PREPARATION AND CHARACTERISATION OF TECHNETIUM METAL AND TECHNETIUM-RUTHENIUM ALLOYS

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Abstract

Technetium metal and Tc-Ru alloys were characterised to build a database of the Tc metal target for transmutation. The lattice parameters of Tc-Ru alloys including Tc and Ru metals measured by X-ray diffraction decrease with increasing Ru concentration. The thermal conductivity of Tc-Ru alloys including Tc and Ru metals was determined by the thermal diffusivity measured by the laser flash method from room temperature to about 1 200 K. The thermal conductivity of Tc metal shows a minimum around 400 K, above which it increases with temperature. The thermal conductivity of Tc metal is smaller than that of Ru metal and the thermal conductivity of Tc-25% Ru, Tc-50% Ru and Tc-75% Ru alloys increases with temperature as well as Ru concentration.

Introduction

Technetium-99 is a long-lived fission product with a half-life of 2.111 x 10^5 years, which decays by beta emission with a maximum energy of 293.5 keV [1]. The cumulative yields for ^{99}Tc from thermal neutron fission of ^{235}U and ^{239}Pu are 6.11 and 6.16 %, respectively [2]. The yields for other long-lived technetium, ^{97}Tc and ^{98}Tc, are 1.2×10^{-10} and 8.7×10^{-7} % from ^{235}U and 4.7×10^{-9} and 2.7×10^{-7}% from ^{239}Pu, respectively [2].

In storage of high-level waste (HLW) from nuclear reactors, ^{99}Tc contributes dominantly to the beta radiotoxicity for a very long time. Since the transmutation of ^{99}Tc to stable ^{100}Ru is an attractive option to reduce the long-term risk of the storage of HLW, irradiation experiments for the transmutation, together with the related experiments, were performed [3-7]. The EFTTRA-T1 experiment revealed no technical limitations to the use of Tc metal as a target for transmutation [5].

We, JAERI, also started an experimental study concerning transmutation of Tc [8,9]. Based on the result of the EFTTRA-T1 experiment, Tc metal was placed in the reliable chemical form of the target to be transmuted. When the target of Tc metal is transmuted, the target will change to Tc-Ru alloy, whose Ru concentration increases with irradiation dose. Although the basic properties of Tc metal and some of its alloys were studied mainly in 1960s and 1970s, the data needed for a design of the target and for evaluation of the irradiation behaviour of the target are very limited.

The present paper describes results of out-of-reactor experiments on alloying behaviour of Tc-Ru and thermal conductivity of Tc-Ru alloys including Tc and Ru metals, which contribute to the formation of a database of the Tc metal target.

Preparation of Tc and Tc-Ru samples

Powder of Tc metal was purchased from Oak Ridge National Laboratory. The as-received powder was heated at 1 073 K in flowing hydrogen to reduce technetium oxide, if any, contained in the sample. The heat-treated powder was analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The main impurities were found to be iron and aluminium, and the total amount of impurities was about 15 ppm, as shown in Table 1.

Table 1. **Analysis of technetium powder by ICP-AES and ICP-MS**

Element	Amount (ppm)
Al	4.0
Ti	0.94
V	< 0.5
Cr	1.5
Mn	< 0.5
Fe	6.4
Co	< 0.5
Ni	1.9
Cu	< 0.5
Zn	< 0.5
U	< 0.5

The X-ray diffraction analysis of the powder was carried out at room temperature, using Ni-filtered Cu Kα radiation. The measured X-ray diffraction pattern of the powder from 25 to 140° was identical with the data of Tc metal reported by Muller *et al* [10]. The lattice parameters obtained were a = 0.27409 nm and c = 0.43983 nm, which were almost the same as the previously reported values [10-13]. The theoretical X-ray density was found to be 11.479 Mg/m^3 when an atomic weight of 98.913 was assumed [14].

For the characterisation of Tc-Ru alloys, five disk-shaped samples of Tc metal, Tc-25%Ru, Tc-50%Ru, Tc-75%Ru, and Ru metal were prepared by arc-melting technique. About 2 g of mixed powder of Tc metal and Ru metal (>99.9%) was pressed into a tablet of 10 mm in diameter and about 3 mm in thickness at room temperature and a pressure of 980 MPa. The tablet was then arc-melted to form a button on a water-cooled copper hearth in an atmosphere of purified argon. The button was remelted several times to assure homogenisation, followed by arc drop-cast to form a rod of 5 mm in diameter and about 10 mm in length. The rod was cut by a diamond cutter to obtain a disk of 5 mm in diameter and 1 mm in thickness.

The disk samples were then annealed at 1 573 K for 1 h in vacuum. The present annealing temperature was selected on the basis of the results of the annealing experiment by Spitsyn *et al* [15].

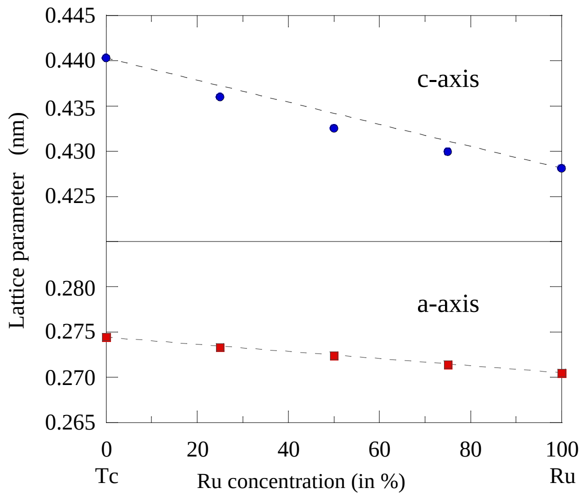
Characterisation of Tc and Tc-Ru alloys

Lattice parameters

The disk samples were analysed by X-ray diffraction method, using Ni-filtered Cu Kα radiation. Tc and Ru metals are isostructural, having a hexagonal close packed structure (space group $P6_3/mmc$), and form a complete solid solution [16].

The formation of a solid solution with a single phase was confirmed in each sample and the lattice parameters of the a- and c-axes of the five samples were obtained. Figure 1 shows the lattice parameters of the alloys as a function of Ru concentration. Both the lattice parameters of the a- and c-axes decrease with increasing the Ru concentration, which almost follow Vegard's law. The present result of the lattice parameters agreed well with the reported ones [16].

Figure 1. **Lattice parameters of Tc-Ru alloys including Tc and Ru metals**



The immersion density of each disk sample measured with methylene iodide was found to be almost the same as the theoretical X-ray density.

Thermal diffusivity

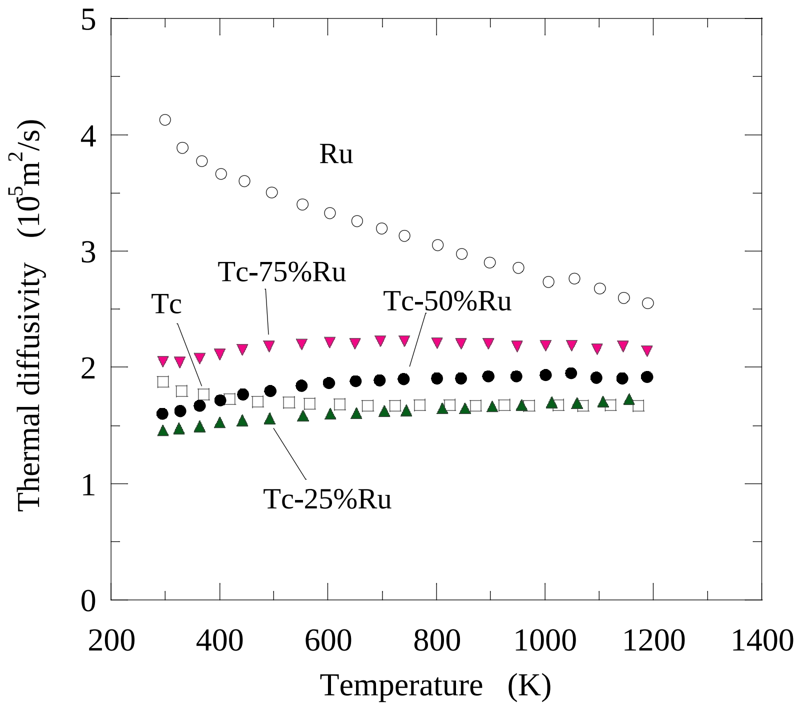
The thermal diffusivity was measured on the disk samples from room temperature to about 1 200 K by the laser flash method. The measurements were performed in a vacuum below 3×10^{-3} Pa. The apparatus for the thermal diffusivity measurement was tested using a stainless steel sample as standard. The experimental uncertainties were less than 3%.

Since the samples had metallic luster, the surface of the disk samples was treated with carbon to absorb the laser beam efficiently. The influence of this treatment on the measured thermal diffusivity was less than 1%.

The sample was heated in an electric furnace to the desired temperatures and the sample temperature was measured with an R-thermocouple placed near the sample. The thermal diffusivity was determined from the temperature rise at the rear surface measured with an In-Sb infrared detector after the front surface of the sample was heated by the pulse of a ruby laser. The data of the temperature rise were analysed by the logarithmic method [17-18].

Figure 2 shows the thermal diffusivity of Tc metal, Tc-25%Ru, Tc-50%Ru, Tc-75%Ru, and Ru metal as a function of temperature.

Figure 2. **Thermal diffusivity of Tc-Ru alloys including Tc and Ru metals**



Heat capacity

When the thermal conductivity is determined from the thermal diffusivity, the specific heat capacity is needed:

$$\lambda = \alpha C_p \rho , (1)$$

where λ is the thermal conductivity, α the thermal diffusivity, C_p the specific heat capacity and ρ the density of the sample.

As no specific heat capacity was measured in the present study, the data from the literature on the heat capacity of Tc [19-22] and Ru [21-23] are presented in Figures 3 and 4, respectively. For Tc, the data reported by Spitsyn *et al* [19] were experimental values, whereas others [20-22] were theoretically estimated ones. The recent compilation of the thermochemical data by Cordfunke and Konings [21] adopted the estimations by Guillermet and Grimvall [24]. Another recent compilation by Barin [22] adopted the same values as those of Stull and Sinke [23]. In the case of Ru, the compilation by Cordfunke and Konings [21] recommended the values based on their measurement, whereas the compilation by Barin [22] adopted the same values as those of Hultgren *et al* [25].

Figure 3. **Specific heat of Tc metal taken from the literature** [19-22]

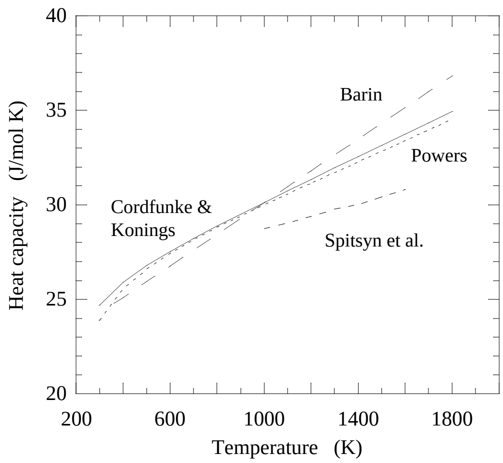
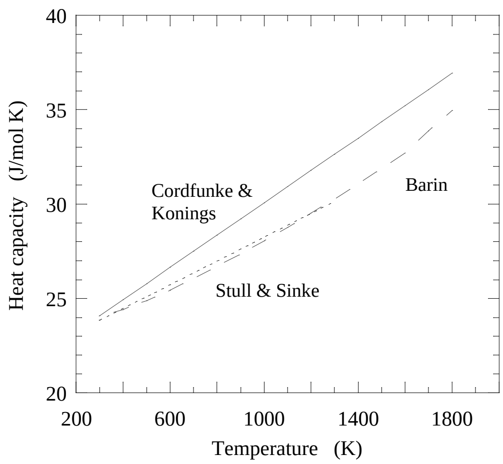


Figure 4. **Specific heat of Ru metal taken from the literature** [21-23]



In the present study the values for heat capacity of Tc and Ru were taken from the compilation by Cordfunke and Konings [21] and those for Tc-Ru alloys were estimated by Neumann-Kopp rule.

Thermal conductivity

Figure 5 shows the thermal conductivity of Tc and Ru metals calculated through Eq.(1) as a function of temperature, together with the reported values [11,19,26-27]. It is noted that the thermal conductivity of Tc metal is smaller than that of Ru metal in the present temperature range. The thermal conductivity of Tc metal in the present experiment shows a minimum around 400 K, above which the thermal conductivity increases with temperature. The thermal conductivity of Ru metal, on the other hand, decreases with increasing temperature.

Figure 6 shows the thermal conductivity of the Tc-Ru alloys as a function of temperature, together with those of Tc and Ru metals. For Tc-25%Ru, Tc-50%Ru and Tc-75%Ru alloys, the thermal conductivity increases with temperature as well as Ru concentration.

Figure 5. **Thermal conductivity of Tc and Ru metals, together with the reported ones** [11,19,26-27]

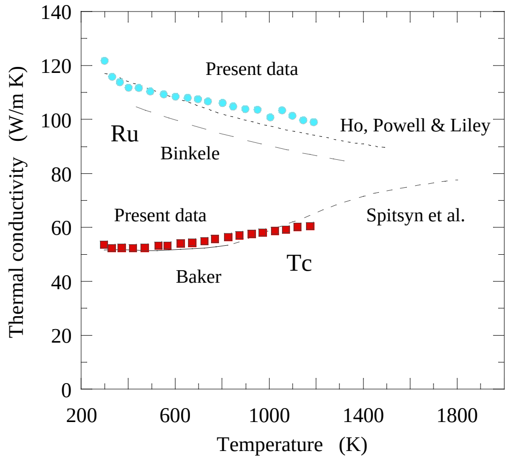
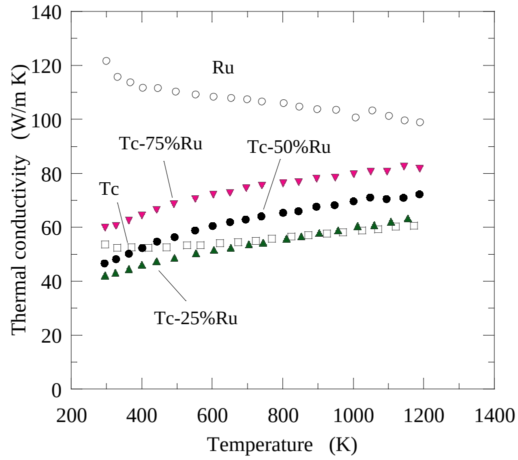


Figure 6. **Thermal conductivity of Tc-Ru alloys including Tc and Ru metals**



Conclusions

In order to build a database of the Tc metal target for transmutation, the lattice parameters of Tc-Ru alloys including Tc and Ru metals were measured by X-ray diffraction and the thermal conductivity of Tc-Ru alloys including Tc and Ru metals was determined by the thermal diffusivity measured by the laser flash method from room temperature to about 1 200 K. The following was concluded:

– The lattice parameters of Tc-Ru alloys decrease with increasing Ru concentration.

– The thermal conductivity of Tc metal shows a minimum around 400 K, above which it increases with temperature. The thermal conductivity of Tc metal is smaller than that of Ru metal.

– The thermal conductivity of Tc-25%Ru, Tc-50%Ru and Tc-75%Ru alloys increases with temperature as well as Ru concentration.

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