Materials Science & Engineering A 729 (2018) 357–361

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Fine-grained W-NiTi heavy alloys with enhanced performance

Yang Shao[a], Huan Ma[b], Lishan Cui[b,*]

[a] Department of Materials Science and Engineering, Dalian Maritime University, Dalian 116026, China
[b] State Key Laboratory of Heavy Oil Processing and Department of Materials Science and Engineering, China University of Petroleum, Beijing 102249, China

ARTICLE INFO

Keywords:
Tungsten heavy alloys
Fine-grained
W-NiTi heavy alloys
Infiltration

ABSTRACT

In this study, the effect of infiltration temperature and holding time on the microstructure, transformation behaviors and mechanical properties of W-NiTi heavy alloys prepared by infiltration and hot pressing were investigated by SEM, DSC and compression tests. It was found that the average W grain sizes of all the W-NiTi heavy alloys prepared at temperatures varied from 1350 to 1450 °C with different holding times were less than 5 μm. The average W grain size was found to increase with increasing sintering temperature and holding time. The morphology of W grain was still polygonal with less growth. The NiTi matrix in these alloys was observed to dissolve up to 8.75 wt% W, significantly less than that of conventional tungsten heavy alloys, which could suppress the growth of W grains and make W grains more stable in NiTi matrix than in NiFe or NiCu matrix. All the W-NiTi alloys exhibited reversible martensite transformation. The stable microstructure and the increasing bonding strength resulted in the increasing of the strength and ductility of the alloys with infiltration temperature and holding time in compression tests.

1. Introduction

Tungsten heavy alloys (WHAs) have been widely used in kinetic energy penetrators, counter weight balances, radiation shields and electrical contacts due to their high density, high thermal conductivity and excellent mechanical properties [1–5]. Conventional WHAs, likely W-Ni-Fe and W-Ni-Cu, are usually fabricated by liquid-phase sintering (LPS) process from elemental powder mixtures at a temperature above 1460 °C [2]. During sintering, W particles coarsen remarkably primarily by the solution-reprecipitation [6] and the final microstructure consists of coarsened-large spherical body-centered cubic (BCC) tungsten grains of about 20 ~ 60 μm in diameter, dispersing in face-centered cubic (FCC) solidified matrix [2]. The large grain size results in low strength, according to the Hall–Petch relation [7]. Therefore, several efforts have been taken to obtain fine-grained WHAs, including using advanced sintering techniques, such as two-stage sintering [8], solid state sintering [9], spark plasma sintering [10], micro-wave sintering [11], or preparing by intensive plastic deformation [12,13].

Many researches have shown that reducing the solubility of W in the matrix is an effective way to suppress the grain growth of W during LPS [14,15]. W-Cu composites are the typical examples [14]. The low solubility of W in Cu matrix makes the contribution of solution-reprecipitation negligible, which retains the coarsening of W grains. The Mo addition in matrix can also restrain the growth of tungsten during LPS by reducing the solubility of W in matrix [15]. So if we could replace the matrix of NiFe/NiCu with other matrix, in which W solubility is very low, then fine-grained WHAs with high strength could be obtained by LPS.

Recently, novel W-NiTi shape memory alloy (SMA) composites have been prepared by infiltration and hot pressing by our group [16,17]. The W-NiTi SMA composites exhibited excellent mechanical properties in tensile and compression tests. The reports also shows that the solubility of tungsten in NiTi SMA matrix is about 10 wt%, which is much lower than that of conventional W-Ni-Fe and W-Ni-Cu alloys (above 20 wt%)[18–20]. Therefore, it is expected to prepare W-NiTi WHAs with fine-grained tungsten and high strength.

In this paper, we prepared fine-grained W-NiTi WHAs by infiltration and hot pressing and investigated the effects of infiltration condition on the microstructure, transformation behaviors and mechanical properties of W-NiTi tungsten heavy alloys. We have found that the W grains in NiTi matrix have high stability and the W-NiTi heavy alloys exhibited excellent mechanical properties in compression tests.

2. Experiments

Commercial elemental W powders were selected as the starting materials for fabricating W-NiTi heavy alloys. The morphology of the W powders is shown in Fig. 1. A master alloy with nominal compositions of $Ti_{53}Ni_{42}Nb_5$ (at%) was prepared from high-purity components (purity 99.8 wt%) by vacuum induction melting. The composition of the

* Corresponding author.
E-mail addresses: shaoyangok@163.com (Y. Shao), lscui@cup.edu.cn (L. Cui).

https://doi.org/10.1016/j.msea.2018.05.088
Received 10 May 2018; Received in revised form 22 May 2018; Accepted 23 May 2018
Available online 25 May 2018
0921-5093/

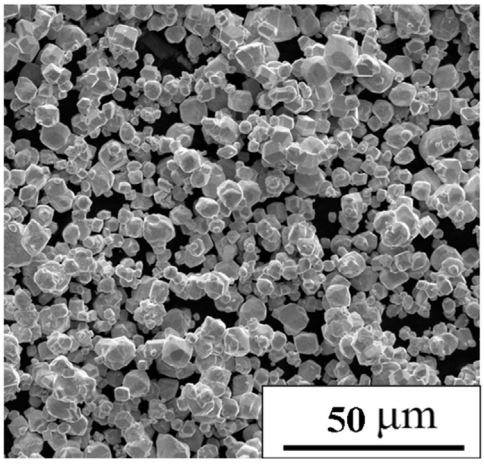

Fig. 1. SEM images of the W powders.

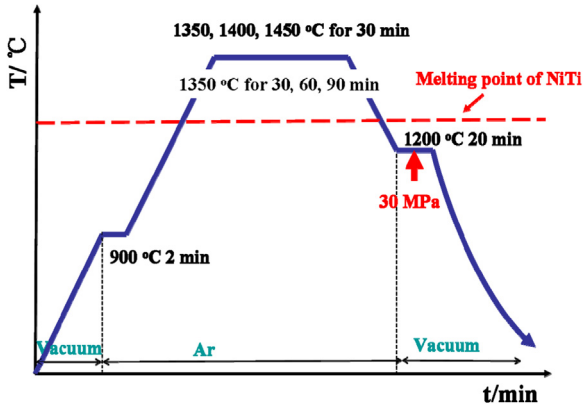

Fig. 2. Preparing cycle of W-NiTi heavy alloys.

master alloy was designed based on our previous work [17]. The W-NiTi heavy alloys were prepared by combining $Ti_{53}Ni_{42}Nb_5$ (at%) alloys and W powders at the mass ratio 1: 5, namely the tungsten content were 83.3% in weight. The W-NiTi heavy alloys were prepared by infiltration and hot pressing process. which can refer our previous work [17]. To obtain the optimum condition, the infiltration temperatures were varied from 1350° to 1450°C for 30 min and holding times at 1350 °C for were varied from 30 to 90 min. The samples were first heated up to 900 °C in vacuum to eliminate of oxygen and water vapor adsorbed on the surface of the initial W powders, and changed atmosphere to argon gas to prevent the vaporization of titanium afterwards. Then the alloys were heated to the infiltration temperatures at a rate of 10 °C/min in vacuum. After holding for different time, the alloys were cooled at a controlled rate of 10 °C/min to a temperature of 1200 °C, below the melting point of NiTi of 1310 °C [21]. A constant pressure of 30 MPa was applied on the alloys for 20 min, and then freely cooled to ambient temperature. The sintering cycle is shown in Fig. 2. Discs of 50 mm diameter of approximately 20 mm in height were produced. All of the alloys were ground to remove surface graphite contamination.

The microstructure of these W-NiTi heavy alloys was observed by scanning electron microscope (SEM, FEI) incorporating with energy dispersive spectroscopy (EDS) to detect W content in matrix phase. The average tungsten grain size was acquired by measuring about 400 individual grains from SEM images of polished surfaces manually using the digital micrograph software. Q20 instrument was used for differential scanning calorimetry (DSC) to study the martensitic transformation of the W-NiTi heavy alloys with a heating and cooling ramping speed of 10 °C/min at N_2 atmosphere. The samples for compression tests with dimension of Φ5 × 10 mm were obtained by wire electrode cutting. The compression tests were conducted by universal testing machine (WDW-200) with a strain rate of 5×10^{-3}.

3. Results and discussion

Fig. 3 shows the back scattering electron images of the W-NiTi heavy alloys prepared at different conditions. It can be seen that the images consisted of white and black areas. The white areas in the figures were tungsten grains, while the grey areas are NiTi matrix. The W grains distributed homogeneously in NiTi matrix and the microstructure of the W-NiTi heavy alloys has little change with increasing the infiltration temperature and holding time. Seen from Fig. 1(a), the raw tungsten powders have faceted morphology. While the W grains in the W-NiTi heavy alloys barely coarsened and incompletely spheroidized, which was different from conventional W-Ni-Fe and W-Ni-Cu alloys with remarkably grain growth sintering at a comparable temperature [22,23].

Fig. 4 displays the variation of average W grain size of W-NiTi heavy alloys with infiltration temperature and holding time. When sintered from 1350° to 1450 °C, W-NiTi heavy alloys with W grain sizes ranging from 4.0 to 4.11 μm can be obtained. It is worth noticing that the average particle size of original W powders was about 4 μm seen form Fig. 1. It can be seen that negligible grain growth of W occurs during infiltration. The compositions of NiTi matrix in different W-NiTi heavy alloys were given in Table 1. As can be seen from Table 1, there seems to be no significant variation of the W content with increasing infiltration temperature and holding time for the alloys investigated in this study. The maximum content of W in matrix was 8.75 wt% obtained in the alloy infiltrated at 1450 °C for 30 min. It should be noted that the date obtained by EDS is not exact due to the semi-quantitative nature of EDS analysis, so it can not be used to explain the increasing solubility of tungsten with increasing the infiltration temperature and holding time. But we can conclude from the results that the solubility of W in NiTi matrix is remarkable lower than those of W-Ni-Fe heavy alloys reported before (above 20 wt%)[18–20]. We speculated that the low solubility of W in NiTi matrix suppressed the solution-reprecipitation process in infiltration, which restrain the growth of tungsten particles, just like that case in W-Cu composites during LPS [14]. Meanwhile, the tungsten grains coarsen mainly by coalescence as evident by grain fusion without a grain boundary at several points in the microstructure of W-NiTi alloys shown in Fig. 3.

Fig. 5 shows the effect of infiltration condition on the transformation behaviors of W-NiTi heavy alloys. It can be seen that all the alloys display reversible martensite transformation during heating and cooling. Meanwhile, the martensite transformation temperatures of the alloys were almost the same. The martensite start temperature (M_s) and martensite finish temperature (M_f) of the alloys was about 48 °C and 12 °C, respectively, which means that the NiTi matrix of all the alloys consisted of martensite and present at room temperature. From the results shown in Fig. 5 and the analysis above, we can conclude that the infiltration condition has little effect on the martensite transformation behavior of NiTi matrix in W-NiTi heavy alloys.

Compression tests were performed to characterize the mechanical properties of the W-NiTi heavy alloys prepared with different infiltration conditions at room temperature. The compression stress–strain