Int. Journal of Refractory Metals and Hard Materials 58 (2016) 206–210

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

# Synthesis and characterization of chromium carbide nanopowders processed by mechanical alloying assisted microwave heating route

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ARTICLE INFO

*Article history:*
Received 15 February 2016
Received in revised form 2 May 2016
Accepted 10 May 2016
Available online 12 May 2016

*Keywords:*
Chromium carbide
Microwave heating
Nanopowders
Mechanical alloying
Microstructure

ABSTRACT

Chromium carbide nanopowders were synthesized via mechanical alloying assisted microwave heating route using micron-sized chromic oxide ($Cr_2O_3$) and nano-sized carbon black as raw materials. The samples were characterized by X-ray diffractometry (XRD), thermogravimetric and differential scanning calorimetry (TG-DSC), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The results show that the ultimate weight loss revealed by TG curve is 47.6 wt%. The transformation temperature (1030 °C) of the mixture after mechanical alloying is much lower than that of the traditional mixing method (1122 °C). Chromium carbide nanopowders have been successfully synthesized at 1000 °C for 1 h. The powders show good dispersion and are mainly composed of spherical or near-spherical particles with a mean diameter of about 50 nm. Compared with the traditional carbon thermal reduction method, the reaction temperature and time synthesized by mechanical alloying assisted microwave heating method can be reduced and shortened by 400 °C and 3 h, respectively.



## 1. Introduction

The transition metal carbides are a class of ceramics that are known for their high hardness and refractory nature whose constituents form part of the class of ultrahigh temperature ceramics [1–3]. Besides, these materials also exhibit good electrical and thermal conductivities. Therefore, they have wide uses in metallurgy, electronics, and catalysts [4,5]. There are three forms of chromium carbides ($Cr_3C_2$, $Cr_7C_3$, and $Cr_{23}C_6$) with different atomic ratios of carbon to chromium element [6]. Among them, chromium carbide ($Cr_3C_2$) is the most stable carbide and it exhibits high hardness, good strength, high Young's modulus, high corrosion and erosion properties, good chemical stability and high oxidation resistance [7]. Therefore, it has been widely used in a variety of industrial applications, such as seals, nozzles, shaft bearings, metal machining molds and high-temperature furnaces [8,9].

Commonly, carbide powders are synthesized by carbon thermal reduction of micron-sized oxides and carbon. This method has some disadvantages such as a high reaction temperature (>1400 °C), a long reaction time (>4 h) and a high cost. Furthermore, the prepared carbide powders exhibit grains in the μm-range, which cannot satisfy the demands of carbide powders for modern industry [10]. Nowadays, various methods for synthesizing carbide powders have been researched, e.g. direct element reaction [11], temperature programmed reaction [12] and gas reduction–carburization [13]. However, industrial applications of these methods are still limited due to the low yields, wide size distributions, complex monitoring and high costs.

Mechanical alloying assisted microwave heating is a promising preparation method that may resolve the problems arising from conventional synthesis methods. Mechanical alloying as production process in cemented carbides has attracted many interests due to its capability of producing nano-crystalline powders prior to sintering [14,15]. Furthermore, microwave heating has a number of potential advantages. It generates first heat within the material and then heats the entire volume. This heating mechanism is advantageous due to uniform, rapid, and volumetric heating, high reaction rates and selectivity, dramatically reduced reaction times, and high product-yields [16–18].

In this study, chromium carbide nanopowders were prepared via mechanical alloying assisted microwave heating route at relatively low temperature. The raw materials were micron-sized $Cr_2O_3$ and nano-sized carbon black. After mechanical alloying, micro-scale raw materials were transformed into nano-scale materials, which exhibit a higher specific surface area and activity. Thus the reaction temperature and time can be reduced and shortened, respectively. Furthermore, microwave heating is a novel heating technology with higher effectiveness than the traditional heating method [18]. As far as we know, it has not been reported that chromium carbide nanopowders have been synthesized by the method. In this investigation, the effect of reaction temperature on phase composition and microstructure of chromium carbide nanopowders was researched.

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http://dx.doi.org/10.1016/j.ijrmhm.2016.05.003
0263-4368/

## 2. Experimental

### 2.1. Synthesis of chromium carbide nanopowders

Micron-sized $Cr_2O_3$ (Tianjin Bodi Chemical Co., Ltd., China, A.R., purity > 99%) and nano-sized carbon black (Panzhihua Qianjin Chemical Co., Ltd., China, average particle size < 50 nm) were used as raw materials. 66 wt% $Cr_2O_3$ and 34 wt% C were put into the QM-3SP2 high-energy planetary ball mill (Nanjing Lai Technology Industrial Co., Ltd., China). The mixing and milling medium were absolute alcohol and cemented carbide balls, respectively. The ball to powder mass ratio and the speed were 20:1 and 300 rpm, respectively. After being milled for 64 h, the mixture was dried in a vacuum drying oven at 90 °C for 12 h. Finally, the mixture was heated at different temperatures (900 °C, 1000 °C, 1100 °C and 1200 °C) for 1 h in a multimode 2.45 GHz RWS microwave furnace (Zhongsheng Thermal Technology Co., Ltd., China) in argon gas atmosphere to prepare chromium carbide nanopowders.

### 2.2. Characterization

The structure of the powder was examined via X-ray diffraction using a Bruker D8 Advance diffractometer with Cu-$K_\alpha$ radiation in the range of $2\theta = 15$ to 85°. Simultaneous thermogravimetric and differential scanning calorimetry (TG-DSC) were performed on the mixture using a NETZSCH STA 409 PC thermogravimetric analyzer under a constant Ar gas flow of 20 ml/min with a heating rate of 10 °C/min. The X-ray photoelectron spectroscopy (XPS) was carried out using a XSAM 800 spectrometer (Kratos, England) using a MgK(alpha 1) X-ray source. Particle morphology and size of the synthesized powders were observed by JSM-6700F scanning electron microscopy (SEM) and JEM-1000CX transmission electron microscopy (TEM).

## 3. Results and discussion

To determine the physical phenomena occurring during the microwave heating process, simultaneous TG-DSC measurements were carried out for the mixture after mechanical alloying and the results given in Fig. 1. As shown in Fig. 1, the ultimate weight loss revealed by TG curve is 47.6 wt%. The change of weight is relatively smooth (15.1 wt%) below 900 °C, but it is abrupt between 900 °C and 1100 °C (32.5 wt%). Then the weight is almost no change between 1100 °C and 1200 °C. Two broad endothermic peaks occur at 500 °C–600 °C in the DSC curve, which is induced by the reaction between $Cr_2O_3$ and C ($Cr_2O_3 + C = 2CrO + CO\uparrow$) [19]. An apparent exothermic peak occurs at 890 °C, which is ascribed to the crystallization of CrO. Then a sharp endothermic peak appears at 894 °C, which is ascribed to the formation of the intermediate carbides ($3Cr_2O_3 + (13 - 2\times)C = 2Cr_3C_{2-x} + 9CO\uparrow$, $0 \le x \le 0.5$). An obvious endothermic peak occurs at 1030 °C in the DSC curve, which is induced by the transformation from chromic oxide to chromium carbide ($3Cr_2O_3 + 13C = 2Cr_3C_2 + 9CO\uparrow$) [20]. A broad exothermic peak occurs at 1104 °C, which is ascribed to the crystallization of chromium carbide. The transformation temperature (1030 °C) of the mixture after mechanical alloying is much lower than that of the traditional mixing method (1122 °C) [19]. This phenomenon can be attributed to the intense mechanical deformation of powders during mechanical alloying, which leads to the formation of various crystalline defects including dislocations, grain boundaries, stacking faults, and vacancies. These defects will result in the occurrence of the short circuit diffusion paths and make diffusion take place easily. As a result, many chemical reactions, that normally require high temperatures, occur at relatively lower temperatures [21]. Furthermore, the transformation temperature (1030 °C) is very close to the minimum synthesis temperature (993 °C) of chromium carbide ($Cr_3C_2$) calculated by thermodynamics. The relationship between $\Delta G$ and $T$ is illustrated in the literature [22].

Fig. 2 shows the XRD patterns of the mixture before and after microwave heating. From Fig. 2(a), it can be seen that all peaks are identified as $Cr_2O_3$ without carbon phase, which is mainly because carbon exists in

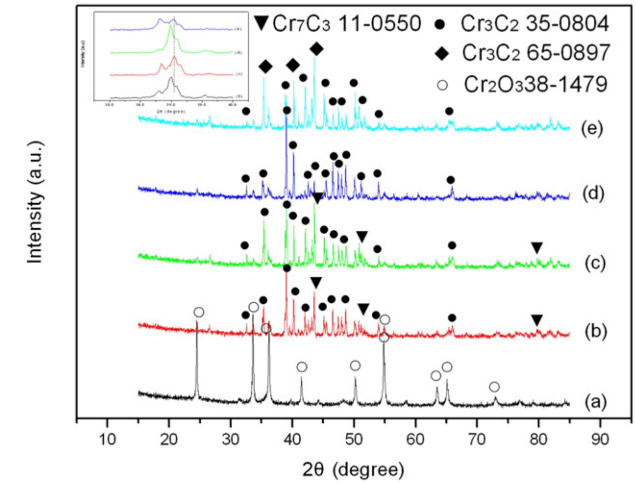


**Fig. 2.** X-ray diffraction patterns of the mixture before and after microwave heating: (a) after mechanical alloying; (b) 900 °C; (c) 1000 °C; (d) 1100 °C; and (e) 1200 °C.

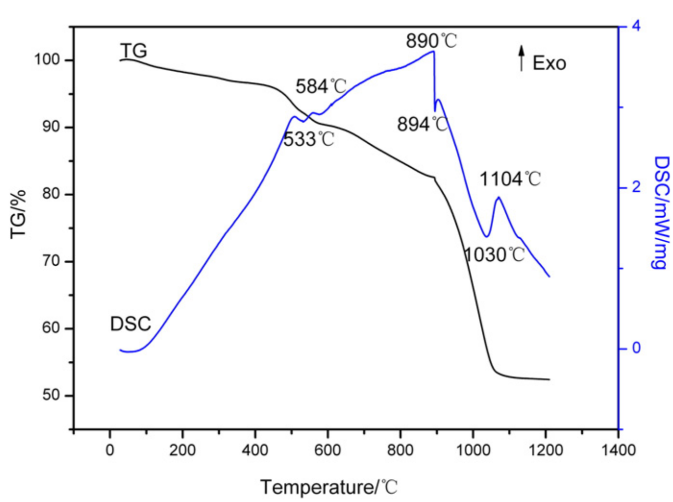


**Fig. 1.** TG-DSC curves of the mixture after mechanical alloying for 64 h measured in Ar atmosphere.

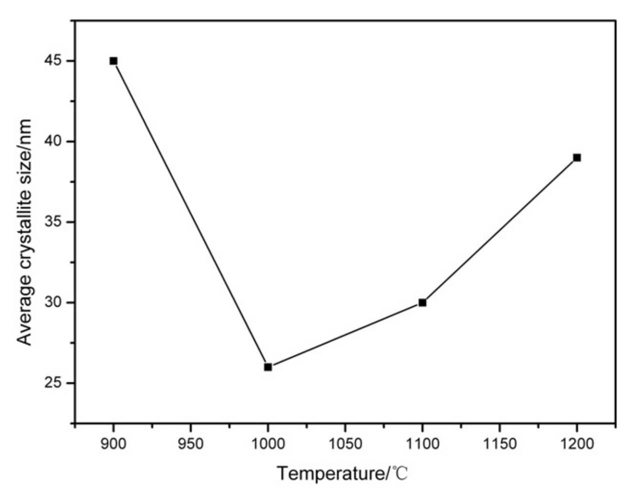


**Fig. 3.** The average crystallite sizes of the powders synthesized at different temperatures for 1 h.