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Synthesis and characterization of $(W_{0.8}Al_{0.2})C_{0.8}$ deduction solid solution

Junmin Yan[a,b], Xianfeng Ma[a,*], Wei Zhao[a,b], Huaguo Tang[a,b],
Changjun Zhu[a,b], Shuguang Cai[a,b]

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

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Abstract

A new solid solution of Al in tungsten carbide (WC) with carbon vacancies, which can be expressed by the chemical formula $(W_{0.8}Al_{0.2})C_{0.8}$, has been synthesized by a mechanical alloying and high-pressure (MAAHP) technique. $W_{0.8}Al_{0.2}$ alloy and proper amount of carbon are firstly ball milled for about 15 h, and then the ball milled mixture is proceeded with the reaction sintering (RA) under the condition of high pressure (4.5 GPa) and high temperature (1873 K) to form the final deduction solid solution $(W_{0.8}Al_{0.2})C_{0.8}$. $(W_{0.8}Al_{0.2})C_{0.8}$ has been identified to crystallize in the hexagonal space group P-6m2 (No. 187) and belongs to the WC structure type. The carbon vacancy concentration has reached a value of 20%. Environment scanning electron microscope (ESEM)–energy dispersive analysis of X-rays (EDAX) has been used to investigate the morphology and the quantitative material composition of the sintered sample. The Vickers micro hardness of the sample has been tested to be 2636 kg mm^{-2} that is much harder than WC, while the density of sintered body is about 12.94 g cm^{-3}, which is lighter than WC.

Keywords: Reaction sintering; High-pressure; Deduction solid solution; Crystal structure; Hardness; Density

1. Introduction

Tungsten carbide (WC) is one of the most important carbides as the major constituent in hard materials. The main use of WC is in high wear resistance parts such as cutting tools, seals, bearings, etc., a use that requires a combination of high hardness and sufficient toughness [1].

We have reported that the substitutional solid solution of Al in WC, which has the stoichiometry $(W_{1-x}Al_x)C$, can be synthesized directly by mechanical alloying of W, Al, C elemental powders [2]. $(W_{1-x}Al_x)C$ has been identified to crystallize in the hexagonal structure of WC type. Atoms of Al partially substitute the lattice sites of W, and are stable in the hexagonal structure at high temperature. Aluminum is more ductile and lighter than tungsten metal, so dissolving Al into the lattice of WC to form a solid solution is expected to enhance the bend strength of WC and reduce its high density (15.63 g cm^{-3}) [3]. In addition, aluminum is inexpensive compared with tungsten, thus operating costs of ternary carbide Al–W–C are surely less than those of WC.

It is reported that vacancies have a profound influence on the physical properties of materials. For instance, the hardness of NbC_x and TaC_x increase consistently as the carbon vacancy concentration increases up to the value of about 12% [4,5]. Other researchers have found that vacancies influence the hardness of iron aluminides, where hardness is proportional to the square root of vacancy concentration [6]. Therefore, we report work on the solid solution of Al in WC with many carbon vacancies, and expect that these vacancies will endow this type of materials with the good mechanical properties such as the high hardness and wear resistance as WC.

In this paper, we describe the synthesis of the pure $(W_{0.8}Al_{0.2})C_{0.8}$ deduction solid solution, which has about 20% carbon vacancies compared with WC, by the following two steps: firstly, mechanical alloying of $W_{0.8}Al_{0.2}$ and

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[*] Corresponding author. Tel.: +86 431 5262220; fax: +86 431 5685653.
E-mail address: xfma@ns.ciac.jl.cn (X. Ma).

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carbon for certain hours; secondly, reaction sintering of the ball milled powders at high pressure. This mechanical alloying and high-pressure technique (MAAHP) has been investigated to synthesize the new intermetallic compound WMg in our previous work [7]. Incidentally, the precursor $W_{0.8}Al_{0.2}$ alloy can be synthesized by mechanical alloying, as proved by our previous paper [8]. Moreover, $W_{0.8}Al_{0.2}$ has the same body-centered cubic structure as W, and is stable even up to 1673 K, so we choose $W_{0.8}Al_{0.2}$ to be the precursor for the solid state reaction with carbon to form $(W_{0.8}Al_{0.2})C_{0.8}$ deduction solid solution as the reaction between W and C to form WC.

In addition, the crystal structure, morphology, elemental composition, hardness and density of the prepared sample are also discussed.

2. Experimental details

The precursor $W_{0.8}Al_{0.2}$ was prepared as follows [8]: firstly, the elemental powders of tungsten (−200 mesh, 99.8% purity) and aluminum (−200 mesh, 99.5% purity) were weighed out with the atomic ratio W:Al = 4:1; secondly, the mixed powders were sealed under an argon atmosphere into the WC vial with ball-to-powder weight ratio of 15:1. Finally, materials were ball milled at the rotation speed of 650 rpm for about 8 h, and then the pure $W_{0.8}Al_{0.2}$ alloy was obtained.

The prepared $W_{0.8}Al_{0.2}$ alloy (<1 μm, 99% purity) and carbon (<34 μm, 99% purity) were ball milled stoichiometric amounts of $W_{0.8}Al_{0.2}$ and C powder with molar ratio of 1:0.8. The rotation speed was also 650 rpm, and the ball:powder ratio was about 10:1. The total milling time is 15 h.

The ball milled powders were then pressed into a column of 10 mm diameter and 5 mm thick with a compaction pressure of 400 MPa, and then reaction sintered at high pressure (4.5 GPa) and high temperature (1873 K) for 30 min.

The materials for various reaction times were examined by X-ray diffraction (XRD) using a Rigaku D/max-II B 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) and the energy dispersive analysis of X-rays (EDAX) measurements were conducted to investigate the morphology and the quantitative material composition of the prepared powders.

The density of the sample was determined by using the Archimedes' principle using distilled water. The hardness was determined with a Vickers micro hardness tester (HX-1, China) with a load of 200 gf and dwell time of 15 s.

3. Results and discussion

3.1. X-ray diffractometry

XRD patterns of the $(W_{0.8}Al_{0.2})C_{0.8}$ powders for various milling times are presented in Fig. 1. The diffraction of the carbon powder to X-ray is weak in our system, so only diffraction peaks corresponding to $W_{0.8}Al_{0.2}$ are observed in the figure of the starting materials. No new phase is formed after milling for 15 h; this means that the mechanical alloying process for synthesis of $(W_{0.8}Al_{0.2})C_{0.8}$ does not produce a solid state reaction between the alloy and the carbon powders. However, the diffraction peaks of $W_{0.8}Al_{0.2}$ obviously broaden and shorten, due to the reduction of crystallite size and accumulation of lattice strain. The long time milling is in order to make the carbon and the alloy particles disperse uniformly, and the reduction in crystallite size of the alloy may enhance the solid state reaction speed in the following high pressure and high temperature process.

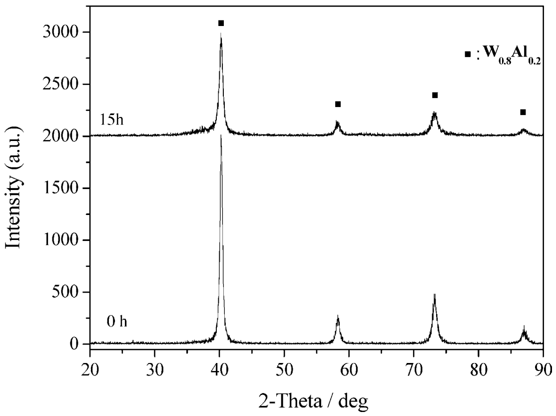

Fig. 1. XRD patterns of the mixture between $W_{0.8}Al_{0.2}$ and carbon after milling for the times indicated.

Fig. 2 shows the XRD pattern of the milled mixture after the treatment at 1873 K and 4.5 GPa for 30 min. No characteristic diffraction peaks of $W_{0.8}Al_{0.2}$ and carbon are observed. A new phase is apparently formed under this condition, and this phase is identified as the hexagonal structure of WC type and belongs to the hexagonal space group P-6m2 from the position of the diffraction peaks. Considering the component of the starting materials, the WC phase in our system is deduced to have the stoichiometry $(W_{0.8}Al_{0.2})C_{0.8}$. This means that the MAAHP process for synthesizing of $(W_{0.8}Al_{0.2})C_{0.8}$

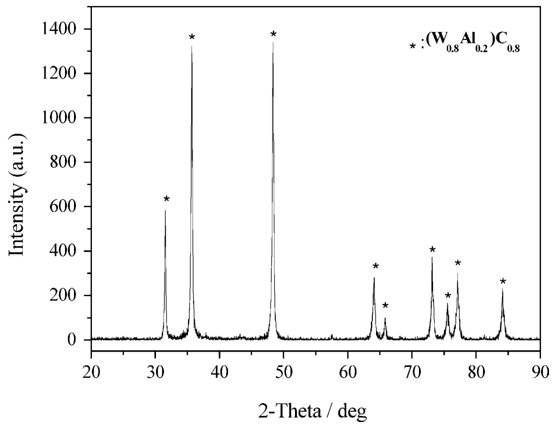

Fig. 2. XRD pattern of the $(W_{0.8}Al_{0.2})C_{0.8}$ phase after reaction sintering at 4.5 GPa and 1873 K for 30 min.