ARTICLE IN PRESS
RMHM-04358; No of Pages 7
Int. Journal of Refractory Metals and Hard Materials xxx (2016) xxx–xxx
Contents lists available at ScienceDirect
Int. Journal of Refractory Metals and Hard Materials
journal homepage: www.elsevier.com/locate/IJRMHM

Synthesis of Cr-doped APT in the evaporation and crystallization process and its effect on properties of WC-Co cemented carbide alloy

Linsheng Wan [a], Liang Yang [a,*], Xuepin Zeng [a], Xingren Lai [b], Lifu Zhao [b]

[a] School of Metallurgical and Chemical Engineering, Jiangxi University of Science & Technology, Ganzhou 341000, Jiangxi, China
[b] Zhangyuan Tungsten Industry Co., Ltd. Chongyi, Ganzhou 341300, Jingxi, China

ARTICLE INFO

Article history:
Received 26 August 2016
Received in revised form 22 October 2016
Accepted 23 October 2016
Available online xxxx

Keywords:
Ammonium paratungstate
Chromium
Evaporation and crystallization
Grain growth inhibitor
Cemented carbides
Physicochemical properties

ABSTRACT

WC grain size has significant effect on WC-Co cemented carbide alloy properties. In order to inhibit WC grain growth during sintering process, grain growth-inhibitor Cr_3C_2 is usually added to tungsten carbide powder in advance through mechanical milling. While, homogeneous distribution of Cr_3C_2 in the tungsten carbide powder is difficult to achieve and result in abnormal growth of WC grains. For this purpose of growth-inhibitor uniform distribution, $(CH_3COO)_3Cr$ is added into ammonium tungstate solution during evaporation and crystallization process to prepare Cr-doped APT powder, which can be used as precursor for ultrafine-grained WC-Co cemented carbide alloy preparation. Compared with conventional APT powder, the Cr-doped APT has smaller particle size and bulk density, moreover, chromium is evenly distributed within it. The Cr-doped APT is then used to produce Cr-doped tungsten powder, which also has smaller particle size than that of conventional tungsten powder. Cr-doped tungsten powder is subsequently prepared into tungsten carbide powder and WC-Co cemented carbide alloy through carbonization and sintering process, respectively. Compared with conventional WC-Co cemented carbide alloy, the obtained WC-Co cemented carbide alloy has smaller mean WC grain size (0.36 μm), and more uniform microstructure. Furthermore, the phenomenon of WC grain abnormal growth during sintering process is not observed, because the grain growth-inhibitor Cr_3C_2 is well dispersed in tungsten carbide and cobalt composite powder. Results show that the obtained WC-Co cemented carbide alloy presents better mechanical properties (HRA, bending strength, coercive force) than those of conventional WC-Co cemented carbide alloy. Accordingly, the novel addition of $(CH_3COO)_3Cr$ during the evaporation and crystallization process is the key factor of ultrafine-grained WC-Co cemented carbide alloy production.

1. Introduction

The cemented tungsten carbide hard metals have been widely used in machining, cutting, mining and drilling tools as well as for wear-resistant equipment [1–5]. Their wide application stems from their combination of desirable properties, including large hardness, wear-resistance and fracture toughness values. WC-based carbides are usually synthesized by sintering the WC-based composites with addition of ductile metal cobalt (binder) [6]. The mechanical properties of these materials depend on their composition and microstructure, especially on the grain size of the carbide phase [7–8]. During sintering process, undesirable grain growth usually occurs and results in substantial deterioration of the carbide's mechanical properties [9–10]. To improve mechanical properties of cemented tungsten carbide hard metals, intensive research efforts have been devoted to reducing the grain size of WC by various technologies. In order to limit growth of the tungsten carbide grain during sintering process, grain growth-inhibitors are added to the powder composition. Early research which employed different grain growth-inhibitors has found that Cr_3C_2 and VC are most effective in restricting grain growth, owing to their appreciable solubility and mobility in liquid cobalt at lower sintering temperatures [11–13]. Actually, homogenous distribution of inhibitors, which depends on the adding process, is also an important factor to obtain uniform WC grains. In current cemented tungsten carbide manufacturing process, grain growth-inhibitors are usually added to the tungsten carbide powder during the ball mill operation [14–15]. The drawback of this method is a bad mixing uniformity of the mixture of grain growth-inhibitors and tungsten carbide powder, which also result in abnormal grain growth of partial tungsten carbide during subsequent sintering process [16]. Thus, choosing an appropriate adding method to improve the dispersion property of grain growth-inhibitors within the tungsten carbide is the key to ultrafine-grained cemented carbide production.

It is known that preparation of tungsten carbide mainly consists of the following steps. Firstly, ammonium paratungstate (APT) is obtained from ammonium tungstate solution through evaporation and crystallization, and then tungsten trioxide is produced by calcining APT, finally,

* Corresponding author.
E-mail address: yangliang_1010@163.com (L. Yang).

http://dx.doi.org/10.1016/j.ijrmhm.2016.10.022
0263-4368/© 2016 Elsevier Ltd. All rights reserved.

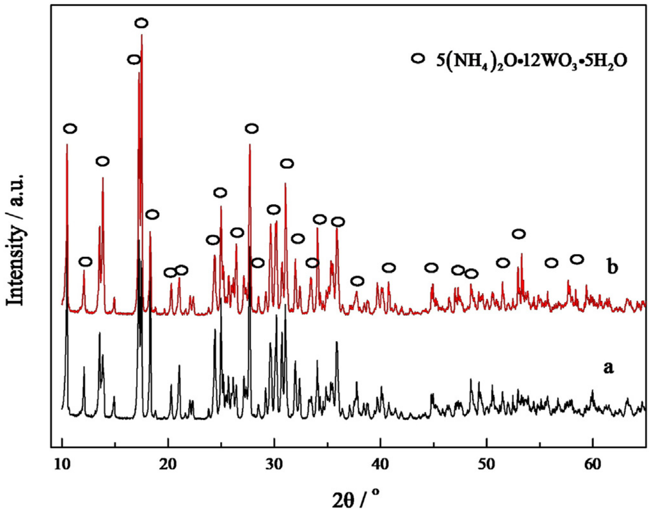

Fig. 1. XRD pattern of Cr-doped APT powder (a represents standard diffraction patterns of APT; b represents diffraction patterns of Cr-doped APT).

tungsten carbide is prepared by hydrogen reduction and followed carbonization [17]. As we all know, homogeneously dispersed powders could be easily prepared by homogenous precipitation method in aqueous solution [18–20]. Thus, preparation of APT doped with chromium is attempted by adding $(CH_3COO)_3Cr$ into ammonium tungstate solution during the evaporation and crystallization process. Chromium acetate in the solution hydrolyzes into chromium hydroxide. It is well known that addition of chromium into the solution effectively enhances nucleation of APT grains, which is favorable for the formation of fine APT grains. Many studies have shown that genetic relationship between grain size of ammonium paratungstate and tungsten powder as well as tungsten carbide is obvious [21]. In this way, tungsten powder and tungsten carbide with evenly distributed chromium could be prepared using the Cr-doped APT as precursor in following processes. In this study, physicochemical properties of the Cr-doped APT, such as particle size distribution, chromium uniformity and apparent density are analyzed. It is also demonstrated that tungsten powder prepared with Cr-doped APT shows much advantageous physicochemical properties over conventional tungsten powder under the same process conditions. In order to investigate effect of the novel addition of grain growth-inhibitors during evaporation and crystallization process on properties of WC-Co cemented carbide alloy, the obtained tungsten prepared with Cr-doped APT is further processed into tungsten carbide powders and WC-Co alloy by carbonization and sintering operation. Compared with conventional products, these products of tungsten powder, tungsten carbide powders and WC-Co alloy prepared by using Cr-doped APT as precursor show more superior physical and chemical properties.

2. Experimental

Experiments of preparing Cr-doped APT were carried out in a reactor equipped with a temperature and stirring speed controller. A certain volume of ammonium tungstate solution ($[WO_3] = 202.8$ g/L, $[NH_4OH] = 96.6$ g/L) was added into the reactor, and then a certain amount of $(CH_3COO)_3Cr$ was added into the solution with Cr concentration of 0.4 wt.% (WO_3-0.4Cr) under a temperature of 100 °C and a stirring speed of 50 rpm. After a specified amount of time, Cr-doped APT particles were precipitated from the solution and then filtered and dried. The Cr-doped APT powder was also used to prepare tungsten powder, tungsten carbide powder and WC-Co cemented carbide alloy in subsequent processes.

Table 2
Chromium content in the Cr-doped APT powder.

Specimens number	Cr/APT (wt.%)
1	0.354
2	0.351
3	0.352
4	0.350
5	0.352

Quantitative analyses of chromium within these samples were conducted with atomic absorption spectrophotometer (WFX-100B). Structural characterization of the Cr-doped APT was performed by Infrared spectrograph. The microstructure of specimens was observed by a scanning electron microscope (JSM-6701F). XRD examinations were performed with the diffractometer (RigakuD/max 2500). Micro-area chemical analysis of specimens was conducted with X-ray energy dispersive spectrum (INCA). The average size of specimens was determined with a particle size analyzer. Sieving method and standard funnel method were used to determine the size distribution and apparent density of specimens, respectively. W grain size, WC grain size and porosity percentage were evaluated employing SigmaScan Pro image analysis software. Determination of oxygen in specimens was conducted by pulse heating and infrared absorption method. Specific surface area of specimens was analyzed by BET nitrogen adsorption method. High frequency melting and infrared absorption method was used to determine total carbon and free carbon content of specimens. Digital display Rockwell Hardness Machine (200HRS-150) was used to measure the hardness of specimens. The density of WC-Co cemented carbide alloy was determined by Archimedes' principle using the water immersion method. Metallographic microstructure examination of alloys was carried out by a metallographic microscope (11XD-PC).

3. Results and discussion

3.1. Characterization of Cr-doped APT

Phase analysis of Cr-doped APT powder is identified by the X-ray diffractometer and illustrated in Fig. 1.

From Fig. 1, it is obviously that all diffraction peaks of the Cr-doped APT are essentially identified to ammonium paratungstate (JCPDS file No. 18-0128), which indicating the Cr-doped APT that has high degree of crystallinity. It is important to point out that the diffraction peaks of chromium are not observed. Accord to quantitative analysis of chromium, the content of chromium in the APT is 0.352 wt.%. Results indicate that chromium hasn't entered into the APT crystal lattice. It is probable that chromium is existed in the form of noncrystalline chromium hydroxide.

3.2. Particle size of the Cr-doped APT powder

To study the effect of chromium addition on growth of APT grains, two experiments of chromium doped and non-chromium doped are

Table 1
Physical properties of the Cr-doped APT and Non-chromium doped APT powder.

Two kinds of APT powder	Fsss/μm	Particle size distribution/%					Apparent density/g·cm^{-3}
		>150 μm	109–150 μm	75–109 μm	45–75 μm	<45 μm	
Chromium doped APT	29.0	0.1	8.2	34.1	35.7	21.9	1.54
Non-chromium doped APT	58.3	0.2	9.5	45.3	32.9	12.1	1.92

Please cite this article as: L. Wan, et al., Synthesis of Cr-doped APT in the evaporation and crystallization process and its effect on properties of WC-Co cemented carbide al..., Int J Refract Met Hard Mater (2016), http://dx.doi.org/10.1016/j.ijrmhm.2016.10.022