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Original Research Paper

Study on the synthesis behavior of Fe–W–B powders and the preparation of bulk

Cheng Li [a], Jialin Li [a], Jun Li [a,b], Ying Liu [a,b,*]

[a] School of Materials Science and Engineering, Sichuan University, Chengdu 610065, People's Republic of China
[b] Key Laboratory of Advanced Special Material and Technology, Ministry of Education, Chengdu 610065, People's Republic of China

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ABSTRACT

FeWB alloy powders were successfully produced by reactive synthesis. In this paper, effects of particle size of raw materials on the synthesis behavior of FeWB alloy powders were systematically investigated and powders with a high density of 13.99 g/cm^3 were fabricated into bulk materials by Spark Plasma Sintering (SPS) technique. Both W and FeB with varying particle sizes ranging from 3 μm to 15 μm were used as raw materials to prepare FeWB alloy powders. Microstructural analysis was performed using X-ray diffraction (XRD), scanning electron microscopes (SEM) equipped with an energy dispersive spectroscopy (EDS), and Mössbauer spectrometry at room temperature. Mean particle sizes were determined by laser granulometry. The results showed that particle size of raw materials had noticeable influence on both microstructure and amount of the resultant FeWB powders. Hardness of the bulk materials was measured by HR-150A Rockwell hardness tester. It had been significantly enhanced and reached 91.8 HRA, which could be comparable to that of cemented carbides.

1. Introduction

In recent years, various functional materials have been developed through appropriate consideration on their compositions and microstructures [1–3]. Especially, materials synthesis of selected raw materials based on well designed structures such as particle sizes is a crucial key for preparation of well functionalized materials [4–7]. For example, borides, especially transition metal borides, are great potential candidates for wear resistant applications due to their unique combination of high hardness, high melting point and relatively high electrical conductivity among hard materials [8–13]. In the last several decades, bunches of researches related to the conventional ternary borides such as Mo_2FeB_2, Mo_2NiB_2 and WCoB have already been reported intensively [14–17]. Those ternary borides have been employed widely in wear resistant applications, for instance, injection molding machine parts, can forming tools, and dies for the extrusion of copper.

On the basis of the bright prospect of ternary borides, we propose a new kind of transition metal boride FeWB to broaden the scope and accelerate the development in this exciting research domain. With high content of W (73.4 wt.%) and B (4.3 wt.%), FeWB possesses the superior properties of transition metal boride, among which excellent thermal stability and high theoretical density (13.27 g/cm^3) are impressing and must be highlighted. Accordingly, FeWB is anticipated to present significant potential in extensive fields, e.g. hard materials, wear resistant materials, and high temperature resistant materials.

Among the ternary borides, however, scant attention has been paid to FeWB since it is an emerging ternary boride. The existing preparation methods of FeWB [18–21] can hardly be realized in industrial production because of their high cost of raw materials, high requirements on equipment and unfriendliness to environment, i.e. their production process is not satisfactory. The author prepared FeWB alloy powders successfully by reactive synthesis with cheap raw materials, simple preparation procedures for the first time, which has attracted growing attention from various research communities. The previous work [22] revealed that the FeWB alloy powders (with a density of 12.896 g/cm^3) were obtained at 1050 °C holding for 1 h with low-density phases remained using FeB and W powders (around 3 μm) as raw materials. The corresponding bulk materials exhibited a Rockwell hardness of 90.4 HRA.

Particle size could influence reaction behavior significantly since the synthesis of FeWB alloy powder mainly relies on diffusion mechanism. Here in this work, the author systematically

* Corresponding author at: School of Materials Science and Engineering, Sichuan University, Chengdu 610065, People's Republic of China. Tel./fax: +86 028 85405332.
E-mail addresses: licmic@126.com (C. Li), jialin320@163.com (J. Li), li_jun@scu.edu.cn (J. Li), liuying5536@163.com (Y. Liu).

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investigated the influence of particle size of raw materials on the reactive behavior of FeWB, in particular, on particle morphology, phase composition of resultants, and the amount of Fe-containing phase. FeWB bulk materials were fabricated by the Spark Plasma Sintering (SPS) technique and the mechanical properties were also presented in this study.

2. Materials and methods

Commercially available tungsten (W) powders (99.95 wt.% W) and ferro-boron (FeB) powders (19.65 wt.% B) with different mean sizes were used as the raw materials. The ferro-boron and tungsten powders were blended at weight percent of 22.5% and 77.5% respectively. The dried mixed powders were reactive synthesized in SDZK furnace at 1050–1150 °C holding for 3 h in argon atmosphere. For comparison purposes, experiments using different W, FeB particle sizes both in the range of 3–15 μm under the same reaction condition were carried out.

The alloy powders with a density of 13.99 g/cm^3 obtained at 1150 °C with holding for 3 h were put into a cylindrical graphite die with an inside diameter of 20 mm and sintered in vacuum Spark Plasma Sintering apparatus (model SPS 1050, Sumitomo Coal Mining Co., Japan) with 5–35 min holding time and 50 MPa pressure.

The X-ray diffraction analysis of phase transformation was performed by DX-2000 diffractometer with a graphite monochromator using Cu Kα radiation operated at 30 kV and 40 mA. To track the evolution of the particle size, the powders were observed by JSM-6490LV scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS). The mean particle sizes were also determined by Mastersizer 2000 laser particle characterization system. The amount of Fe-containing phases in the sintered alloy powders was tested by room temperature transmission MS-500 Mössbauer spectrometry with a ^{57}Co/Pd source.

The bulk density of the sintered specimen was determined by Archimedes' method using water immersion. The Rockwell hardness (HRA) of the sintered specimen was measured by HR-150A Rockwell hardness tester. The fracture toughness was calculated by indentation technology with the help of Vickers hardness tester (452SVA) at the load of 30 kgf. For conversion of the sum of crack lengths values into fracture toughness values, the formula was used [23]:

$$\mathrm{KIC} = 0.15\sqrt{(HV30/\textstyle\sum l)} \tag{1}$$

where $\sum l$ is the sum of crack lengths (mm). Five indentations are made for the sample to measure the length of indentation diagonals.

3. Results and discussion

3.1. Effect of particle size variation of raw materials

3.1.1. Effect of particle size variation of raw W

Microstructure of mixed raw powders using FeB in uniform size (3 μm) and W in a range of different particle sizes was shown in Fig. 1a–d. According to the previous EDS results [22], irregular fine particles and flat particles which were marked in Fig. 1c generally correspond to ferro-boron and tungsten. The XRD patterns of alloy powders after sintered at 1050 °C for 3 h were detected in Fig. 2. It could be observed that synthesized reaction processed sufficiently with smaller W size (3 μm, 6 μm and 8 μm) of the mixed raw powders, containing two dominant phases, FeWB and W_2B merely. The phase W_2B exists in alloy steadily and it is also a transition metal boride with high hardness and high melting point which is beneficial to the mechanical properties of bulk materials. Therefore, W_2B is not regarded as an impurity phase in FeWB alloy powders. Reducing particle size produced higher specific surface areas and surface energy which could contribute to atom diffusion, promoting the synthesis of the alloy powders. When particle size increased to 15 μm, however, it was noted that the reaction process could not be complete with holding time of 3 h (Fig. 2d). Oversize particles of 15 μm resulted in more complicated phase composition which contained a great amount of Fe_2B, even with FeB and W remaining. It can be assumed that particle size of raw materials influenced the synthesis of alloy powders to a certain extent. On the one hand, larger particle size of raw materials brought about initial non-uniform mix (Fig. 1d), then B-rich areas and W-rich areas existed in raw mixed powders, making composition partly stray from the design (FeB:W = 0.225:0.775). On the other hand, the large size difference between W and FeB particles restrained uniform diffusion of the powders during reaction. Since the reactive synthesis of FeWB alloy powders depended on a solid diffusion process, the interparticle distance generally increased with larger particles, thus enlarging the difficulty of complete reaction. Therefore, Fick's second law is reduced to a simple form as given below for the case where a special concentration of the diffusing element is desired in the diffused metal or alloy [24].

$$\chi/2\sqrt{Dt} = c_1 \tag{2}$$

where c_1 is a constant. Thus, it shows that diffusion distance is proportional to the square root of time which is a parabolic dependence.

Fig. 1 also characterized the morphology of sintered alloy powders with different W particle size (Fig. 1e–h). It could be seen that particle size of FeWB alloy powders distributed uniformly when raw powders were finer (Fig. 1e and f), whereas particle size was of wide range when using coarse raw powders (Fig. 1g and h). Comparing the morphology before and after sinter treatment, it was interesting to find that particle size of FeWB alloy powders presented a dependence on that of the raw powders especially W. Increasing the W size generally led to correspondingly larger FeWB particle size after reactive synthesis. Fig. 3 highlighted the dependency of sintered powders' particle size on raw materials' size. FeWB powders' particle size increased approximately in proportion to the increase of W's particle size. The measured data did support the observation that particle size of sintered alloy increased with the particle size of W. We took into account that boron atom can diffuse into tungsten particle first as faster diffusion partly depends on distinctly larger diameter ratios [25,26]. It could be deduced that the synthesis of FeWB alloy powders mainly relied on the diffusion of FeB, thus basically remaining the original size of W after sintering. The results were well in agreement with generation of the W_2B and Fe_2B phases detected by XRD [22], indicating the reaction equation:

$$2\mathrm{FeB} + 2\mathrm{W} \rightarrow \mathrm{Fe_2B} + \mathrm{W_2B} \tag{3}$$

3.1.2. Effect of particle size variation of raw FeB

The morphology and phase composition of the powders using W in uniform size (3 μm) and FeB in a range of different particle sizes were also investigated. SEM investigation was recorded to monitor the microstructure of the mixed powder samples before sintering, with both FeB (point 1, Fig. 4c) and W (point 2, Fig. 4c) particles conducted by EDS. According to the XRD patterns after 1050 °C–3 h process (Fig. 5), similarly, alloy phase was mainly FeWB with some W_2B coexisting when the mean size of FeB was relatively small (Fig. 4a–c). When FeB particle size increased to 15 μm, the dominant phases comprised W_2B, W, Fe_2B and FeB, with merely a few FeWB appearing. As the particle size increased,