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Facile Synthesis and Thermal Stability of Nanocrystalline Molybdenum Carbide

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ABSTRACT

Nanocrystalline molybdenum carbide (*Mo_2C*) *was prepared via one simple route by the reaction of metallic magnesium powders with molybdenum trioxide and potassium acetate in an autoclave at the condition of* 600*˚C and* 4 *h. X-ray powder diffraction* (*XRD*) *pattern indicated that the product was hexagonal α-Mo_2C, and the cell constant was a =* 3.0091 *Å, c =* 4.7368 *Å. Scanning electron microscopy* (*SEM*) *image showed that the sample consisted of particles with an average size of about* 100 *nm in diameter. The product was also studied by the thermogravimetric analysis* (*TGA*). *It had good thermal stability and oxidation resistance below* 450*˚C in air.*

***Keywords*:** *Molybdenum Carbide*, *Chemical Synthesis*, *X-Ray Diffraction*, *Thermogravimetric Analysis*

1. Introduction

Molybdenum carbide, one of the most important compounds among transition metal carbides, due to its promising physical and chemical properties, such as a high melting temperature, high hardness, and high resistance to corrosion and oxidation, high abrasion resistance, good electrical conductivity. So it is widely used for cutting materials, abrasive, anti-wear and aerospace materials [1-4]. At the same time, Mo_2C is used as a kind of catalyst in various reactions [5-10]; even it is usually superior to the noble metal catalysts in selectivity, stability and resistance to poison, so that Mo_2C might be considered as a cheaper substitute for the noble metal catalysts. Because of the promising properties and extensive application of Mo_2C, it is meaningful to synthesize nanocrystalline Mo_2C, in a simple route at low temperature and with convenient manipulations.

Traditionally, mixing molybdenum powder with carbon black by annealing under argon flow or vacuum at a temperature between 1400˚C and 1500˚C can produce Mo_2C. Later, Mo_2C is synthesised via the reaction of molybdenum oxide and high specific surface-active carbon at the lower reaction temperature [11]. Up to now, many approaches have been developed for the preparation of Mo_2C. Wang and co-workers [12] have shown that bulk face-centered-cubic (fcc)-based η-MoC_{1-x} and hexagonal-close-packed (hcp)-based β-Mo_2C have been prepared using C_3H_8/H_2 by temperature-programmed reaction method and a rapid heating method. Arceo *et al* [13] have reported hexagonal Mo_2C have been synthesized by mechanical alloying with a mixture of carbon and molybdenum powder under argon atmosphere at 25 h, consequently. Norin *et al.* [14] have deposited single-phase molybdenum carbide films on sapphire by chemical vapour deposition using C_{60} as a carbon source. Yao [15] has used carbothermal reduction route to produce the β-Mo_2C in the presence of a small amount of H_2 at 950˚C. T. Miyao *et al.* [16] have prepared molybdenum carbide by nitridation of 12.5 wt% MoO_3/Al_2O_3 in a flow of NH_3 at 700˚C, followed by carburization in a flow of 20% CH_4/H_2 also at 700˚C for 3 h.

In this paper, we have developed a new convenient route to synthesize nanocrystalline hexagonal α-Mo_2C at low temperature by the reaction of metallic magnesium powders with MoO_3 and CH_3COOK in an autoclave at 600˚C. In this route, MoO_3 as molybdenum source is more stable and safe in operation than other molybdenum source (e.g. $MoCl_5$) and metallic magnesium powders as reductant are also more safe and convenient than other reductants (e.g. metallic sodium). Due to the whole syn-

thesis route which is carried out in the sealed autoclave, so it can be obtained that all manipulations are rather safe and convenient, etc.

2. Experimental

In a typical experiment, analytical grade MoO_3, analytical grade CH_3COOK and analytical grade metallic magnesium powders were put into a mortar, followed by mixing these powders thoroughly. Then the mixture was put into a stainless steel autoclave. After sealing under argon atmosphere, the autoclave was heated at 600˚C for 10 h, followed by cooling to room temperature in the furnace. The obtained product from the autoclave was washed several times with absolute ethanol, dilute HCl aqueous solution, distilled water to remove the impurities. Finally the product was washed three times with absolute ethanol to remove water. The final product was vacuum-dried at 60˚C for 8 h. Black powders were obtained.

The obtained sample was analyzed by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray powder diffractometer using Cu K-α radiation (wavelength λ = 1.54178 Å). The operating voltagewas 40 kV. 2 theta angles were from 20˚ to 90˚. The morphology of the sample was observed from a JEOL JSM-6700F scanning electron microscope, the operating voltage was 10 kV. The thermogravimetric analysis was performed on a thermal analyzer (Model: Q600) below 900˚C in air at a rate of $5^{\circ}C \cdot min^{-1}$ to study its thermal stability and oxidation behavior.

3. Results and Discussion

Figure 1 shows the XRD patterns of the as-prepared samples and Mo_2C (JCPDS Card no. 35-0787). Pattern (a) shows the sample prepared under the condition of 600˚C and 10 h, there are eight obvious diffraction peaks in the pattern in **Figure 1(a)**. And all these diffraction peaks ((1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1)) at different *d*-space can be indexed as hexagonal α-Mo_2C. The refinement gives the cell constants (a = 3.0091 Å, c = 4.7368 Å), which is consistent with the value reported in the literature (a = 3.0124 Å, c = 4.7352 Å) (JCPDS card no. 35-0787). No evidences of crystal impurities such as molybdenum, molybdenum trioxide, other molybdenum carbides, can be found in this XRD pattern.

The morphology of the prepared Mo_2C sample was investigated by field emission scanning electron microscopy. The SEM image of the as-prepared Mo_2C sample is shown in **Figure 2**. In this figure, the samples show that it consists of particles with an average diameter of 100 nm. These particles exhibit slightly agglomerated particle morphology due to the ultrafine size of the sample.

In order to investigate the thermal stability and the

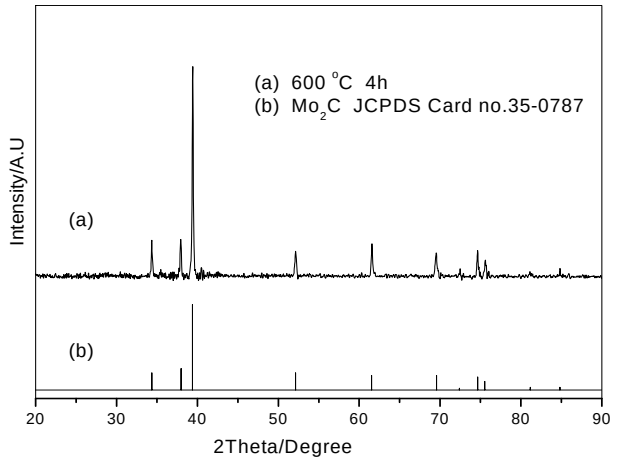

Figure 1. XRD patterns of the (a) as-prepared sample and (b) Mo_2C (JCPDS Card no. 35-0787).

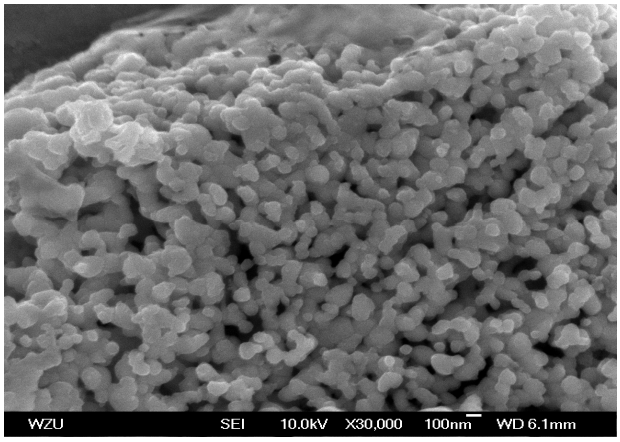

Figure 2. SEM image of the as-prepared sample prepared under the reaction condition of 600˚C and 4 h.

oxidation resistance of the as-prepared Mo_2C powder by the thermogravimetric analysis (TGA), which was carried out at temperatures below 900˚C under flowing air in **Figure 3**. In the figure, we can find that the weight of the product has not changed significantly below 350˚C. A slight weight loss indicates that the sample might adsorb a little water on the surface. However, an obvious weight loss step occurred in the temperature range of about 350˚C to 450˚C, which may be attributed to oxidation of the graphite to form CO_2 [17]. In this stage, the sample Mo_2C is very stable. The Mo_2C sample begines to oxidize at the temperature about 450˚C, indicating that the sample is oxidized to form molybdenum trioxide and carbon dioxide. The sample can be oxidized thoroughly at 550˚C. Therefore, the weight gain remains almost constant on the TGA curve when the temperature ranges of about 550˚C to 720˚C. When the temperature exceeds 720˚C, the curve of the as-prepared Mo_2C sample has suddenly declined, which is attributed to molybdenum

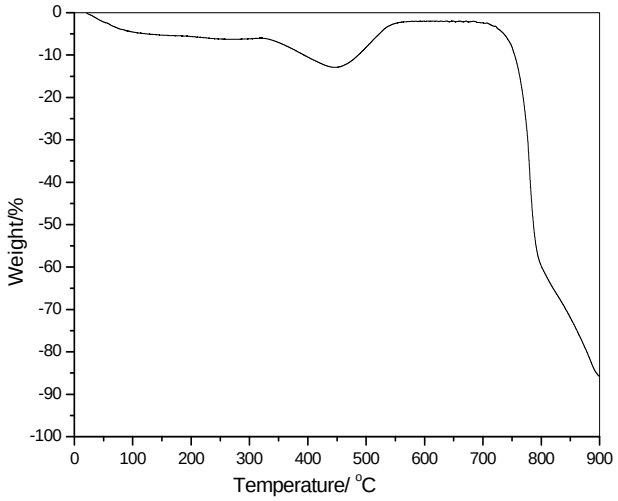

Figure 3. TGA curve of the as-prepared Mo_2C sample in flowing air.

trioxide evaporated at this high temperature (about 740˚C). In a word, because of the ultrafine particles, the sample can be oxidized thoroughly at about 550˚C. But the sample has good thermal stability below 450˚C.

4. Conclusions

In summary, nanocrystalline molybdenum carbide (Mo_2C) powder has been prepared via a simple thermal route by the reaction of metallic magnesium powders with molybdenum trioxide and potassium acetate in an autoclave at 600˚C for 4 h. The product crystalline structure is hexagonal. It consists of particles with an average size of 100 nm. The product has good thermal stability and oxidation resistance below 450˚C.

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