

Synthesis of $\text{Al}_2\text{O}_3/\text{WC}$ powder by aluminothermic reduction and carbonization method^①

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Abstract: $\text{Al}_2\text{O}_3/\text{WC}$ powder was synthesized by means of aluminothermic reduction-carbonization with metallic Al powder, yellow tungsten oxide and carbon black or graphite as raw materials under the protection of coke granules. The effects of Al_2O_3 content, temperature, C/ WO_3 molar ratio, and atmosphere on the synthesis of $\text{Al}_2\text{O}_3/\text{WC}$ powder were studied. The results show that the relative content of WC and W_2C is strongly influenced by the factors mentioned above. Carbon black has higher reactivity than graphite. $\text{Al}_2\text{O}_3\text{-WC}$ composite is easier to obtain under the protection of coke granules than under argon atmosphere. The CO in the coke layer can easily react with tungsten to form WC and to transfer from W_2C to WC.

Key words: aluminothermic reduction; carbonization; phase composition; composite; thermodynamics

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1 INTRODUCTION

Alumina ceramics are the most familiar ceramics for industry applications such as cutting tools, wear resistant components, refractories materials, because of their superior properties such as high hardness, high corrosion resistance, high insulation, high melting point, high modulus and good chemical stability. In order to improve the performance of the alumina ceramics, the second phase, such as metal powder, fiber and whisker, is introduced to toughen the ceramics. Tungsten carbide toughened alumina is one of the cutting-tool composites. $\text{Al}_2\text{O}_3/\text{WC}$ composite can be prepared by hot pressing the mixture of Al_2O_3 and WC at high temperature^[1-6]. Recently, self-high temperature synthesis method was used to prepare $\text{Al}_2\text{O}_3/\text{WC}$ composite^[7, 8]. $\text{Al}_2\text{O}_3/\text{WC}$ powder can be obtained by heating the mixture of Al_2O_3 and tungsten in flowing CO. In such condition, it is very important to control the partial pressure of CO.

WC, WC_{1-x} and W_2C are the three stable phases in the W-C binary phase diagram^[9]. From the thermodynamics calculation, both WC and W_2C are very easy to form. So it is difficult to get very pure WC powder. W_2C phase is brittle and has inferior tribological properties. So the content of W_2C must be controlled.

Zhang et al^[7] also found the conversion of W_2C to WC, but he didn't give an explanation. Martin et al^[10] also observed the similar phenomena in the

study of copyrolysis of polysilane and metallic tungsten. He indicated that the formation of W_2C is preferred at lower temperature between 1 100 and 1 200 °C. High temperature causes a transformation to WC for the previously formed W_2C and the transformation is caused by transport kinetics of the carbon phase from the inorganic silicon-carbon network. Gao and Kear^[11] studied the carburization of large surface area tungsten powders in flowing CO gas. He analyzed the formation of WC and W_2C from $\alpha\text{-W}$ and $\beta\text{-W}$ at low temperature and found that the former was easy to be carburized directly to WC, however, the latter was easy to be carburized to W_2C . Similar studies have been taken by Swift and Hatano et al^[12, 13].

Carbon-containing materials play an important role in refractories industries. The refractories containing carbon were usually heated in coke bed and the coke can protect the material from oxidizing. Study on the formation of tungsten carbides in the carbon bed to obtain tungsten carbides cheaply is interesting. In our previous work, WC and W_2C were found in the Al- WO_3 system when the experiments were carried out under the protection of coke granules^[14, 15]. We also studied the synthesis of $\text{MgAl}_2\text{O}_4\text{-W}$ under the protection of coke granules^[16]. In this study, $\text{Al}_2\text{O}_3/\text{WC}$ composite was prepared by aluminothermic reduction and carbonization method under the protection of coke from mixtures of Al, WO_3 and carbon black or graphite. The effects of Al_2O_3 content, temperature, C/ WO_3 molar

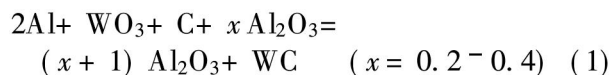
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ratio, and atmosphere on the synthesis of $\text{Al}_2\text{O}_3/\text{WC}$ powder were studied.

2 EXPERIMENTAL

Yellow WO_3 (> 99.98%), metal aluminum powder (> 98.45%, average particle size 88 μm) and fused corundum powder (< 88 μm) were chosen as the starting raw materials. Carbon black (average particle size 22 μm) and graphite (< 88 μm) were selected as the carbon sources. The overall reaction is as follows:



The starting mixed powders with composition based on reaction (1) stoichiometrically were dry mixed in a planetary mill for 60 min. Then the mixture was pressed into specimens with 20 mm in diameter and 12–18 mm in height under uniaxial pressure of 200 MPa. Specimens were dried for 24 h and calcined at various temperatures for 3 h under the protection of coke granules or under argon atmosphere.

The phase of the composites was determined by X-ray diffraction analysis (XRD) using CuK_α radiation (model Philips X'pert SW). The microstructure of the composites was observed by scanning electron microscope (SEM) (model Philips XL30 TMP).

3 RESULTS AND DISCUSSION

3.1 Phase identification

Fig. 1 shows the XRD patterns of the products soaked at 1373 K for 3 h under the protection of coke granules. The main phases in the products are WC, $\alpha\text{-Al}_2\text{O}_3$ and W_2C . No residual WO_3 can be detected, which means that WO_3 has been reduced completely by Al. The intensity of WC increases but the intensity of W_2C decreases with the content of corundum increasing. However, the intensity of W_2C in the sample with molar ratio of C/ WO_3 being 3 decreases more quickly than that with molar ratio of C/ WO_3 being 1. When $x = 0.4$, WC and $\alpha\text{-Al}_2\text{O}_3$ are the dominant crystal phases. Fig. 2 shows the relative intensity of $I(\text{WC}(101)) / [I(\text{WC}(101)) + I(\text{W}_2\text{C}(101)) + I(\text{W}(110))]$ as a function of corundum content and the molar ratio of C/ WO_3 . The relative intensity is calculated from XRD patterns in Fig. 1. It is obvious that the relative intensity increases with increasing of corundum content and the relative intensity of the sample with molar ratio of C/ WO_3 being 3 is higher than that with molar ratio of C/ WO_3 being 1.

When carbon black was replaced by graphite and other conditions were kept unchanged, the samples with molar ratio of C/ WO_3 being 3 were achieved.

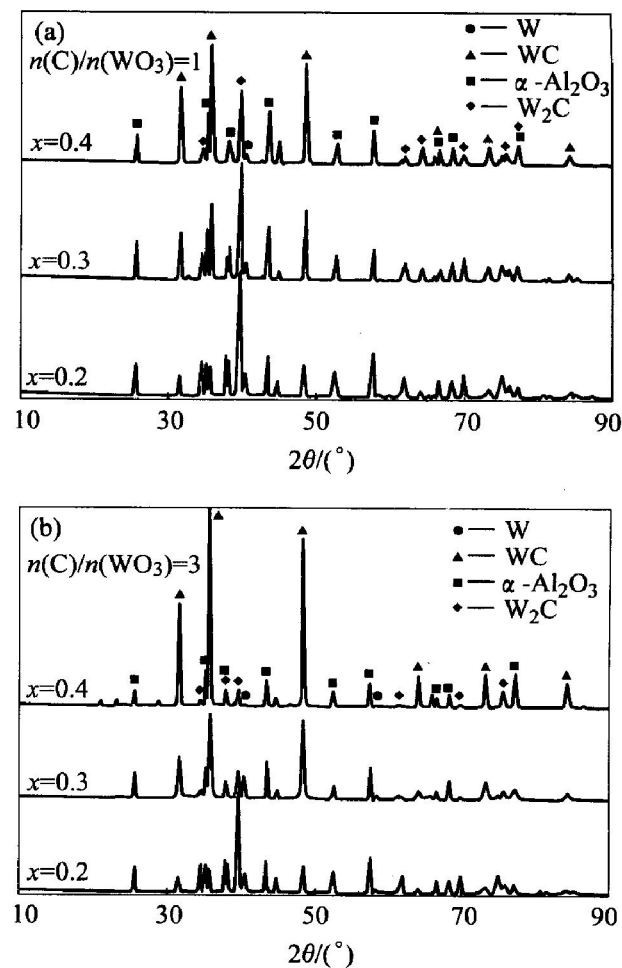


Fig. 1 XRD patterns of reaction products with different corundum content and molar ratio of C/ WO_3 soaked at 1373 K for 3 h under protection of coke granules

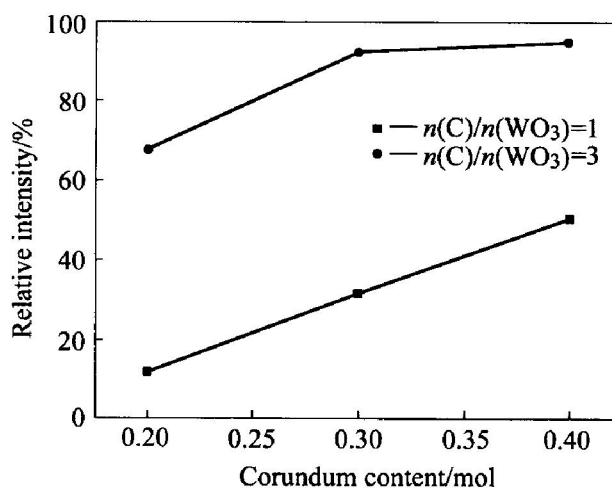


Fig. 2 Effect of corundum content and C/ WO_3 molar ratio on relative intensity of WC(101)

The XRD patterns are shown in Fig. 3. Comparing Fig. 1(b) with Fig. 3(a), it is found that a great amount of tungsten and unreacted graphite exist in the sample. But in the sample with carbon black almost no tungsten can be detected even though the two samples were heated at the same temperature. However when the calcination temperature was increased

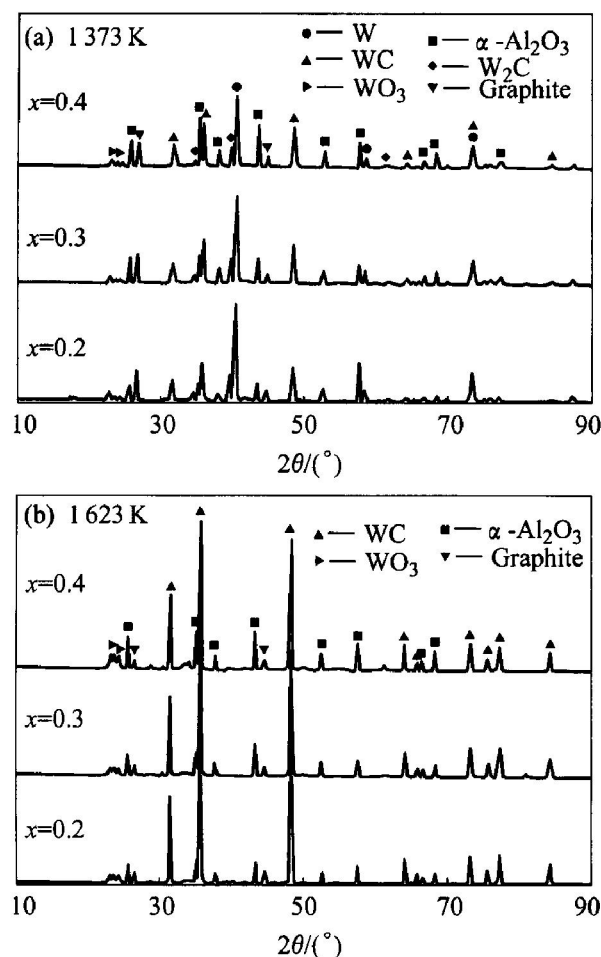


Fig. 3 XRD patterns of reaction products with different corundum content (molar ratio of C/ WO₃ is 3)

to 1 623 K, only WC, α -Al₂O₃ and a little unreacted WO₃ were found in the XRD patterns, indicating that W₂C has converted to WC completely.

Fig. 4 shows the XRD patterns of the sample with the molar ratio of C/ WO₃ being 3 and heated in atmosphere of argon. Carbon black was chosen as the source of carbon. Comparing Fig. 1(a) with Fig. 4 (a), it is found that the samples heated at 1 373 K in the atmosphere of argon have more tungsten content and less WC and W₂C content than the samples heated under the protection of coke.

The results mentioned above show that carbon black is more reactive than graphite, and coke protection during heating of the sample is more beneficial to formation of WC and conversion of W₂C to WC than argon protection.

3.2 Morphology

Fig. 5 shows the SEM photographs of the products soaked at 1 373 K for 3 h under the protection of coke granules. Fig. 5(a) shows the photograph of the products with carbon black as carbon source, in which tungsten can be found, and irregular tungsten carbides coexist with corundum. Fig. 5(b) shows the SEM photograph of the products with graphite as car-

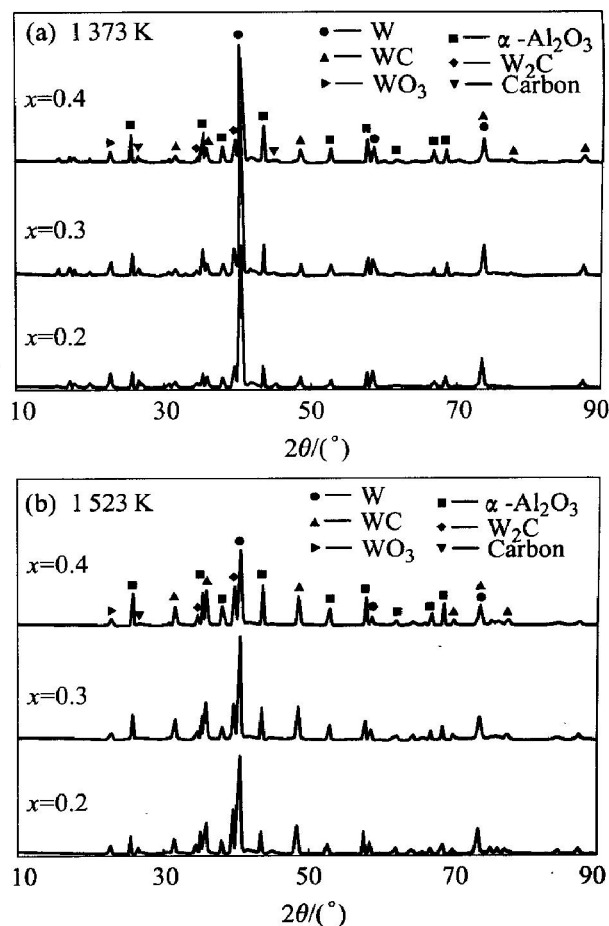


Fig. 4 XRD patterns of reaction products with different corundum content under argon atmosphere (molar ratio of C/ WO₃ is 3)

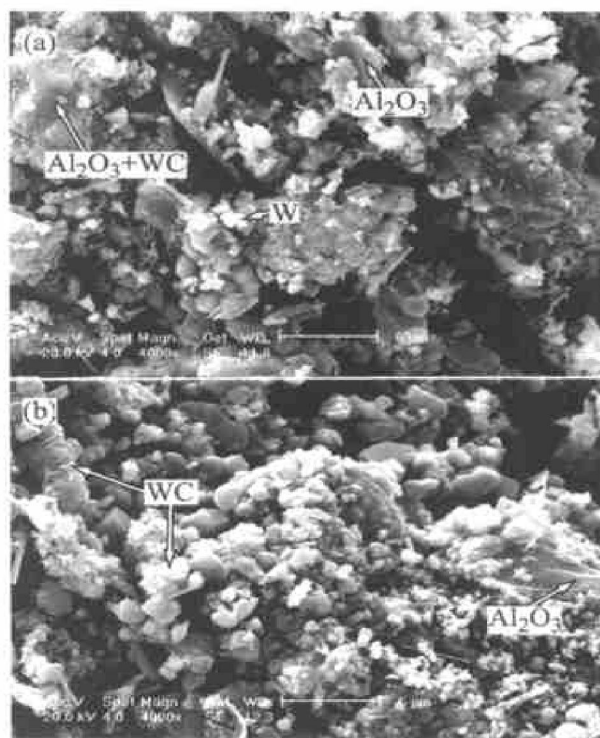
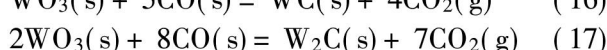
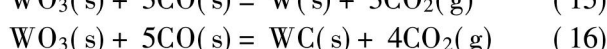
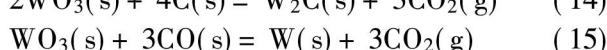
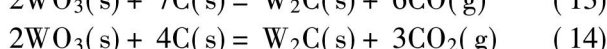
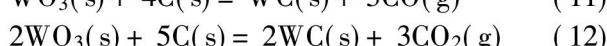
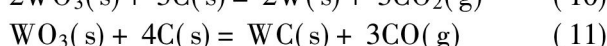
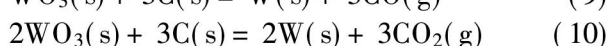
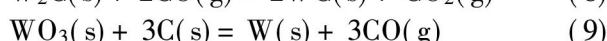
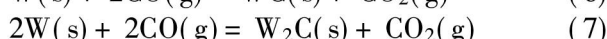
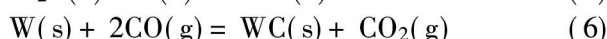
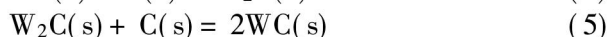
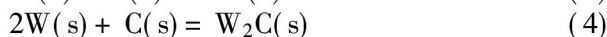
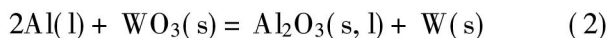


Fig. 5 SEM photographs of products soaked at 1 373 K for 3 h
(a) —Carbon black; (b) —Graphite
(molar ratio of C/ WO₃ is 1)

bon source, in which some tungsten carbide particles have obvious hexagonal platelike characteristics. Maybe the structure of flake graphite can help to form regular tungsten carbides. Some fine tungsten carbide particles can also be observed.

3.3 Discussion

In the $\text{Al}-\text{WO}_3-\text{C}$ system, the possible reactions are as follows:



The reaction (2) is an instant reaction and can finish quickly. But when there is residual WO_3 and no Al, the reactions (9–17) can take place.

When the experiments are carried out under the protection of coke granules, there are mainly N_2 , O_2 , CO , CO_2 in atmosphere. According to the thermodynamic calculation, when the system comes to balance at high temperature, CO and N_2 are the dominant gases and the partial pressures of CO_2 and O_2 are very low. Under the protection of coke granules, the possible reactions are reactions (2–8) because N_2 doesn't react with W at the studied temperature. These reactions give important effects on final products of synthesis.

Based on the Dalton's law of partial pressure, the equilibrium partial pressures of CO and N_2 are 35 170 Pa and 66 154 Pa respectively, and the partial pressure of CO is unchanged with the temperature changing. Thus the equilibrium partial pressure of CO_2 and O_2 can be calculated by the following reactions:



Assume that WO_3 is reduced completely by Al based on reaction (2), ΔG of the possible reactions in $\text{Al}-\text{WO}_3-\text{C}$ system as a function of temperature are shown in Fig. 6. The ΔG of reaction (5) increases with the temperature increasing and is above zero when the temperature is above 1 500 K. ΔG of other reactions are still below zero so the reactions always

occur at the designed heat treatment condition. It is noticeable that the reactions (6–8) are more easy to take place according to thermodynamics calculation because CO participates in the reactions. It is maybe the reason that the formation of WC and the transition of W_2C to WC occur more easily under the coke protection.

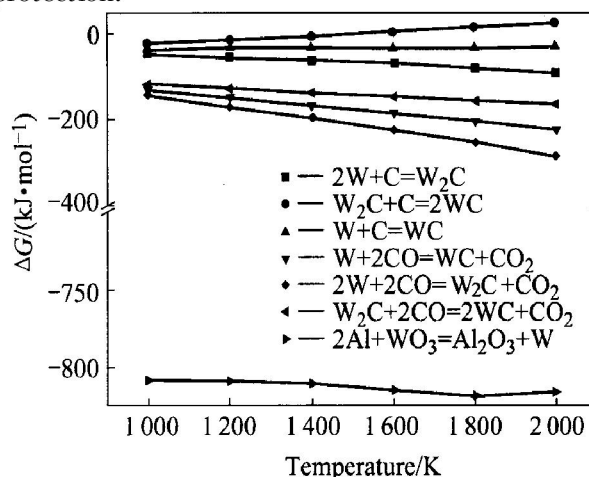


Fig. 6 Reaction Gibbs free energies for potential reactions in $\text{Al}-\text{WO}_3-\text{C}$ system^[17]

When WO_3 is not reduced completely by Al, which often occurs when the diluent content is high and a part of Al is isolated by diluent from WO_3 , all of the reactions (2–17) must be studied in the $\text{Al}-\text{WO}_3-\text{C}$ system. Similarly, the correlations between ΔG and temperature are shown in Fig. 7. From Fig. 7, the ΔG of the reactions between WO_3 and C or CO are more negative than that between W and C or CO. That is to say, if there is unreacted WO_3 in the system, the unreacted WO_3 will be reduced by CO or C to form WC and W_2C . At last, the formed W_2C will convert to WC by the reaction (5) and (16). So it can be concluded that coke protection is beneficial to the formation of WC because WC_2 can convert to WC more easily.

When the heating process is taken in flowing argon atmosphere, reactions (6–8) and (15–17) can be ignored because the formed CO has escaped from the system. Though the reactions (9–14) can take place according to the thermodynamics calculation in standard conditions, they aren't the main reactions and can be ignored because the reaction (2) takes place more easily. So under the protection of Ar, the main reactions in $\text{Al}-\text{WO}_3-\text{C}$ system are reactions (2–5). It is clear that the carbonization of tungsten is difficult without the participation of CO. Moreover, from the XRD patterns (Fig. 4), the intensity of W_2C increases with temperature increasing, which means that the transition of W_2C to WC is difficult. It can also be explained with the above discussion.

From the previous discussion, it should be noted that the conversion from W_2C to WC increases with the increment of corundum content, especially for the

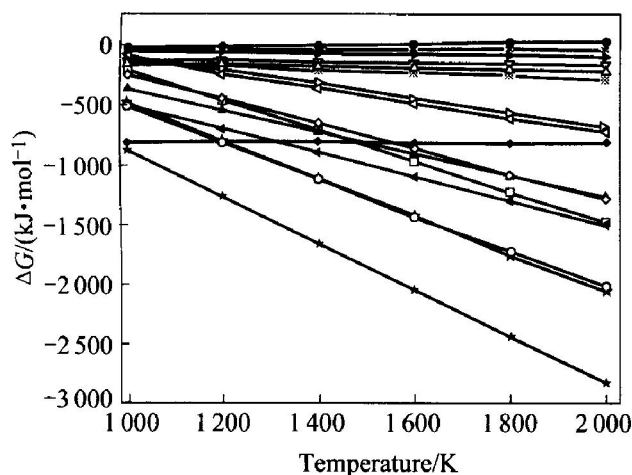


Fig. 7 Reaction Gibbs free energies for potential reactions in $\text{Al-WO}_3\text{-C}$ system^[17]

- $\triangleright -\text{WO}_3 + 3\text{C} = \text{W} + 3\text{CO}$; $* -\text{W} + \text{C} = \text{WC}$;
 $\diamond -2\text{WO}_3 + 3\text{C} = 2\text{W} + 3\text{CO}_2$; $\triangle -\text{W} + 2\text{CO} = \text{WC} + \text{CO}_2$;
 $\blacktriangle -\text{WO}_3 + 3\text{CO} = \text{W} + 3\text{CO}_2$; $\ast -2\text{W} + 2\text{CO} = \text{W}_2\text{C} + \text{CO}_2$;
 $\triangleleft -\text{WO}_3 + 4\text{C} = \text{WC} + 3\text{CO}$; $\nabla -\text{W}_2\text{C} + 2\text{CO} = 2\text{WC} + \text{CO}_2$;
 $\circ -2\text{WO}_3 + 5\text{C} = 2\text{WC} + 3\text{CO}_2$; $\blacklozenge -2\text{Al} + \text{WO}_3 = \text{Al}_2\text{O}_3 + \text{W}$;
 $\blacktriangleright -\text{WO}_3 + 5\text{CO} = \text{WC} + 4\text{CO}_2$; $\square -2\text{WO}_3 + 7\text{C} = \text{W}_2\text{C} + 6\text{CO}$;
 $\blacktriangleleft -2\text{W} + \text{C} = \text{W}_2\text{C}$; $\ast -2\text{WO}_3 + 4\text{C} = \text{W}_2\text{C} + 3\text{CO}_2$;
 $\bullet -\text{W}_2\text{C} + \text{C} = 2\text{WC}$; $\star -2\text{WO}_3 + 8\text{CO} = \text{W}_2\text{C} + 7\text{CO}_2$

samples heated under the protection of coke granules. It is difficult to explain with thermodynamics consideration. Maybe the distribution of formed tungsten and corundum particles has great influence on the carbonization of tungsten and the conversion. In our previous reports about Al-WO_3 system, it was observed that when the content of corundum was less than 30%, tungsten was continuous; when the content of corundum was above 30%, tungsten was disperse^[14, 15]. Dispersive tungsten is easy to react with CO to form WC and beneficial to the transition of W_2C to WC.

4 CONCLUSION

$\text{Al}_2\text{O}_3\text{-WC}$ composite powder can be more easily prepared using Al powder, yellow tungsten oxide and carbon black or graphite as raw materials under the protection of coke granules than under argon atmosphere. Carbon black has higher reactivity than graphite and makes the carbonization of tungsten and the transition of W_2C to WC more easy. Atmosphere is an important factor influencing the synthesis of $\text{Al}_2\text{O}_3\text{-WC}$. The participation of CO in coke bed is beneficial to the formation of WC and the transition of W_2C to WC. Temperature, C/ WO_3 molar ratio and corundum content are the other important factors affecting the synthesis of $\text{Al}_2\text{O}_3\text{-WC}$. Increasing the content of corundum and C/ WO_3 molar ratio also prompts the formation of WC and transition of W_2C to WC.

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