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Synthesis of nanocrystalline cubic substoichiometric WC_{1-z} powders by mechanochemical technology

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Nanocrystalline cubic substoichiometric WC_{1-z} powders were synthesized by a mechanochemical method at room temperature, a process of highly reactive energetic ball milling of $WO_3 + 3Mg$ mixtures containing excessive graphite as a source of carbon for W phase. The excessive graphite plays a very important role in the formation of cubic phase, otherwise the h.c.p. phase is formed. The entropy evaluation shows that the reduction reaction is a self-propagating process. After millimg for 90 hours and excluding MgO from the product by using HCl solution, the cubic substoichiometric WC_{1-z} powders containing a little excessive graphite with the grain size in the range of 4 to 20 nm were obtained.

1. Introduction

Cemented carbides are a group of sintered materials with outstanding mechanical properties, such as high hardness and excellent wear resistance. Tungsten monocarbide ranks the most important role of all hard phases in cemented carbides. More than 98% of all hard metal grades contain WC, and more than half of them are pure WC-Co alloys [1]. The success of tungsten carbides in technical application is closely related to their method of manufacture [2], owing to the fact that WC melts incongruently (i.e. decomposes before melting). The modification of W_2C and the additional phase, the cubic substoichiometric WC_{1-z}, can be readily produced as an accessory phase of WC during carbonization of tungsten [3]. Meanwhile tungsten carbides had been shown to be an effective catalyst in some chemical reactions that are usually catalyzed by noble metals such as Pt and Pd [4]. There is some practical significance to investigate the kinetic behavior for the formation of these metastable modifications during the carbonization of tungsten, and their influence on the properties of tungsten carbides.

Mechanochemical methods activating solid phase reactions have been known for a long time with a wide practical applications [5, 6]. Many alloys, intermetallic compounds, sulfides and phosphates have been obtained by means of this method [7]. Nowadays, this method is used for carrying out chemical reactions under the conditions of heat explosion. Its exothermal effect raises the reaction temperature to such an extent that it is convenient to prepare refractory alloys at room temperature in a short period, while it is difficult to do so by conventional method. Popovich [8] had successfully synthesized tungsten carbide powders in an atmosphere of H_2 and obtained a mixture powders of WC and W_2C in air ambient by mechanochemical method, but further research work on preparing nanocrystalline powders was not developed.

Though many papers investigating on the synthesis of nanocrystalline tungsten carbides are reported, most of them are concerned with h.c.p. WC by chemical method [9–11]. Porat [12] has recently prepared nanocrystalline WC powders by lasted ball milling of mixtures of W and C powders for over 300 hours. However, few papers are concerned with the synthesis of single phase WC_{1-z} compound by chemical or physical method. This paper deals with the synthesis of pure nanocrystalline WC_{1-z} powders by a mechanochemical process and the study of their microstructures.

2. Experimental procedure

Mixture of WO_3 (>99% purity) and elemental Mg (99.9% purity) powders was used as source materials. Graphite (99.9%) was added to the mixture under the W/C atomic ratio of 1 : 2. The excessive amount of graphite was used to form desired substoichiometric structure of WC_{1-z}. The milling balls with the diameters of 5 to 10 mm and vials were constructed from hardened steel. The weight ration of milling balls to powder was ranged from 20 : 1 to 50 : 1 and the milling speed was 250 rpm. Since Mg powders are very pyrophoric and easy to explode, the milling was conducted in an inert atmosphere of N_2 for various duration. Unless otherwise mentioned, the milling process was periodically interrupted to remove small quantity of as-milling powders for analysis after treated by HCl. Phase identification of as-milled powders was performed by x-ray diffraction analysis. The crystalline phases of milling powders were determined by using Cu-K_α radiation. The morphology and crystalline structure of as-milling powders were determined by a JEOL 100CX Transmission Electron Microscope (TEM).

3. Results and discussion

3.1. As-milled powders

The mixture of WO_3, graphite and magnesium powders was milled under N_2 atmosphere for different periods. The x-ray diffraction pattern of initial materials in Fig. 1 shows the existence of reflections for WO_3, Mg and C only. The x-ray diffraction patterns of the mixture powders milled for different duration are shown in Fig. 2 and Fig. 3. It can be seen from Fig. 2 that raw powders transform to a mixture of W, MgO and some remnants of WO_3 after milled for about 6 hours. No WC reflections are detectable. The reductive reaction process is completed as follows:

$$WO_3 + 3Mg \Rightarrow \alpha\text{-}W + 3MgO + Q(\text{kJ}) \qquad (1)$$

The values of the reactive heat (Q) and the energy of formation ($-\Delta G$) in Equation 1 are 320 kJ/mol and 280 kJ/mol, respectively [12].

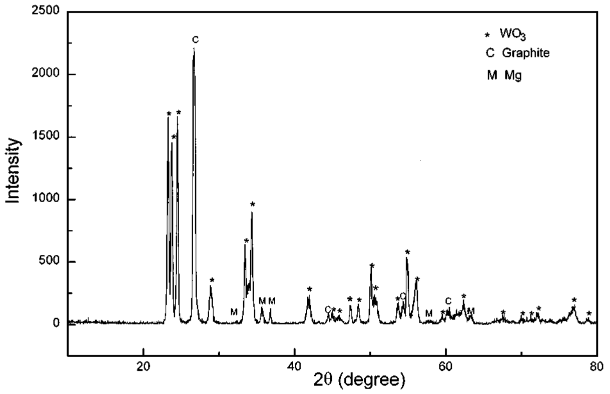


Figure 1 X-ray diffraction pattern of initial mixture of WO_3, Mg and C powders.

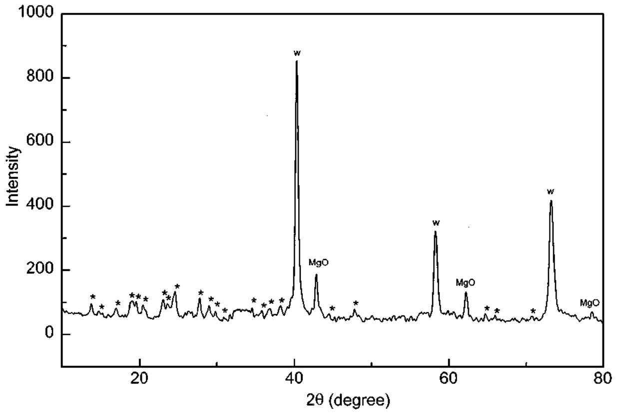


Figure 2 X-ray diffraction pattern of mixture powders milled for 6 hours.

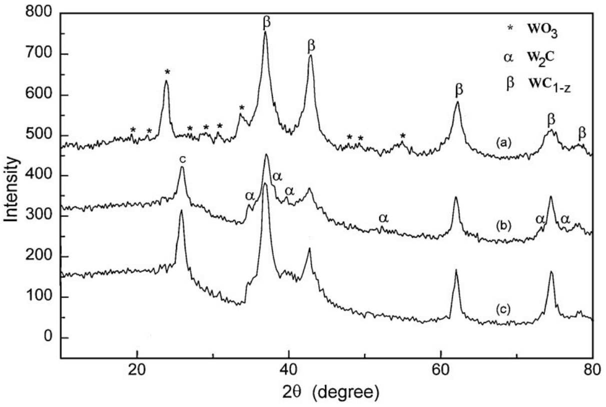


Figure 3 X-ray diffraction patterns of mixture powders milled for different period: (a) 38 hours; (b) 70 hours; and (c) 90 hours, respectively.

Under normal synthesis condition (i.e. without milling), the reaction mentioned above is not self-propagating. In our milling process, the self propagating reaction may take place if the contribution of milling impact to the energy of formation ($-\Delta G$) is big enough that the entropy becomes positive ($\Delta S > 0$). Since $\Delta S = (\Delta H - \Delta G)/T$, if $\Delta S > 0$, then $\Delta H > \Delta G$. That is to say, if the change of enthalpy is larger than that of energy of formation, the reaction is a self-propagating one. In reaction (1), ΔH is equal to -320 kJ/mol (the value is negative since the reaction is exothermal), ΔG is equal to -280 kJ/mol. In the case of no milling, $\Delta S = (\Delta H - \Delta G)/T < 0$, the reaction is not a self-propagating one. Taking the contribution of milling impact energy to the energy of formation into account, the situation will be changed. In such case, the energy of formation (ΔG) will increase and may lead the entropy to be positive. The milling impact energy is calculated by Magini [13] model as follows. For each collision in a planetary mill, the energy transferred from milling balls to the powder per unit of mass is calculated by following formula:

$$E_i = \left(\left[7.66 * 10^{-2} R_P^{1.2} \rho^{0.6} E^{0.4}\right] d_b \omega_P^{1.2}\right)/\sigma \qquad (2)$$

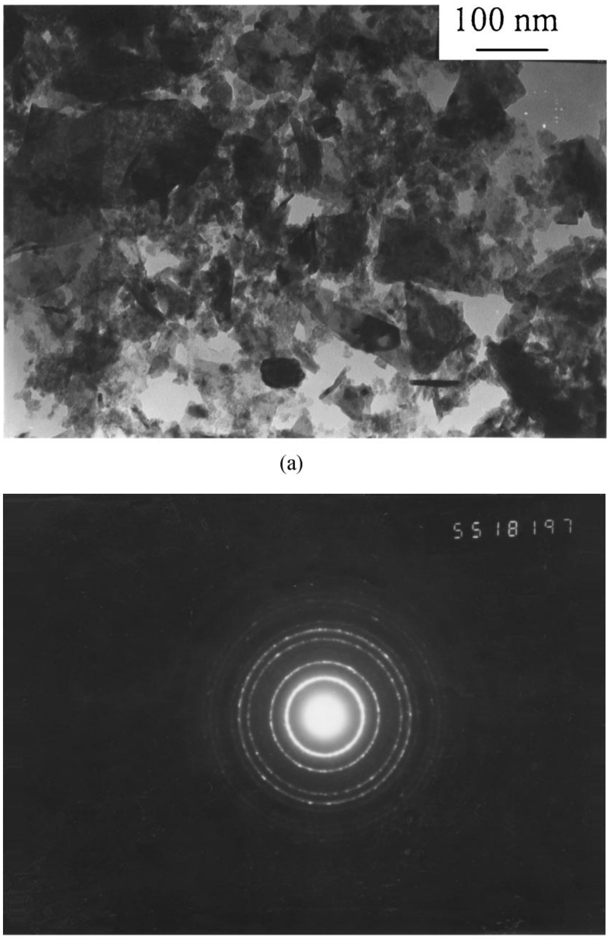
where E_i is the energy absorbed by the powder per unit of mass, R_P is the radius of the plate of the mill, ρ is the ball material density, E is the elastic modulus of the ball material, d_b is the diameter of balls, ω_P is the angular velocity of the mill, σ is the surface density of trapped powder. In our case, taking $R_P = 0.09$ m, $\rho = 7.64 * 10^3$ kg/m^3, $E = 2.1 * 10^{11}$ N/m^2, $d_b = 0.01$ m, $\omega_P = 2\pi * 250/60 = 26.18$ rad/s, $\sigma = 0.2$ kg/m^2, then E_i is equal to 77.4 kJ/kg. Since the powder is composed of $WO_3 + Mg + C$ with the atomic ratio of $1:3:2$, the average mole mass is estimated to be 0.547 kg/mol, which gives $E_i = 4.2$ kJ/mol. This is the energy absorbed by the powder in one collision. For the collision frequency of 14 per second when $\omega = 250$ rpm [13], the total energy (E_P) absorbed by the powder in one second is 58.8 kJ/mol. Due to the contribution of E_P, the energy of formation for the reaction (1) becomes $\Delta G' = -280 - 58.8 = -338.8$ kJ/mol and the entropy changes to be $\Delta S = (\Delta H - \Delta G)/T = (-320 + 338.8)/T > 0$. In this case, reaction (1) will be a self-propagating reaction. It is worth mentioning that σ is a variable in the milling process and is a key parameter for the above evaluation. When the milling proceeds, the grain size of the powders become smaller, the specific surface area becomes larger, namely the surface density σ decreases and the impact energy transferred to the powders increases. Above milling process leads to the enhancement of the entropy. Therefore, only when the powders are milled to a certain extent can the self-propagating reaction occur.

According to the above evaluation, we may conclude that the mechanochemical process initiates spontaneous exothermal reaction (1), which raises the temperature of mixture powders to such an extent that a self-propagating reduction reaction is incurred and the reaction completes instantly. The high temperature in the vial and the excessive graphite are favorable to expedite the subsequent diffusion reaction of high activity α-W with C. After 38 hours of milling, x-ray diffraction pattern indicates that the sample is composed of WC_{1-z} and W_2C, while the diffraction peaks of W disappears, as shown in Fig. 3a. The diffusion reaction could be expressed as follows:

$$3W + 2C \Rightarrow WC_{1-z} + W_2C \qquad (3)$$

Tungsten and graphite are converted to cubic WC_{1-z} phase and a little W_2C phase after 52 hours milling. As shown in Fig. 3b, further milling for 70 hours leads to the disappearance of the diffraction peaks of WO_3, which is converted to WC_{1-z} through diffusion reaction. The other peaks remain unchanged. After milling for about 90 hours, only WC_{1-z} and C are detectable and the diffraction peaks of W_2C disappear, as shown in Fig. 3c. Note that the products are different from those of Poppvich [12], who obtained a mixture powders of W_2C, WC and MgO through the process under an air atmosphere. The present samples don't contain any hexagonal phase. From above result, it can be seen that the products of the mechanochemical reaction depend mainly on the graphite content, milling atmosphere, and the milling energy. The final grain size of the mixture powders milled for 90 hours is in the range of 4 to 20 nm.

The heat explosion of mixture powders did not take place even after milling for 90 hours. One reason may relate to the excessive carbon packing the surface of the WO_3 which reduces opportunity of Mg powder to react with WO_3. That is why excessive graphite may alleviate heat accumulation and thus prevents the reaction from explosion. When stoichiometric or a little deficient graphite is used, such layer will be absent and the reduction reaction will take place very quickly. Therefore a lot of reaction heat will accumulate in the vial within a very short period and will result in the explosion and the formation of W_2C. This case was discussed in detail elsewhere [14]. Furthermore, the other reason why heat explosion did not occur after 90 hours milling could be explained according to Magini's model [13]. After a long periodic milling, the size of the mixture powders will approach to a limited value, that means that the impact energy contributed to the mixture powders will reach a constant after long periodic milling. In such case, the temperature of the mixture powders will not rise and the explosion is avoidable.



(a)

(b)

Figure 4 (a) TEM bright field micrograph of mixture powders of WC_{1-z} and C; (b) electron diffraction pattern of one WC_{1-z} grain.

3.2. Microstructure of as-milling powders

Fig. 4 illustrates the morphology of the final mixture powders of WC_{1-z} and C in a TEM bright field and the electron diffraction pattern of one WC_{1-z} grain. The large particles exhibit a laminated rectangular contour which is different from that of W_2C with a round shape synthesized under a carbon deficient condition [14]. The small particles still show a round shape. The large laminated particles come from graphite phase and the small particles come from WC_{1-z} phase. It can be also seen from Fig. 4a that the secondary particles are formed due to cohesion of fine particles with high surface activity, which resulted in aggregation of fine particles. The final crystal particle size for the 90 hours milled powders is in the range of 4 to 20 nm, as shown in Fig. 4a. The electron diffraction pattern of one f.c.c. structured WC_{1-z} grain is congruous with the x-ray diffraction result.

4. Conclusions

Nanocrystalline cubic substoichiometric WC_{1-z} powders were successfully synthesized by reactive milling of $WO_3 + Mg$ mixture powders containing graphite as a source of carbon. The synthesis procedure consisted of two steps: namely the synthesis of α-W by reductive reaction of Mg with WO_3 and the diffusion reaction of high activity α-W with C. During reductive reaction, a great deal of heat was released and accumulated in the vial to a certain temperature which expedited the subsequent diffusion reaction. An entropy evaluation indicated that the reduction reaction could be self-propagating after mixture powders milling to a certain extent. The nanocrystalline powders of single phase WC_{1-z}, with the grain size ranged from 4 to 20 nm, are obtained by mechnochemical milling for 90 hours.

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