FORMATION OF SUPERCONDUCTING COMPOUNDS, WHICH ARE METASTABLE AT ROOM TEMPERATURE, BY PLASMA HEATING

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ABSTRCT

Superconducting compounds, such as cubic β-WC_{1-x}, hexagonal MoB_2 and δ-TaN, which were metastable at room temperature, were formed by heating and quenching of respective equilibrium phases which were not superconductors in the plasma jet.

1. INTRODUCTION

Metastable phases of transition metal carbides, nitrides, and boride, such as cubic α-MoC_{1-x} (1), cubic β-WC_{1-x} (2), cubic δ-TaN (3) and hexagonal MoB_2 (4) are superconductors, the transition temperature of which are higher than those of respective stable phases. Quenching of these metastable phases from higher temperatures have been carried out by means of splat melting (4,5) or sintering under high pressures (6). Using plasma jet for powder heating very high quenching rate of 10^8 deg s^{-1} is possible (7).

The authors have studied the formation of various transition metal carbides and nitrides, such as NbC (8), TaC (9), TiN and ZrN (10) by means of plasma arc. The metastable transition metal compounds described above could not be prepared by means of plasma arc because of low quenching rate.

In this paper, formation of cubic β-WC_{1-x}, hexagonal MoB_2 and cubic δ-TaN which are metastable superconductors at room temperature by heating of respective equilibrium phases, such as hexagonal WC, rhombohedral Mo_2B_5 and hexagonal TaN, in the plasma jet and solid solutions of W-Ti-C and Mo-Zr-B systems are described together with the identification and some properties of products.

2. EXPERIMENTAL

Materials : Elemental and oxide powders used in this study were described in each parts. Powders were mixed in desired

molar ratios and pressed into tablet. Purified argon and nitrogen were used as plasma gas.

Apparatus and Procedures : Plasma arc furnace and heating procedure are the same as described previously (11). After the products obtained by plasma arc heating crushed into powder below 44μm in size, powder was heated again in the argon or argon-nitrogen plasma jet. The plasma jet furnace is the same as described previously (12). The products were investigated by X-ray diffraction and chemical analyses. The superconducting transition temperature of the product was measured with a 100 kHz self inductance bridge and germanium thermometer.

3. RESULTS AND DISCUSSION

3.1 W-C system (12)

Tungsten carbide is known to form high temperature phase of the composition of WC with hexagonal unit cell. Cubic modification of the carbide, β-WC_{1-x}, has been found at above 2500°C. Since β-WC_{1-x} transforms into hexagonal WC and W_2C below 2500°C, rapid quenching of the carbide from high temperature is necessary to obtain cubic β-WC_{1-x} at an ordinary temperature.

Powder of WO_3 was mixed with graphite powder at a desired molar ratios. About one gram of the mixture was pressed into tablet. The tablet was heated in an argon plasma arc at about 3000°C. Heating was continued for 3 min and then the plasma arc was stopped. After the product was crushed into powder, the powder was injected into an argon plasma jet and heated again. (Optimum conditions were as follows : Power input was 2.2 kW (22 V, 100 A), Ar flow rate 20 l min^{-1}, powder injection rate 0.5 g min^{-1}.) Heating the powder in the plasma jet produced spherical particle below 20 m in size, so the powder injected into the plasma jet was melted. The products obtained by plasma arc heating was identified to be WC and W_2C. By the plasma arc heating procedure, the quenching rate was about 10^2 deg s^{-1}. It was too small to obtain the cubic phase. The formation of cubic β-WC_{1-x} was observed by heating of the mixture of WC and W_2C in the plasma jet. By the plasma jet heating procedure, the quenching rate was about 10^8 deg s^{-1}, so the cubic phase could be obtained. The lattice parameter of β-WC_{1-x} was 4.25 A and was comparable to that reported in the literature (2).

The contents of combined carbon, free carbon and oxygen remarkably decreased by heating in the plasma jet. Both of CO and CO_2 were detected with argon in the off gas from the plasma jet reactor by gas chromatogram. So carbon and oxygen would be removed as CO and CO_2.

The relation between the out put of the self inductance bridge and temperature was shown in Fig. 1. The product obtained by the heating in the plasma jet, having the superconducting temperature of 6.9 K, was obtained from hexagonal WC that was normal down to 4.2 K.

Tungsten carbide formed solid solutions having a cubic lattice with TiC, ZrC or HfC (13). Tungsten oxide was mixed with TiO_2, ZrO_2 or HfO_2 and graphite at the desired ratios and

the mixture was heated in the argon plasma arc at about 3000°C to form cubic solid solution. The cubic solid solution was identified when the additive metal content was larger than 2 at.%. From the change of the lattice parameter and the density caused by the addition of Ti, Zr or Hf, it seems that Ti, Zr or Hf in W-C system replaces the W atom in W-C lattice and stabilizes the cubic form.

Cubic phases containing 14% of Ti, 10% of Zr or Hf have the highest Tc in each case and were 8.4 K, 6.2 K and 6.2K, respectively. The curve for W-Ti-C system is shown in Fig. 1 as an example.

3.2 Mo-B system (14)

Hexagonal AlB_2 type molybdenum diboride, MoB_2, is stable above 1500°C and has a homogeneity range of 62-67 at.% B (15). As MoB_2 decomposes into α-MoB and Mo_2B_5 below 1500°C, rapid quenching from high temperatures is necessary to obtain hexagonal MoB_2. Hexagonal MoB_2 was prepared by arc melting of mixture of elemental powders, but the product as cast was close to $MoB_{1.7}$. When the nominal composition of $MoB_{2.5}$ was splat melted, excess B was forced into the hexagonal lattice (4).

Hexagonal MoB_2 was formed by the melting of mixture of Mo and B powders in the argon plasma arc following heating in the plasma jet in the same way describing in the W-C system.

Chemical and X-ray analysis data for the products obtained by the melting of Mo and B in the argon plasma arc are given in Table 2. Hexagonal AlB_2 type phase was obtained in $MoB_{2.0}$. When the boron content exceeded $MoB_{2.0}$, rhombohedral Mo_2B_5 was the main phase in the products. The rhombohedral phase obtained by the plasma arc melting were heated again in the plasma jet. Chemical and X-ray analysis data of the product are also given in Table 2. The hexagonal phase including trace of the rhombohedral phase was obtained. The boron content considerably decreased by the plasma jet heating procedures.

The hexagonal MoB_2 was formed in the range of $MoB_{2.0}$-$MoB_{2.3}$ in almost single phase by means of plasma arc melting following plasma jet heating. One lattice parameter of the hexagonal phase, c, increased with increasing boron content from 3.07 to 3.13 A, but a was almost constant in spite of the change of boron content. The density of products with a single phase increased with increasing boron content. The measured values agreed with those determined by means of X-ray diffraction, if we assumed that the Mo atom and B atom positioned in the hexagonal lattice were occupied and the excess B atoms are positioned in the interstitial site.

Hexagonal $MoB_{2.0}$ was found to be superconductor with a Tc of 4.2 K as shown in Fig. 2. The samples containing more than 70 at.% B obtained by plasma arc melting were rhombohedral and normal down to 2.2 K. Plasma jet heating of the rhombohedral phase caused transformation to the hexagonal phase also changed it to a superconductor. The maximum value of Tc was 7.0 K and was comparable that reported by Cooper et al. (4). The hexagonal phase of molybdenum diboride containing excess boron in the lattice is a superconductor with a high Tc.

These samples were easily formed by plasma arc melting followed by plasma jet heating of a mixture of molybdenum and boron.

Since a hexagonal solid solution was formed in Mo-Zr-B system(4), the mixture of Mo, Zr and B powders was heated in the argon plasma arc at about 3000°C and prepared the hexagonal solid solution. The hexagonal phase was identified when the Zr content was more than 1 at.%. From the increase of the lattice parameter and the change of the density caused by the addition of Zr, it seems that Zr in Mo-B system replace the Mo atom in Mo-B lattice. The products were superconductors, Tc of which were higher than 8 K as shown in Fig. 2.

3.3 Ta-N system (16)

Since δ-TaN, which has the NaCl crystal structure type, is a high temperature phase and it transforms into hexagonal ε-TaN and Ta_2N below 1950°C, it was prepared by heating hexagonal TaN above 1950°C under high pressures of nitrogen atmosphere to prevent a decomposition of TaN to Ta_2N (3).

Hexagonal TaN was prepared by heating of tantalum powder in a nitrogen atmosphere under normal pressure at 1200°C for 30 hours. After crushing the product into powder finer than 44 μm in size, it was heated again in a nitrogen-argon mixed plasma jet. (Optimum conditions were as follows : Power input was 4 kW (50 V, 80 A), N_2 flow rate 5 l min^{-1}, Ar flow rate 15 l min^{-1}, powder injection rate 0.5 g min^{-1}).

The product obtained by heating tantalum powder in the nitrogen atmosphere was hexagonal -TaN with lattice parameters a=5.20 A and c=2.89 A, respectively. The lattice parameters were approximately equal to those of hexagonal -TaN. The nitrogen content of product was 6.98 % and was comparable with that of stoichiometric TaN.

The product obtained by heating ε-TaN in the nitrogen-argon mixed plasma jet was identified as a mixture of hexagonal ε-TaN, Ta_2N and cubic NaCl type TaN. The lattice parameter of the cubic phase was 4.33 A and was approximately equal to that of cubic TaN prepared under high pressures (3). Nitrogen content of the product was 5.00 %.

When ε-TaN that was normal down to 4.2 K was heated in the nitrogen-argon mixed plasma jet, the product having the transition temperature at 8.3 K was prepared. It is higher than Tc's value in literature (3). As a superconducting transition is not observed in Ta_2N down to 4.2 K, it is considered that the transition point is based on cubic TaN. By heating and quenching powdered hexagonal ε-TaN using a plasma jet, superconducting cubic TaN with a high transition temperature was easily formed under normal pressure.

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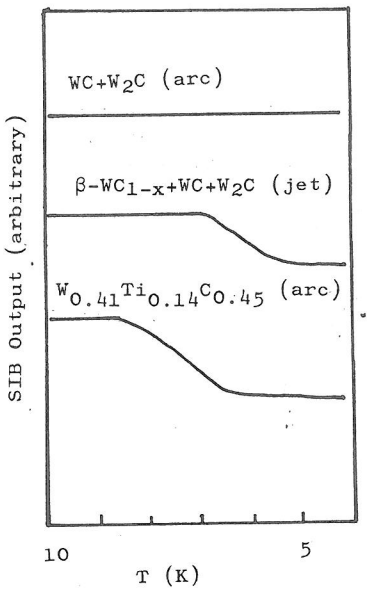

Fig. 1

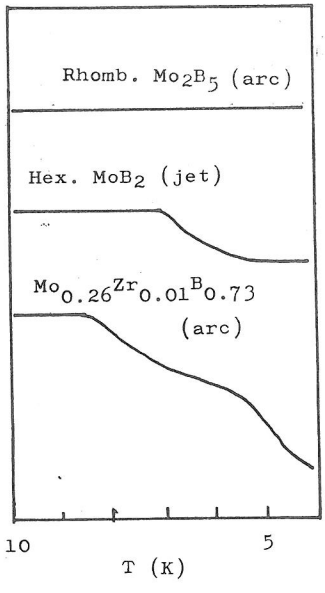

Fig. 2

Table 1 Chemical and X-ray analysis data of products in W-C system

	W_xC_y x	W_xC_y y	Free C wt.%	O wt.%	Identified phases	a of cubic phase A
Plasma arc heated	0.49	0.51	3.15	0.58	WC, α-W_2C	-----
Plasma jet heated	0.58	0.42	1.41	0.07	β-WC_{1-x}, WC α-W_2C	4.25

Table 2 Chemical and X-ray analysis data of products in Mo-B system

	No.	Mo_xB_y x	Mo_xB_y y	Identified phases	Lattice parameters A a	Lattice parameters A c
Plasma arc heated	1	0.33	0.67	MoB_2	3.05	3.07
	2	0.30	0.70	Mo_2B_5 + tr.MoB_2	(3.00)	(21.0)
	3	0.28	0.72	Mo_2B_5 + tr.MoB_2	(3.00)	(21.0)
Plasma jet heated	2	0.33	0.67	MoB_2 + tr.Mo_2B_5	3.05	3.12
	3	0.30	0.70	MoB_2 + tr.Mo_2B_5	3.05	3.13

( ) represents the hexagonal parameters for rhombohedral phase.