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First synthesis of Cr_3C_2 nanowhiskers by low-temperature vaccum carburization from precursor

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HIGHLIGHTS

- Cr_3C_2 nanowhiskers were first synthesized at 800 °C by a novel LVCP method.
- A homogeneous chemical composition from precursor reduces synthesis temperature.
- Cr_3C_2 nanowhiskers have a single-phase structure and a diameter size of ~50 nm.

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ABSTRACT

To assist a widespread application of chromium carbide (Cr_3C_2), it is important to synthesize Cr_3C_2 nanowhiskers and but there are almost no related reports. In this letter, we first reported a low-lost synthesis of Cr_3C_2 nanowhiskers at 800 °C by vacuum carburization process using precursor powders as raw materials without Fe/Co/Ni catalysts. X-ray diffraction (XRD) data confirm that Cr_3C_2 nanowhiskers have a single-phase orthorhombic structure. A homogeneous chemical composition can be obtained in the calcining product from precursor, which reduces significantly the synthesis temperature. Morphological studies using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) show Cr_3C_2 nanowhiskers have a clean and smooth surface with a diameter size of ~50 nm.

1. Introduction

Whiskers of transition metal carbides, nitrides, and borides are now being used to reinforce and toughen the metal matrix composites and ceramic matrix composites [1,2]. So far, although a large number of ceramic whiskers such as SiC [3], TiC [4], Si_3N_4 [5] and TiB [6] have been reported in recent years by various synthesis methods, there are very few types of whiskers commercially available on a large scale, except SiC whiskers. But SiC has some limitations for use at high temperature because of its chemical stability [4]. Of these carbides, Chromium carbide (Cr_3C_2) has a good set of properties of high hardness, high melting point, excellent resistance to chemical corrosion and good chemical stability [7]. For example, Cr_3C_2 can resist against corrosion and oxidation up to 900 °C, and it dissociates only at very high temperature of 1813 °C [8].

At present, there are many researches concerning about powder synthesis of Cr_3C_2. For example, Zhao et al. [9] used ammonium dichromate and nanometer carbon black as raw materials to synthesize Cr_3C_2 nanopowders at 1100 °C by solution-derived precursor method. Cintho et al. [10] prepared Cr_3C_2 and Cr_7C_3 powders at 800 °C by mechanical-thermal synthesis method. Wang et al. [11] produced Cr_3C_2 nanopowders at 800–850 °C by metal-organic chemical vapor deposition method. However, there are few investigations about Cr_3C_2 whiskers in recent decades. Motojima et al. [12] reported the growth of Cr_3C_2 microwhiskers by chemical vapor deposition (CVD) process only in 1985, but unfortunately Cr_3C_2 nanowhiskers have not yet been reported. In this study, Cr_3C_2 nanowhiskers were first synthesized at 800 °C by a novel method, namely low-temperature vacuum carburization from precursor (LVCP).

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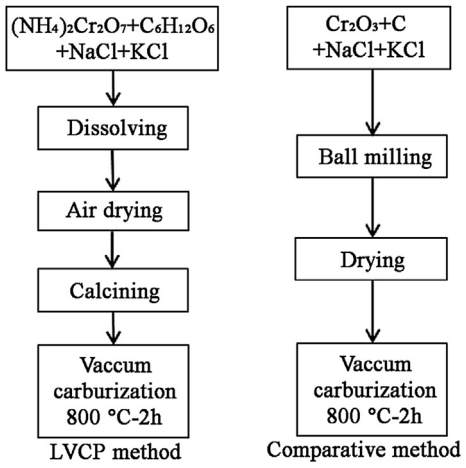

Fig. 1. Different methods of synthesizing Cr_3C_2 nanowhiskers.

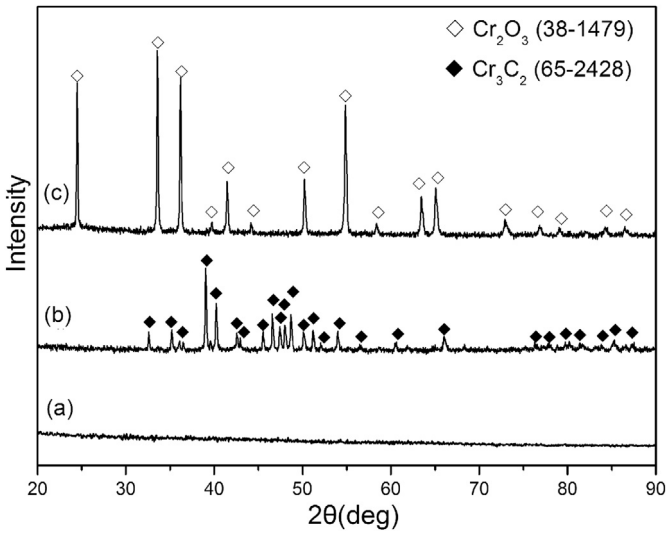

Fig. 2. XRD patterns of the reaction products: (a) calcined at 400 °C for 1 h by LVCP method; (b) carburized at 800 °C for 2 h by LVCP method; (c) carburized at 800 °C for 2 h by comparative method.

2. Material and methods

During the LVCP process, commercially available raw materials of ammonium dichromate (Cr source), glucose (C source) and halogenating agent (NaCl + KCl, molar ratio of 1:1) were put into hot purified water and mixed uniformly. The purity of all the raw materials is more than 99%. The well-proportioned precursor mixture was obtained after the precursor solution was dried in the air for 40 h, and then calcined with flowing argon atmosphere at 400 °C for 1 h to form the complex chromic oxide-carbon-chloride mixture. All the carburization reactions were carried out with 50 g of the calcined mixture in vacuum carbon tube furnace (Model XLJ-S-ZKL-005, China). The furnace was evacuated to less than 50 Pa by using a vacuum pump and then heated at a rate of 5–8 °C/min. After reaching the carburization temperature, the samples were isothermal treated for 2 h.

In order to evaluate the effect of the LVCP method on the synthesis of Cr_3C_2 nanowhiskers, the comparative synthesis method was used in this study, as shown in Fig. 1. For the comparative method, the milling mixture of Cr_2O_3 and C powders with the same stoichiometric proportion was carburized at the same carburization process.

The phase composition analysis of reaction products was investigated by X-ray diffractometry (XRD, DX-2000, Dandong Fangyuan Instrument co., LTD, China) using Cu Kα radiation with a step size of 0.03°/s. Microstructural examinations of samples were observed by scanning electron microscopy (SEM, VEGA 3 SBU, TESCAN, Czech), field emission scanning electron microscopy equipped with energy dispersive spectroscopy (FESEM-EDS, JSM-7800F, JEOL, Japan) and transmission electron microscopy (TEM, JEM-100CX, JEOL, Japan and Titan G2 60-300, FEI, USA).

3. Results and discussion

Fig. 2 shows XRD patterns of reaction products. According to Ref. [9], $(NH_4)_2Cr_2O_7$ can transform into Cr_2O_3 at ~ 180 °C. Therefore, the calcined products at 400 °C (in Fig. 2a) are just Cr_2O_3−⊕C−NaCl−KCl mixtures. All diffraction peaks in Fig. 2a are so smooth that the pattern appears more like amorphous structure. So, it can be deduced that all the elements have been mixed homogeneously on a molecular level by LVCP method. As shown in Fig. 2b, All diffraction peaks of the product can be indexed to a Pnma phase of Cr_3C_2 (JCPDS 65-2428). It can be stated that a single-phase Cr_3C_2 product with orthorhombic structure was obtained at 800 °C for 2 h by LVCP method. Note that in Fig. 2c, no other phase is present, except Cr_2O_3 (JCPDS 38-1479) at 800 °C for 2 h, showing that the transformation temperature of $Cr_2O_3 \rightarrow Cr_3C_2$ is very high in the comparative method. It is concluded that the calcining product from precursor with homogeneous chemical composition contributes to the decrease of synthesis temperature for LVCP method.

Fig. 3 shows typical SEM micrographs of reaction products. A

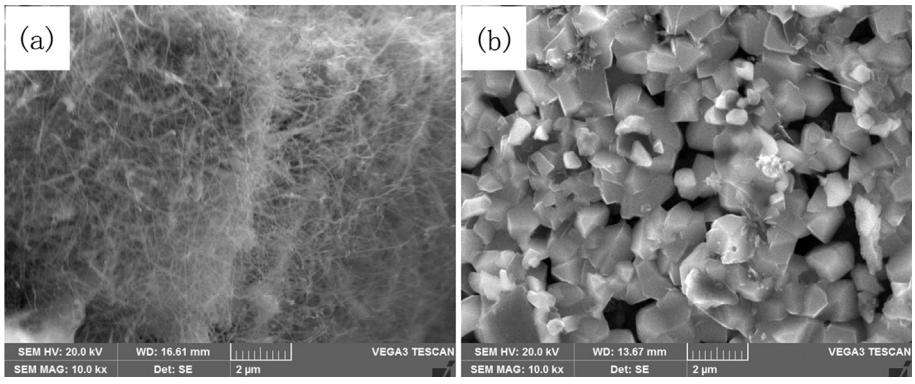

Fig. 3. SEM images of the products obtained at 800 °C for 2 h: (a) LVCP method, (b) comparative method.