研 究

Synthesis of New Mono-Carbonitride (W,Mo)(C,N) Powder by Heating W-Mo Alloy + C Mixed Powder in High-Pressure Nitrogen Gas

Nobuaki Asada^{★1}, Yoshiharu Yamamoto^{★1}, Tadashi Igarashi^{★2}, Yoshihiko Doi^{★3} and Koji Hayashi^{★4}^{★1}Allied Material Corp., Ltd., 2 Iwasekoshi-machi, Toyama 931-8543.^{★2}Formerly, Tokyo Tungsten Co., Ltd., 2-23-1 Kitarokkohdai, Nishinomiya 651-1413.^{★3}Allied Material Corp., Ltd., 5-24-8 Higashi-Ueno, Taito-ku, Tokyo 110-0015.^{★4}Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505.

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SYNOPSIS

We have already succeeded in synthesizing new mono-carbonitrides W(C,N) and Mo(C,N) with 11~20 at%N and 14~25 at%N respectively by heating W + C and Mo + C mixed powder in high-pressure N₂ gas of 10~160 MPa at 1523~1673 K. In this study, the synthesis of new (W,Mo)(C,N) powder was tried by heating W + Mo + C mixed elemental powder and W-Mo solid solution alloy + C mixed powder in such high-pressure-N₂ gas. (W,Mo)(C,N) with N content of 14~24 at% could be synthesized at 25~160 MPa in case of (W-Mo)+C mixed powder (Metal/C atomic ratio is 1/1), while (W,Mo)(C,N) could not in case of W + Mo + C mixed elemental powder.

KEY WORDS

tungsten, molybdenum, carbonitride, (W,Mo)(C,N), nitrogen, high-pressure, powder, synthesis

1 Introduction

Carbonitride powders including Ti such as Ti(C,N) and (W,Ti)(C,N) powders are used as the main component or additive for TiC base cermets and WC base hardmetals, respectively^{1,2)}. However, carbonitride powder of W itself and also of Mo, i.e., W(C,N) and Mo(C,N) powders, were not synthesized before our previous studies^{3,4)}: we have already succeeded in synthesizing W(C,N) and Mo(C,N) with 11~20 at%N and 14~25 at%N respectively by heating W + C and Mo + C mixed powders in high-pressure N₂ gas of 10~160 MPa at 1523~1673 K for 3.6 ks. Here, the at%N is N content to metal, not in mono-carbonitride: 100 at% corresponds to the N/metal atomic ratio of 1/1. It was also clarified that WN and MoN could not be synthesized at pressure even up to 190 MPa.

The syntheses of W(C,N) and Mo(C,N) powders have been also succeeded by normal-pressure method, i.e., by heating W and Mo powders respectively in CH₄ + NH₃ mixed gas of normal-pressure (0.1 MPa)⁵⁻⁸⁾. Their N contents depend greatly on the heating profile, and the maximum content obtained up to now were 9 and 22 at%, respectively⁹⁾. These values are small and comparable respectively with those of mono-carbonitrides obtained by the above high-pressure method. Furthermore, it was also found that the mono-carbonitride of solid solution of these W(C,N) and Mo(C,N), i.e., (W,Mo)(C,N) powder with N

content of 23 at% can be synthesized from W-70at%Mo solid solution alloy powder⁹⁾ (abbreviated as (W-Mo) or W-Mo powder), and not from W + Mo mixed elemental powder by the normal-pressure method. WN and (W,Mo)N were not synthesized and MoN containing a large amount of Mo₂N was synthesized by this normal-pressure method as far as the heating time was 3.6 ks^{5,9,10)}.

In this work, the synthesis of (W,Mo)(C,N) was attempted by the high-pressure method, i.e., by heating W + Mo + C and (W-Mo) + C mixed powders in N₂ gas of high-pressure gas up to 160 MPa. The possibility of synthesizing the mono-nitride of W-Mo, i.e., (W,Mo)N powder by the high-pressure method was also investigated beforehand.

2 Starting Materials and Experimental Procedures

W and Mo elemental powders and W-70at%Mo solid solution alloy powder with mean secondary particle size of 0.3, 4.5 and 1.0 μm and with primary particle size of 0.3, 1.0 and 0.5 μm, respectively, were used as starting materials. The contents of C, N and O in these three kinds of powders were commonly 0.01, 0.002 and 0.04~0.07 mass%, respectively. Carbon powder with mean secondary particle size of 0.7 μm was used as the carbon source, differing from CH₄ in the normal-pressure method⁵⁻⁸⁾. This is because CH₄ gas is not generally used in HIP-furnace. The content of N and O of the carbon powder were 0.24 and 0.062

mass%, respectively, which were considered to be due to the adsorbed N_2 , O_2 and H_2O from air, because the compounds of C with N, O or H are not solids, but gases.

In case of W+Mo mixed elemental powders, W, Mo and C powders were combined so that the W/Mo atomic ratio (hereafter, also expressed as W/Mo) becomes 2/1, 1/1, and 1/2 and that (W+Mo)/C atomic ratio becomes 1/0 (i.e., free from C) and 1/1. In case of W-Mo solid solution alloy powder, W-Mo and C powders were combined so that W-Mo/C atomic ratio becomes 2/1 and 1/2 as well as the above 1/0 and 1/1. Then, these combined powders were mixed by ball-milling for 86.4 ks, differing from in the normal-pressure method where a pestle and agate mortar were used for mixing. The reason for the difference in the mixing method is that C powder with low reactivity was used as the carbon source in the high-pressure method instead of CH_4 gas in the normal-pressure method and thus the refinement of C particles and sufficient mixing are needed. In case of normal-pressure method, active nascent C atoms are generated by the decomposition of CH_4 . These mixed powders were weakly compacted by die-pressing under 1 MPa. The relative density of the compact was about 50%.

These powder compacts were heated in N_2 of 0.1 ~ 150 or 160 MPa at 973 ~ 1773 K for 3.6 ks by using N_2 -HIP furnace where the materials of both heating element and insulator were both graphite, as in the previous studies on W(C,N)³ and Mo(C,N)⁴. The heating time was varied in

the range of 0 ~ 14.4 ks, if necessary. Each product was porous and easily crushed to powder.

For each product powder, the contents of total-carbon, free-carbon, and combined-carbon, -nitrogen and -oxygen were analyzed by using WR-112 and TC-136, LECO Co. Ltd. as in the previous studies³⁻⁸. The phases in the product powders were identified by X-ray diffraction analysis. The particle sizes and morphologies of the starting and product powders were investigated with SEM. From these results, the possibilities of synthesizing (W,Mo)N and (W,Mo)(C, N) by high-pressure method were judged.

3 Experimental Results and Discussion

3.1 W+Mo mixed elemental powder

3.1.1 W+Mo free from C

Fig. 1 (a)~(c) show the effect of N_2 pressure (P_{N_2}) on the mass% of C (combined-carbon), N and O of the product powders which were obtained by heating W+Mo mixed elemental powder with W/Mo of 2/1, 1/1 and 1/2 respectively in N_2 at 1673 K for 3.6 ks. The N content of the product powder was 0.0 mass% at 0.1 MPa for all W/Mo and increased with increasing P_{N_2} particularly up to 100 ~ 150 MPa. The N contents increased with decreasing W/Mo: the N contents, e.g., at 150 MPa, were 0.8, 2.4 and 4.3 mass% for W/Mo of 2/1, 1/1 and 1/2, respectively. The C and O contents for all W/Mo did not vary by increasing P_{N_2} .

The (C+N)/(W+Mo) atomic ratio of the product powders was shown by the lower curve in Fig. 2. The ratio can be said to be substantially N/(W+Mo) atomic ratio by taking into consideration that C content was nearly zero as shown in Fig. 1. The ratio became about 0.25 at 150 MPa.

Fig. 3 (a)~(c) show the effect of P_{N_2} on the X-ray diffraction profiles of the starting W+Mo mixed elemental

Fig.1 Effect of N_2 pressure (P_{N_2}) on mass% of C (combined-carbon), N and O of product powders which were obtained by heating (W+Mo)/C of 1/0 with W/Mo of 2/1, 1/1 and 1/2 in N_2 at 1673 K for 3.6 ks.

Fig.2 Effect of P_{N_2} up to 150 MPa on (C+N)/(W+Mo) atomic ratio of products which were obtained by heating W+Mo of 1/1 with (W+Mo)/C of 1/1 and 1/0 in N_2 at 1673 K for 3.6 ks.

powder with W/Mo of 1/2, 1/1 and 2/1, respectively, and of the product obtained by heating them in N_2 of 0.1, 10 and 150 MPa at 1673 K for 3.6 ks. Fig. 4 (a)~(c) show the X-ray diffraction profiles at 2θ of about 100~102 degree where the peaks of W and Mo are clearly separated from each other. The results at 50, 100 and 160 MPa which are not shown in Fig. 3 were nearly similar to those at 10, 150 and 150 MPa, respectively. The phases which were identified by taking into consideration the above C, N and O at%, the (C+N)/(W+Mo) atomic ratio and the previous results^{3,4)} on W and Mo, were shown in the figure. The profiles for the product powder for all W/Mo atomic ratios were the same as those of each starting powder up to 50

MPa. At 100 and 150 MPa, γ - Mo_2N peaks appeared and Mo peaks disappeared. However, W_2N did not appeared and W peaks did not disappeared. Thus, the product was identified to be Mo_2N +W mixture. This corresponds to the results that W_2N and γ - Mo_2N were not and were generated respectively by heating W and Mo powder^{3,4)}. This suggests that the diffusion distances of W and Mo are both very short.

Namely, it was clarified that (W,Mo)N mono-nitride can not be synthesized by heating the mixed elemental powder of W and Mo in high-pressure N_2 gas, in the same way as by the normal-pressure method⁹⁾, as far as the P_{N_2} is below 160 MPa

3.1.2 (W+Mo)/C of 1/1

Fig. 5 show the effects of P_{N_2} and W/Mo of mixed powder on the chemical composition of the product which were obtained by heating W+Mo+C mixed elemental powders with (W+Mo)/C of 1/1 in N_2 at 1673 K for 3.6 ks. The C contents at 0.1 MPa were about 6.0 mass% for all W/Mo.

Fig. 3 Effect of P_{N_2} on X-ray diffraction profiles of the product obtained by heating (W+Mo)/C of 1/0 with W/Mo of 2/1, 1/1 and 1/2 in N_2 at 1673 K for 3.6 ks.

Fig. 4 X-ray diffraction profiles near diffraction angle 2θ of 95~102 degree for the products obtained by heating W+Mo+C with (W+Mo)/C of 1/1 and with W/Mo of 2/1, 1/1 and 1/2 in N_2 at 1673 K for 3.6 ks.

With increasing P_{N_2} up to 50 MPa, the C content hardly varied in case of W/Mo of 2/1, but increased up to about 6.5 and 7.2 mass% in cases of W/Mo of 1/1 and 1/2, respectively, and it slightly decreased from 6.0, 6.5 and 7.2 mass% to about 5.7, 6.3 and 7.0 mass% for each W/Mo at 150 MPa, respectively. On the other hand, the N content at 0.1 MPa was about 0.4 mass% for all W/Mo. It increased with increasing P_{N_2} and reached to 1.6, 1.7 and 2.0 mass% at 150 MPa for W/Mo of 2/1, 1/1 and 1/2, respectively. The O contents for all W/Mo hardly varied by changing P_{N_2} . The free carbon content of the products from mixed

powder with (W+Mo)/C of 1/1 were 0.5~1.5 mass%.

The atomic ratios of (C+N)/(W+Mo) of the product powder for W/Mo of 1/1 which were calculated based on the above mass%, are shown by the upper curve in the previous Fig. 2. The ratio became nearly unit at 100~150 MPa. The same result was also obtained for another W/Mo.

Fig. 6 (a)~(c) show the effect of P_{N_2} on the X-ray diffraction profiles of the above product. Fig. 7 (a)~(c) show the X-ray diffraction profiles at 2θ of about 98~100 degree where the peaks of W(C,N) and Mo(C,N) are clearly separated from each other. In these figures, the phases of W(C,N), Mo(C,N) and Mo₂C, which were identified by taking into consideration also the above results on the C

Fig. 5 Effect of P_{N_2} and W/Mo of starting powder on the mass% of C (combined-carbon), N and O of products obtained by heating (W+Mo)/C of 1/1 with W/Mo of 2/1, 1/1 and 1/2 in N_2 at 1673 K for 3.6 ks.

Fig. 6 Effect of P_{N_2} on X-ray diffraction profiles of products obtained by heating (W+Mo)/C of 1/1 with W/Mo of 2/1, W/Mo and 1/2 in N_2 at 1673 K for 3.6 ks.

Fig.7 (a)~(d) X-ray diffraction profiles near 2θ of 98~100 degree for the product obtained by heating W+Mo+C with (W+Mo)/C of 1/1, and with W/Mo of 1/2 (a), 1/1 (b), 2/1 (c), and also (W-Mo)+C with W-Mo/C of 1/1 (d) in N_2 at 1673 K for 3.6 ks.

and N contents, etc., were shown.

It was concluded that W(C,N)+Mo(C,N) mixture were generated, and (W,Mo)(C,N) could not be synthesized by heating W+Mo+C mixed elemental powder in high-pressure N_2 gas of up to 150 MPa, in the same way as by the normal-pressure method⁹⁾.

3.2 W-Mo solid solution alloy, i.e., W-Mo powder

3.2.1 W-Mo free from C

Fig. 8(a) shows the effect of P_{N_2} on the mass% of C, N and O of the product powder which was obtained by heating W-Mo powder without C powder in N_2 at 1673 K for 3.6 ks. The C content was of course nearly zero for all P_{N_2} . The N content increased with increasing P_{N_2} , and reached about 5 mass% at 150 MPa. Fig. 9(a) shows the effect of the heating temperature (T_h) on the chemical composition of the product, which was obtained by heating the alloy powder at 160 MPa for 3.6 ks. The N content increased firstly and then decreased with decreasing T_h from the above 1673 K to 1473 and 973 K, and it decreased with increasing T_h from 1673 K to 1773 K. Such decrease of N content in the temperature range from 1473 K to 973 K was thought to be because the product did not reach an equilibrium state by heating for 3.6 ks at 973 K, taking into consideration that carbonitride becomes more stable with decreasing temperature.

The lowest curve in Fig. 10 shows the effect of P_{N_2} on the (C+N)/(W+Mo) of the product, which is substantially

Fig.8 Effect of P_{N_2} on mass% of C (combined-carbon), N and O of the products obtained by heating W-Mo with W-Mo/C of 1/0, 2/1 and 1/1 in N_2 at 1673 K for 3.6 ks.

N/(W+Mo). It became about 0.5 at 160 MPa.

Fig. 11 (a) shows the effects of P_{N_2} and W-Mo/C on the X-ray diffraction profiles of the product obtained by heating (W-Mo)+C mixed powders in N_2 at 1673 K for 3.6 ks, and so on. The results at 50, 100 and 150 MPa for all W-Mo/C were nearly similar to those at 10, 150 and 150 MPa, respectively. The phases which were identified by taking into consideration also the above chemical composition, the (C+N)/(W+Mo) atomic ratio and the previous results^{3,4)} on W and Mo, were shown in the figure. The products were the same as those of each starting powder, i.e., the W-Mo did not change up to 50 MPa, and were (W,Mo)₂N at 100, 150 and 160 MPa.

Namely, it was clarified that (W,Mo)N mono-nitride could not be synthesized by heating the W-70at%Mo solid solution powder in high-pressure N_2 gas up to 160 MPa, in the same way as by the normal-pressure method⁹⁾.

Fig.9 Effect of T_h on mass% of C, N and O of products obtained by heating W-Mo with W-Mo/C of 1/0 and 1/1 in N_2 of 160MPa for 3.6 ks.

Fig.10 Effect of P_{N_2} on $(C+N)/(W+Mo)$ atomic ratio of products obtained by heating W-Mo with W-Mo/C of 1/0, 2/1, 1/1 and 1/2 in N_2 at 1673 K for 3.6 ks.

3.2.2 W-Mo/C of 1/1

Fig. 8 (b) and (c) show the effect of P_{N_2} on the mass% of C, N and O of the product which were obtained by heating (W-Mo)+C mixed powders with W-Mo/C of 2/1 and 1/1

Fig.11 Effect of P_{N_2} on X-ray diffraction profiles of product obtained by heating W-Mo with W-Mo/C of 1/0, 2/1 and 1/1 in N_2 at 1673 K for 3.6 ks.

in N_2 at 1673 K for 3.6 ks. The C contents at 0.1 MPa were about 4.2 and 8.3 mass% for W-Mo/C of 2/1 and 1/1 respectively. With increasing P_{N_2} up to 50 MPa, the C content did not vary in case of W-Mo/C of 2/1, but in case of W-Mo/C of 1/1 it decreased gradually from 10 MPa and became about 4.0 and 6.7 mass% for W-Mo/C of 2/1 and 1/1 at 160 MPa, respectively. On the other hand, the N content at 0.1 MPa was about 0.2 mass% for W-Mo/C of 2/1 and 1/1. With increasing P_{N_2} , it increased from 10 MPa and reached 0.9 and 2.5 mass% for W-Mo/C of 2/1 and 1/1 at 160 MPa, respectively. The O contents hardly varied by P_{N_2} . The free-C contents of the product from mixed powder with W-Mo/C of 2/1 and 1/1 were 0.0 and 0.0~1.3 mass%,

respectively.

The atomic ratios of (C+N)/(W+Mo) of the product for W-Mo/C of 2/1, 1/1 and 1/2 of the mixed powder, which were calculated based on the above mass%, are shown by the upper three curves in the previous Fig. 10. The ratios became nearly 1.0, 0.5 and 0.6 for W-Mo/C of 1/2, 1/1 and 2/1, respectively, at 100~160 MPa.

Fig. 9 (b) shows the effect of T_h on the chemical composition of the product which was obtained by heating the powder with W-Mo/C of 1/1 at 160 MPa for 3.6 ks.

Fig.12 Effects of P_{N_2} and T_h on atomic composition of (W,Mo)(C,N) obtained by heating W-Mo with W-Mo/C of 1/1 for 3.6 ks.

The N and C contents were 1.9 and 7.1 mass%, e.g., at 1773 K, respectively.

Fig. 11 (b) and (c) show the effect of P_{N_2} on the X-ray diffraction profiles of the above product powder. Fig. 7 (d) shows the X-ray diffraction profiles at 2θ of about 98~100 degree. The phases above 1473 K for W-Mo/C of 1/1 and 1/2 were the targeted (W-Mo)(C,N), which were identified by taking into consideration the above all results.

Fig. 12 shows the effects of T_h and P_{N_2} on the C and N atomic ratios, i.e., x and y values of C_xN_y of the product powders which were obtained by heating (W-Mo)+C mixed powder with W-Mo/C of 1/1 in N_2 for 3.6 ks. At a fixed T_h of 1673 K, where the products were all (W,Mo)(C,N), the N content increased from 2 at% to 24 at% with increasing P_{N_2} from 0.1 to 160 MPa. On the other hand, at a fixed P_{N_2} of 160 MPa, the products were not pure (W,Mo)(C,N), but (W,Mo)(C,N)+ Mo_2N mixed powder at 973 K, and (W,Mo)(C,N) with N content of 24 and 19 at% at 1473 and 1773 K respectively.

It was concluded that (W,Mo)(C,N) with N contents of 11~24 at% could be synthesized by heating (W-Mo)+C mixed powder with W-Mo/C of 1/1 in N_2 of 10~160 MPa and above 1473 K.

Fig. 13 (a) and (b) show SEM micrographs of product powders which were obtained by heating W-Mo and (W-Mo)

	Starting materials	(a) Products (1673 K)			(b) Products (160 MPa)		
		Pressure of nitrogen gas, P_{N_2} /MPa			Heating temperature, T_h / K		
		0.1	10	100	973	1273	1773
W-Mo							
W-Mo/C(1/1)							

Fig.13 Effects of P_{N_2} and T_h on SEM micrographs of product powders obtained from W-Mo and (W-Mo)+C with W-Mo/C of 1/1.

Table 1 All results on products obtained from W, Mo, W+Mo and (W-Mo) by high-pressure and normal-pressure processes. (W-Mo) is W-70at%Mo alloy.

High-Pressure Process			
Starting Powders	Nitrogen Pressure P_{N_2} /MPa	Temperature T_h /K	Product Powders
W	10~190	973~1673	W ³⁾
Mo	50~160	1273~1773	Mo ₂ N ⁴⁾
W+Mo	100~150	1523~1673	W+Mo ₂ N
(W-Mo)	100~150	1523~1673	(W,Mo) ₂ N
W+C	10~160	1523~1673	W(C _{0.89~0.80} N _{0.11~0.20}) ³⁾
Mo+C	25~160	1523~1673	Mo(C _{0.86~0.75} N _{0.14~0.25}) ⁴⁾
W+Mo+C	10~160	1523~1673	W(C,N)+Mo(C,N)
(W-Mo)+C	10~160	1523~1673	(W,Mo)(C _{0.89~0.76} N _{0.11~0.24}) ³⁾
Normal-Pressure Process			
Starting Powders	Gas	Temperature T_h /K	Product Powders
W	NH ₃ +H ₂	973~1573	W ₂ N ⁵⁾
Mo	NH ₃	1173~1373	Mo+Mo ₂ N ⁶⁾
(W-Mo)	NH ₃	973~1573	(W,Mo)+(W,Mo) ₂ N ¹¹⁾
W	CH ₄ +NH ₃	1573	W(C _{0.91} N _{0.09}) ⁵⁾
W+C	NH ₃ +H ₂	1573	W(C _{0.97} N _{0.03}) ⁵⁾
Mo+C	NH ₃	1173~1573	Mo ₂ C ¹⁰⁾
Mo	CH ₄ +NH ₃	<1173	MoN+Mo ₂ C ¹⁰⁾
Mo	CH ₄ +NH ₃	1373~1573	Mo(C _{0.78~0.85} N _{0.22~0.15}) ^{7,8)}
(W-Mo)+C	N ₂	1573	(W,Mo)+(W,Mo) ₂ C ⁹⁾
(W-Mo)	CH ₄ +NH ₃	1573	(W,Mo)C ⁹⁾
(W-Mo)	CH ₄ +N ₂	1573	(W,Mo)C+(W,Mo) ₂ C ⁹⁾
(W-Mo)	CH ₄ +NH ₃	1373~1573	(W,Mo)(C _{0.77~0.79} N _{0.23~0.21}) ⁹⁾

+C mixed powder as a function of P_{N_2} and T_h , respectively. In case of W-Mo, the particles became coarser with increasing P_{N_2} and T_h especially above 10 MPa and 1673 K. The primary particle size of product powder was about 2 μ m, e.g., at 1773 K and 160 MPa, while the initial particle size was 1 μ m. In case of (W-Mo)+C mixed powder with W-Mo/C of 1/1, the primary particle size was hardly affected by P_{N_2} and T_h in the same way as in the case of W(C,N) and Mo(C,N), and they were all about 0.6 μ m.

Table 1 shows the all results on the products which were generated by high-pressure and normal-pressure processes on W, Mo, W+Mo and (W-Mo)³⁻¹¹⁾. The N content of (W,Mo) (C,N) is nearly the same as that of Mo(C,N), not of W(C,N). Generally speaking, the N contents of the product generated by high-pressure process were a little or considerably larger than those by normal-pressure process. The cause for the similarities or differences in the N content between two processes will be discussed hereafter.

4 Summary

The syntheses of (W,Mo)(C,N) and also (W,Mo)N were

tried by heating mixed powders of W+Mo or (W-70at% Mo)+C with and without C in high-pressure nitrogen gas of 0.1~160 MPa at 973~1773 K for 3.6 ks. The atomic ratio of metal/C was varied in the range of 1/0~1/2. The following results were obtained.

- (1) (W,Mo)N was not synthesized for two kinds of mixed powders, in the same way by the normal-pressure method.
- (2) (W,Mo)(C,N) with nitrogen content of 14~24 at% could be synthesized from (W-Mo)+C mixed powder, and not from W+Mo+C mixed elemental powder. The maximum N content was nearly the same as that (23 at%) by the normal-pressure method.
- (3) The product (W,Mo)(C,N) was easily crushed to powder, and the mean primary particle size was 0.6 μ m, which was nearly the same as that of the starting W-Mo alloy powder.

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