Journal of Alloys and Compounds 692 (2017) 420–426

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

The effects of alumina reinforcement and nickel activated sintering on nanosized tungsten matrix

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ARTICLE INFO

Article history:
Received 9 August 2016
Received in revised form
5 September 2016
Accepted 7 September 2016
Available online 9 September 2016

Keywords:
Nanosized tungsten
Al_2O_3 reinforcement
Activated sintering
Microstructure
Hardness

ABSTRACT

In this work, the effects of aluminum oxide reinforcement and Ni activated sintering on nanosized tungsten matrix was investigated by analysis obtained W compacts sintered at 1400 °C for 1 h. Experimental results show that the effect of alumina reinforcement on tungsten compacts exhibit improved mechanical strength with high densification at relatively low sintering temperature during nickel activated sintering process. The densification of sintered compacts could be effectively enhanced with Ni addition, and near-full dense samples (98.0% of theoretical density) could be obtained by 0.6 wt% Ni adding. Furthermore, the grain growth of sintered compacts could be restrained from 10.55 μm to 2.57 μm with ultrafine Al_2O_3 addition, which results in about 32% improvement of Vickers microhardness value of 515 ± 7 (VHN) compared to that of W-Ni composite without Al_2O_3 addition. The results well illustrate the advantage of alumina reinforcement of nanosized tungsten matrix under nickel activated sintering process for their structural applications.

1. Introduction

Tungsten has been a primary candidate material for various structural applications due to its brilliant properties such as high melting point and mechanical strength, well thermal conductivity, low coefficient of thermal expansion and good resistance to oxidation [1]. Generally, tungsten is hard to be fully sintered because of its highest melting point among all the metals and partially sintered tungsten will deteriorate its mechanical strength and limit its application. Using nanosized tungsten and adding transition metals are two efficient activated sintering methods, which could reduce the sintering temperature of tungsten and obtain near-full dense compacts [2–5]. Refining the particle size to nanoscale could improve the activity of powders and small additions of transition metals such as Ni, Pt enhance grain boundary diffusion, which could both reduce the activated energy of sintering process and decrease the sintering temperature [6,7].

Another important issue for structural applications of tungsten is the stability of its mechanical properties, and monolithic tungsten chooses to lose its high strength at elevated temperatures due to the weakness of grain boundary at high temperatures [8], which limits its further structural applications. In order to improve the mechanical properties of tungsten matrix, oxides (such as Y_2O_3, La_2O_3, HfO_2, Al_2O_3) reinforce W matrix have been widely investigated and show their superiority in high strength at elevated temperatures [9–13]. For example, La_2O_3 and Y_2O_3 reinforced tungsten matrix shows an improvement of Vickers microhardness by 30% compared to that of pure tungsten [13]. After that, a question is natural raised about how the coupled effects of oxides reinforced tungsten matrix during activated sintering process. However, there are few report on the coupled effects on microsized tungsten by oxides reinforced with activated sintering process, and the coupled effects on nanosized tungsten (although possessing more excellent properties), especially the sintering behavior and mechanical strength of tungsten matrix, are rather less reported and need to be further investigated.

In this work, the sintering performance, microstructure evolution and mechanical strength of quasi-spherical nanotungsten compacts co-strengthened by nickel and ultrafine Al_2O_3 particles were investigated in detail. Experimental results indicate near full dense compacts (98% of theoretical density) could be obtained with 0.6 wt% Ni addition and the grain size grows up to around 10 μm. Importantly, grain growth could be well suppressed and microhardness of obtained compacts improves by adding ultrafine Al_2O_3

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http://dx.doi.org/10.1016/j.jallcom.2016.09.081
0925-8388/

particles as oxide dispersed strengthener. The average grain size declines to 2.57 μm from 10.55 μm when Al_2O_3 proportion is 1.5 wt %, and Vickers microhardness of sintered compacts promotes up to 515 ± 7 (VHN), which increases about 32% compare to that of no Al_2O_3 addition. These results well illustrate that co-strengthened tungsten compacts exhibit improved mechanical strength with high relative density at relatively low sintering temperatures.

2. Experimental

2.1. Materials

Spherical ultrafine Al_2O_3 particles with the average size of 286 nm and quasi-spherical tungsten nanoparticles used in this study were produced by Radio-Frequency induction thermal plasma, and the synthesis process of quasi-spherical nanotungsten powders was presented elsewhere [14]. Nickel chloride ($NiCl_2 \cdot 6H_2O$, analytical pure) was used as Ni source.

2.2. Fabrication of composite powder

Composite powder was obtained by liquid mixing method. Firstly, tungsten nanopowders were mixed with nickel chloride which dissolved in absolute ethyl alcohol, and then dried at 80 °C using water bath. Then the absolutely dried powder was calcined under H_2 atmosphere in a tube furnace to form W-Ni composite powders. As obtained powders were mixed with spherical ultrafine Al_2O_3 powder under ethanol medium with the assistance of ultrasonic. Finally, the liquid mixture was absolutely dried at 80 °C while stirred constantly using a glass bar to obtain W-Ni-Al_2O_3 composite powders.

2.3. Fabrication of tungsten matrix composites

As obtained composite powders in Section 2.2 were compacted under a uniaxial pressure of 250 MPa and holding for 1 min with 1.5 wt% stearic acid assistance. The green compacts were firstly sintered at 400 °C for 2 h to remove the stearic acid under a constantly heating rate of 2 °C/min, followed by sintering for 1 h at 1400 °C with 10 °C/min to obtain tungsten matrix composites. All experiments were carried out under hydrogen atmosphere.

2.4. Characterization

The morphologies of the powders and sintered compacts were examined by transmission electron microscope (TEM, JEM-2100) and field-emission scanning electron microscopy (FESEM, JEOL JSM-7001F). Energy Dispersive Spectrometer (EDS, INCA Microanalysis Suite) was applied to analyze the elements distribution. The structure of nanotungsten powders used in this study was analyzed by X-ray diffractometer (XRD, Philips X'Pert PRO MPD). Laser particle size analyzer (Beckman Coulter, LS 13320) was used to examine the particle size distribution of Al_2O_3 powders. Grain size of nanotungsten powders and sintered compacts were measured by particle size analysis software of Nano-measurer. The Brunauer-Emmett-Teller (BET) specific surface area of powders was determined by N_2 adsorption measurement (Builder, SSA-7300). Linear shrinkage of sintered samples was based on diameter variation. The density of green compacts was calculated directly by the ratio of weight to volume, and the densities of sintered samples were measured according Archimedes principle and relative densities of sintered compacts were calculated using theoretical density of the composite ρ_c, $\rho_c = \frac{1}{\frac{w_W}{\rho_W}+\frac{w_{Ni}}{\rho_{Ni}}+\frac{w_{Al_2O_3}}{\rho_{Al_2O_3}}}$ (w_x and ρ_x, x = W, Ni and Al_2O_3, mean the weight percent and density of tungsten, nickel and Al_2O_3). Vickers microhardness test was conducted on the polished samples using microhardness tester under a 200 g·f loading and 10 s duration, and an average of ten readings with standard deviations is used as the final value.

3. Results and discussions

3.1. Powders characterization

Fig. 1 exhibits the typical morphology and structure of tungsten and Al_2O_3 powders synthesized by thermal plasma. SEM and TEM images show that the obtained tungsten powders exhibit quasi-spherical shape and well-dispersed state with the particle size of about 50 nm, as presented in Fig. 1a, b. Scanning electron micrograph of Al_2O_3 exhibited in Fig. 1c indicates that ultrafine Al_2O_3 powders produced by thermal plasma process possess perfect spherical shape and good dispersity. The XRD pattern of tungsten powders shown in Fig. 1d reveals that the dominant phase is α-W structure, coexisting with small amounts of non-equilibrium β-W phase and tungsten oxide. The particle size distribution of quasi-spherical tungsten shown in Fig. 1e indicates that quasi-spherical tungsten powders used in this study have an average size of 52.9 nm and above 95% particles are under 100 nm. Besides, spherical Al_2O_3 powders have an average size of 287 nm with uniform particle size distribution, as presented in Fig. 1f.

3.2. The effect of nickel on sintering behavior of tungsten matrix

Fig. 2 exhibits the evolution of linear shrinkage and relative density of sintered compact with different nickel contents when sintered at 1400 °C for 1 h. Sharply increasing of linear shrinkage occurs from 17.5% to 20.85% when Ni proportion is under 0.6 wt%, as shown in Fig. 2a, and the tendency of linear shrinkage turns to relatively smooth as Ni contents increasing above 0.6 wt%. The variation of relative density vs. Ni contents is shown in Fig. 2b, which is in accordance with the linear shrinkage variation. The relative density increases remarkably from 89.8% to 98.0% while Ni contents increase from 0 to 0.6 wt%, and the relative density is around 98.0% in this study while Ni proportion keeps increasing. The thickness of Ni on tungsten in terms of monolayers can be estimated as [15,16]:

$$\delta = \frac{N_A X_{Ni}}{\rho_0 M_{Ni} S_W} \quad (1)$$

where N_A means Avogadro's number, X_{Ni} and M_{Ni} are the weight ratio and the molecular weight of nickel, respectively, ρ_0 represents the atomic density of Ni on W (9.7×10^{18} atoms/m^2) [17,18] and S_W means the specific surface area of tungsten powders (6.53 m^2/g in this work). The parameter of average coverage (δ) is calculated to be 1.03 in this study. The results indicate that 0.6 wt% Ni additives could show good performance on the densification of tungsten matrix, which is selected as an optimal nickel contents in later Al_2O_3 adding experiments.

As discussed the physical parameters of sintered compacts with different nickel additives above, microstructures of typical sintered bodies are obtained by analyzing the fractured and as-sintered surface of sintered compacts, as presented in Fig. 3. The microstructure of compacts fabricated by quasi-spherical nanotungsten powders when sintered at 1400 °C for 1 h was shown in Fig. 3a, and the grain size mainly ranges from 2 μm to 4 μm. However, there exist some pores when sintered at 1400 °C, which indicates tungsten is hard to be fully sintered because of its highest melting point among all the metals [19]. Fig. 3b, c displays SEM images of