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Effect of growth promoters on chemistry synthesis of Cr_3C_2 nanowhiskers from water-soluble precursors

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ABSTRACT

Cr_3C_2 nanowhiskers with a diameter size of ~50 nm were synthesized at mild condition (800 °C for 2 h) by a new precursor method. The process has two steps in which the amorphous Cr_2O_3-C mixtures containing whisker growth promoters were first produced from water-soluble precursor solution by air drying and subsequent calcining at 400 °C for 1 h, and secondly carburized at 750–800 °C. Phase composition and morphology of as-prepared products were discussed by X-ray diffraction and scanning electron microscopy, respectively. Furthermore the transmission electron microscope was used to identify the fine structure of the as-prepared products. The results showed that the melting point and addition amount of the selected grow agent were two critical controlling factors during synthesizing Cr_3C_2 nanowhiskers, in which the addition of 4 wt% NaCl + KCl (molar ratio of 1:1) mixture with the melting point of ~650 °C is optimal. Fe/Co/Ni catalysts are not suitable for the synthesis of Cr_3C_2 nanowhiskers as whisker growth promoters by the precursor method.

1. Introduction

Chromium carbides have three typical crystallographic structures, namely cubic $Cr_{23}C_6$, hexagonal Cr_7C_3 and orthorhombic Cr_3C_2. Of these carbides, Cr_3C_2 has a good set of properties of high hardness, high melting point, excellent resistance to chemical corrosion and good chemical stability [1,2]. 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 [3]. Therefore, Cr_3C_2 has been widely used as one of the most effective grain growth inhibitors for sintering WC-Co cemented carbide [4], thermal spray powder for corrosion and wear resistance coatings [5], sputtering thin film for nanomechanical and nanowear properties [6].

Whiskers of transition metal carbides, nitrides, and borides are now being used to reinforce and toughen the metal matrix composites and ceramic matrix composites, such as SiC [7], TiC [8], Si_3N_4 [9] and TiB [10]. However, there are few reports about the synthesis of nano Cr_3C_2 in low temperature, except producing Cr_3C_2 microwhiskers by chemical vapor deposition (CVD) method [11] and Cr_3C_2 nanopowders by chemical-reduction route [12]. So far, Cr_3C_2 nanowhiskers have not yet been reported. So the study on synthesis of Cr_3C_2 nanowhiskers is very important to develop some new whisker-reinforced composites.

In this study, Cr_3C_2 nanowhiskers were synthetized for the first time by a novel method, namely low-temperature vacuum carburization from water-soluble precursors. The goal of this work was to explain the formation mechanism of Cr_3C_2 nanowhiskers by investigating the phase and microstructure evolution of various reaction products with different whisker growth promoters and to provide fundamental basis for the production of high-quality Cr_3C_2 nanowhiskers.

2. Material and methods

In this experiment, the water-soluble precursors of ammonium dichromate ($(NH_4)_2Cr_2O_7$), glucose ($C_6H_{12}O_6$) were used as chromium source, carbon source, respectively. In addition, six kinds of grow promoters with the different melting point at the range of ~550–800 °C and three kinds of Fe/Co/Ni catalysts were selectively used as whisker growth promoters, as shown in Table 1. The purity of all the raw materials is more than 99%. In order to ensure synthesis reaction to finish entirely, glucose was added according to 150 wt% of theoretical carbon contents. At first, all the raw material powders were put into hot purified water and mixed to be homogeneous. The well-proportioned precursor mixtures were obtained after the precursor solutions were dried in the air for 40 h, and then calcined with flowing argon atmosphere at 400 °C for 1 h to form the complex Cr_2O_3-C mixtures containing whisker growth promoters. All the carburization reactions were carried out with 50 g of the calcined mixtures 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

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Table 1
Growth promoters used to synthesize Cr_3C_2 nanowhiskers.

Samples	Halogenating agents		Fe/Co/Ni catalysts
	Chemical composition (molar ratio)	Melting point (°C) [13]	
1	$CaCl_2$+NaCl (0.54:0.46)	~550	—
2	$CaCl_2$+KCl (0.26:0.74)	~600	—
3	NaCl+KCl (0.5:0.5)	~650	—
4	$MgCl_2$	~710	—
5	KCl	~770	—
6	NaCl	~800	—
7	NaCl+KCl (0.5:0.5)	~650	$NiCl_2{\cdot}6H_2O$
8	NaCl+KCl (0.5:0.5)	~650	$FeCl_3{\cdot}6H_2O$
9	NaCl+KCl (0.5:0.5)	~650	$CoCl_2{\cdot}6H_2O$

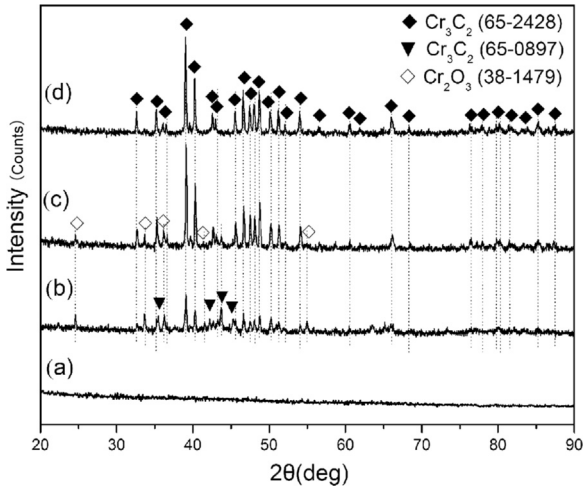

Fig. 1. Effect of synthesis temperature on XRD patterns of reaction products: (a) calcined at 400 °C for 1 h; (b) carburized at 750 °C for 2 h; (c) carburized at 800 °C for 1 h; (d) carburized at 800 °C for 2 h..

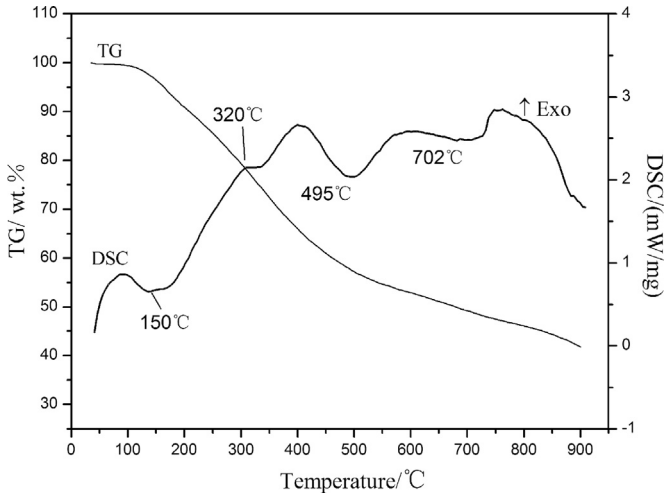

Fig. 2. DSC/TG analysis of reaction products from room temperature to 900 °C..

rate of 5–8 °C/min. After reaching the carburization temperature, the samples were isothermally treated for 1–2 h.

The phase composition analysis of reaction products was investigated by X-ray diffraction (XRD, DX-2000, China) using Cu Kα radiation with a step size of 0.03°/s. Microstructural examinations of the samples were observed by scanning electron microscopy (SEM, VEGA 3 SBU, Czech Republic) and Transmission electron microscopy (TEM, JEM-100CX, Japan and Titan G2 60–300, USA). TG-DSC (NETZSCH STA 409 PC/PG, Germany) was performed under a

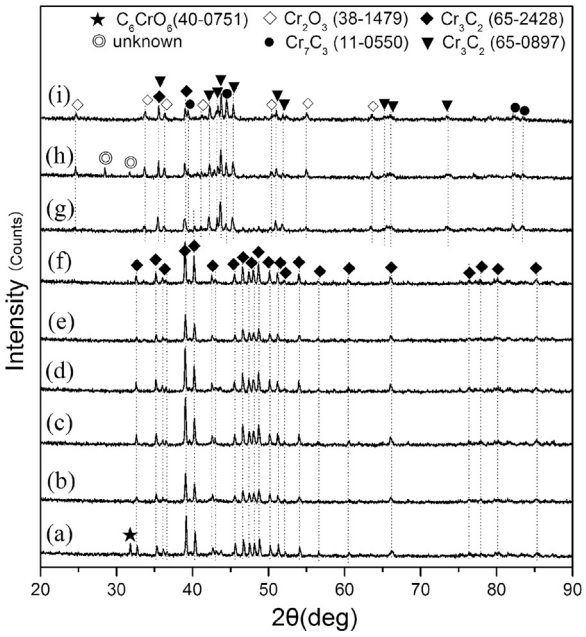

Fig. 3. Effect of whisker growth promoter on XRD patterns of reaction products: (a) $CaCl_2$ + NaCl; (b) $CaCl_2$ + KCl; (c) NaCl + KCl; (d) $MgCl_2$; (e) KCl; (f) NaCl; (g) NaCl + KCl + $NiCl_2{\cdot}6H_2O$; (h) NaCl + KCl + $FeCl_3{\cdot}6H_2O$; (i) NaCl + KCl + $CoCl_2{\cdot}6H_2O$..

constant argon gas flow of 20 ml/min with a heating rate of 10 °C/min.

3. Results and discussion

Fig. 1 shows XRD patterns of the products obtained by using NaCl +KCl (molar ratio of 0.5:0.5) as whisker growth promoter at different synthesis temperature. At 400 °C, all diffraction peaks in Fig. 1a are so smooth that the pattern appears more like amorphous structure. According to Ref. [14], $(NH_4)_2Cr_2O_7$ can transform into Cr_2O_3 at ~180 °C(as shown in Eq. (1)). Therefore, the calcined products at 400 °C are just Cr_2O_3-C-NaCl-KCl mixtures. It suggests that all the elements in the mixtures have been mixed homogeneously on a molecular level. Well, if the carburized temperature is high enough that Cr_2O_3 would be reduced into Cr_3C_2 as shown in Eq. (2).

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2\uparrow \quad (1)$$

$$3Cr_2O_3 + 13\,C = 2Cr_3C_2 + 9CO\uparrow \quad (2)$$

At 750 °C for 2 h (in Fig. 1b), the formed phases are mainly two kinds of Cr_3C_2 (JCPDS 65-2428 and 65-0897) and Cr_2O_3 (JCPDS 38-1479) phases. These two kinds of Cr_3C_2 phases belong to orthorhombic system with different lattice parameters. Compared with the formed phases at 750 °C for 2 h, the diffraction intensities of Cr_3C_2 (JCPDS 65-0897) phase decrease significantly at 800 °C for 1 h (in Fig. 1c), while the intensities of Cr_3C_2 (JCPDS 65-2428) increase accordingly. It implies that the complete transformation reaction from Cr_3C_2 (JCPDS 65-0897, low-temperature phase) to Cr_3C_2 (JCPDS 65-2428, high-temperature phase) occurs at 800 °C. The existence of Cr_2O_3 phase (in Fig. 1b and c) shows that the synthesis temperature and time of $Cr_2O_3 \rightarrow Cr_3C_2$ should increase to make the reaction be completed. Note that in Fig. 1d, no other phase is present, except Cr_3C_2 (JCPDS 65-2428) at 800 °C for 2 h, indicating that all the oxides of chromium have disappeared and single-phase Cr_3C_2 has formed. It is concluded that the single-phase Cr_3C_2 can be synthesized at 800 °C for 2 h from the calcining product of precursor powders with homogeneous chemical composition.

The transformation reaction of $Cr_2O_3 \rightarrow Cr_3C_2$ can be further analyzed by DSC/TG in Fig. 2. The first mass loss at 130–500 °C is due to the decomposition of the ammonium dichromate and glucose.