows [5]:

$$k = k_f \times (1.0 - a \times P), \quad (2)$$

where k_f and k are the thermal conductivities of 100% TD and porous material with the porosity P, respectively, and a is a constant.

This correlation with porosity dependence is applied to the thermal conductivity of Cs_2MoO_4 and the constant a in Eq. (2) is evaluated.

Since the experimental value of thermal conductivity with 100% TD was not obtained, the constant a was

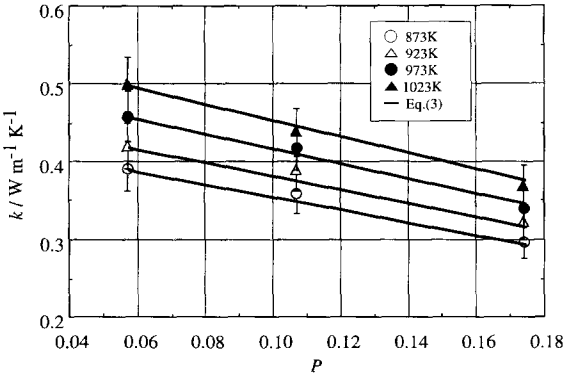

Fig. 3. Effect of porosity on thermal conductivities (k) of Cs_2MoO_4 at 873, 923, 973 and 1023 K. P is the porosity. The solid lines are the results of the calculations using Eq. (3).

determined by using the thermal conductivity of the 94.3% TD Cs_2MoO_4 sample as reference.

By using the ratio of thermal conductivity of the different densities to the 94.3% TD sample, the following equation was obtained:

$$k = (1.0 - a \times P)/(1.0 - a \times 0.057) \times k_{ref}, \quad (3)$$

where k_{ref} is the thermal conductivity of 94.3% TD Cs_2MoO_4 obtained in the preceding study [2].

The calculation was carried out using the least squares method to fit the obtained thermal conductivity data with the assumption that the constant a was independent of temperature. This constant a in Eq. (3) was found to be 1.848. The calculated thermal conductivities at the four temperatures using this value are shown as solid lines in Fig. 3. The deviation of experimental thermal conductivities from the lines calculated by Eq. (3) is less than the uncertainty in the experimental values. Therefore, it is considered that the constant a in Eq. (3) has a negligibly small temperature dependence. This implies that the assumption to set a as a constant is acceptably consistent with the experimental results.

3.4. Evaluation of thermal conductivity

In our preceding study, a simple correlation was determined for the thermal conductivity of 94.3% TD Cs_2MoO_4 from RT to 1073 K. This correlation was modified for the density dependence evaluated above.

The original correlation for 94.3% TD Cs_2MoO_4 is as follows [2]:

In the temperature below the transition temperature (845 K [3,4]):

$$k_{ref} = (78.242/T + 0.15 + 1.7 \times 10^{-10} \times T^3). \quad (4a)$$

In the temperature above the transition temperature:

$$k_{ref} = (132.56/T + 0.03 + 3.2 \times 10^{-10} \times T^3), \quad (4b)$$

where the first, second and third terms correspond to the contributions of the phonon, phonon plus electron and photon conduction, respectively, and T is the temperature (K). The thermal conductivity (k_{ref}) is expressed in units of W m^{-1} K^{-1}.

In the present study, the thermal conductivity was considered to have an identical correlation but two different sets of constants in the temperatures above and below the transition temperature, because the thermal conductivity was assumed to be discontinuous at the transition temperature, based on the following considerations [2]:

(1) The phonon conduction could be closely related to the crystal symmetry [5]. Since the crystal structure of Cs_2MoO_4 in the low temperature phase is an orthorhombic and that in the high temperature phase is a hexagonal, the symmetry is subjected to change due to the phase transition. Therefore, at the transition temperature of 845 K, the contribution of phonon conduction changes. As cited above, the second terms of Eqs. (4a) and (4b) correspond to the contribution of phonon plus electron conduction for each phase. Hence, the change in the value of the constant would occur not only in the first term of Eqs. (4a) and (4b) but also in the second term.

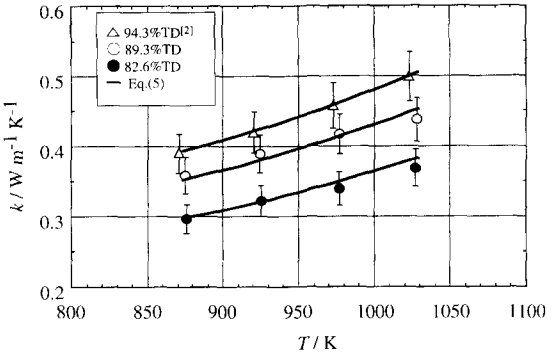

Fig. 4. Thermal conductivity (k) of Cs_2MoO_4 in the temperature from 873 to 1073 K and in the density from 82.6 to 94.3% TD. The solid lines are the results of the calculations using Eq. (5).

(2) The photon conduction could depend on the refractive index and transmittance [5]. Since the two properties are related to the crystal structures, they can also change due to the phase transition, resulting in the change of contribution of photon conduction. Therefore, there will also be a change in the constant in the third term of the above equation.

Consequently, the equation was rewritten for the thermal conductivity of Cs_2MoO_4 in the high temperature phase, in order to take account of the density dependence of thermal conductivity, as follows:

$$k = (1.0 - 1.848 \times P)/(1.0 - 1.848 \times P_{ref}) \times k_{ref}, \quad (5)$$

where $k_{ref} = 132.56/T + 0.03 + 3.2 \times 10^{-10} \times T^3$, $P_{ref} = 1.0 - 0.943 = 0.057$ and the thermal conductivity (k) is expressed in units of W m^{-1} K^{-1}.

The calculated values using Eq. (5) are shown as solid lines in Fig. 4. The correlation, Eq. (5), agrees well with the thermal conductivity data for each density.

Therefore, it is considered that Eq. (5) is an applicable correlation for the thermal conductivity of Cs_2MoO_4 from 82.6 to 94.3% TD over the temperature range 873 to 1023 K.

4. Conclusion

The thermal conductivity of Cs_2MoO_4 from 873 to 1023 K was studied taking the density as a parameter.

In the present study, the thermal diffusivities of 82.6 and 89.3% TD Cs_2MoO_4 specimens were measured by the laser flash method and the thermal conductivities of these specimens were calculated. The range of the thermal conductivity of these specimens was found to be 0.3 to 0.5 W m^{-1} K^{-1}.

The density dependence of thermal conductivity was found to be linear from 82.6 to 94.3% TD.

The simple correlation for the thermal conductivity of Cs_2MoO_4 is as follows:

$$k = (1.0 - 1.848 \times P)/(1.0 - 1.848 \times P_{ref}) \times k_{ref},$$

where $k_{ref} = 132.56/T + 0.03 + 3.2 \times 10^{-10} \times T^3$, $P_{ref} = 1.0 - 0.943 = 0.057$ and k, k_{ref}, P, P_{ref} and T have the same meaning as described in the text. The above equation is applicable for 82.6 to 94.3% TD dense Cs_2MoO_4 from 873 to 1023 K.

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