

Synthesis of V_8C_7 – Cr_3C_2 nanocomposite via a novel in-situ precursor method

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ABSTRACT

V_8C_7 – Cr_3C_2 nanocomposite has been synthesized by a novel in-situ precursor method, and the raw materials are ammonium vanadate (NH_4VO_3), ammonium dichromate ($(NH_4)_2Cr_2O_7$) and glucose ($C_6H_{12}O_6$). The products were characterized by thermogravimetric and differential scanning calorimetry (TG–DSC), X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. The results show that V_8C_7 – Cr_3C_2 nanocomposite with an average crystallite size of 31.5 nm can be synthesized at 900 °C for 1 h. The powders show good dispersion and are mainly composed of spherical or nearly spherical particles with a mean diameter of about 100 nm. The weight loss ratio of the precursor throughout the reaction process reaches 70 wt.%, and it changes rapidly before 400 °C (about 35 wt.%). Four endothermic peaks and three exothermic peaks occur during the reaction. The surface of the specimen is mainly composed of V, Cr, C and O four elements. The synthesis temperature of V_8C_7 – Cr_3C_2 nanocomposite by the method (900 °C) is 500 °C lower than that of the conventional method (1400 °C).

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1. Introduction

The transition metal carbides have very high melting points, hardness and high temperature strength. Particularly, vanadium carbide (V_8C_7) shows very high melting point (2810 °C), good wear resistance and high mechanical hardness [1,2]. Chromium carbide (Cr_3C_2) has high melting point (1890 °C), good toughness and high antioxidant properties [3,4]. Research shows that V_8C_7 and Cr_3C_2 are the most effective grain growth inhibitors for cemented tungsten carbides. However, single V_8C_7 or Cr_3C_2 cannot effectively inhibit the grain growth of WC particles. Nowadays, V_8C_7 and Cr_3C_2 are commonly used as a mixture in the WC–Co materials, which cannot disperse uniformly by mechanical mixing. Consequently, the nonuniformity of inhibitors will cause abnormal growth of WC grains and reduce the mechanical properties of the cemented carbides [5–7]. V_8C_7 – Cr_3C_2 nanocomposite combines the advantages of V_8C_7 and Cr_3C_2 , and can effectively solve the problems mentioned above. Moreover, it has potential applications in various fields such as catalysts, electronics and aerospace [8–11].

Commonly, carbide powders are synthesized by carbon thermal reduction of micron-sized oxides and carbon. This method has a number of weaknesses such as a higher reaction temperature (>1400 °C), a longer reaction time (>4 h) and a higher cost. Furthermore, the prepared carbide powders exhibit grains in the μ m-range, which cannot satisfy the demands of carbide powders for modern industry. Nowadays, various methods for synthesizing carbide powders have been researched, e.g. direct element reaction [12], mechanical alloying [13,14], temperature

programmed reaction [15] and gas reduction–carburization [16]. However, industrial applications of these methods are still limited due to the agglomeration problems, wide size distributions, low yields, complex monitoring and high costs.

In this study, V_8C_7 – Cr_3C_2 nanocomposite was synthesized by a novel in-situ precursor method. The raw materials were NH_4VO_3 , $(NH_4)_2Cr_2O_7$ and $C_6H_{12}O_6$, which were used as vanadium source, chromium source and carbon source, respectively. This is mainly because they can easily dissolve in water and decompose at about 200 °C. Besides, this method [17,18] can prepare V_8C_7 – Cr_3C_2 nanocomposite under milder conditions in comparison with conventional methods. This not only helps save energy and cause lower costs, but also prepare V_8C_7 – Cr_3C_2 nanocomposite with excellent properties. As we know, it has not been reported that V_8C_7 – Cr_3C_2 nanocomposite has been synthesized by the method using NH_4VO_3 , $(NH_4)_2Cr_2O_7$ and $C_6H_{12}O_6$ as raw materials. In this study, the effect of reaction temperature on phase composition and microstructure of V_8C_7 – Cr_3C_2 nanocomposite was researched.

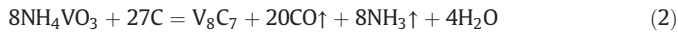
2. Experimental

2.1. Synthesis of V_8C_7 – Cr_3C_2 nanocomposite

V_8C_7 – Cr_3C_2 nanocomposite was prepared by a novel solution-derived precursor method, and the raw materials were NH_4VO_3 , $(NH_4)_2Cr_2O_7$ and $C_6H_{12}O_6$. 28 wt.% NH_4VO_3 (purity >99%), 34 wt.% $(NH_4)_2Cr_2O_7$ (purity >99%) and 38 wt.% $C_6H_{12}O_6$ (purity >99%) were mixed uniformly in 100 ml heated de-ionized water until they were

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completely dissolved in water. Therefore, a homogeneous solution could be obtained. The composition of NH_4VO_3 , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and $\text{C}_6\text{H}_{12}\text{O}_6$ is the stoichiometric proportion according to the following reaction equations:



After the solution was dried at 200 °C for 1 h, a precursor with well-proportioned vanadium source, chromium source and carbon source could be obtained. Finally, the precursor was heated at different temperatures (800 °C, 900 °C, 1000 °C and 1100 °C) for 1 h in vacuum. V_8C_7 - Cr_3C_2 nanocomposite can thus be prepared at a certain temperature.

2.2. Characterization of V_8C_7 - Cr_3C_2 nanocomposite

The structure of the powder was examined at room temperature via X-ray diffractometry (X'Pert Powder, Philips, Netherlands) using $\text{Cu-K}\alpha_1$ radiation in the range of $2\theta = 15\text{--}85^\circ$ with a scanning rate of $0.017^\circ/\text{s}$. The average crystallite size of the powder was estimated from the Scherrer equation [19]:

$$D = k\lambda/(\beta \cos\theta), \quad (4)$$

where D is the crystallite size, λ is the X-ray wavelength (0.15406 nm), θ is the Bragg angle, k is a constant taken to be 0.9, and β is the full width at half maximum (FWHM) of an XRD line which has been corrected for instrumental broadening.

Particle morphology and size of the synthesized powders were observed by JSM-6700F scanning electron microscopy (SEM) and JEM-1000CX transmission electron microscopy (TEM). Simultaneous thermogravimetric and differential scanning calorimetry (TG-DSC) were performed on the precursor using a NETZSCH STA 409 PC thermogravimetric analyzer under a constant Ar gas flow of 20 ml/min with a heating rate of $10^\circ\text{C}/\text{min}$. The X-ray photoelectron spectroscopy (XPS) was carried out using a XSAM 800 spectrometer (Kratos, England) using a $\text{MgK}(\alpha_1)$ X-ray source.

3. Results and discussion

To determine the physical phenomena occurring during the thermal processing, simultaneous TG-DSC measurements were performed on the precursor and the results given in Fig. 1. TG result shows that the

weight loss ratio of the precursor during the reaction reaches 70 wt.%, and it changes rapidly before 400 °C (about 35 wt.%), which is caused by the decomposition of NH_4VO_3 , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and $\text{C}_6\text{H}_{12}\text{O}_6$. DSC curve shows that three exothermic peaks and four endothermic peaks occur during the reaction. A sharp endothermic peak appears at 110 °C, which is induced by the carbonization of $\text{C}_6\text{H}_{12}\text{O}_6$ ($\text{C}_6\text{H}_{12}\text{O}_6 = 6\text{C} + 6\text{H}_2\text{O}$). Similar phenomenon has been observed in the reference [20]. A wide endothermic peak occurs at 200–300 °C, which is ascribed to the decomposition of NH_4VO_3 ($2\text{NH}_4\text{VO}_3 = \text{V}_2\text{O}_5 + 2\text{NH}_3\uparrow + \text{H}_2\text{O}$) and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ($(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{N}_2\uparrow$) [21]. An apparent endothermic peak appears at 461 °C, which is induced by the transformation from V_2O_5 to VO_2 ($\text{V}_2\text{O}_5 + \text{C} = 2\text{VO}_2 + \text{CO}\uparrow$) [22]. A weak exothermic peak occurs at 500–600 °C, which is caused by the crystallization of amorphous VO_2 and Cr_2O_3 [21]. A wide exothermic peak occurs at 600–900 °C, which is ascribed to the transformation from VO_2 to V_2O_3 ($2\text{VO}_2 + \text{C} = \text{V}_2\text{O}_3 + \text{CO}\uparrow$) and the crystallization of amorphous V_2O_3 [22]. A sharp endothermic peak occurs at 989 °C, which is induced by the transformation from V_2O_3 (Cr_2O_3) to V_8C_7 (Cr_3C_2). A wide exothermic peak occurs at 1000–1100 °C, which is ascribed to the crystallization of V_8C_7 and Cr_3C_2 .

The XRD patterns of the powders synthesized at different temperatures are shown in Fig. 2. As shown in Fig. 2(a), all peaks are identified as V_2O_3 (JCPDS 34-0187) and Cr_2O_3 (JCPDS 38-1479) when the temperature is 800 °C, and the diffraction peaks of carbon are not observable. This is mainly because carbon exists in a noncrystalline form at 800 °C, and similar phenomenon has been observed in the literature [23]. This result is well consistent with the TG-DSC result. V_2O_3 mainly originates from the decomposition of NH_4VO_3 and the subsequent carbothermal reduction of V_2O_5 . Cr_2O_3 originates from the decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and the crystallization of the product. V_2O_3 (JCPDS 34-0187) and Cr_2O_3 (JCPDS 38-1479) belong to the $R\text{-}3\text{c}$ trigonal system and their lattice parameters are $0.4954 \text{ nm} \times 0.4954 \text{ nm} \times 1.4008 \text{ nm}$ and $0.4959 \text{ nm} \times 0.4959 \text{ nm} \times 1.3594 \text{ nm}$, respectively. When the temperature reaches 900 °C, the product is mainly composed of V_8C_7 (JCPDS 35-0786) and Cr_3C_2 (JCPDS 35-0804), indicating that the carbothermal-reduction reactions among V_2O_3 , Cr_2O_3 and C have completed at 900 °C for 1 h, and the reactants are V_8C_7 and Cr_3C_2 , as shown in Fig. 2(b). V_8C_7 and Cr_3C_2 may be regarded as substoichiometric carbides with ordered C vacancies. V_8C_7 (JCPDS 35-0786) and Cr_3C_2 (JCPDS 35-0804) belong to the $P4_332$ [212] cubic system and Cmcm [63] orthorhombic system, respectively. During the reaction process, V_2O_3 and Cr_2O_3 may transform firstly into the interphases of VC_{1-x} ($1-x = 0.66\text{--}0.88$) and $\text{Cr}_3\text{C}_{2-x}$ ($0 \leq x \leq 0.5$) and then into V_8C_7 and Cr_3C_2 [24], respectively. From TG-DSC and XRD results, it can be seen that the conversion of the precursor follows the principle of step-by-step reduction and

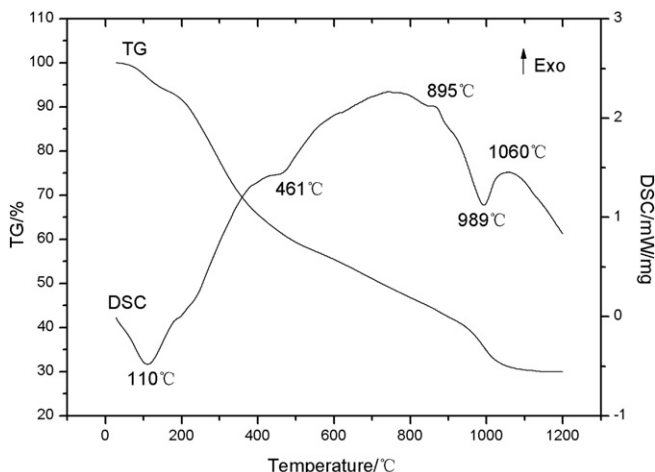


Fig. 1. TG-DSC curves of the precursor measured in Ar atmosphere.

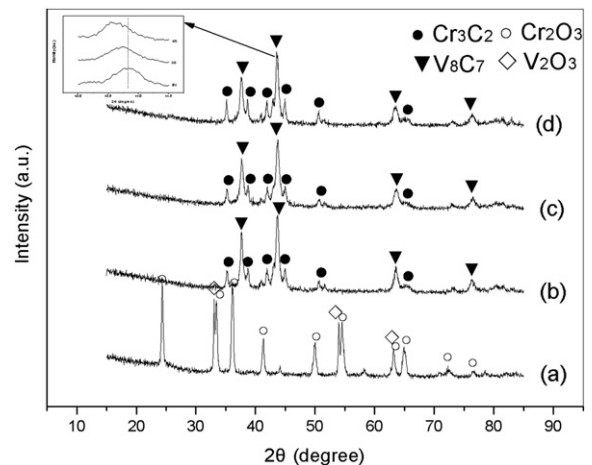


Fig. 2. X-ray diffraction patterns of the powders synthesized at different temperatures for 1 h: (a) 800 °C; (b) 900 °C; (c) 1000 °C; (d) 1100 °C.

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