Powder Technology 360 (2020) 430–443

Contents lists available at ScienceDirect

Powder Technology

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

Densification behavior of ultrafine W-Ni-Fe composite powders produced by a two-stage reduction process

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ARTICLE INFO

Article history:
Received 12 August 2019
Received in revised form 18 October 2019
Accepted 6 November 2019
Available online 6 November 2019

Keywords:
Carbothermic reduction
Tungsten heavy alloys
Microstructure evolution
Hardness
Bending strength

ABSTRACT

The ultrafine composite powders of two different compositions (90W-7Ni-3Fe and 93W-4.9Ni-2.1Fe, wt%) were synthesized by a two-stage reduction process consisting of carbothermic pre-reduction and the following deep reduction by hydrogen, and then the densification behaviors of them were investigated. The prepared W-Ni-Fe composite powders by the new proposed two-stage method had the particle size ranged from 200 nm to 400 nm. The sintered compacts of these two kinds of W-Ni-Fe powders achieved nearly full densification at a sintering temperature of 1400 °C within 3 h. The maximum hardness of the alloys obtained at 1300 °C were 411 HV and 358 HV, and the bending strength of >1500 MPa was achieved at 1400 °C for the compositions of 90W-7Ni-3Fe and 93W-4.9Ni-2.1Fe, respectively. Meanwhile, the bending fracture mechanism was also investigated, which was different for the samples sintered at different temperatures.

1. Introduction

Tungsten heavy alloys (WHAs) possess a two-phase microstructure consisting of 80–97 wt% nearly spherically-shaped BCC tungsten grains homogeneously interspersed in a low melting temperature ductile FCC γ-(Ni-Fe-W) matrix phase [1,2]. WHAs provide an outstanding combination of properties, such as high density (16–18 g/cm^3), prominent mechanical properties, good ductility, great corrosion resistance, easy machinability, high absorption capacity against X-ray and Gama-ray and harmless to health and environment [3–6]. Considering these excellent properties listed above, WHAs are extensively used as counter weight balances, radiation shields, vibrating damping devices, electrical contacts, as well as for defense purposes (kinetic energy penetrators, fragmentation devices, etc.) and are even considered as plasma facing components in fusion reactors [7–12]. With the development of science and technology, the high-performance W-Ni-Fe heavy alloys are used as an attractive alternative to replace depleted uranium alloys (DUAs) for armor piercing ammunition, due to the serious radioactive contamination problem of DUAs cause [13–16].

Owing to the high refractoriness of tungsten (melting point 3420 °C), it is difficult to fabricate tungsten heavy alloys by melting and casting processes. Therefore, WHAs are traditionally processed by conventional powder metallurgy (PM) techniques. Pressed compacts are usually sintered in hydrogen atmosphere and the eutectic liquid phase forms at 1465 °C [17]. W-Ni-Fe ternary system with a Ni: Fe ratio of 7:3 is the most commonly used in preventing intermetallic compounds from developing to achieve the best mechanical properties [18]. According to the literature [19], Rabin et al. confirmed that strength of WHAs continuously decreases with increasing tungsten content. Meanwhile, Belhadjhamida et al. [20] found the strength of WHAs gains the maximum value at approximately 93 wt% tungsten. After that, Akhtar [21] successfully produced 90W-7Ni-3Fe heavy alloy and investigated its mechanical properties, microstructure development and fracture behavior after solid state sintering. Tang et al. [22] carried out the researches on the preparation and shielding properties of 90W-Ni-Fe alloy with different Ni/Fe ratios by liquid phase sintering. Zhang et al. [23] fabricated the tungsten heavy alloys with the composition of 93W-4.9Ni-2.1Fe by mechanical alloying process followed by a sintering process in hydrogen atmosphere, and it was concluded that 93W-4.9Ni-2.1Fe alloy sintered at 1150 °C shows homogeneous microstructure and good mechanical properties. Consequently, a large amount of work has been performed to prove that 90W-7Ni-3Fe and 93W-4.9Ni-2.1Fe alloys (wt%) are two typical WHAs with good performances [24].

Many newly developed sintering techniques in the preparation of WHAs were also proposed, such as microwave sintering and spark plasma sintering (SPS), which have tremendous advantages over conventional sintering technology. For example, Liu et al. [25] carried out studies on mechanical properties and microstructure evolution of 93W-4.9Ni-2.1Fe alloys, and found that with the increase of sintering temperature from 1250 °C to 1500 °C, the relative density and mechanical properties were improved. Upadhyaya et al. [26] sintered the compacts at 1500 °C in a conventional furnace and a microwave furnace to demonstrate that microwave sintering could reduce about 75% processing time, which led to less grain coarsening of W. In addition,

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https://doi.org/10.1016/j.powtec.2019.11.019
0032-5910/

Ding et al. [27] used the HEBM assisted SPS method to successfully produce fine-grained WHAs at different sintering temperatures (1000 °C–1200 °C). Hu et al. [28] synthesized 93W-5.6Ni-1.4Fe alloy on a spark plasma sintering system and investigated the sintering behavior and microstructure evolution. Besides, there are still an enormous amount of research and significant technology developments with respect to grain size reduction and microstructural parameters control to improve mechanical properties, such as employing mechanical alloying (MA) to increase powder activation and decrease motivation energy of sintering [24,27,29,30], adding rare earth oxide to refine grain size [24,29,31], selective laser melting (SLM) [32], laser sintering (LS) [33], and gel-casting [34].

As summaried above, over the past several decades, substantial research efforts have been focused on technological innovation of sintering and mechanical properties enhancement. The grain size of WHAs was found to be dependent on particle size of initial powder, which is controllable through powder preparation process distinctly. The particle size of the initial powder and microstructure of the alloy are the intrinsic factors to affect mechanical properties [35]. Many approaches have been proposed to prepare ultrafine W-Ni-Fe composite powder, including mechanical alloying [24,27,29,30], sol-spray drying and hydrogen reduction process [36,37], and gaseous reduction of their mixed oxides [38]. It is well known that mechanical alloying (MA) is an important method to prepare the ultrafine powder [29,30]. In spite of the advantages of this method, lots of impurities might be introduced during long time high-energy ball milling (HEBM) process. By severe plastic deformation, cold welding and fracture during MA, a large number of gas molecules have been absorbed on the particles. It is deteriorated for these gases to generate water vapor during hydrogen reduction as well as the swelling or bubbles on the surface of the sintered microstructures, which causes a decline in the relative density of the WHAs [27]. Gong et al. [36] and Fan et al. [37] synthesized 93W-4.9Ni-2.1Fe-0.03Y and 93W-4.9Ni-2.1Fe ultrafine composite powder, respectively, by the method of sol-spray drying combined with hydrogen reduction process. Nevertheless, the production cost of this method is higher. Furthermore, due to the formation of tungsten bearing volatile intermediate ($WO_2(OH)_2$) in the hydrogen reduction process, the chemical vapor transport (CVT) mechanism dominates the reduction process, which makes it hard to control the growth of W particles, especially when the material layer is thick. [40].

According to our previous work, it was revealed that the preparation of nanocrystalline W powder is feasible via the combination of carbothermic reduction with insufficient carbon black and the secondary hydrogen reduction process [41], due to the formation of large numbers of nano nuclei by using nano carbon black and the absence of tungsten bearing volatile intermediate like $WO_2(OH)_2$. In this work, we extended this method to prepare ultrafine and high purity W-Ni-Fe composite powders. Subsequently, the obtained powders will be pressed into compact and sintered for densification. Meanwhile, the mechanical properties of WHAs with different compositions (90W-7Ni-3Fe and 93W-4.9Ni-2.1Fe alloys, wt%) were also investigated.

2. Material and methods

2.1. Powders preparation

Tungsten trioxide powders (WO_3, > 99 mass%, Sinopharm Chemical Reagent Co., Ltd), nickel oxide powders (NiO, > 99 mass%, Aladdin Industrial Co., Ltd) and iron oxide powders (Fe_2O_3, > 99 mass%, Sinopharm Chemical Reagent Co., Ltd) were selected as the raw materials. Carbon black (MA100, Mitsubishi Chemical Corporation) was used as the primary reducing agent. The micromorphologies of the four as-received samples were observed with a field emission scanning electron microscopy (FE-SEM, ZEISS SUPRA 55, Oberkochen, Germany), and shown in Fig. 1(a)–(d), from which it can be seen that the polyhedral shaped WO_3 particles (Fig. 1(a)) have an average grain size of 45 μm; the average particle sizes of NiO (Fig. 1(b)) and Fe_2O_3 powders (Fig. 1(c)) were

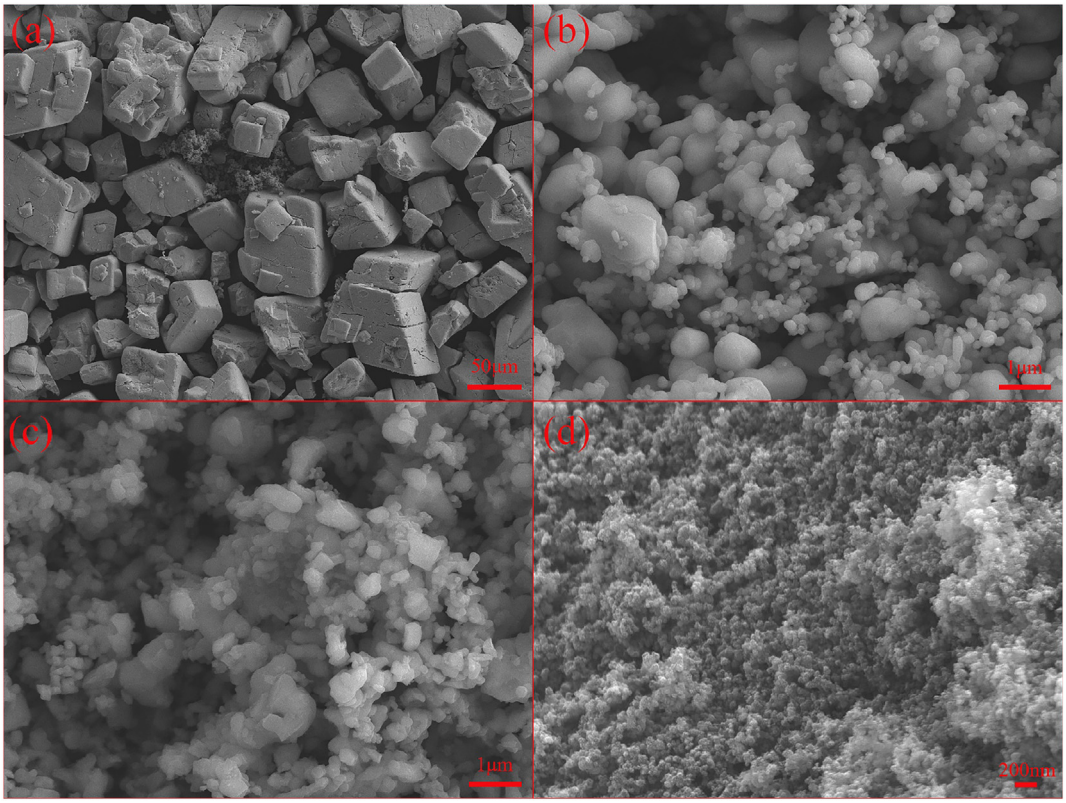

Fig. 1. Micromorphologies of raw materials: (a) WO_3, (b) NiO, (c) Fe_2O_3, (d) carbon black.