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Section 5. Thermophysical properties and the thermo-electric effect

Thermal properties of Mo_3Te_4

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Abstract

The thermal properties of Mo_3Te_4 were investigated in the temperature range from 300 to 1000 K. The linear thermal expansion coefficient of Mo_3Te_4 was evaluated from high-temperature X-ray diffraction. The thermal conductivity was calculated from the heat capacity, the pycnometric density, and the thermal diffusivity measured by the laser flash method. The thermal conductivity of Mo_3Te_4 is relatively low and is increased from 2.2 W m^{-1} K^{-1} at 300 K to 3.1 W m^{-1} K^{-1} at 1000 K. The electrical conductivity was measured by the standard four-probe dc method. The electronic contribution to the thermal conductivity was calculated using the Wiedemann–Franz law, and the lattice thermal conductivity was estimated. The mechanism of the thermal conduction of Mo_3Te_4 was discussed.

1. Introduction

Molybdenum and tellurium have comparatively high fission yields, and these elements are the predominant fission products in several types of metallic precipitates of spent fast reactor fuel [1,2]. In order to evaluate the safety of the fuel, it is important to understand the effect of the fission products on thermal and mechanical properties of the fuel under irradiation. However, the thermal properties on the molybdenum telluride intermetallic compounds have scarcely reported. In the present study, several thermal properties such as the linear thermal expansion coefficient and the thermal conductivity of Mo_3Te_4 were investigated in the temperature range from 300 to 1000 K.

2. Experimental

Mo_3Te_4 was prepared by mixing stoichiometric amounts of the elements followed by heating in sealed quartz ampoules for 2 days at 1023 K. The powder was then hot-pressed in graphite dies into dense samples. The hot-pressing was conducted at a pressure of about 8 MPa and at the temperature 1273 K for 2 h under argon atmosphere. The crystal structure of the sample was analyzed by the powder X-ray diffraction method at room temperature using Cu–K_α radiation. For thermal and electrical properties measurements, appropriate shapes of the samples were cut from the pellet. The density of the samples was calculated from the measured weight and dimensions.

The linear thermal expansion coefficient of Mo_3Te_4 was evaluated by the high temperature X-ray diffraction method in the temperature range from room temperature to about 700 K under argon atmosphere. Between room temperature and about 1200 K, the thermal conductivity of Mo_3Te_4 was calculated from the heat capacity [3], the pycnometric density, and the thermal diffusivity measured by the laser flash method using ULVAC TC-7000 in vacuum. The electrical conductivity was measured by using the standard four-probe dc method under helium atmosphere between room temperature and about 923 K.

3. Results and discussion

The powder X-ray diffraction pattern of the sample is shown in Fig. 1 together with the literature data [4]. This figure shows that single-phase Mo_3Te_4 with a hexagonal structure (Chevrel phase) is obtained in the present

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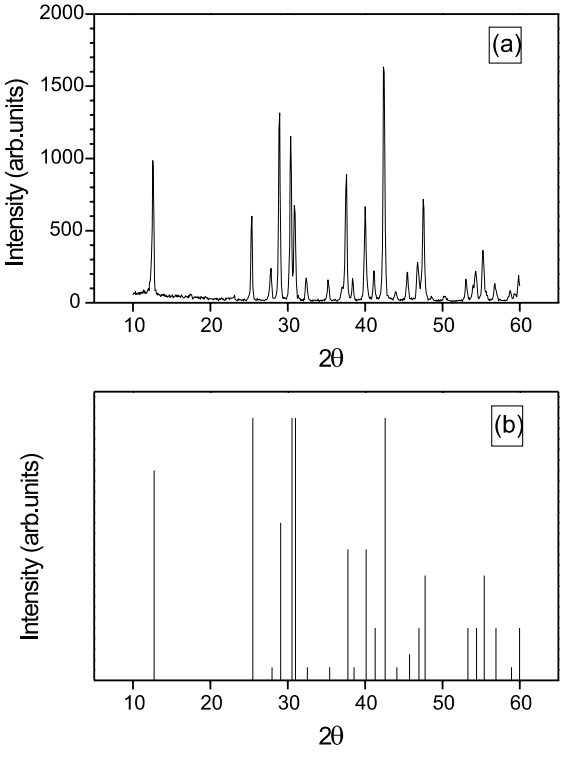

Fig. 1. (a) X-ray powder diffraction pattern for Mo_3Te_4; (b) simulated X-ray powder diffraction pattern for Mo_3Te_4 [4].

study. The lattice parameters and X-ray density of Mo_3Te_4 were obtained from the X-ray diffraction analysis. The bulk densities of the samples are about 80% of the theoretical density. Although the Mo/Te ratio was not measured in the present study, the deviation from the stoichiometry is small. This is because the lattice parameters of Mo_3Te_4 prepared in the present study are close to the previously reported literature data [5–7]. The sample characterizations of Mo_3Te_4 are shown in Table 1.

Fig. 2 shows the temperature dependence of the hexagonal unit cell parameters a, c and V of Mo_3Te_4. All parameters increase smoothly with increasing temperature. These temperature dependences can be expressed as a linear function of temperature. Between room temperature and about 623 K the linear and volumetric thermal expansion coefficients $(\alpha_a, \alpha_c, \alpha_V)$ were calculated from change in the lattice parameters and lattice volume with temperature by using the following equation:

$$\alpha_a = \frac{1}{a_0}\left(\frac{\partial a(T)}{\partial T}\right)_P, \tag{1}$$

$$\alpha_c = \frac{1}{c_0}\left(\frac{\partial c(T)}{\partial T}\right)_P, \tag{2}$$

Table 1
Lattice parameters at room temperature, pycnometric and X-ray densities, and linear and volumetric thermal expansion coefficient between room temperature and 623 K for Mo_3Te_4

Lattice parameters (at room temperature) (nm)	
a	1.0179
c	1.1725
X-ray density (Mg/m^3)	7.6
Bulk density	
(Mg/m^3)	6.2
(%T.D.)	82
Linear thermal expansion coefficient (K^{-1})	
α_a	1.58×10^{-5}
α_c	8.25×10^{-6}
Volumetric thermal expansion coefficient (K^{-1})	
α_V	4.04×10^{-5}

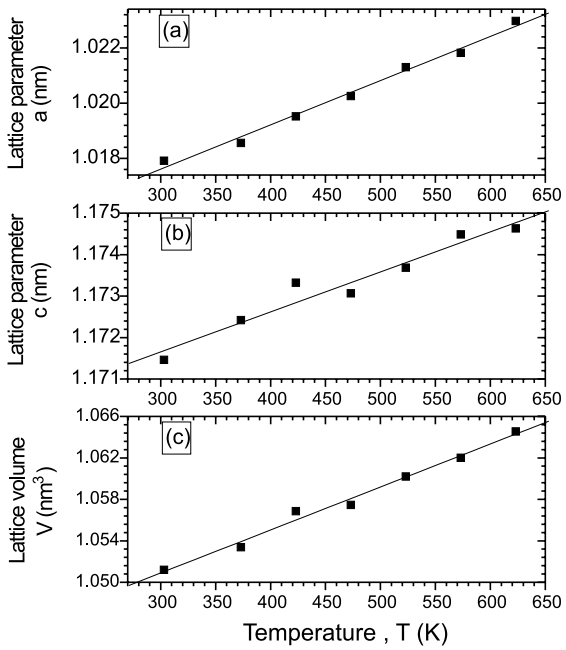

Fig. 2. Temperature dependence of hexagonal unit cell parameters a, c and lattice volume V for Mo_3Te_4.

$$\alpha_V = \frac{1}{V_0}\left(\frac{\partial V(T)}{\partial T}\right)_P, \tag{3}$$

where a_0, c_0 and V_0 are the lattice parameters at room temperature. These results are shown in Table 1. It is found that the linear thermal expansion coefficient in a direction α_a is larger than that in c direction α_c.

It is empirically found that the product of α_L and T_m is a constant for many substances, where α_L equals one-third of α_V and T_m is the melting temperature in K [8,9].

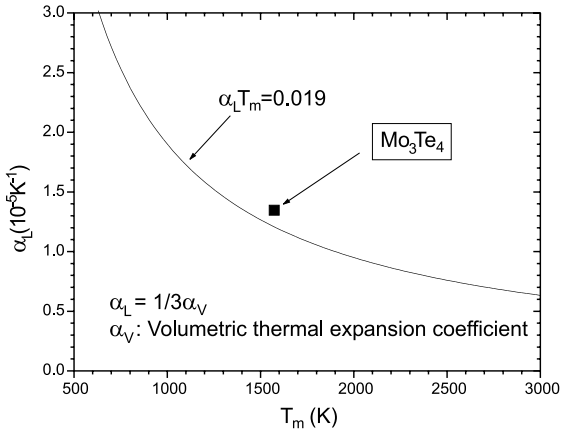

Fig. 3. Relationship between α_L and T_m for Mo_3Te_4.

For pure metals the following relationship between α_L and T_m was reported [8,9]:

$$\alpha_L T_m = 0.019. \tag{4}$$

The variation of α_L with T_m [10,11] are shown in Fig. 3. It is found from this figure that the relationship between α_L and T_m of Mo_3Te_4 has the same tendency as for pure metals.

The thermal conductivity λ was calculated from the measured thermal diffusivity a, specific heat capacity c_p, and density d using the following relationship:

$$\lambda = ac_p d. \tag{5}$$

The temperature dependence of the thermal conductivity of Mo_3Te_4 is shown in Fig. 4. These experimental data were corrected to 100% T.D. by using Schulz's equation [12]. At around room temperature the thermal conductivity of Mo_3Te_4 is extremely lower than that of UO_2 [13], while it is increased gradually with increasing temperature, and becomes higher than that of UO_2. This temperature dependence shows metallic behavior.

It is well known that the total thermal conductivity of the material λ_{total} of solids can be written as

$$\lambda_{total} = \lambda_{el} + \lambda_{ph}, \tag{6}$$

where λ_{el} is the electronic contribution and λ_{ph} is the lattice contribution. In order to separate λ_{ph} from λ_{el}, the electronic contribution to the thermal conductivity was calculated using the Wiedemann–Franz law,

$$\lambda_{el} = L\sigma T, \tag{7}$$

where L is the Lorentz number, σ is the electrical conductivity, and T is the absolute temperature. In the present study, the electrical conductivity of Mo_3Te_4 was measured by using the standard four-probe dc method in the temperature range from room temperature to about 1000 K, and this result is shown in Fig. 5. The electrical conductivity of Mo_3Te_4 are almost independent of the temperature, and the values are about $1.4 \times 10^5\ \Omega^{-1}\ m^{-1}$. The lattice contribution was obtained by subtracting λ_{el} from λ_{total}. Variations of λ_{ph}, λ_{el}, and λ_{total} with temperature are shown in Fig. 4. The temperature dependence of λ_{ph} follows a $1/T$ law, which indicates that the λ_{ph} is composed of phonon contribution. In the low temperature range, the lattice contribution is more predominant than the electronic contribution, while in the high temperature range the electronic contribution increases rapidly and it becomes comparable to the lattice contribution. From the present study, it is found that the characteristics of the thermal properties such as the thermal expansion, melting point, and thermal conductivity of Mo_3Te_4 show metallic behavior.

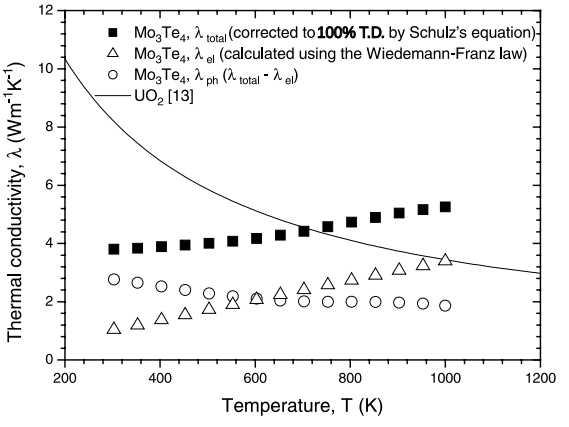

Fig. 4. Temperature dependence of thermal conductivity for Mo_3Te_4.

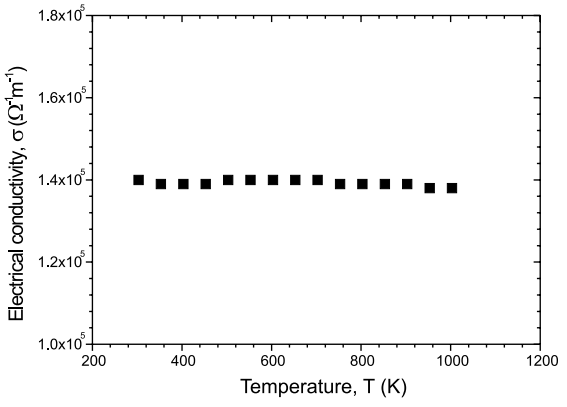

Fig. 5. Temperature dependence of electrical conductivity for Mo_3Te_4.

4. Conclusion

The thermal properties of Mo_3Te_4 were investigated in the temperature range from 300 to 1000 K. The hexagonal unit cell parameters increased smoothly with increasing temperature. The relationship between the thermal expansion coefficient and the melting temperature of Mo_3Te_4 had the same tendency as for pure metals. The thermal conductivity of Mo_3Te_4 increased with increasing temperature, indicating metallic behavior. The electrical conductivity of Mo_3Te_4 was measured by using the standard four-probe dc method, and the electronic contribution to the thermal conductivity was evaluated by using the Wiedemann–Franz law. In the low temperature range, the lattice contribution to the thermal conductivity was more predominant than the electronic contribution, while in the high temperature range the electronic contribution became comparable to the lattice contribution.

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