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Change of thermal diffusivity and lattice constants of W–5% Re–HfC alloys irradiated in a fission reactor

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Abstract

W–5% Re–HfC alloys with aimed HfC contents of 0.5, 1 and 3 wt% were fabricated by powder metallurgy. Their thermal diffusivity and lattice constant were measured before and after neutron irradiation at 330 K up to a fast neutron ($E > 1$ MeV) fluence of 1×10^{24} n/m^2. Chemical analysis and lattice constant measurements revealed that Hf existed not as HfC but mainly as a solute in the alloys. The thermal diffusivity of the alloys with HfC less than 1% nominal content was higher than that of W–5% Re, specifically at higher temperatures, while the diffusivity of the alloy with 3% HfC (nominal content) was lower than that of W–5% Re. Only the alloy with 3% HfC showed a distinct decrease of the thermal diffusivity after neutron irradiation and its recovery after annealing. The lattice constants of the W–5% Re alloys increased with the increase of the Hf content. Only the lattice constant of the alloy with 3% HfC represented a considerable increase after neutron irradiation.

1. Introduction

The development of high heat flux materials will be one of the technical key issues for establishing nuclear fusion technologies. High atomic number refractory metals such as molybdenum (Mo) and tungsten (W) will be among a variety of candidates [1]. Specifically, W has many favorite properties as a plasma facing material [2]. Thus, some tungsten alloys were developed [3].

The addition of dispersoids in the materials are now one of the usual ways for strengthening. In W alloys, if these dispersoids are stable at high temperatures, this will provide many improvements, such as an increase in recrystallization temperature and in ductility. HfC was selected as dispersoid, because it is known as one of the highest melting point materials. W–5% Re was selected as the W base alloy because it has the possibility of higher ductility than W. Further, it has a better thermal diffusivity than W–10% Re or W–25% Re [3].

The aims of this study are the fabrication of a W–5% Re alloy with HfC as dispersoid by powder metallurgy and the investigation of the effect of neutron irradiation on the thermal diffusivity and lattice constant of the obtained alloys. Measurements of the thermal diffusivity and lattice constants of W–Re–HfC alloys (up to 3 wt% HfC) were carried out before and after neutron irradiation in the JMTR reactor.

2. Experimental procedure

W, W–5.3% Re and W–5% Re–HfC alloys were used in this study. As to the W–Re alloys, their details were described elsewhere [3]. W–5% Re–HfC alloys were fabricated by powder metallurgy. Powders of W,

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Table 1
Fabrication process of W–5% Re–HfC alloys

1	Raw materials (powders)	W powder (2 μm)
		NH_4ReO_4 powder
		HfC powder (0.9 μm)
2	Mixing	W–Re powder + HfC powder
3	Forming	CIP
4	Sintering	Hydrogen furnace (2073 K–5 h)
		Vacuum furnace (2273 K, 20 h)
		HIP treatment (2073 K, 200 MPa, 5 h)

NH_4ReO_4 and HfC were mixed and formed to rectangular plates with $10 \times 50 \times 30$ mm^3 by cold isostatic pressing (CIP). They were annealed in vacuum at 2273 K after hydrogen furnace annealing at 2073 K, and finally were HIP-treated at 2073 K under 200 MPa for 5 h (see Table 1). The aimed HfC contents in the W–5% Re alloys were 0.5%, 1% and 3% (in wt%). The chemical compositions of the obtained alloys together with the analyzed W and W–5% Re are listed in Table 2.

Disks with 8 mm diameter and about 1 mm thickness were cut by a wire spark cutting tool for measurements of the thermal diffusivity and the lattice constants. All specimens were polished with Al_2O_3 (0.05 μm) before the tests.

Some of the 8 mm disks were irradiated at about 330 K in the JMTR (Japan Materials Testing Reactor) at Oarai Research Establishment of Japan Atomic Energy Research Institute. The fast neutron fluence ($E > 1$ MeV) was 1×10^{24} n/m^2. After cooling, the influence of the neutron irradiation on the thermal diffusivity was investigated.

The apparatus (Sinku Rikou Co. Ltd.) reported previously [3] was used for the measurement of the thermal diffusivity of the specimens before and after irradiation. The thermal diffusivity was evaluated by the conventional 'half-time method' [4]. The measurement was carried out from room temperature up to about 1000 K under vacuum of $<3 \times 10^{-3}$ Pa. The irradiated specimens were kept at 1000 K for 10 min and the treatment was also named 'annealing' as in the previous paper [3]. The measurement was continued on cooling from 973 K to room temperature.

Lattice constants of the specimens before and after neutron irradiation and after 'annealing' were evaluated from X-ray diffraction using Cu Kα_1 ($\lambda = 0.154060$ nm). The determination of the lattice constants of the specimens was done according to Cohen's method [5].

3. Results and discussion

The chemical analysis data of Hf and carbon in the W–Re–HfC alloys show that carbon content in the alloys is too low compared to the Hf content to form HfC; carbon in HfC should be 0.025, 0.059 and 0.16 wt% compared to hafnium of 0.37, 0.88 and 2.41 wt%, respectively. This may be due to the hydrogen treatment adopted to remove oxygen from the products during the fabrication process. From energy dispersive X-ray analysis, a residual HfC particle present at the grain boundary was accidentally identified in 0.5% HfC alloys (Fig. 1). Therefore, for the present it is suitable to assume that hafnium exists mainly as a solute in the alloys according to the W–Re–Hf phase diagram [6]. This means that the alloys should be named W–Re–Hf alloys.

Thermal diffusivities of W–Re alloys before and after neutron irradiation have been described elsewhere [3]. Fig. 2 shows the temperature dependence of the thermal diffusivity of W–Re–Hf alloys in the as-received condition. As shown previously, the thermal diffusivity of W decreases largely with the increase of the test temperature. In comparison, that of W–5% Re showed a small decrease as the temperature rose. With an addition of Hf(C) to W–5% Re, the temperature dependence of the thermal diffusivity seems to disappear above 500 K. Further, the addition of Hf less than 1% increases the diffusivity of W–5% Re to some extent in the higher temperature range. These are useful properties from the viewpoint of fusion reactor design.

Figs. 3–5 show the temperature dependence of the thermal diffusivity of W–Re–Hf alloys after neutron irradiation. There was a difficulty to measure the diffusivity of the alloys with 0.33% and 0.88% Hf near the room temperature range because of their relatively high thermal diffusivity values related to their specimen

Table 2
Chemical composition of the W–Re–Hf(C) alloys (wt%)

Component	Alloy				
	W	W–5% Re	W–5Re–0.5%HfC	W–5Re–1%HfC	W–5Re–3%HfC
W	100	Balance	Balance	Balance	Balance
Re	–	5.24	4.97	4.98	4.87
Hf	–	–	0.37	0.88	2.41
C	–	0.001	0.001	0.016	0.013
O	–	<0.001	0.026	0.019	0.0065
N	–	<0.0001	0.001	0.003	<0.001

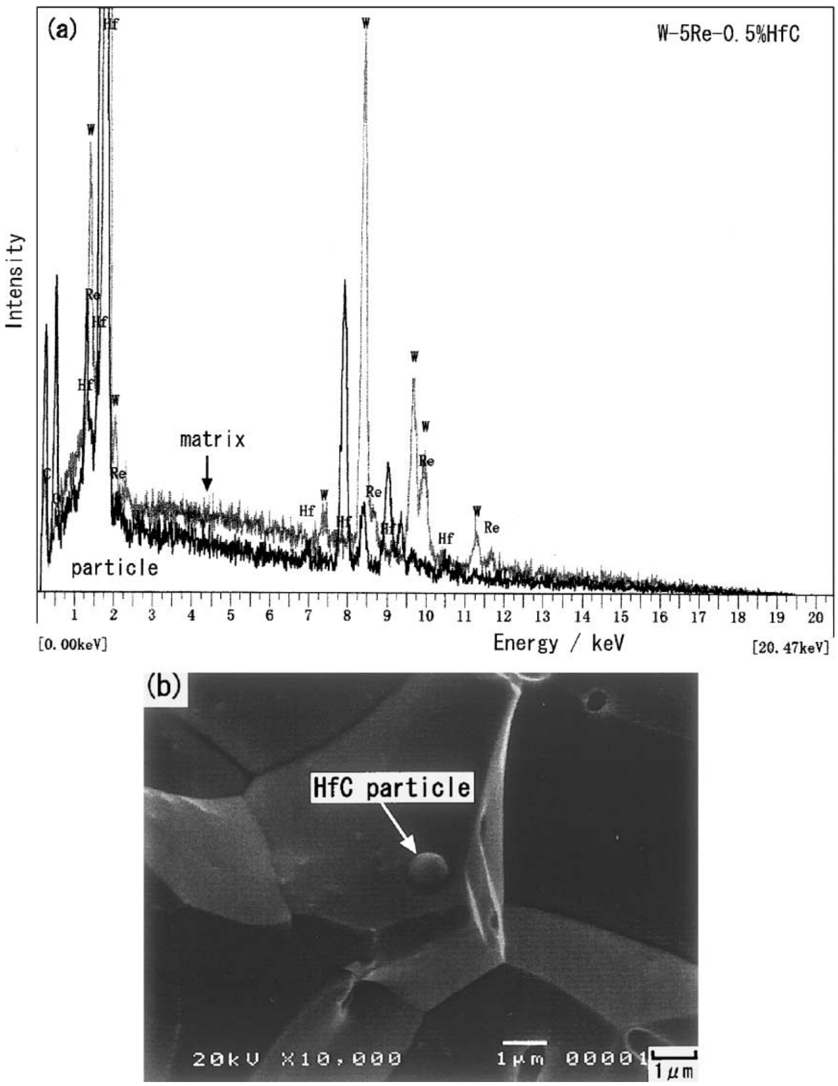

Fig. 1. EDX analysis of grain or particle and SEM image of W–5% Re–0.5%HfC: (a) composition of HfC particle; (b) SEM image of HfC particle at a grain boundary.

thickness. Therefore, the room temperature data were obtained by using thicker unirradiated specimens than the irradiated ones. The lack of the data near room temperature in the 0.33% and 0.88% Hf alloys makes it difficult to judge whether they recovered the original values after heating and annealing (at 1023 K for 10 min). In the 2.4% Hf alloy, on the other hand, it is obvious that the diffusivity decreased due to neutron irradiation and that the diffusivity increased as the temperature increased. On cooling, the alloy keeps almost the same value equal to the one obtained from the unirradiated specimen. Therefore, it can be said that a restoration occurred in the 2.41% Hf alloy after annealing.

The thermal diffusivities of W–Re–Hf alloys before and after neutron irradiation were summarized in Fig. 6. Due to the lack of the data in some alloys near room temperature, it is not possible to understand the general feature of the influence of neutron irradiation on the property. However, as to the thermal diffusivity, in each case the inferiority of the 2.4% Hf alloy to other alloys with lesser Hf contents is obvious.

So far, we did not take the porosity of the sintered W–5% Re–Hf products into consideration. The measured densities of the alloys in g/cm^3 were 19.36, 18.45, 18.26 and 17.15, and the porosities calculated from their ideal densities are 0.003, 0.047, 0.055 and 0.111 for 0%, 0.37%, 0.88% and 2.41% Hf alloys, respectively. Then,

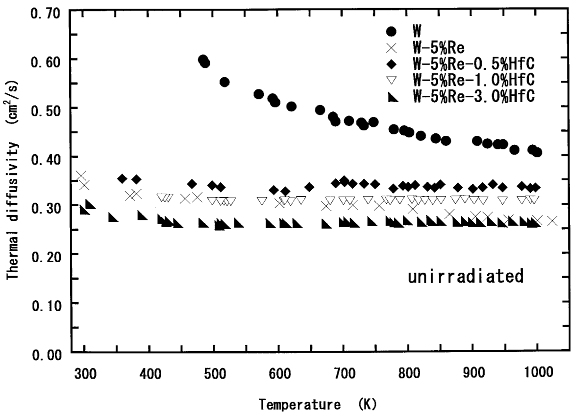

Fig. 2. Temperature dependence of the thermal diffusivity of W–Re–Hf alloys in the as-received condition.

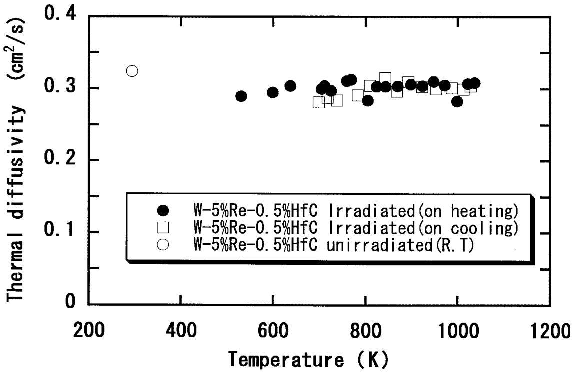

Fig. 3. Thermal diffusivity of W 5% Re–0.37%Hf after neutron irradiation as a function of temperature.

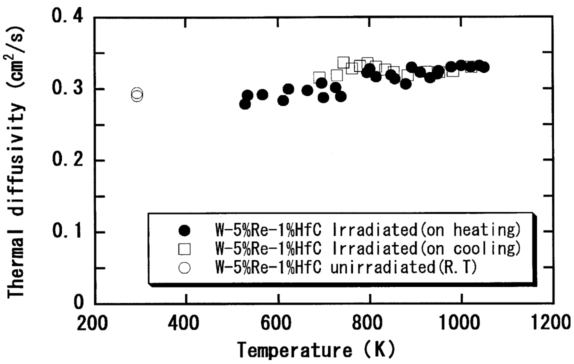

Fig. 4. Thermal diffusivity of W–5% Re–0.88%Hf after neutron irradiation as a function of temperature.

for example, their measured diffusivities of 0.3, 0.33, 0.307 and 0.263 cm^2/s at about 600 K are estimated to be 0.301, 0.354, 0.334 and 0.312 cm^2/s for 0%, 0.33%, 0.88% and 2.41% Hf alloys without porosity, respectively,

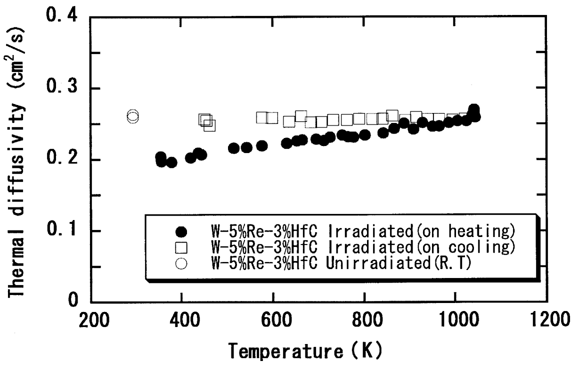

Fig. 5. Thermal diffusivity of W–5% Re–2.4%Hf after neutron irradiation as a function of temperature.

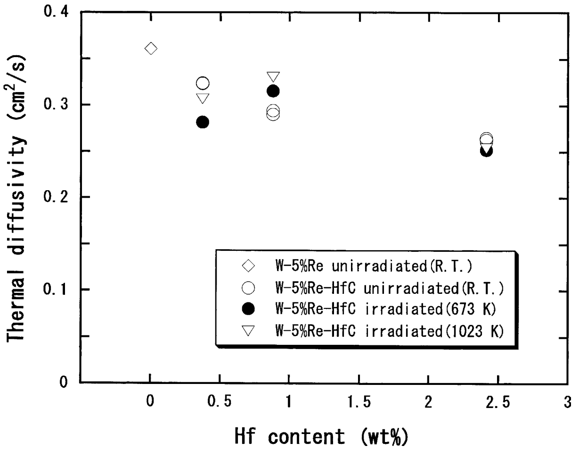

Fig. 6. Thermal diffusivity of W–5%Re–Hf alloys as a function of the Hf content before and after neutron irradiation.

when using the equation for porous solids shown in the literature [7]. So, even if the porosity is taken into account, the inferiority of the thermal diffusivity in the 2.41% Hf alloy to others is obvious.

The change in lattice constants of the W–Re–Hf alloys before and after irradiation is shown in Fig. 7. In the unirradiated condition, the lattice constants increase as the Hf content increases. This is due to the difference of the atomic radius between solute (Hf) and solvent (W–Re); the atomic radius of Hf (0.1747 nm) is much larger than that of W (0.1558 nm) and Re (0.1527 nm) [8].

The change of lattice constant due to Hf addition to W–5% Re alloys also indicates that Hf atoms exist not as HfC but mainly as a solute in the matrix of the alloys.

It should be noted that as far as X-ray diffraction patterns are concerned in this study, there exist no other peaks than those corresponding to the bcc W(Hf, Re) solid solution.

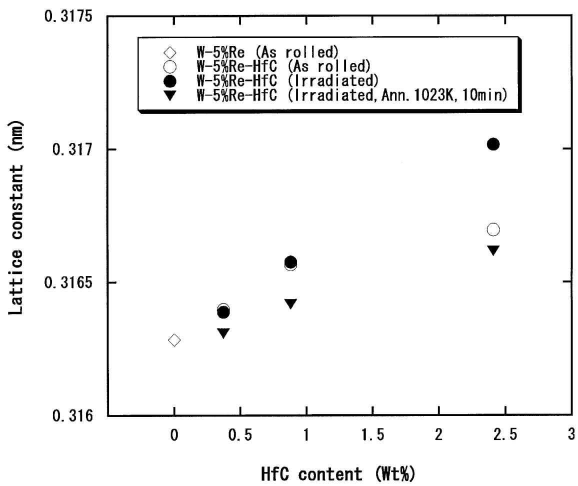

Fig. 7. Lattice constant of W–5% Re–Hf alloys as a function of the Hf content before and after neutron irradiation.

After neutron irradiation, the increase of the lattice constants for 0.37% and 0.88% Hf alloys was low, however, that of 2.41% Hf alloy was large. It is unclear whether the lattice constants of all specimens decreased after annealing below the values of the as-received condition. However, the large decrease of the lattice constant in the 2.41% Hf alloy after annealing may suggest that defects caused by the irradiation were annealed out in this alloy. Further studies are needed to ascertain the phenomenon.

4. Conclusions

The thermal diffusivity and lattice constants of three W–5% Re alloys with HfC (up to 3 wt%) as dispersoids fabricated by powder metallurgy were measured before and after JMTR irradiation with a fast neutron (>1 MeV) fluence of 1×10^{24} n/m^2. The results obtained are as follows:

(1) In the fabricated alloys, HfC particles were scarcely observed. Hf exists mainly as a solute in the alloys.
(2) The thermal diffusivity of the alloys with <1 wt% Hf was a bit higher, and that of the alloy with 2.4 wt% Hf was a bit lower than the diffusivity of W–5% Re. Each alloy with Hf showed an almost constant thermal diffusivity value at temperatures higher than 500 K, while that of W–5% Re decreased gradually with temperature.
(3) Though neutron irradiation may not seriously cause a change in the thermal diffusivity of the alloys with <1% Hf, a decrease of the thermal diffusivity was observed in the alloy with 2.4% Hf. Further, it recovers its original value through heating to 1000 K.
(4) The lattice constants increased with the increase of the Hf content in the W–5% Re alloy. After neutron irradiation, only the alloy with 2.4% Hf showed a considerable increase in lattice constant.
(5) As far as X-ray diffraction patterns are concerned in this study, there exist no other peaks than those corresponding to bcc W.

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