



Tungsten carbide powder obtained by direct carburization of tungsten trioxide using mechanical alloying method



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ABSTRACT

Tungsten carbide is widely used in the production of cutting tools and parts with very good resistance to wear. It is well known that the properties of sintered carbides are closely related to the carbide particles size. Tungsten carbide production is a laborious process, which always includes a milling step. This article aims to study the manufacturing of tungsten carbide by carburizing tungsten trioxide using mechanical alloying (MA) method, thus concentrating the process in one step. Experimental tests were performed with a Fritch planetary mill and complete conversion of tungsten trioxide in carbide was observed after 30 h of milling. The average value of D50 for the synthesized WC is $6.73 \pm 0.62 \mu\text{m}$.

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1. Introduction

Due to its high hardness, tungsten carbide is widely used in the production of cemented carbides, used in the making of cutting tools and parts with very good resistance to wear [1]. In early studies, it was observed that there is a close relationship between the properties of manufactured parts and the particles size of tungsten carbide [2]: When the particles are fine enough, both the hardness and toughness improve. This discovery stimulated the initiation of several endeavors to obtain tungsten carbide powders with the smallest dimensions possible to counterbalance the increase of carbide particles size during sintering and therefore to maintain satisfactory mechanical properties [3]. Some recent researches [4–7] have shown that it was possible to raise the toughness and hardness of a WC-Co alloy powder by using ultrafine carbide particles size ($<1 \mu\text{m}$).

Among the methods for producing tungsten carbide, the following can be cited: chemical precipitation from solutions, carburization of tungsten in horizontal furnaces with hydrogen atmosphere, and chemical synthesis methods [8]. Those methods present advantages in productivity, but the carbide particles obtained are not in the acceptable size range for use in cutting tools

(carbide grain sizes from 0.5 to 5 μm are commonly used). For this reason the powder is subjected to a grinding process, usually by attrition, to achieve the required fineness.

Development of the mechanical alloying (MA) process [9] for the production of alloys which are not achievable by melting opened the opportunity to produce tungsten carbide by this method. In recent years a large number of studies have been carried out [10–24] aimed at developing the manufacturing of WC-Co mixtures by mechanical milling or mechanical alloying by different approaches: (i) the carburization of tungsten powders with black carbon or graphite; (ii) the creation of a homogeneous mixture of WO_3 and carbon that is reduced in a furnace at high temperature; and (iii) the grinding in high-energy mills of tungsten carbide obtained by chemical methods, mixed or not with cobalt [7,12,14,17,18,23,24,25]. All these researches have allowed, after certain periods of time, the production of ultra-fine tungsten carbide.

Using mechanical alloying to transform tungsten trioxide into tungsten carbide is a difficult approach because of the high temperature ($>1300 \text{ }^\circ\text{C}$) required for direct carburization. The solution is to use a mill able to develop large amounts of energy to obtain tungsten carbide directly from the oxide, without other technological steps. This study aims to examine the conditions in which the carburizing reaction can take place as well as the required technological parameters.

2. Thermodynamic conditions

To demonstrate the viability of the process, we present a

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thermodynamic study of the reaction. This first approximation study allows us to determine the thermodynamic conditions in which the carburizing reaction of tungsten trioxide can occur.



From the Chaudron–Boudouard diagram, in the range of temperatures at which the grinding process takes place (lower than 600 K), CO_2 is the stable oxidized form of carbon (even in the presence of excess carbon), which explains the choice of reaction (1) in the thermodynamic calculations.

From the standard enthalpies of formation of the various compounds involved in the reaction and by means of equation (2), it is possible to determine the standard enthalpy of the reaction and its endothermic or exothermic nature.

$$\Delta H_{\text{reaction}}^{\circ} = \sum n \Delta H_{\text{(products)}}^{\circ} - \sum m \Delta H_{\text{(reagents)}}^{\circ} \quad (2)$$

Since the standard enthalpy of formation of WO_3 (s), WC (s) and CO_2 (g) at 298 K are [26,27], respectively: -842.91 kJ/mol, -40.40 kJ/mol, -393.52 kJ/mol, we obtain from (2):

$$\begin{aligned} \Delta H_{\text{reaction}}^{\circ} &= [2(-40,40) + 3(-393,52)] - [2(-842,91)] \\ &= 424.46 \cdot 10^3 \text{ J/mol} \end{aligned}$$

Consequently the reaction is endothermic in nature and energy must therefore be provided to make it occur. The amount of energy required is determined from the Gibbs free energy by means of equation (3).

$$\Delta G_{\text{reac}}^{\circ} = \Delta H_{\text{reac}}^{\circ} - T \Delta S_{\text{reac}}^{\circ} \quad (3)$$

As the entropies of formation of WO_3 , WC and CO_2 are respectively [26,27]: 75.91 J/K mol, -6.28 J/K mol, 213.79 J/K mol, 5.74 J/K mol, from equation (4), we can calculate the entropy of the reaction.

$$\Delta S_{\text{reac}}^{\circ} = \sum n \Delta S_{\text{(products)}}^{\circ} - \sum m \Delta S_{\text{(reagents)}}^{\circ} \quad (4)$$

So we have:

$$\begin{aligned} \Delta S_{\text{reac}}^{\circ} &= [2(-6.28) + 3(213.79)] - [2(75.91) + 5 \cdot 5.74] \\ &= 448.29 \text{ J/K mol.} \end{aligned}$$

Considering that a reaction occurs spontaneously when its Gibbs free energy is negative, through equation (5), we can determine the minimum temperature at which the reaction happens, using the Ellingham approximation and considering a pressure of CO_2 of 1 atm.

$$T = \frac{\Delta H_{\text{reac}}^{298}}{\Delta S_{\text{reac}}^{298}} \quad (5)$$

$$T = \frac{424460}{448.29} = 946.84 \text{ K}$$

The reaction should thus occur for temperatures higher than 946.84 K, or 673.7 °C for a pressure of 1 atm of CO_2 .

Once we know the reaction enthalpy ($\Delta H_{\text{reac}}^{\circ}$) and the entropy ($\Delta S_{\text{reac}}^{\circ}$) as well as Gibbs free energy ($\Delta G_{\text{reac}}^{\circ}$), we can achieve a balance study of the reaction (1) to determine how the pressure affects the course of the reaction. From the law of mass action, we obtain equation (6), and from the latter, the value of the equilibrium constant of the reaction (K_C).

$$K_C = e^{\frac{-\Delta G^{\circ}}{RT}} \quad (6)$$

where R is the gas constant and T the absolute temperature.

From equation (5), the Gibbs free energy is calculated for a temperature $T = 393$ K (temperature reached during test grinding).

$$\Delta G_{\text{reac}}^{\circ} = \Delta H_{\text{reac}}^{\circ} - T \Delta S_{\text{reac}}^{\circ} \quad (7)$$

$$\Delta G_{\text{reac}}^{\circ} = 248.23 \frac{\text{kJ}}{\text{mol}}$$

Which leads from (6) to an equilibrium constant:

$$K_C = 9.6188 \cdot 10^{-34}$$

K_C is linked to the activities of reagents and products according to (8):

$$K_C = \frac{a_{\text{WC}}^2 \times a_{\text{CO}_2}^3}{a_{\text{WO}_3}^2 \times a_{\text{C}}^5} \quad (8)$$

Given that the reactants and the solid products of reaction are not miscible, their activity can be supposed as equal to 1; K_C depends thus only of gaseous elements, therefore:

$$K_C = a_{\text{CO}_2}^3 \quad (9)$$

Similarly, the constant K_p depends on the partial pressures of the reactants and products.

$$K_p = P_{\text{CO}_2}^3 \quad (10)$$

If we consider our system as a closed system, both constants (K_C and K_p) can be connected by means of the equation (11):

$$K_p = K_C (RT)^{\Delta\alpha} \quad (11)$$

where $\Delta\alpha$ is the increase in the number of moles of the gas reaction.

Using the working conditions of our system (volume = 63.4 ml and amount of reactants = 20.1 g), with $\Delta\alpha = 3$ and $R = 8.31$ J/mol·K, at $T = 393.15$ K, the P_{CO_2} limit value is:

$$P_{\text{CO}_2} = 5.8406 \times 10^{-5} \text{ Pa}$$

At ambient temperature (298 K), the P_{CO_2} limit value is:

$$P_{\text{CO}_2} = 4.434 \times 10^{-5} \text{ Pa}$$

This value of the CO_2 partial pressure is very low, probably due to the fact that the temperature increase in the system causes already an important increase of the internal pressure.

However, as the system is open at regular intervals for sampling and is also not fully air tight, considering it as a closed system may not be the best approach: the CO_2 can disperse during sampling.

3. Experimental methods

Milling was carried out in a Fritch Pulverisette 7 Premium line planetary ball mill which can reach 850 revolutions per minute, equipped with two tungsten carbide bowls of 80 ml capacity. In each bowl (jar), tungsten carbide balls of different diameter were placed: 200 g of balls of 10 mm in the first and a mixture of 150 g of 3 mm balls with 50 g of 1.6 mm balls in the second.

The mass ratio of balls and ground powder was fixed to 10: 1. A tungsten trioxide powder with 99.98% purity supplied by Inframat Advanced Material, having a particles size of about 100 μm , was used. The carbon powder was supplied by Alfa Aesar, with a particles size in the range of 25 nm and a purity of 99.9%. The mixture

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