Ceramics International 42 (2016) 9371–9374

Contents lists available at ScienceDirect

Ceramics International

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

In situ synthesis of vanadium carbide–copper nanocomposite by a modified mechanochemical combustion method

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ARTICLE INFO

Article history:
Received 4 October 2015
Received in revised form
21 January 2016
Accepted 22 February 2016
Available online 5 March 2016

Keywords:
B. Nanocomposite
Mechanochemical processing
Combustion
Vanadium carbide
Copper

ABSTRACT

Synthesis of vanadium carbide–copper nanocomposite was achieved via mechanochemical combustion method from reactant mixture of V_2O_5, CuO, C and Mg powders. The obtained samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS). X-ray diffraction investigations indicated that the combustion products were V_4C_3, V_2C and Cu phases. Microstructural studies showed that a nanostructured powder with a mean particle size of about 100 nm was procured in the samples milled for 90 min.

1. Introduction

Some of the transition metal carbides such as WC, VC and TiC are used as cutting tools and abrasive materials due to their significant properties, including high hardness, high melting temperature, high thermal conductivity and a relatively high chemical stability [1,2]. These carbides are widely used in above applications as single phase or in combination with other phases to produce cemented carbides. In the case of VC, this involves the formation of a composite with a binder metal such as Co, Ag or Fe [3–5]. Because of its excellent high chemical stability, high hardness (9–9.5 Mohs) and high temperature properties (melting point = 2810 °C), VC has also been considered for use as a catalyst, an inhibitor for the grain growth in hard alloys and reinforced phase in matrix or coating materials [6–8].

In recent years, copper-based metal matrix composites containing ceramic particulates have attracted wide interest. These composite materials possess excellent thermal and electrical conductivities, high temperature strength and good microstructural stability because of copper's good electrical and thermal conductivities in addition to chemical stability [9,10].

A current challenge in manufacturing of cermets is the development of simple synthesis method providing required characteristics of products. Numerous methods have been used to synthesize ultrafine and nano-cermet such as hydrothermal [11], spark plasma sintering [12], sol–gel [13] and hot isostatic pressing [14]. However, because of the time, economy and efficiency, most of the processes have not been widely used in the practical production. In this paper, we report a facile, fast and high-efficiency route to synthesize vanadium carbide–copper nanocomposite in a high-energy ball mill by a combustion reaction of magnesium powders with V_2O_5, graphite and copper oxide without further heat treatment in the furnace. In comparison with high temperature conventional methods, it is an economical and effective method to obtain vanadium carbide–copper nanocomposite.

2. Experimental procedure

The starting materials consisted of vanadium oxide (99.7% purity, 250 μm, Merck), copper oxide (99.9, 5 μm, Merck), magnesium (99.8% purity, 300 μm, Merck) and graphite (95% purity, 0.3 μm, Merck) powders were mixed with the molar ratio of 1:1:6:1. Mechanical activation was carried out in a hardened chromium steel vial using hardened carbon steel balls (diameter: 20 mm). In all experiments, the weight ratio of the ball to powder and rotational speed were 20:1 and 600 rpm, respectively. To control temperature and prevent from excessive heating, the millings were carried out with 15 min interval pauses. Details of ball mill procedure are given in Table 1. All the milling

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http://dx.doi.org/10.1016/j.ceramint.2016.02.129
0272-8842/

Table 1
Details of ball mill machine and milling conditions.

Rotation speed of vial (rpm)	600
Diameter of vial (mm)	125
Vial material	Hardened chromium steel
Ball material	Hardened carbon steel
Diameter of balls (mm)	20
Number of balls	5
Balls to powder weight ratio	20:1
Total powder mass (g)	6.65

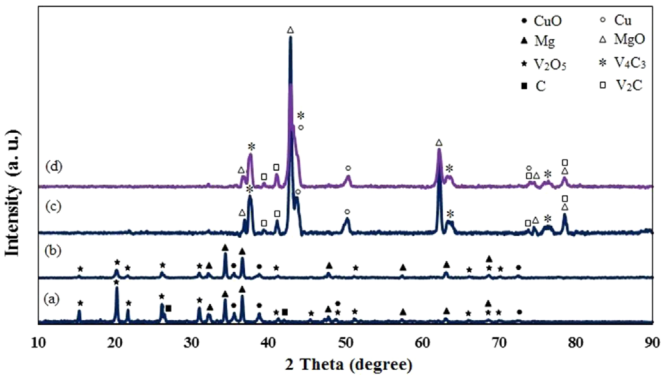

Fig. 1. X-ray diffraction patterns of stoichiometric mixture of V_2O_5, CuO, Mg and graphite powder mixture (according to stoichiometric ratio) milled for different times: (a) 0 min, (b) 45 min, (c) 73 min and (d) 90 min.

Table 2
Crystallite size and lattice strain of 73 and 90 min milled samples.

Phase	Crystallite size (nm)				Lattice strain	
	Scherrer		Williamson–Hall			
	73 min	90 min	73 min	90 min	73 min	90 min
V_2C	30	22	36	30	0.00435	0.00524
V_4C_3	33	24	35	25	0.00415	0.0057
Cu	28	17	44	33	0.00195	0.0051

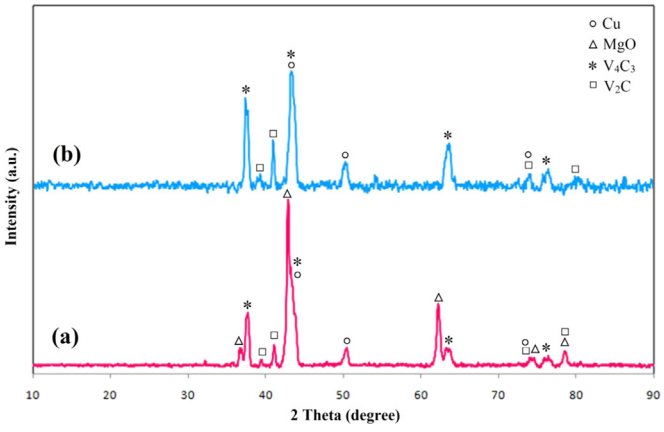

Fig. 2. X-ray diffraction patterns of the 90 min milled sample (a) before leaching; (b) after leaching.

experiments were carried out under high-purity argon gas; and as a by-product, the magnesium oxide was removed by leaching the as-milled powder in 1 M HCl at 60 °C for 40 min.

The crystal phase identification was performed by X-ray diffraction (XRD) using a PhilipsTW3710 X'Pert diffractometer with CuKα radiation. The average crystallite size (D) of the powder during milling was determined using the Scherrer [15] (Eq. (1)) and Williamson–Hall [16] (Eq. (2)) equations.

$$D = \frac{K.\lambda}{\beta.\cos\theta} \quad (1)$$

where λ is the wavelength of the radiation used (λ=0.15418 nm for CuKα); β is the full-width at the half-maximum (FWHM); K is a shape factor, taken to be 0.98 and θ is the Bragg angle (°) at which the peak appears.

The Williamson–Hall formula (Eq. (2)) separates the effects of size and strain in the crystals.

$$\beta\cos\theta = \frac{0.98\lambda}{D} + 2\varepsilon\,\mathrm{Sin}\,\theta \quad (2)$$

The values of $\beta\cos(\theta)$ calculated for each peak were plotted as a function of $\sin(\theta)$. The linear regression of the obtained data allows the determination of the mean crystallite size (D) and lattice distortion (ε).

Microstructure and elemental mapping of the milled powder were investigated using a CamScan MV2300 scanning electron microscope equipped with an energy-dispersive spectroscopy analysis (EDS). TEM electron micrograph of the powders was recorded with JEM-100CX transmission electron microscope.

3. Results and discussion

The proposed mechanism for the synthesis of vanadium carbide–copper composite by ball milling of V_2O_5, CuO, C and Mg in the present system involves two subsequent steps: reduction of CuO and V_2O_5 to form elemental Cu and V as described in the reactions (3) and (4) followed by reaction of vanadium with carbon (reaction (5)) [17].

$$CuO + Mg \rightarrow Cu + MgO \quad (3)$$

$$\Delta H^0_{298} = -445\ \mathrm{KJ/mol}\quad \Delta G^0_{298} = -441\mathrm{KJ/mol}$$

$$V_2O_5 + 5Mg \rightarrow 2V + 5MgO \quad (4)$$

$$\Delta H^0_{298} = -1456\mathrm{kJ/mol}\quad \Delta G^0_{298} = -1428\mathrm{kJ/mol}$$

$$2V + C \rightarrow V_2C \quad (5)$$

$$\Delta H^0_{298} = -117\mathrm{KJ/mol}\quad \Delta G^0_{298} = -112\mathrm{KJ/mol}$$

In general, the as received powders were mixed on the basis of the above reactions to give the final composition of vanadium carbide–copper.

The X-ray diffraction (XRD) patterns of powder mixture (V_2O_5, CuO, Mg and graphite (1:1:6:1)) as-blended and after milling are shown in Fig. 1. The XRD pattern of the as-blended mixture exhibited the peaks of Mg (ICDD PDF #004-0770), V_2O_5 (ICDD PDF #041-1426), CuO (ICDD PDF #048-1548) and C (ICDD PDF #008-0415). It can be seen that after 45 min of milling, only peaks of raw materials (V_2O_5, CuO, Mg and C) are present in the XRD patterns, and there is no evidence of reaction at this interval. As milling time was increased from 45 to 73 min, a combustion reaction happened and the peaks of the V_4C_3 (ICDD PDF #001- 1159), V_2C (ICDD PDF #071-1258), Cu (ICDD PDF #085-1326) and MgO (ICDD PDF #074-1225) appeared. It seems that a thermic reaction occurred after 73 min of ball milling. It is well known that a sudden increase in the vial temperature during milling is an indication of combustion reactions [18,19]. During the milling with increase the concentration of volume and surface defects and hence the enhancement of the internal energy of the reactive system, reduction happened, which resulted in vanadium carbide–copper composite. Reactions (3)–(5) take place, when the internal energy reaches to their