研 究

Synthesis of New W(C,N) Powder by Heating W+C and WO₃+C Mixed Powders in NH₃+H₂ and CH₄+NH₃ Mixed Gases

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SYNOPSIS

New tungsten carbonitride W(C,N) powder with 11~20 at% nitrogen had already been found by us to be synthesized by heating W+C mixed powder in N₂ gas of high pressure (10~160 MPa) at 1523~1773 K. In this work, the synthesis of W(C,N) powder was tried by heating W+C and WO₃+C mixed powders in NH₃+H₂ mixed gas of normal pressure (method I) and by heating W powder in CH₄+NH₃ mixed gas of normal pressure (method II), mainly at 1573 K for 3.6 ks. This try was based on the general concepts that the reactivities or activities of nitrogen and carbon atoms formed by the dissociation of NH₃ and CH₄ respectively are enormously high, compared with those of N₂ and solid carbon, respectively. It was found that the products obtained by methods I and II were W(C,N) with nitrogen contents of 3 and 5 at%, respectively. The functions of NH₃ and CH₄ in the carbonitridation of W powder were also experimentally investigated in comparison with those of N₂ and solid carbon, respectively.

KEY WORDS

tungsten, carbonitride, W(C,N), nitridation, carburization, ammonia, methane, synthesis

1 Introduction

The nitrides and carbonitrides of transition metals such as TiN, Ti(C,N), (W,Ti), (C,N) and (W,Ti,Ta) (C,N) are used in the form of powder as the starting materials or additives for TiC base cermets and WC base cemented carbides^{1,2)}. Nitride powders such as TiN powder are produced by heating the metal (Ti) powder in N₂ gas of normal pressure (0.1 MPa)^{2,3)}. One method for producing carbonitride powders such as titanium carbonitride {Ti(C,N)} powder is the heating of the mixed powder of the carbide (TiC) and the nitride (TiN) in N₂ gas of normal pressure^{2,4)}. However, tungsten carbonitride {W(C,N)} powder cannot be synthesized by the same process as that for Ti(C,N) powder. This is because tungsten mononitride (WN) which is thermodynamically stable at low temperature decomposes to W₂N and N₂ at high temperatures above 900 K⁵⁾, differing from tungsten monocarbide (WC) which is thermodynamically stable up to 2900 K in vacuum⁶⁾. Probably because of this, the carbonitride as well as nitride powders of tungsten are not on the market today.

In the previous studies^{7,8)}, we had assumed the following, mainly based on Le Chatelier's principle⁹⁾: (1) WN and W(C,N) are formed even above 900 K by heating W powder and W+C mixed powder in N₂ of high pressure,

respectively, and (2) W(C,N) powder is formed under lower N₂ pressure than WN, because WC is more thermally stable than WN as described above and thus the solid solution of WC and WN, i.e., W(C,N) has a possibility to be stable under lower N₂ pressure, compared with WN. The experimental results were partly as expected: W(C,N) with nitrogen contents of 11~20 at% could be obtained by heating at 1523~1773 K in N₂ of 10~160 MPa, although WN powder could not even in N₂ of 190 MPa^{7,8)}. These results indicated that W(C,N) is surely more stable than WN under low N₂ pressure. The crystal structure of W(C,N) was clarified to be hexagonal in accordance with those of WC and WN. This result would be reasonable, considering that the difference in lattice parameters between WC and WN is small (*a*₀ are 2.906 and 2.896 Å respectively and *c*₀ are 2.838 and 2.826 Å respectively¹⁰⁾).

In this work, the other two kinds of methods using gas of normal pressure were tried for the synthesis of W(C,N) powder. The first method (method I) was the heating of W+C and WO₃+C mixed powders in NH₃+H₂ mixed gas. The reason for using also WO₃ powder instead of W powder was that W powder generated by the reduction of WO₃ powder with C or H₂ was considered to be finer¹¹⁾ and thus more reactive than W powder as starting material. The method I is based on the fact that nitride such as Fe₄N,

which is thermodynamically unstable in N₂ of normal pressure even at room temperature, is generated by heating the metal in NH₃+H₂ gas of normal pressure^{12,13}. There are following two kinds of theoretical standpoints on the mechanism for such formation of unstable nitride under normal pressure. (1) Virtual-pressure concept¹⁴: the activity of N atoms or N₂ molecules generated by the dissociation of NH₃ gas is so high, corresponding to that of N₂ of high pressure up to 100 MPa. In other words, the nitriding chemical potential of such N atoms or "virtual-pressure" of such N₂ gas is much higher than that of N₂ gas of normal pressure. (2) Ostwald's rule¹⁵: when a system undergoing reaction (the decomposition of NH₃ on the surface of Fe particles in this case) proceeds from a less stable state, the most stable state (N₂) is not formed directly, but rather the next more stable state (Fe₄N) is formed, and so on, step by step until the most stable state is formed.

The second method (method II) is the heating of W powder in CH₄+NH₃ mixed gas of normal pressure. This method is based on the following facts: (1) the temperature (about 1100 K) needed for the generation of WC by heating W powder in CH₄+H₂ mixed gas is considerably lower than the temperature (1700~1900 K) needed for the generation of WC by heating W+C mixed powder in H₂ gas⁶, and (2) diamond which is unstable under normal pressure can be generated by the dissociation of CH₄ of low pressure¹⁶. Namely, the reactivity or activity of C atom generated by the dissociation of CH₄ is also considered to be extremely higher than that of solid carbon.

If W(C,N) powder can be obtained by the normal-pressure methods, the methods have advantages in terms of apparatus and cost, compared with the high-pressure method.

2 Experimental procedures

2.1 Preparation of powders

The starting powders were W (mean particle size by Fisher subsieve sizer and scanning electron microscope methods : 0.50 and 0.2 μm respectively, the contents of C, N and O: 0.01, 0.03 and 0.47 mass% respectively, or 0.08, 0.34 and 5.13 at% respectively. The oxygen is assumed to exist in the form of WO₃ surface layer on the particle. Tokyo Tungsten Co. Ltd.), WO₃ (0.68 μm , Tokyo Tungsten Co. Ltd.) and C (carbon black, 0.03 μm , Electrochemical Industry Co. Ltd.). Using these powders, methods I and II described in the chapter of "1. Introduction" were carried out as below.

In method I, W+C mixed powder with atomic or molar ratio of W:C=1:1.5 and WO₃+C mixed powder with

WO₃:C=1:1.5 and 1:2 were prepared as follows. Each 50 gram of the combined powder was dispersed in a beaker with 200 ml of acetone using an ultrasonic pulverizer for 0.6 ks, stirred with a pestle in an agate mortar for 1.2 ks, and then dried with a vacuum-dryer. Each 4 gram of the mixed powder was placed in alumina boat and heated in silica tube with a siliconite tube furnace in NH₃+H₂ flowing mixed gas. The temperature gradient of the siliconite furnace from the end to the maximum temperature region was about 65 K/cm, when the heating temperature was 1573 K. The purities of NH₃ and H₂ were >99.8 and 99.99% (the dew point of the latter was 213 K), respectively. The volume ratio of NH₃:H₂ was 1:1 and the total flow rate was 400 cm³/min. The powders were isothermally heated at temperatures between 973 and 1573 K, and also at 873 and 1673 K, if necessary. The heating rate was 0.17 K/s. The heating time was mainly 3.6 ks, and 1.8~14.4 ks in some cases. In order to investigate whether NH₃ has actually higher nitriding potential for W than N₂, the products obtained by heating W+C (1:1.5) and WO₃+C (1:2) mixed powders in N₂+H₂ mixed gas and by heating W+C (1:1.5) and WO₃+C (1:5) in N₂ gas were investigated. Here, the purity and dew point of N₂ were 99.99 % and 213 K, respectively. Additionally describing on the molar ratio in the WO₃+C mixed powders, the molar ratio of 1:2 in the case of N₂+H₂ mixed gas is insufficient for completely reducing WO₃, if the reduction is taken place only by the carbon. However, WO₃ in WO₃+C was clarified to be reduced mainly by H₂ in NH₃+H₂ and N₂+H₂ mixed gases, as shown later. The molar ratio of 1:5 in the case of N₂ was selected, taking into consideration that the reduction of WO₃ is possible only by the solid carbon and a sufficient amount of free-C is necessary for the full carbonitriding reaction^{7,8}.

In method II, each 4 gram of W powder was heated isothermally at temperatures between 973 and 1573 K for 3.6 ks with the above tube furnace in CH₄+NH₃ (1:2) flowing mixed gas. The purity of CH₄ was 99.5 %. The total flow rate and the heating rate were the same as the above. CH₄+N₂ (1:2) was also used instead of CH₄+NH₃ in order to investigate whether the nitriding potential of NH₃ in CH₄+NH₃ is higher than N₂ in CH₄+N₂.

2.2 Evaluation of the products

The contents of total-C, free-C, N and O of the products, which were easily crushed to powder, were analyzed with the elemental analyzers (WR-112 and TC-136, LECO Co. Ltd.). The combined-C content was determined by subtracting the free-C content from the total-C content. The phases in the products were identified with X-ray diffractometer (M03X-HF Model No.1031, Mac Science

Fig.1 X-ray diffraction profiles of W, WO_3 , W_2C , W_2N , WC and WN in ASTM cards, which were used to identify the phases of the products. The lines with black spots are the highest ones, which were used for the calculation of X-ray relative intensity of each phase.

Co. Ltd.). The X-ray diffraction profiles of the substances related to the reactants and products such as W (crystal structure; cubic), WO_3 (rhombohedral), W_2C (hexagonal), W_2N (cubic), WC (hexagonal) and WN (hexagonal) in ASTM cards were shown in Fig.1 as a reference. The morphology of the products was observed with scanning electron microscope (SEM: JSM-T220, JEOL Co. Ltd.).

3 Experimental results and discussion

3.1 Heating in NH_3+H_2 flowing mixed gas

3.1.1 W and WO_3 powders

Fig.2 shows the effect of isothermal heating temperature

Fig.2 Effect of heating temperature (T_h) on atomic ratios of N and O to W in products obtained by heating W powder in NH_3+H_2 (the volume ratio; 1:1) mixed gas for 3.6 ks and X-ray relative intensity of each phase. The peak of W_2N was observed up to 1573 K.

(T_h) on the atomic ratios of N and O to W (abbreviated as the atomic ratio of N/W, etc.) in each product obtained by heating W powder in NH_3+H_2 mixed gas and the X-ray relative intensity of each phase. T_h was in the range of 973~1573 K and the heating time (t_h) was 3.6 ks. The X-ray relative intensity of each phase is defined as $(I_i / \sum I_i) \times 100$ (%). Where, I_i (cps) is the detected count of the highest peak among all diffraction line peaks in ASTM cards, which are indicated with black spots in Fig.1, and $\sum I_i$ is the sum of each I_i . This relative intensity does not show the quantitative amount of each phase, but relative amount, as understood from the definition. The quantitative amount can be estimated using the mass% or atomic ratio of the elements, only when the product is one phase. The products were identified as W and W_2N from these results. Namely, no WN was obtained by heating W in NH_3+H_2 . The molar ratio of W_2N in the products was estimated to decrease from 16 to 8 mol% with increasing T_h from 973 to 1573 K.

Fig.3 shows the effect of T_h on the atomic ratios of N/W and O/W in the products obtained by heating WO_3 in NH_3+H_2 for 3.6 ks and the X-ray relative intensity of each phase. Here, the scale in the vertical axis of the upper figure is different from that in Fig.2 (the scales in Figs.5 and 6 shown later are also the same as that in this Fig.3). No peaks of WO_3 were observed at 873~1673 K. The products were different from those in the case of W described above. The products at 873~973 K were only W_2N -type compound. However, the atomic ratios of N/W and O/W in the product at 873~973 K were both >0.5 , and the atomic ratio of (N+O)/W was 2.9 at 873 K and 1.3 at 973 K. Based on these results, the product was judged to be not W_2N , but tungsten oxinitride $\text{W}(\text{N},\text{O})$ ^{17) with W_2N -type structure. Here, the X-ray peak pattern of $\text{W}(\text{N},\text{O})$ was not separated from that of W_2N under the conditions used, because of small}

difference (0.3 %) between their lattice parameters {W(N,O): $a=4.138 \text{ \AA}$ ¹⁷, W₂N: $a=4.126 \text{ \AA}$ }. Both atomic ratios of N/W and O/W decreased with increasing T_h . The atomic ratios of N/W and O/W in the product obtained at 1373~1673 K were 0.04 and <0.01, respectively: the compound was W₂N at these temperatures. The cause why the crystal structure of W(N,O) is the same as that of W₂N irrespective of the large difference in the atomic ratio of the nonmetal elements to W between them was not clear.

In short, the phases in the products related to W, which were obtained by heating WO₃ in NH₃+H₂, were found to change with increasing T_h as follows.

Namely, WN could not be also obtained by heating WO₃ in NH₃+H₂, in the same way as by heating W.

3.1.2 W+C and WO₃+C powders

Fig.4 shows the effect of T_h ($t_h=3.6$ ks) on the atomic ratios of free-C/W, combined C/W(C/W), N/W and O/W in the products obtained by heating W+C with W:C molar ratio of 1:1.5 {abbreviated as W+C (1:1.5)} in NH₃+H₂ (1:1) and the X-ray relative intensity of each phase. The phases in the products related to W were clarified to change with increasing T_h as follows:

Namely, W(C,N) with nitrogen content of 3 at% and with

Fig.3 Effect of T_h on atomic ratios of N and O to W in products obtained by heating WO₃ powder in NH₃+H₂ for 3.6 ks and X-ray relative intensity of each phase.

crystal structure of WC-type was found to generate at 1573 K. The nitrogen content of W(C,N) at 1173~1373 K could not be estimated, because there were W+W₂C in the products besides W(C,N).

Figs.5 and 6 show the effect of T_h on the atomic ratios of each element to W in the products obtained by heating WO₃+C (1:1.5) and (1:2) respectively in NH₃+H₂ for 3.6 ks and the X-ray relative intensity of each phase. The results for two kinds of mixed powders were nearly the same,

Fig.4 Effect of T_h on atomic ratios of free-C, combined-C (C), N and O to W in products obtained by heating W+C (the atomic ratio; 1:1.5) in NH₃+H₂ for 3.6 ks and X-ray relative intensity of each phase.

Fig.5 Effect of T_h on atomic ratio of each element to W in products obtained by heating WO₃+C (1:1.5) in NH₃+H₂ and X-ray relative intensity of each phase.

except for the free-C content and the amount of W(C,N). The atomic ratio of O/W in the products became nearly zero above 1373 K, indicating that the reduction of tungsten oxinitride, i.e., W(N,O) formed at low temperatures became complete at high temperature. The reduction was judged to occur mainly by the reaction with H₂, because the atomic ratio of free-C/W did not vary corresponding to the decrease in that of O/W. The dependence of the kind of phase on T_h was not similar at low T_h to that for W+C shown in Fig.4: a large amount of W(N,O) was formed instead of W₂N and the maximum ratio of W₂C was higher than those for W+C. However, the atomic ratio of N/W in W(C,N) formed at high T_h was 0.03 for every specimen, which was nearly the same as that in the case of W+C.

Fig.7 shows SEM photographs of starting W and WO₃ powders and of the product powders obtained by heating W+C (1:1.5) and WO₃+C (1:1.5) powders at 1573 K for 3.6 ks. The primary particle sizes of the product powders were 0.3~0.6 μm for W+C and 0.1~0.2 μm for WO₃+C. The product of the latter was much finer than the former as well as the starting material. This result was expected, although the initial products in the sequence of the reaction were not W, but W(N,O) with high O content and W₂C.

Next, the effect of t_h was investigated at 1573 K. Figs.8 and 9 show the results obtained by heating W+C (1:1.5) and WO₃+C (1:2) in NH₃+H₂. The product was W (C_{0.97}N_{0.03}), irrespective of t_h. This indicates that the product is equilibrium one under the experimental conditions. The amount of W(C,N) in both cases slightly decreased at long t_h. This was considered to be due to the extinction of free-

C which was caused by the escape of carbon from the powder probably through the reaction of C+2H₂ → CH₄.

In short, the nitrogen content of W(C,N) obtained from WO₃+C was found to be the same as that from W+C: the kind of the final product at high T_h did not depend on the starting powder, although the particle size depended. This indicates that the W(C_{0.97}N_{0.03}) is the equilibrium phase at high T_h in NH₃+H₂ and the coexistence of solid carbon.

3.2 In N₂+H₂ and N₂ flowing mixed gas

The products obtained by heating W+C (1:1.5) and WO₃+C (1:2) at 1573 K for 3.6 ks in N₂+H₂ instead of NH₃+H₂ were also investigated to evaluate whether NH₃ has actually higher nitriding potential than N₂. The figures were abbreviated. The products for two kinds of mixed powders were confirmed to be both W(C,N) which had the atomic ratio of N/W of 0.03 and 0.02 respectively. Namely, they were nearly the same values as those obtained by heating these powders in NH₃+H₂ (Figs.4 and 6). This shows that the nitriding potential of NH₃ in NH₃+H₂ was unexpectedly nearly the same as that of N₂ in N₂+H₂.

Next, the function of H₂ in the formation of the products was investigated. W+C (1:1.5) and WO₃+C (1:5) mixed powders were heated at 1573 K in N₂, instead of N₂+H₂ (1:1). Figs.10 and 11 show the atomic ratio of each element to W in the products and the X-ray relative intensity of each phase, as a function of t_h. The following large difference was observed in both results, compared with those in the case of NH₃+H₂ or N₂+H₂: 4~5 at% O remained in the products. The kinds and amount of the products

Fig.6 Effect of T_h on atomic ratio of each element to W in products obtained by heating WO₃+C (1:2) in NH₃+H₂ for 3.6 ks and X-ray relative intensity of each phase.

Fig.7 SEM photographs of starting powders (W and WO₃ powders) and products obtained by heating W+C (1:1.5) and WO₃+C (1:1.5) in NH₃+H₂ (1:1) at 1573 K for 3.6 ks.

depended on the kind of mixed powders. In the case of W+C shown in Fig.10, the phases were mainly tungsten carboxynitride W(C,N,O) with crystal structure of WC-type and partly W at short t_h and the amount ratio of W(C,N,O) and W decreased and increased respectively with increasing t_h : this suggests that W(C,N,O) was formed during rising temperature and was decomposing during isothermal heating at 1573 K. The N content in W(C,N,O) could not be estimated due to the existence of W phase, but

Fig.8 Effect of heating time (t_h) on atomic ratio of each element to W in products obtained by heating W+C in NH₃+H₂ at 1573 K and X-ray relative intensity of each phase.

Fig.9 Effect of t_h on atomic ratio of each element to W in products obtained by heating WO₃+C and in NH₃+H₂ at 1573 K and X-ray relative intensity of each phase.

the atomic ratio was suggested to be less than 3 at%. It was noted that W(C,N,O) formed at low temperatures below about 1573 K in N₂ became unstable at 1573 K, in contrast to the pure WC without N which is stable up to 2900 K even in vacuum. The source of the oxygen in W(C,N,O) was considered to be the starting W powder (the oxygen content was 5.13 at%) and the impurity water in N₂ gas.

On the other hand, in the case of WO₃+C shown in Fig.11, the phases in the products were mainly carboxynitride W(C,N,O) with C:N:O of nearly 0.92:0.02:0.06. The amount of W(C,N,O) hardly depended on t_h , differing from W(C,N,O) for W+C. Such difference seemed to be related to the amount of free-C between them: the amount in this case is larger than that in the case of W+C.

From these results and those in N₂+H₂, it was known that H₂ in N₂+H₂ has a promoting effect of carburization at high temperatures as well as a reducing effect of WO₃. These effects were thought to arise, probably because hydrocarbon gases such as CH₄ are formed by the reactions between carbon powder and H₂. It was also noted that the total amount of free-C and combined-C decreased with increasing t_h , in the same way as in the case of W+C shown in Fig.10. This suggests that a small amount of water contained in N₂ reacted with C to form CO and CH₄ gases which escape from the reaction system.

Additionally describing, the atmosphere for heating W+C mixed powder in the production of commercial WC powder is not N₂, but H₂¹⁸⁾. This selection of the atmosphere was thought to be in correspondence with the above results that

Fig.10 Effect of t_h on atomic ratio of each element to W in products obtained by heating W+C in N₂ at 1573 K and X-ray relative intensity of each phase.

the full carburization of W by heating W+C at high temperature did not occur in N_2 , but under the existence of H_2 . It was assumed that the full carburization or carbonitridation of W by heating W+C in N_2 will occur at low temperatures below 1573 K. However, it was also assumed that the heating time needed for the full carburization at low temperature is extremely long due to low diffusivities of the elements. This issue should be studied in the future.

3.3 In CH_4+NH_3 flowing mixed gas

Fig.12 shows the effect of T_h on the atomic ratio of each element to W in the products obtained by heating W in CH_4+NH_3 (1:2) for 3.6 ks and the X-ray relative intensity of each phase. The phases related to W in the products changed with increasing T_h as follows.

There were two differences, compared with the above results obtained by heating W+C in NH_3+H_2 shown in Fig.4. First, no W_2C formed near 1173 K, but $W(C,N)$, i.e., the compound with higher C content than W_2C did. This suggests that CH_4 gas has expectedly a stronger carburizing potential for W than that of solid carbon. Second, the atomic ratio of N/W in $W(C,N)$ at high T_h was 0.05, which was higher than those of any other products in the case of using solid carbon as a carbon source. A large amount of free-carbon, which will be unnecessary for using $W(C,N)$ powder, was formed at high T_h , e.g., at 1573 K. However,

Fig.11 Effect of t_h on atomic ratio of each element to W in products obtained by heating WO_3+C in N_2 at 1573 K and X-ray relative intensity of each phase.

the amount seems to be minimized by selecting T_h and t_h . The particle size of $W(C,N)$, the SEM photograph of which is shown in Fig.13, was confirmed to be nearly the same as that of $W(C,N)$ from W+C in method I (Fig.7 c). The free-C particles could not be distinguished from those of $W(C,N)$.

In order to investigate the function of NH_3 in CH_4+NH_3 in the formation of the products, N_2 was used as nitrogen source, instead of NH_3 . W powder was heated at 1573 K for 3.6 ks in CH_4+N_2 . The product was confirmed to be WC with the atomic ratio of C/W of 1.0 and N/W of <0.01 . This indicates that N_2 in CH_4+N_2 mixed gas has no potential of nitridation for W. It was noted that NH_3 of normal pressure has expectedly higher nitriding potential for W powder than that of N_2 of normal pressure under the coexistence of CH_4 gas, differing from under the coexistence of solid carbon. The cause, however, was not clear.

Fig.12 Effect of T_h on atomic ratio of each element to W in products obtained by heating W in CH_4+NH_3 for 3.6 ks and X-ray relative intensity of each phase.

Fig.13 SEM photograph of products obtained by heating W in CH_4+NH_3 (1:2) at 1573 K for 3.6 ks.

In the high-pressure method where W+C mixed powder was heated in N₂ of 10~160 MPa at 1523~1773 K for 3.6 ks^{7,8)}, the nitrogen content of the product W(C,N) reached 11 and 20 at% at 10 and 160 MPa, respectively, and when solid carbon did not coexist, the nitrogen content of the product was 0.00 at% (the product was W). Namely, the nitridation (substantially carbonitridation) occurred only when the carbon coexisted. Therefore, the following are concluded: (1) NH₃ in NH₃+H₂ has nitriding (carbonitriding) potential for W powder only under the coexistence of carbon above about 1273 K, in the same way as N₂ of high pressure, and (2) NH₃ has a higher nitriding potential for W than N₂ in the presence of CH₄, (3) NH₃ in NH₃+H₂ has no such high nitriding potential for W powder in the presence of CH₄ as well as in the presence of solid carbon, compared with N₂ of even 10 MPa. The result (1) was attributed to the fact that W(C,N) is more stable than WN under low N₂ pressure.

As for the general mechanisms for the generation of unstable substance by heating under gas of normal pressure, there are Virtual-pressure concept and Ostwald's rule as described in "1. Introduction". On the mechanism for the generation of W(C,N) by heating W+C and WO₃+C in NH₃+H₂ and CH₄+NH₃ of normal pressure, we could not conclude which is more appropriate one. This problem and also the effects of heating atmosphere and volume ratio of mixed gas on the formation of products will be precisely investigated after the study on the carbonitridation of Mo metal and W-Mo alloy powders which we will carry out in the near future.

4 Conclusion

The products obtained by heating W+C and WO₃+C mixed powders in NH₃+H₂ of normal pressure (method I) and by heating W powder in CH₄+NH₃ of normal pressure (method II) were investigated mainly at 1573 K, in order to know whether new carbonitride W(C,N) can be synthesized by these methods, in the same way as by heating W+C mixed powder in N₂ of high pressure up to 160 MPa. The products obtained by heating these powders in N₂, N₂+H₂ and CH₄+N₂ of normal pressure were also investigated to know the functions of NH₃ and CH₄.

(1) The products obtained by methods I and II were W(C,N) with nitrogen contents of 3 and 5 at%, respectively. The values were much smaller than those (11~20 at%) of W(C,N) obtained by the previous high-pressure method. The particle size of W(C,N) from WO₃+C in method I was extremely smaller than those of W(C,N) from W+C in method I as well as method II.

- (2) NH₃ had higher nitriding potential to W powder under the coexistence of CH₄ than N₂, but did not under the coexistence of solid carbon. CH₄ was more appropriate for the generation of W(C,N) with high nitrogen content at high temperatures, compared with solid carbon.
- (3) No WN was generated under any conditions by this normal-pressure method, in the same way as by the high-pressure method.

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