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Effect of rare earth elements on the consolidation behavior and microstructure of tungsten alloys

Mingyue Zhao [a], Zhangjian Zhou [a,*], Qingming Ding [a], Ming Zhong [a], Kameel Arshad [b]

[a] School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China
[b] School of Physics and Nuclear Energy Engineering, Beihang University, Beijing 100191, China

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ABSTRACT

The effects of rare earth elements (Y_2O_3, Y and La) on the consolidation behavior, microstructure and mechanical properties of tungsten alloys were investigated in this work. The starting powders were mechanical alloyed (MA) and then consolidated by spark plasma sintering (SPS). It was found that Y doping was beneficial to obtain fully dense tungsten alloys with more refined grains as compared to any other rare earth elements. The maximum values of Vickers microhardness and bending strength obtained from W–0.5 wt.% Y alloy reached up to 614.4 $HV_{0.2}$ and 701.0 MPa, respectively.

Introduction

Tungsten is a promising candidate material for high temperature applications due to its attractive properties, such as high melting point, high conductivity, low thermal expansion coefficients and low sputtering yield [1]. However, a major limitation of its use is the inherently high ductile–brittle transition temperature (DBTT) and low recrystallization temperature. Fine grained tungsten materials have shown improved properties in terms of reduced brittleness and improved toughness and strength [1,2]. However, the improved mechanical properties will be deteriorated when exposed to high temperatures for long time and when the service temperature is higher than the recrystallization temperature of pure tungsten. Recent studies suggested that the dispersion of high temperature oxide nanoparticles, such as La_2O_3 and Y_2O_3, will not only inhibit the grain growth of W during the consolidation but also stabilize the microstructure when exposed to higher temperature [3,4].

It is well known that, the impurities, especially for oxygen, have detrimental influence on the sinterability of tungsten powders and make tungsten materials embrittlement. Thus adding rare earth elements in the metallic state instead of the oxidic state should be better for fabrication of high performance tungsten alloys, due to the high affinity of rare earth elements with oxygen. A recent research conducted by L. Veleva et al. [5] found that the relative density of W–(0.3–2) wt.% Y appeared higher than that of W–(0.3–2) wt.% Y_2O_3, however, the microhardness appeared always lower than that of W–(0.3–2) wt.% Y_2O_3. From the viewpoint of oxygen absorption, it is suggested that La will be better than Y when used as alloying element for fabrication of W [6]. However there are almost no reports on W–La alloy and their comparison with W–Y alloy. It will be interesting and important to investigate the effects of different rare earth elements on the densification of W and their mechanical properties. This is the motivation of this work.

In this study the effect of rare earth elements, including Y_2O_3, Y and La on the consolidation behavior of W under the same sintering condition was investigated. The microstructural evolution and mechanical properties of different rare earth tungsten materials were examined and compared.

Experimental procedures

Powders of commercial pure W (with an average particle size of 2.0 μm and a purity of 99.9%), rare earth element of Y or La (with an average particle size of 48 μm and a purity of 99.9%), and rare earth oxide of Y_2O_3 (with an average particle size of 30 nm and a purity of 99.9%) were used as starting materials. The mixture powders of W–0.5 wt.% Y_2O_3 (named as WYO), W–0.5 wt.% Y (named as WY) or W–0.5 wt.% La (named as WL) were mechanical alloyed (MA) in a planetary ball mill, respectively. The MA parameters can be found in our previous work [7,8]. Then, the MA treated powders were placed into graphite tool in glove box and sintered by spark plasma sintering (SPS) in vacuum. Fig. 1 shows the temperature and pressure profile of SPS as a function of time. In order to get fully dense bulk materials by suppressing the pore-boundary separation, the samples were first sintered at 1373 K for 2 min and then sintered at 1873 K according to [9].

* Corresponding author at: Laboratory of Special Ceramics and Powder Metallurgy, School of Materials Science and Engineering, University of Science & Technology Beijing, Beijing 100083, PR China. Tel./fax: +86 10 62334951.
E-mail address: zhouzhj@mater.ustb.edu.cn (Z. Zhou).

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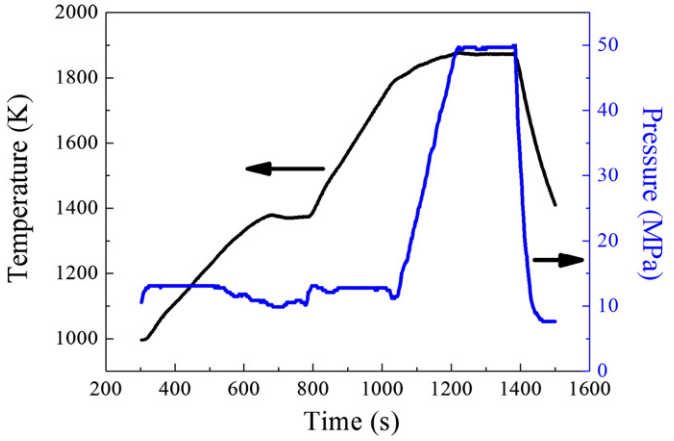

Fig. 1. The temperature and pressure profile as a function of time for the sintering experiments of rare earth tungsten alloys.

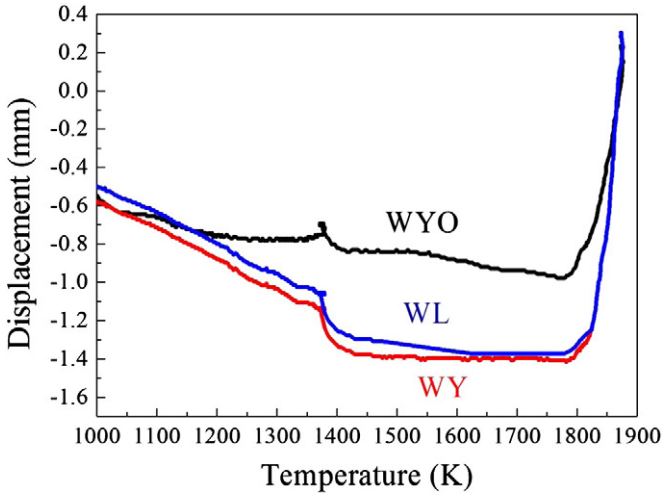

Fig. 2. The real time sintering curves of all samples without removing the contribution of the thermal expansion of the graphite tool and matrix.

The shrinkage of the specimens was continuously monitored by the displacement of the punch rod. The density of the compacts was measured by Archimedes method. A field emission scanning electron microscope (FE-SEM) equipped with Energy-dispersive X-ray Spectroscopy (EDS) and Scanning electron microscope (SEM) were employed to investigate the microstructural features, i.e., the element distribution, and the size and morphology of the grains and the pores of the samples. Moreover, XRD was used to determine the phase and X-ray diffraction analysis was made by the Rietveld method using the Full prof program [10]. The average crystallite size as well as the internal stress of the MA treated powders were determined from the diffraction peak widths taking into account the diffractometer resolution function. Vickers microhardness was measured at room temperature by applying a load of 1.96 N for 15 s. Three point bending tests were conducted on specimens with dimensions of 2 mm × 3 mm × 18 mm with a span of 13.1 mm and a crosshead speed of 0.5 mm/min. The thermal behavior of the MA treated powders in the range 373–1723 K was investigated by differential scanning calorimetry (DSC) at a heating rate of 10 K/min in flowing pure Ar.

Results and discussion

Consolidation behavior

Fig. 2 compares the consolidation behavior of all tungsten alloys as a function of temperature. It can be clearly seen that the displacement of WY alloy is similar with that of WL alloy, and shows quite different tendency from that of WYO alloy, especially at the sintering temperature of 1373 K. For WY and WL alloys, the displacement decreased by 0.6 mm between 993 K and 1373 K due to the thermal expansion of graphite punch rods and the matrix overweighing the contribution of precompaction, and continued to decrease at the sintering temperature of 1373 K. For WYO alloy, the displacement experiences a slower downward trend between 993 K and 1373 K and a weak upward trend at 1373 K. After that, the displacement of WY sees a similar trend with that of WYO. It was found that the WY alloy experienced a substantial decrease in the displacement while the WYO alloy experienced a slight increase at the temperature of 1373 K. This result is likely to arise from the formation of a higher volume of Y_2O_3 due to the oxidation of Y element in the WY system. Chemical analysis of the consolidated compacts was performed by the HORIBA EMIA-820V and LECO TCH600 devices to measure the C and O contents, respectively. It shows that the C contents were about 240 ppm for various tungsten materials fabricated under the same conditions. The amount of oxygen content which existed in MA treated WY powders was 0.4808 wt.%, which is enough for the reaction with added Y particles to form Y_2O_3. Fig. 3 shows the DSC curve of the MA treated WY powders in the range 373–1723 K. A weak exothermic peak at 1500 K with an onset temperature of 1400 K is found. It probably corresponds to the oxidation of the metallic Y with the residual oxygen in a hermetically sealed pan, which also illustrates that the remaining Y particles are likely to start to react with oxygen around 1373 K during SPS. Moreover, a sharp strong and a small exothermic peak can be clearly seen at 1003 K and 1173 K, respectively. According to [11,12], these peaks indicate that the strain relief took place during the heating of MA treated powders. Similar results on the oxygen analysis and the thermal behavior are also found for MA treated WL powders.

Fig. 4 shows the milling and sintering effect on the XRD patterns of the investigated samples. It is obvious that the diffraction peaks are broadened after milling, which was caused by the refinement of powder particles and a high level of internal strain in the W grains fabricated by the MA process. After sintering, the diffraction peaks become narrow again due to the grain growth and strain relief. The quantitative data on such grain growth and strain relief can be obtained by the comparison of lattice parameters after each stage of the powder processing (Table 1). It should be noted that the XRD patterns for all samples after milling exhibit a single BCC phase, suggesting that the rare earth elements were dissolved into the W lattice. This solid solution during

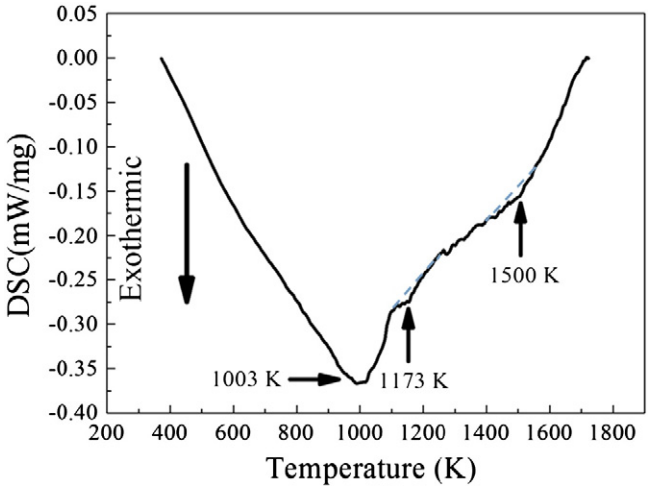

Fig. 3. DSC curve of the MA treated WY powder. The peak temperatures of thermally induced transformation of the powders are indicated by arrows.