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Bulk ultrafine binderless $(W_{0.4}Al_{0.6})C$ prepared by high pressure sintering

Zhuhui Qiao [a,b], XianFeng Ma [a,*], Wei Zhao [a,b], Huaguo Tang [a,b], Junmin Yan [a,b], Shuguang Cai [a,b], Bo Zhao [a,b]

[a] *Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China*
[b] *Graduate School of The Chinese Academy of Sciences, Beijing, PR China*

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Abstract

Pure $(W_{0.4}Al_{0.6})C$ powder of about 1 μm in diameter was sintered by the high pressure sintering (HPS) process without the addition of any binder phase. The microstructure, Vickers micro hardness and density versus the sintering time and temperature are well described. The most suitable sintering condition under pressure of 4.5 GPa is 1873 K for 8 min. Under this sintering condition, the hardness can reach 2295 kg mm^{-2} and the relative density can reach 98.6%.

Keywords: Binderless $(W_{0.4}Al_{0.6})C$; Mechanical properties; Microstructure; High pressure sintering; Vickers micro hardness; Density

1. Introduction

Materials with high hardness, such as WC-Co cemented carbides, where Co is a binder phase, have long been used as cutting tools, dies and wear resistant parts, owing to their high hardness and excellent wear resistance as well as their retention of room temperature hardness at elevated temperatures [1–4].

In our previous work [5], we have synthesized a new compound $(W_{0.4}Al_{0.6})C$ which is a new hard material as we expected. Practically, $(W_{0.4}Al_{0.6})C$ is a deduction solid solution of Al in WC compared with WC, and it is found to crystallize in the hexagonal space group *P*-6*m*2 (187), and has the WC-type structure. Moreover, the cell parameters of $(W_{0.4}Al_{0.6})C$ are $a = 2.9066$ Å and $c = 2.8412$ Å, which is much close to those of WC.

Considering the same crystal structure of $(W_{0.4}Al_{0.6})C$ as WC, we suppose that the sinterability of $(W_{0.4}Al_{0.6})C$ may be similar to that of WC. So some sintering experiences of WC could be helpful to the sintering of $(W_{0.4}Al_{0.6})C$. The densification of conventional WC powder is commonly in liquid phase sintering with the addition of 3–20 wt.% of metallic binder from the iron group (usually cobalt) [7–10]. The binder phase facilitates the sintering to a fully dense bulk, controls the bonding between WC particles and increase the toughness of the sintered bulk [11]. However, addition of the binder phase not only decrease hardness and corrosion/oxidation resistance of materials but also cause heat stress due to the different thermal expansion of WC and the binder phase. Because of the high-melting point of WC, however, it is almost impossible to sinter pure WC without any binder phase by a conventional process in which the liquid phase is partly necessary during the sintering process. Thus, early in the 1980s, several attempts have been made to sinter binderless WC [12,13].

The high pressure sintering (HPS) process has attracted considerable attention because of its high pressure and rapid sintering at relative low temperature in comparison with conventional sintering process. In early 1980s, several attempts have been made to sinter WC without any binder metal, and it was found that it is impossible to reach high levels of density without the use of high temperatures or high external pressure.

Therefore, in order to get the well sintered specimen with high hardness, we aimed to sinter ultrafine pure $(W_{0.4}Al_{0.6})C$ with nearly full densification by the HPS process without any binder metal, which is expected to have excellent properties. The microstructure, Vickers micro hardness and density are well described.

* Corresponding author. Tel.: +86 431 5262220; fax: +86 431 5698041.
E-mail address: xfma@ns.ciac.jl.cn (X. Ma).

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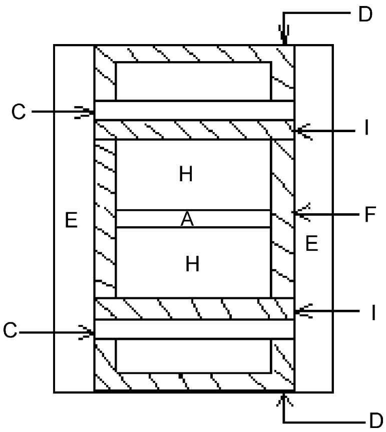

Fig. 1. Schematic diagram of high-pressure cell. A, Sample area; I, graphite disk; C, titanium disk; D, conductive ring; E, pyrophylite; F, graphite tube; H, h-BN.

2. Experimental details

The deduction solid solution powder $(W_{0.4}Al_{0.6})C$ was synthesized as follows: firstly, ball milled the elemental powders of W (−200 mesh, 99.8% purity) and Al (−200 mesh, 99.8% purity) with the atomic ratio of 4:6 for 30 h to form the precursor $W_{0.4}Al_{0.6}$ alloy [6]. Secondly, the prepared $W_{0.4}Al_{0.6}$ alloy (<0.1 μm, 99.8% purity) and carbon (<34 μm, 99.5% purity) were accurately weighed out such that the $(W_{0.4}Al_{0.6})C$ molar ratio was about 1:1. The mixture of the two powders, which has been packed into a corundum crucible, was put into a vacuum furnace (0.067 Pa) for solid-state reaction at 1450 °C. After reaction for about 120 h, the pure deduction solid solution of $(W_{0.4}Al_{0.6})C$ was completely obtained. The prepared $(W_{0.4}Al_{0.6})C$ powder were ball-milled for about 10 h, the superfine $(W_{0.4}Al_{0.6})C$ powder (about 100 nm) was obtained.

Green compacts of $(W_{0.4}Al_{0.6})C$ in column form of 1 cm diameter and 0.5 cm high were produced by uniaxial pressing at 400 MPa. The high-pressure experiments were conducted on a cubic-type high-pressure apparatus with six WC anvils (DS–029C, China). The cubic pyrophyllite sample cell was 3.2 cm on edge and contained a graphite sample tube 1.5 cm in diameter and 2.5 cm in length. The green compacts were loaded into the graphite tube, and the residual space in the tube was filled with h-BN as heat-transmitting medium. The schematic diagram of the cubic pyrophyllite sample cell could be seen in Fig. 1. Compact was then sintered under high pressure (4.5 GPa) at various temperatures and various times.

Samples were ground with a diamond wheel and then carefully grinded and polished. The figure and the average diameter of the initial $(W_{0.4}Al_{0.6})C$ powder were observed by transmission electron microscope (TEM). The microstructures of fractured samples were observed by scanning electron microscopy (SEM).

The hardness was determined with a Vickers micro hardness tester (FM-700, Japan) with a load of 300 gf and dwell time of 15 s. The density of the samples was determined by the Archimedes principle using distilled water.

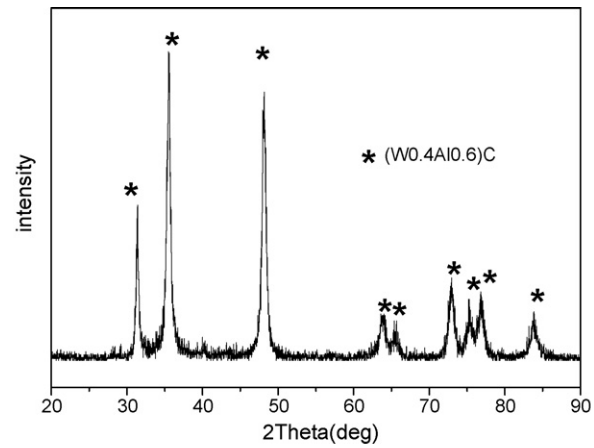

Fig. 2. XRD patterns for the $(W_{0.4}Al_{0.6})C$ bulk after sintered at 1873 K and 4.5 GPa for 8 min.

X-ray diffraction (XRD) was using a Rigaku D/max 2500PC X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). The scan speed was 4° min^{-1}. The environment scanning electron microscope (ESEM, Philips, XL30) was conducted under condition of vacuum (7×10^{-10} mbar).

3. Results and discussion

3.1. X-ray diffractometry

The XRD patterns for $(W_{0.4}Al_{0.6})C$ sintered at different time and temperature are almost the same, so we choose the one detected from which was sintered at 1873 K and 4.5 GPa for 8 min as the representative one. The XRD patterns for $(W_{0.4}Al_{0.6})C$ which sintered at 1873 K and 4.5 GPa for 8 min was shown in Fig. 2. The pure phase of $(W_{0.4}Al_{0.6})C$ in Fig. 2 proves that $(W_{0.4}Al_{0.6})C$ will not decompose under high pressure and high temperature even up to 4.5 GPa and 1873 K. The calculated lattice parameters based on the X-ray data in Fig. 2 are $a = 2.9066$ Å, $c = 2.8412$ Å.

3.2. Densification behavior and microstructure

Pure $(W_{0.4}Al_{0.6})C$ of 100 nm particle size was high pressure sintered at 4.5 GPa at 1573–1973 K for 5–15 min. The theoretical density of $(W_{0.4}Al_{0.6})C$ is 8.095 g cm^{-3}, which is much lower than that of WC. Fig. 3(a) shows the relative density of

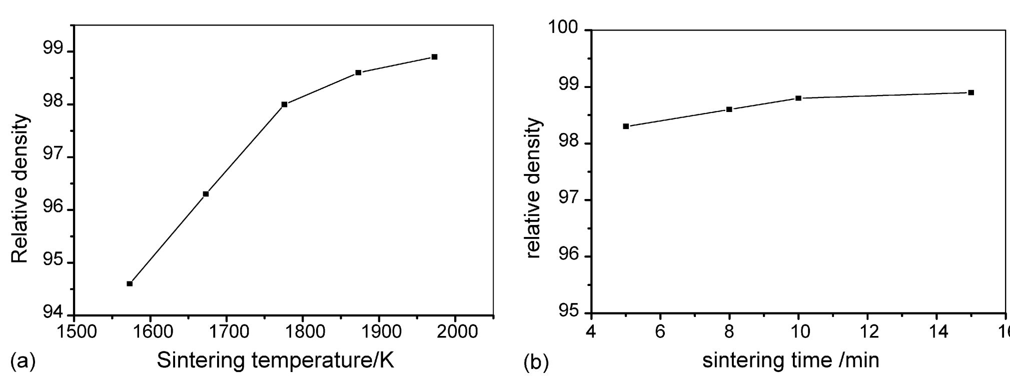

Fig. 3. (a) The relative density of various sintered samples vs. sintering temperature for 8 min and (b) the relative density of various sintered samples.