PHASE TRANSITION OF W-Co OXIDE MIXTURE DURING DIRECT REDUCTION/CARBURIZATION BY $H_2/CH_4$①

Qian, Chongliang Wu, Enxi
Powder Metallurgy Research Institute,
Central South University of Technology, Changsha 410083

ABSTRACT The processes of the H_2-reduction and the carburization by hydrogen/methane mixtures with various gas phase composition for the tungsten-cobalt oxide mixture($W_{20}O_{58}+Co_3O_4$) were investigated by means of XRD and SEM analyses. The results shows that the oxide mixture was reduced to α- W, Co_3W and Co_7W_6 at the temperatures higher than 850 ℃ in H_2. The pure blue tungsten oxide($W_{20}O_{58}$) or W-Co oxide mixture can be carburized with H_2/CH_4 gas mixture at lower temperatures(900～1 000 ℃). Both the carburizing rate and the deposition of free carbon are closely related to the carburizing temperature and the H_2/CH_4 mixture constitution. The present paper gives an optimal combination of processing parameters for the carburization.

Key words tungsten oxide cobalt oxide H_2-reduction carburization X-ray diffraction phase transition

1 INTRODUCTION

The conventional processing route for the production of WC-Co composite powders involves a series of high energy consuming processes. First, metallic tungsten powder is obtained by the H_2-reducing WO_3 or blue tungsten oxide ($W_{20}O_{58}$) at temperatures higher than 800 ℃. Then, the tungsten powder is mixed with carbon black for a long time, before it is carburized over the temperature range 1 300 up to 2 000 ℃ to yield WC powder. Cobalt powder is obtained by the H_2-reduction of Co_3O_4 and subsequently the two powders, WC and Co, are ball milled to produce the composite powder as homogeneous as possible for manufacturing the cemented carbide[1]. In order to simplify the route, many methods for producing WC-Co composite powder by direct reducing/carburizing have been explored. For example, the continuous reduction/carburization of $CoWO_4/WO_3$ mixture in a rotary kiln by H_2/CH_4 mixture or CO/CO_2 mixture is one of these methods[2, 3]. It is clear for these processes that the route is more simple and the reaction temeprature is lower. Therefore, the energy-expense is greatly reduced. But the key of applying these processes to industry effectively is accurate carbon-control. That is to say, not only the carburization must be executed completely, but also the free carbon is not deposited. Besides, additional processes are needed to prepare $CoWO_4$ as raw material. For this reason, in our research, two kinds of commercial powders, $W_{20}O_{58}$ and Co_3O_4, were directly mixed to raw materials with specified composition. The reduction/carburization processes of the mixture by H_2/CH_4 have been studied in order to get optimal process parameters for producing WC-Co composite powder.

2 EXPERIMENTAL

According to final composition requirement of WC-15% Co, two kinds of commercial powders, $W_{20}O_{58}$ and Co_3O_4, were mixed and ball milled homogeneously in the ethylalcohol medium for 15h, and then dried at 80 ℃ in air. The mixture was used as experimental material.

High temperature XRD method was used

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to investigate the H_2-reduction process. The experimental steps are as follows: the mixture of powders was mixed with petrol and rubber dilute solution and pressed into specimen frame made of corundum, then set into the H. T. XRD attachment while H_2 was ventilated. The sample was heated gradually from room temperature till 950 ℃. It was observed that phase transition began at 250 ℃, so the data were accumulated from 250 ℃ at a 25 ℃ temperature interval of the measuring points. The flow rate of the hydrogen was 40 mL/min. The XRD measurements were performed at a goniometer scanning rate of 4 (°)/min and with 2θ scanning angle in the range of 25 ~ 50°. In this way, the dynamic phase transition process during H_2-reduction can be in-situ observed.

In the stage of carburizing, the test was carried out in a wound tube-furnace in which various temperatures and various ratios of gaseous mixture of H_2 and CH_4 with fixed total flow of 400 mL/min were chosen. During the carburization, a series of continuous experiments were carried out, such as the porcelain boat which contained powders was pushed into the high temperature zone to hold and carburization was interrupted by pushing the boat to the cold port of furnace tube in order to get samples for XRD analysis and the kinetic process study of phase transition.

3 RESULTS AND ANALYSIS

3.1 H_2-*Reduction of* W-Co *Oxide Mixture*

Fig. 1 shows the H. T. XRD patterns of the W-Co oxide mixture during H_2-reduction. The dynamic curves of the phase transition obtained by processing these data[4] are shown in Fig. 2. It is obvious from both figures that the Co_3O_4 have been completely reduced to the CoO at 325 ℃ and, subsequently, transited to the metallic β- Co(cubic) and trace amounts of α- Co(Hexa.) at 425 ℃. The transition of the blue tungsten oxide to WO_2 started at 550 ℃. A little of α-W and β-W appeared at 575 ℃. WO_2 was completely reduced to α-W in 750 ℃. At 600 ℃, part of cobalt and tungsten reacted to form an intermetallic compound phase Co_3W. But, other kind of intermetallic com-

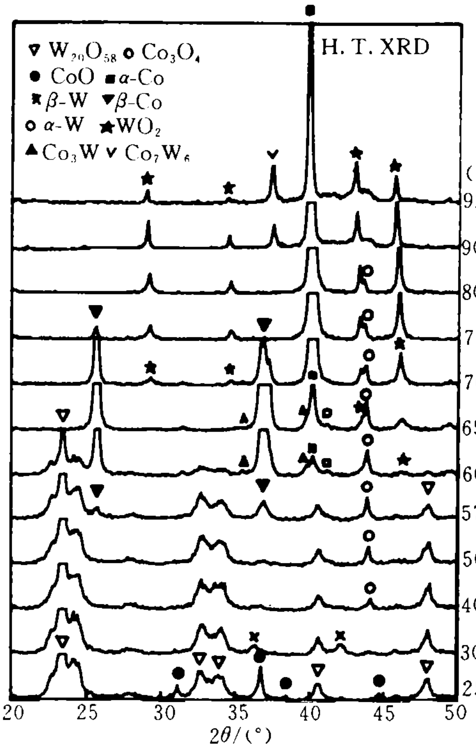

Fig. 1 A part of H. T. XRD patterns of W-Co oxide mixture in H_2-reduction

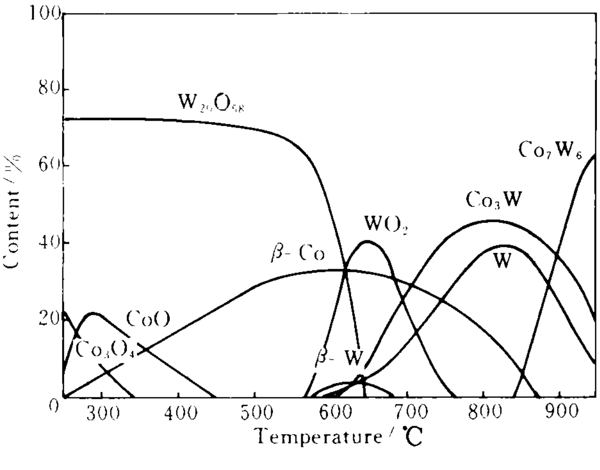

Fig. 2 The phase transition curves of W-Co oxide mixture in H_2-reduction

pound Co_7W_6 appeared only above 850 ℃. At the highest temperature of 950 ℃ in our test, the final product was the three phase mixture of α-W, Co_3W and Co_7W_6.

3. 2 *Carburization in* H_2/CH_4 *Mixed Gas*

The sample obtaind previously by H_2-reducing W-Co oxide mixture was heated as quickly as possible to carburization temeprature in H_2 / CH_4 mixture with flow ratio of $H_2 : CH_4 = 1 : 1$ and total flow of 40 mL/min. Fig. 3 shows a part of H. T. XRD patterns of the carburization products during holding at 950 ℃. It is apparent from the figure that the gaseous phase carburization is a complex phase transition process with multi-phase being coexisted and transited each other. The rapid appearance of both intermediate carbides of Co_2W_4C and Co_6W_6C coincided with the disappearance of the Co_7W_6 and Co_3W, as well as the reduction of W. A part of W was compounded to form above carbides, while a lot of it was carburized to form the phase W_2C, which is an incomplete tungsten carbide. Then, the carbides of Co_2W_4C and Co_6W_6C reduced rapidly with the appearance of a new carbide Co_3W_3C phase (η phase) and metallic β- Co. With the prolonging of the carburization time, the W_2C and Co_3W_3C decreased, a new carbide WC appeared.

For the W-Co oxide mixture, the XRD measurement results of the products, which were obtained by interrupting experiment during the carburization with different H_2/CH_4 mixtures and temperatures in tube-furnace, were shown in Fig. 4 and Fig. 5. It is evident that the carburization rate increases as temperature and content of CH_4 in the gaseous mixture increase. When the carburization process was executed in H_2-20%CH_4(in volume) mixture at 900 ℃, it is incomplete and there are a lot of intermediate carbide Co_3W_3C in spite of hold time up to 15h, while there are a large amount of free carbon which results in volume expansion of the sample powder (see Fig. 4(a)). Increasing the methane concentration up to 50%(in volume), though carburization rate increased rapidly, only a small amount of carbide Co_3W_2C existed after holding for 4 h, but a large amount of free carbon deposited (see Fig. 4 (b)). When increasing temperature up to 1 000 ℃, in 10 h, the sample can be carburized completely, in spite of content of 10% CH_4(in volume) only. In this condition, the η phase Co_3W_3C was eliminated completely while no free carbon was found(see Fig. 5 (a)). When the methane concentration was increased up to 20%(in volume), the same result can be obtained only after holding for 4 h(see Fig. 5(b)). If the methane concentration was increased up to 33%(in volume), a lot of the free carbon deposited, though the carburization rate increased so rapidly that the hold time of 10 min was enough for complete carburization while no Co_3W_3C phase existed (Fig. 5(c)).

Using pure blue tungsten oxide as raw

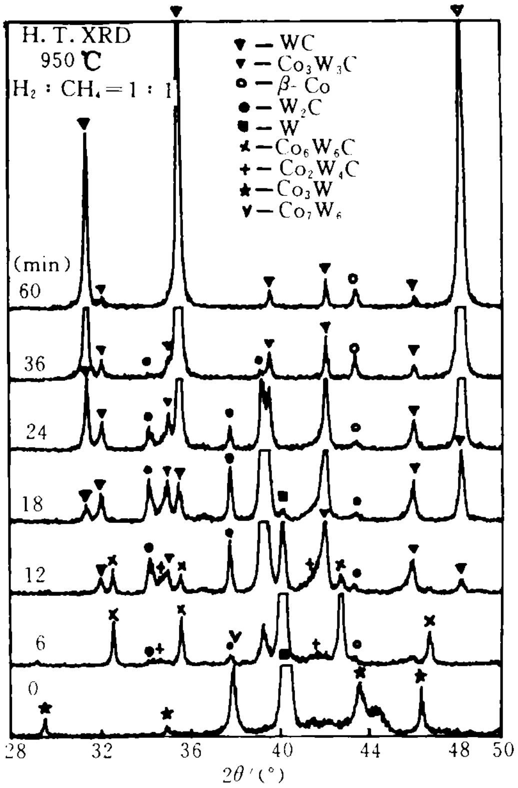

Fig. 3　The H. T. XRD patterns of the gas carburization with H_2+50% CH_4(in volume) at 950 ℃ with increasing hold time

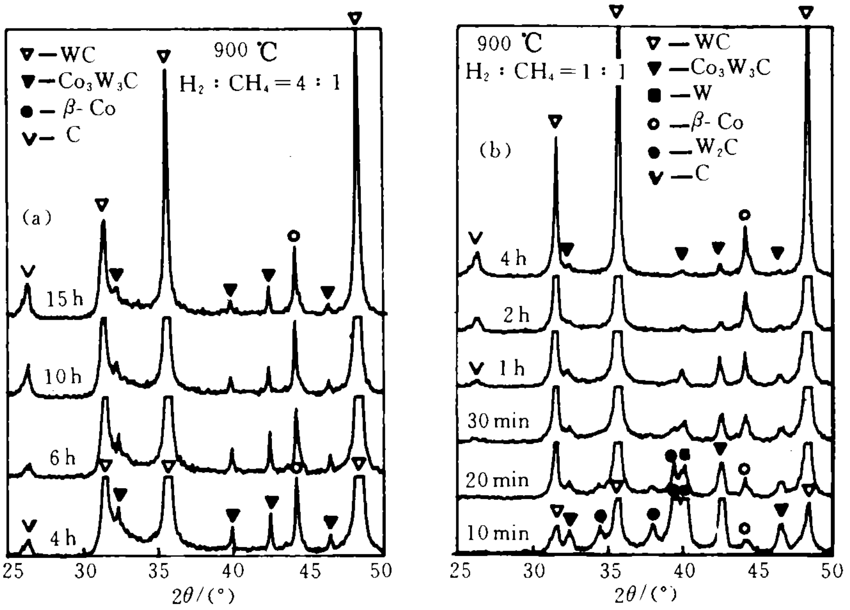

Fig. 4 The XRD patterns of the $W_{20}O_{58}+Co_3O_4$ mixture during gasous phase carburization at 900 ℃

(a)—H_2+20%CH_4(in volume); (b)—H_2+50%CH_4(in volume)

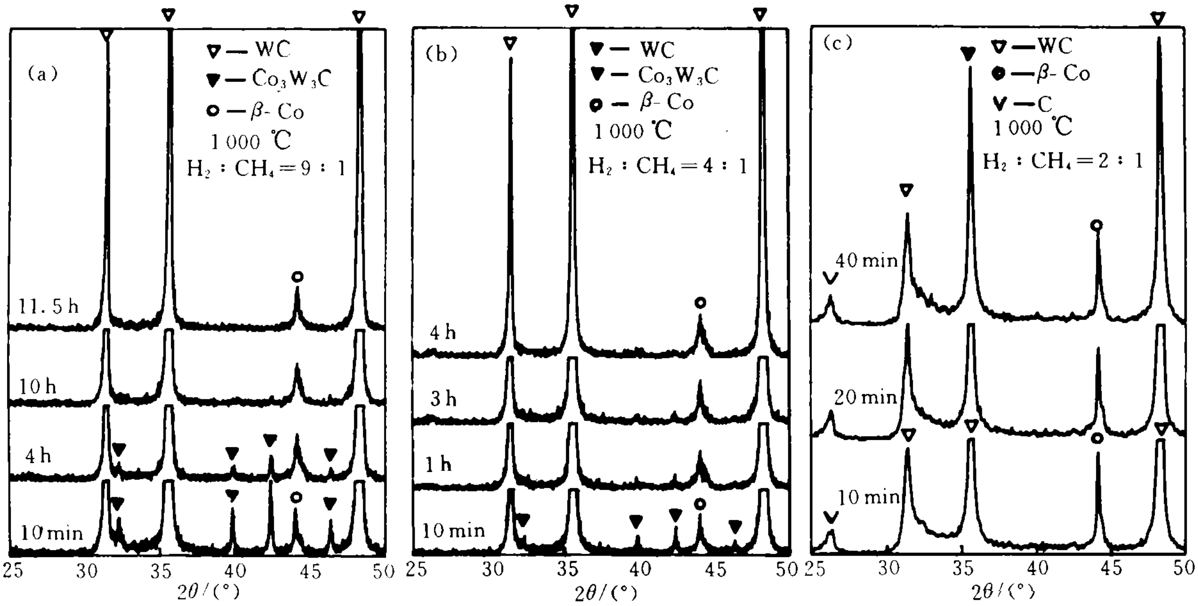

Fig. 5 The XRD patterns of the $W_{20}O_{58}+Co_3O_4$ mixture during gaseous phase carburization at 1 000 ℃

(a)—H_2+10% CH_4(in volume); (b)—H_2+20% CH_4(in volume); (c)—H_2+33%CH_4(in Volume) material and the same experimental procedure as above, similar gaseous phase carburization results can be obtained (Fig. 6). The carburization rate increased dramatically with the increase of the concentration of CH_4. Comparing with W-Co oxide mixture, no free carbon deposited for the pure $W_{20}O_{58}$ sample during the carburization by H_2-33%CH_4(in volume) mixture. It is obvious that the accurate carbon-control is not necessary for the carburization of pure $W_{20}O_{58}$.

In summary, the temperature of 900 ℃ is too low for both of the raw materials to be carburized, because of the time-expense and the incompletely carburizing. Although the concentration of CH_4 has an appreciable effects on the carburization rate, either increasing the concentration of CH_4 ($>20\%$ in volume) or extending hold time can result in the deposition of the free carbon. Therefore, in the present experimental condition, the optimal parameters are carburization temperature of 1 000 ℃, H_2-20% CH_4(in volume) mixed gas and hold time of about 4 h.

3.3 *Product Morphologies*

Fig. 7(a) ~ (d) show the SEM morphologic photographs of both raw materials of the W-Co oxide mixture and the blue tungsten oxide as well as their carburization products at 1 000 ℃ for 4 h in H_2-20%CH_4 (in volume) mixture. It is found that the particle size of the carburization products is very fine (<1 μm). If some additional processes and apparatuses, for example fluid-bed reactor etc, were used, it seems that the direct carburization process by gas mixture for producing superfine WC-Co composite powder is a very prospective route.

4 DISCUSSION

The reduction/carburization characteristic of $W_{20}O_{58}+Co_3O_4$ mixture used in the present investigation agrees basically with that of $CoWO_4$ used as raw material in literature[5], (Fig. 1 and Fig. 3), but there exists lots of

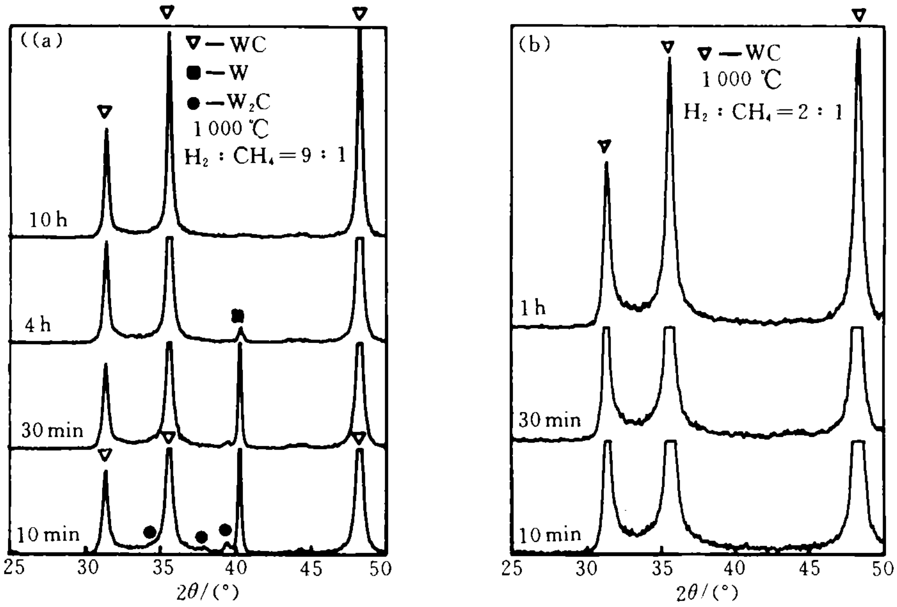

Fig. 6 The XRD patterns of the $W_{20}O_{58}$ sample during gaseous phase carburization at 1 000 ℃

(a)—H_2+10% CH_4(in volume); (b)—H_2+33% CH_4(in volume)

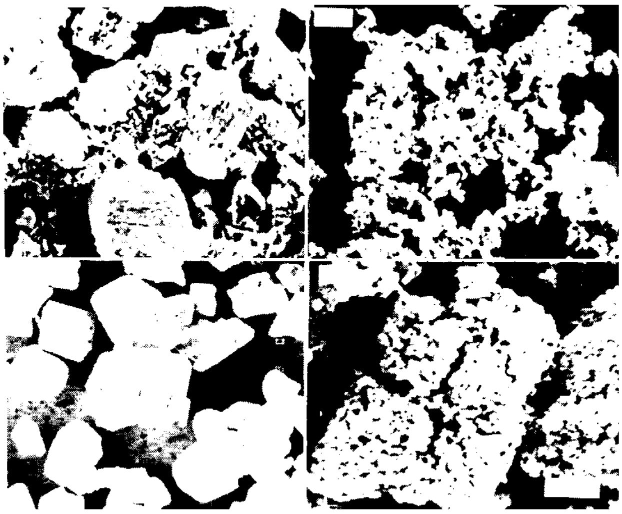

Fig. 7 The SEM morphologic photographes

(a) $W_{20}O_{58}+Co_3O_4$ milled mixture powder; (b) the carburization product of the mixture; (c) $W_{20}O_{58}$ powder raw material; (d) the carburization product of $W_{20}O_{58}$ powder

W_2C phase during carburization of the former. It is probably due to some diferences between above two raw materials on the experimental method and/or the process parameters. A thermal electrobalance was used and a series of interrupted products was obtained for XRD identification for the latter. It is similar to carburization in tube furnace used in this paper.

As only a little mixture gas flowed practically through sample surface, due to the particular structure of the H. T. XRD attachment, and the sample was pressed densely, the result obtained by H. T. XRD (Fig. 3) has some differences from that of loose powder in tube furnace. The advantage of the former is that a series of intermediate phases, such as Co_2W_4C, Co_6W_6C, W_2C etc, can be in-situ measured during the carburization.

Fig. 8 shows an isothermal section at approximate 1 130 ℃ of the W-Co-C system. The β-Co+WC two-phase field can be seen to be a very narrow border between the two three-phase fields, β-Co+WC+graphite and β-Co + WC + M_6C. The gas mixture with higher or lower carbon potential will lead to deviate from the two-phase field and enter the three-phase field, that is to say, excess of carbon (deposition of free carbon) or deficit of carbon (formation of brittle M_6C phase) may be occurred. Therefore, it is practically important for direct reduction/carburization with gaseous mixture that the concentration of CH_4, the carburization temperature and the hold time must be carefully controlled. Because of the differences between the small tube furnace used in this experiment and industrial boat-pushed furnace or rotary kiln, the process parameters must be suitably adjusted for practical application.

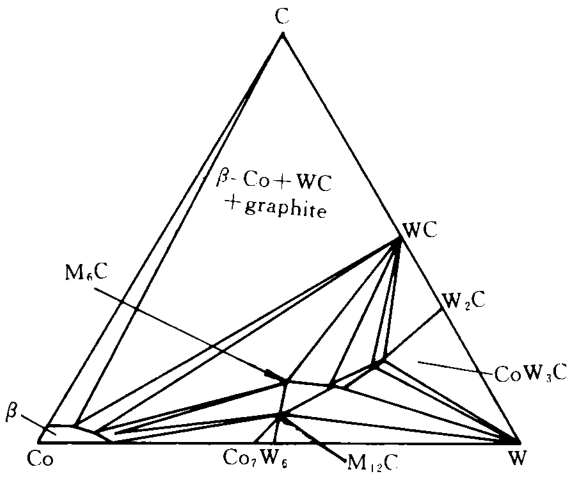

Fig. 8 **The isothermal section of W-Co-C system at** 1 127 ℃

5 CONCLUSIONS

(1) At lower temperature (1 000 ℃), W-Co oxide mixture can be well-reduced/carburized directly by H_2/CH_2 mixture to produce WC-Co composite powder which is used to manufacture cemented carbide.

(2) The gaseous phase carburization is a complex phase transition process with multiphase coexistence and mutual transition.

(3) The carburization rate depends on the temperature and, especially, the CH_4 concentration in the gas mixture.

(4) The carbon control is the key factor of the gaseous phase carburization process. In present experimental condition, it is necessary for complete carburization and no free-carbon deposition that the W-Co oxide mixture is heated in the H_2-20% CH_4 (in volume) mixed gas at 1 000 ℃ holding for 4 h.

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