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Effects of titanium impregnation on the thermal conductivity of carbon/copper composite materials

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Abstract

Carbon/copper-based materials with high thermal conductivity and good stability at high temperatures were developed by adding a small amount of titanium. The isotropic fine-grained nuclear grade graphite and felt type C/C composite, which were impregnated by copper (10–18 vol.%) and titanium (0.5–0.8 vol.%), provided ~1.3 times higher thermal conductivity of 110 and 200 W/mK at 1200 K than the original carbon materials. Microstructural analyses showed that the increase of thermal conductivity is due to the formation of titanium compounds at the carbon/copper interface, and that the thermal energy would pass through both the carbon and copper. The present study indicates that addition of a small amount of a third element with a low enthalphy of alloy formation with carbon and copper will increase the thermal conductivity and the stability of carbon/copper-based materials. These carbon-based materials could be one of candidate materials for the plasma facing components of the fusion devices.

1. Introduction

Plasma facing components for fusion reactors require excellent erosion properties on the surface by high heat loading from plasma and high resistence to radiation damage by high energy neutron. Recently, carbon materials have been extensively used for plasma facing components because of low atomic number and comparatively high thermal conductivity [1–3]. The C/C composites which have been developed so far are considered to be qualified materials for high heat flux components in the present fusion devices in the world. However, it is not sufficient for plasma facing components for the engineering phase operation of fusion reactors, because the effects of radiation damage on the thermal and mechanical properties of carbon materials are more serious. The problem is that the thermal conductivity is quite low at high temperatures during operation of the fusion reactors. Therefore, it is necessary to develop carbon composite materials that have higher thermal conductivity at high temperatures and more stable properties to radiation damage for the use in future fusion reactors.

Carbon/copper composite materials have been used for electrical brushes for many years [4]. However, attention has not been paid to the thermal conductivity of those materials at high temperatures but to the abrasive properties. Recently, the thermal conductivity of C/Cu and C/Ag composite materials has been measured and examined up to 1400 K for fusion applications. In order to increase the thermal conductivity of carbon materials, effects of heat treatments, metallic elements addition and pressure under graphitization on the thermal conductivity of the carbon materials have been investigated [5–7]. In particular, the effect of addition of metallic elements, such as copper (Cu) or silver (Ag), was quite

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effective on the thermal conductivity. However, C/Ag composite materials will not be used for fusion reactors since silver is radioactivated by neutron from them. Although C/Cu composite materials are promising from a standpoint where they have higher thermal conductivity at high temperatures, there are some cases where the thermal conductivity at room temperature becomes smaller than the original C/C composite materials. The reason for this is that the cohesion of the interface between C and Cu or Ag is poor.

This paper describes the effect of titanium addition (0.5–0.8 vol.%) on the thermal conductivity of the copper-impregnated (10–18 vol.%) isotropic graphite and C/C composite materials. The purpose of the present work is twofold. The first is to increase the thermal conductivity of carbon materials by adding Cu and a small amount of titanium (Ti). For the application of fusion devices, Cu was selected as a metallic element because of its high thermal conductivity. In addition, Ti was selected as a third element because Ti has a low enthalphy (ΔH) of alloy formation with carbon (C) ($\Delta H = -656$ kJ/mol) and Cu ($\Delta H = -40$ kJ/mol) [8]. The addition of Ti to C/Cu composite materials is expected to show high thermal conductivity due to strong cohesion at the interface between carbon and copper. The second purpose is to understand the heat conduction mechanism of the carbon materials by analyzing the microstructure using optical microscopy (OM), transmission electron microscopy (TEM), selected area diffraction (SAD = ED, electron diffraction), high resolution electron microscopy (HREM), and energy dispersive X-ray spectroscopy (EDX). In particular, HREM is a powerful method to investigate the interfacial structure of advanced materials [9,10].

2. Experimental

Materials tested here were a nuclear grade fine-grained isotropic graphite (IG-430U) and a C/C composite (CX-2002U) and their composite materials with copper and copper–titanium. Details of the materials are shown in Table 1. The base materials, IG-430U and CX-2002U, are used for the plasma facing components of some fusion devices such as JT-60U [2]. In the metal impregnation processes, the molten copper or copper with titanium was mixed under a pressure of about 15 MPa with the base carbon materials. Since CX-2002U is a felt type C/C composite, the axial direction of the fiber in the felt plane was denoted as XX and YY, and the perpendicular direction to the felt plane was denoted as ZZ. The size of the specimen was 10 mm in diameter and 2–4 mm in thickness.

Thermal conductivity measurements were performed in the range of 293–1200 K using a laser flush device (Rigaku, MJ-800HW) for thermal diffusivity and specific heat. The measurement conditions were as follows: the laser pulse energy of about 0.6 J, the pulse width of 0.5 μs, the temperature increase of 1.8–2.8 K at room temperature and 0.6–0.8 K at 1000 K.

Microstructural analyses were carried out using OM, TEM, ED, HREM and EDX. The morphology of the samples was observed by OM. Cross-sectional samples for HREM and ED were prepared by a dimple grinder and an argon ion miller with an accelerating voltage of 3 kV. HREM, TEM and ED were carried out by a 400 kV transmission electron microscope (JEM-4000EX) equipped with a top-entry goniometer which has a point-to-point resolution of 0.17 nm. An EDX analyzer installed in a 5 kV scanning electron microscope was used to investigate element distribution in selected areas.

3. Results and discussion

Temperature dependencies of thermal conductivity for the two base carbon materials and copper (OFHC) are shown in Figs. 1 and 2 . The thermal conductivity of copper at higher temperatures is larger than that of the base carbon materials.

The thermal conductivity of the copper-impregnated IG-430U was larger than that of the original one at

Table 1
Materials tested

Base materials	Tested materials	wt%	vol.%	Bulk density (g/cm^3)	Electrical resistivity (μΩ m)
Graphite	IG-430U	–	–	1.82	9.0
	IG-430U + Cu	33.1(Cu)	10.2(Cu)	2.74	2.9
	IG-430U + Cu(Ti)	36.0(Cu) 0.8(Ti)	11.4(Cu) 0.5(Ti)	2.84	–
C/C composite	CX-2002U (XX, YY, ZZ)	–	–	1.67	1.7(XX) 3.4(YY) 5.1(ZZ)
	CX-2002U + Cu	44.3(Cu)	14.0(Cu)	2.83	1.4(XX)
	CX-2002U + Cu(Ti)	48.1(Cu) 1.1(Ti)	17.7(Cu) 0.8(Ti)	3.29	–

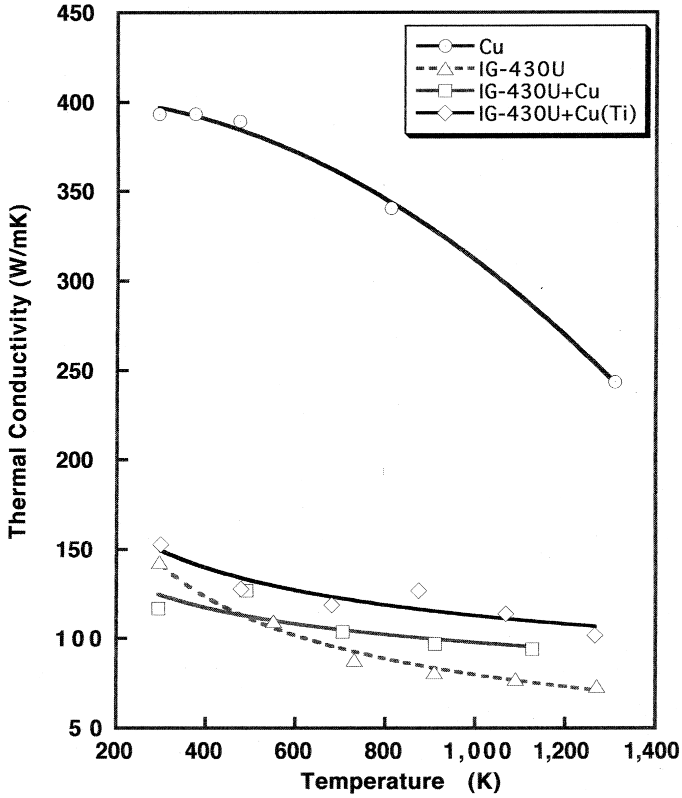

Fig. 1. Temperature dependence of thermal conductivity for Cu(OFHC), IG-430U, IG-430U + Cu and IG-430U + Cu(Ti).

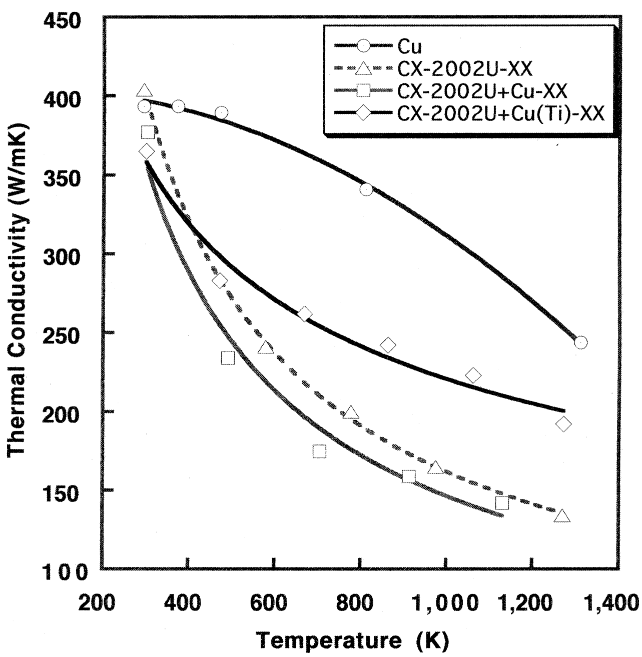

Fig. 2. Temperature dependence of thermal conductivity for Cu(OFHC), CX-2002U, CX-2002U + Cu and CX-2002U + Cu(Ti).

higher temperatures, as shown in Fig. 1, which was also obtained by Takahashi et al. [11], who gave the similar results as described here. However, the thermal conductivity at room temperature was smaller than that of the original one. The reason for this is that there is no good cohesion between carbon and copper particles. To improve the cohesion between carbon and copper particles a small amount of titanium was added to the copper-impregnated composite materials. These are denoted as IG-430 + Cu(Ti) and CX-2002U + Cu(Ti). The temperature dependencies of two composite materials were shown in Figs. 1 and 2. A clear increase in thermal conductivity over the measured temperature range and a decrease in temperature dependence has been detected as expected. CX-2002U is a felt type C/C composite; the thermal conductivity measurement was performed in the high thermal conductivity plane, i.e. within the felt layer. In this case, the effect of titanium addition to the copper-impregnated material on the thermal conductivity was definite. The reason that the thermal conductivity of CX-2002U + Cu is smaller than that of the original material is that no sufficient cohesion is obtained between carbon and copper particles.

To observe the morphology of these carbon materials, OM images were taken as shown in Fig. 3. In the CX-2002U + Cu(Ti) and CX-2002U + Cu samples the large Cu grains (~100 μm) with high reflectivity were observed. On the other hand, many small Cu grains (~20 μm) with high reflectivity were distributed in the IG-430U + Cu(Ti) and IG-430U + Cu samples. In the optical micrographs the homogeneous distribution of Cu grains in the C was observed. No changes were observed in X-ray diffraction patterns by the addition of titanium to carbon/copper composite materials (IG-430U + Cu, CX-2002U + Cu). In order to investigate the microstructure of the composite materials X-ray diffractometry was carried out. TEM is necessary for detecting a small amount of titanium.

To investigate the microstructure of the IG-430U + Cu(Ti) which has a large thermal conductivity, observations by TEM and ED were carried out as shown in Fig. 4. Fig. 4(a) is a low magnification image of the IG-430U + Cu(Ti) sample. The Cu grains are distributed in the fiber-like carbon. Fig. 4(b) is a TEM image at the C/Cu interface in Fig. 4(a). A reaction layer with many grains is observed at the C/Cu interface. To determine the reaction phase, an ED pattern of the C/Cu interface. To determine the reaction phase, an ED pattern of the C/Cu interface was taken as shown in Fig. 4(c), which was taken along [0 $\bar{1}$ 1] of Cu crystal.

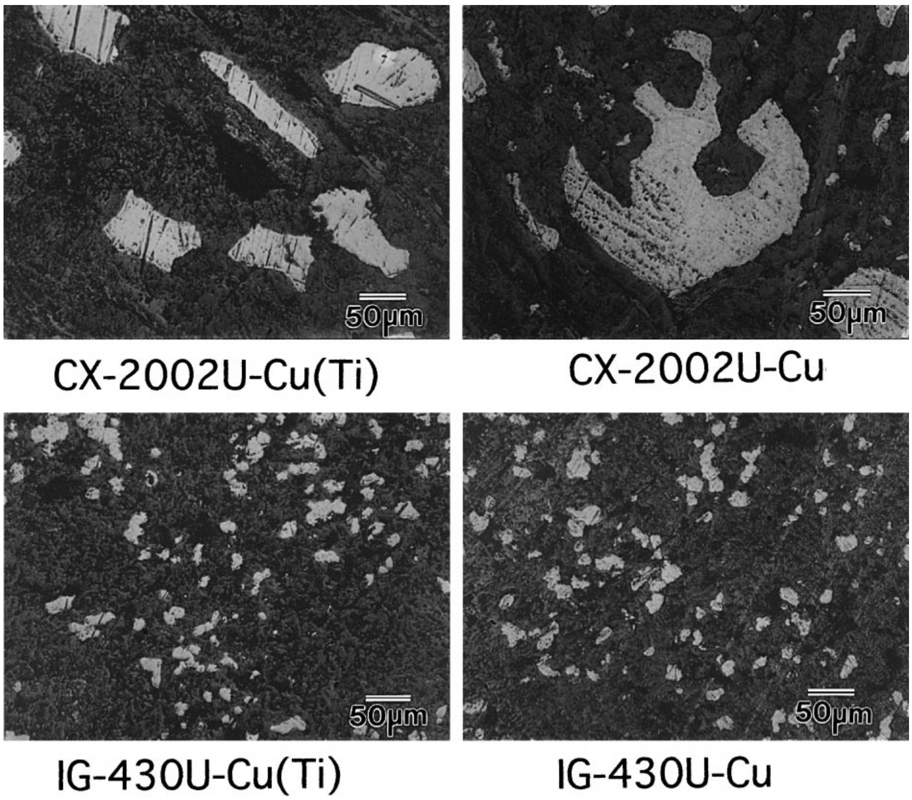

Fig. 3. Optical micrographs of IG-430U + Cu, IG-430U + Cu(Ti), CX-2002U + Cu, and CX-2002U + Cu(Ti).

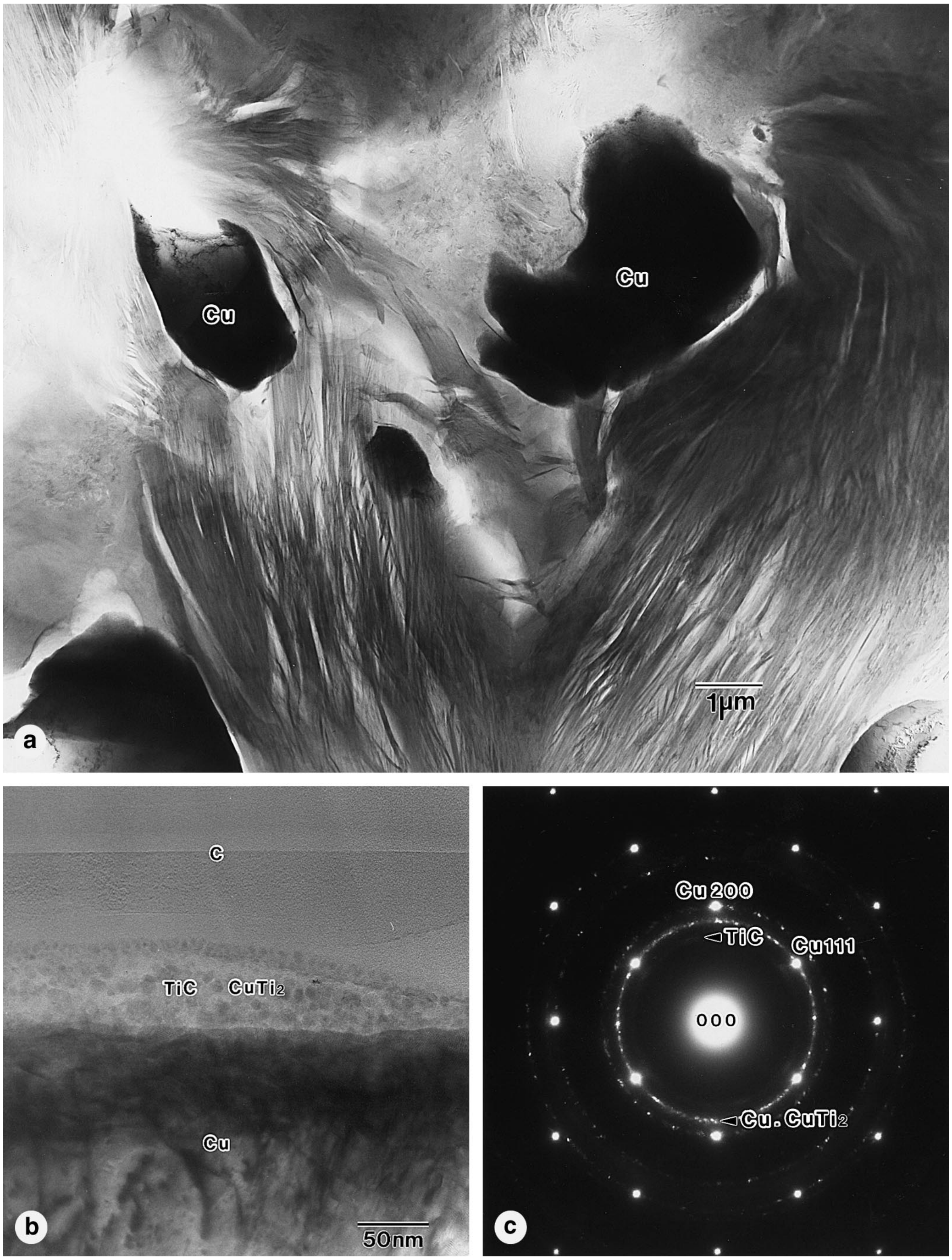

Fig. 4. Results of TEM and ED observations. (a) Low magnification image of IG-430U + Cu(Ti). (b) TEM image of IG-430U + Cu(Ti) at the interface between carbon and copper in Fig. 5(a). (c) ED pattern of the interface between carbon and copper in IG-430U + Cu(Ti).

Debye–Scherrer rings corresponding to TiC and CuTi2 are observed in addition to the Cu reflections.

Fig. 5 shows HREM images at the C/Cu interface in Fig. 4(b). The Cu/TiC and TiC/C interfaces are shown in Fig. 5(a) and (b), respectively. Lattice patterns of Cu, $CuTi_2$ and TiC, which were determined by d-spacings of the pattern, are observed. Grain sizes of the TiC and $CuTi_2$ compounds are $\sim$5 nm.

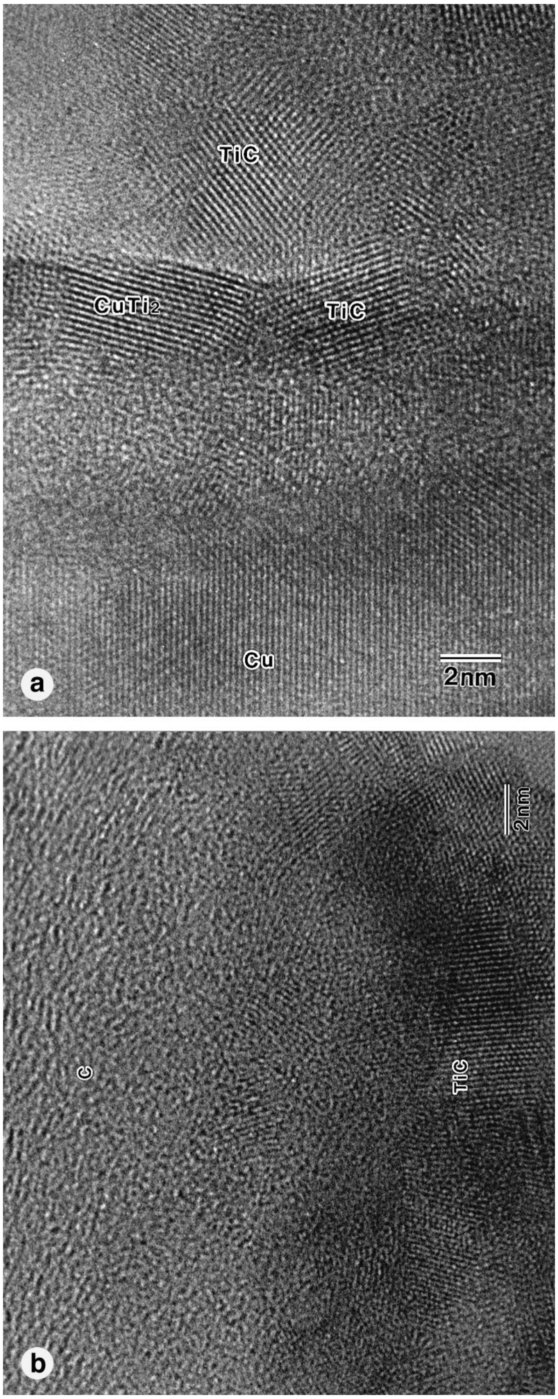

Fig. 5. HREM images at the interface between carbon and copper in Fig. 5(b). (a) Interface between carbon and titanium carbide. (b) Interface between titanium and carbon.

The C/Cu interface of CX-2002U + Cu(Ti) was also investigated by TEM and ED, as shown in Fig. 6(a) and (b), respectively. In the ED pattern of Fig. 6(b) which was taken along [1 $\bar{1}$ 1] of Cu crystal, Debye–Scherrer rings corresponding to TiC and $CuTi_2$ are observed in addition to the Cu reflections. Microcrystals of TiC and $CuTi_2$ are distributed at the C/Cu interface as shown in Fig. 6(a). Grain sizes of the compounds are ~5 nm, which was the same as those seen in Fig. 5.

In order to confirm the interfacial structure, the titanium distribution at the C/Cu interface of IG-430U + Cu(Ti) was investigated by EDX analysis, as shown in Fig. 7. The sample containing the interface between carbon and copper was cut out of the surface portion of the graphite block which was covered with the molten copper. Titanium cocentration in the interface between carbon and copper grain in Fig. 3 is presumed to be almost the same as Fig. 7. Titanium concentration is high at the C/Cu interface, which also indicates formation of TiC and $CuTi_2$ compounds.

The above results indicate that a small amount of titanium reacted wtih C and Cu to form TiC and $CuTi_2$ compounds, which results in the increase of thermal conductivity. Fig. 8 is a model of thermal conduction for the present C/Cu(Ti) composite materials. It is believed that the thermal energy would pass through both C and C/Cu/C. In particular, thermal conductivity is increased by the addition of a small amount of titanium which forms TiC and Ti–Cu compounds at the interface. This compound formation would increase the cohesion at the C/Cu interface, which results in the high thermal conductivity at high temperatures. On the other hand, the influence of titanium on the graphitization of graphite has been investigated [12–14]. They found that an addition of titanium facilitates graphitization of the material. This fact may contribute to the increase in thermal conductivity in addition to that due to the formation of titanium compounds. The present study indicates that the addition of a small amount of the third element with the low enthalphy of alloy formation with C and Cu will increase the thermal conductivity and the stability at high temperatures. Since zirconium has the lowest ΔH values with C and Cu, further increase of the thermal conductivity could be expected by the addition of a small amount of zirconium to C/Cu materials.

4. Conclusions

The thermal conductivity of carbon/copper composite materials was larger than that of the original carbon material at high temperatures. However, the thermal conductivity at room temperature was smaller than that of the original one. The reason for this was that carbon materials were not cohesive with copper and that there may exist some gaps at the interface between carbon and copper. The addition of a small amount of titanium to

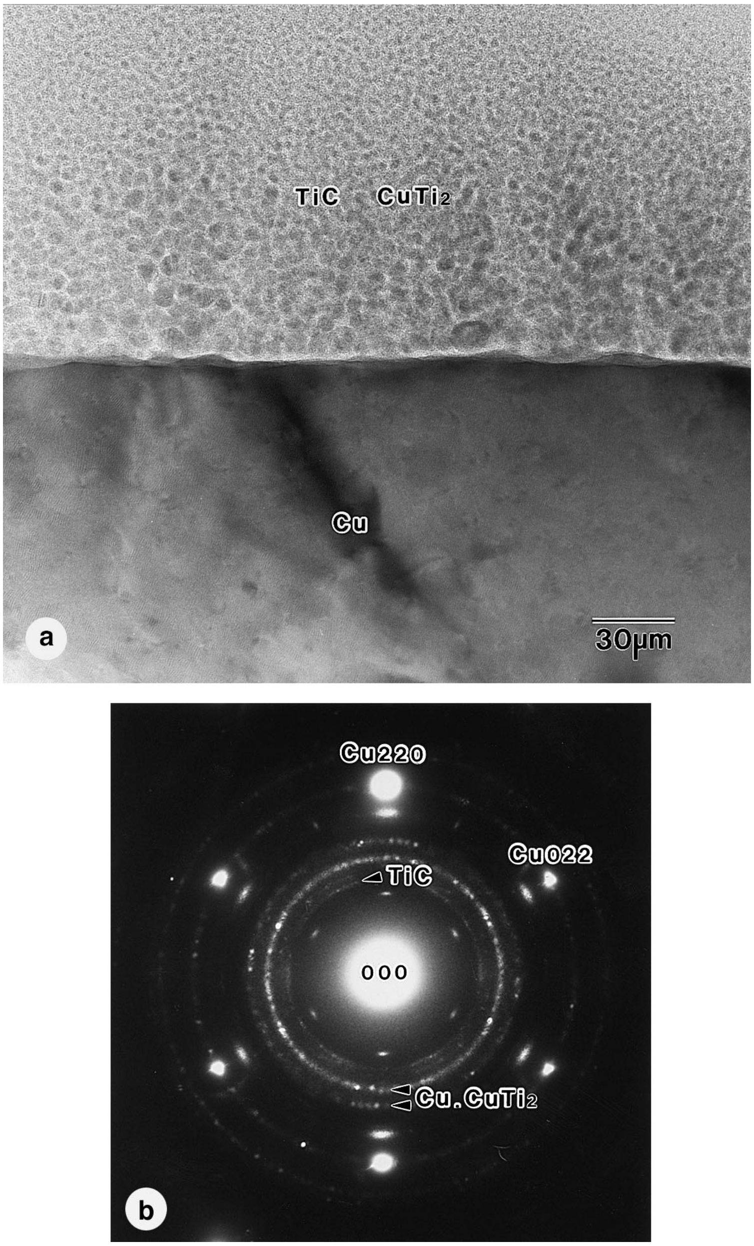

Fig. 6. TEM image (a) and ED pattern (b) of the interface between carbon and copper in CX-2002U + Cu(Ti).

the carbon/copper composite materials increased the thermal conductivity over the temperature range measured here, and decreased the temperature dependencies of thermal conductivity. The effects of titanium addition on the temperature dependence of thermal conductivity of carbon/copper composite materials were confirmed to be due to the existence of cohesive compounds, such as TiC and $CuTi_2$ on the interface between carbon and copper in the copper impregnated carbon materials by TEM analyses. In addition, an increase in graphitization by titanium addition may increase thermal conductivity of the carbon materials.

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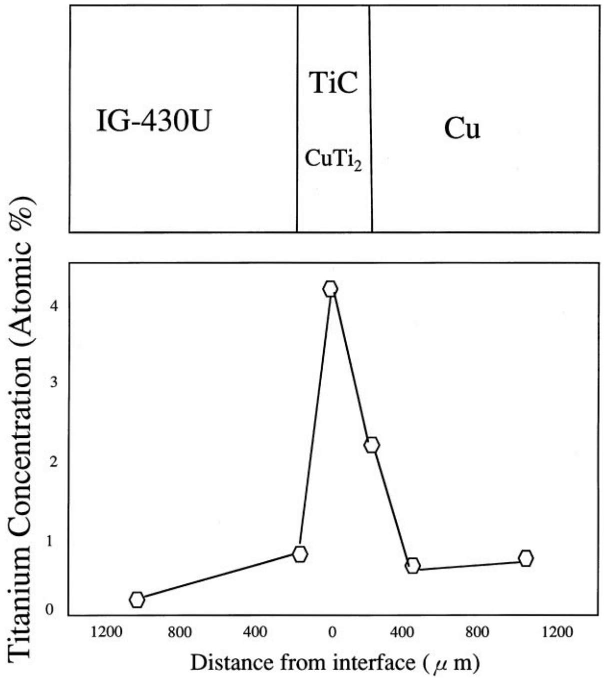

Fig. 7. Titanium concentration near the interface between carbon and copper on the surface of bulk graphite (IG-430U) covered by copper for impregnation.

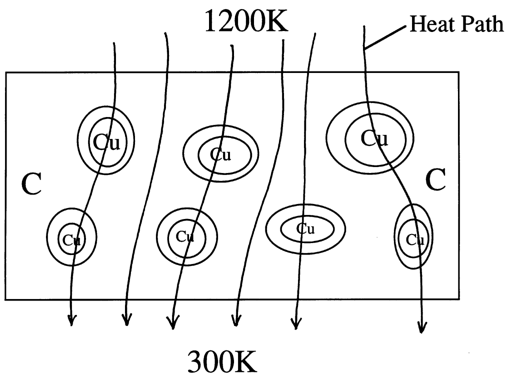

Fig. 8. A model of thermal conduction for the carbon/copper composite materials with titanium.

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References

[1] T.D. Burchell, T. Oku, Atomic and Plasma-Material Interaction Data for Fusion (Supplement to the Journal Nuclear Fusion), vol. 5, IAEA, Vienna, 1994, p. 77.
[2] K. Nakamura et al., J. Nucl. Mater. 196–198 (1992) 627.
[3] J. Linke et al., J. Nucl. Mater. 196–198 (1992) 607.
[4] C.H. Mantell, Carbon and Graphite Handbook, Interscience, New York, 1968, p. 446.
[5] T. Oku et al., Extended Abstracts of Carbon 95, UCSD (1995) 772.
[6] T. Oku et al., J. Nucl. Sci. Technol. 32 (1995) 816.
[7] T. Oku et al., TANSO 170 (1995) 280.
[8] F.R. de Boer et al., Cohesion in Metals, North-Holland, Amsterdam, 1988, p. 133.
[9] T. Oku, H. Wakimoto, A. Otsuki, M. Murakami, J. Appl. Phys. 75 (1994) 2530.
[10] T. Oku, E. Kawakami, M. Uekubo, K. Takahiro, S. Yamaguchi, M. Murakami, Appl. Surf. Sci. 99 (1996) 265.
[11] Y. Takahashi et al., private communication.
[12] T.A. Burtseva et al., J. Nucl. Mater. 191–194 (1992) 309.
[13] L. Mazul et al., Proceedings of the Sixth International Carbon Materials Workshop, Jülich, 1993, p. 43.
[14] V.N. Chernikov et al., J. Nucl. Mater. 209 (1994) 148.