Int. Journal of Refractory Metals and Hard Materials 43 (2014) 141–146

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

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

# Gradient structure induced by molybdenum in 90W–Ni–Fe heavy alloy

Ying Jin, Shunhua Cao *, Jie Zhu, Huiyuan Liu, Binghuang Chen, Huan Xu

*State Key Lab of Powder Metallurgy, Central South University, Changsha 410083, PR China*

ARTICLE INFO

*Article history:*
Received 5 August 2013
Accepted 25 November 2013

*Keyword:*
Gradient structure
Molybdenum diffusion
Liquid phase migration

ABSTRACT

90W(Mo)–Ni–Fe heavy alloy with gradient structure was fabricated by the diffusion of Mo slice from the alloy's surface at 1480 °C. The microstructure and content of binding phase at different regions along the cross section in the samples were investigated by scanning electron microscopy (SEM). The Mo content was determined by energy dispersive analysis (EDS) and the hardness of matrix phase was measured by Vickers' micro-hardness tester. Results show that the grain size, the volume fraction of binding phase and the hardness of matrix phase vary gradually due to the graded distribution of molybdenum. Simultaneously, the interfacial tension gradient induced by the dissolution of molybdenum is the driving force for liquid phase migration during liquid phase sintering.



## 1. Introduction

Tungsten heavy alloys (WHAs) are a kind of composite materials consisted of two-phase microstructure of tungsten particles with bcc structure distributed homogeneously in the matrix with fcc structure, which are generally fabricated by liquid phase sintering process [1]. They are used extensively in military, medical and industrial installations due to their excellent mechanical properties [2]. WHAs are most frequently used as kinetic energy penetrator. However, normal WHA penetrators easily cause the decreasing of self-sharpening effect by shear localization due to the formation of mushroom [3,4]. Therefore, to improve the performance of penetration, many kinds of novel WHA materials are fabricated, such as W–Ni–Mn, W–Hf and W–Ti system [5–7]. However, the pore in the alloy is easily caused by the oxidizability of Mn and Ti. It is also hard to obtain full-density materials due to the high volatility of Mn and hydrogen absorption of Ti at high temperature. The practical application is rare by the lack of Hf raw material and complex fabricating process. These problems limit their broader military applications as kinetic energy penetrator.

There is also a trade-off between wear resistance and toughness of the conventional WC–Co materials [8]. The wear resistance is usually improved at the expense of the toughness, and vice versa [9]. Functionally graded WC–Co (FG WC–Co) material provides an optimum solution to this problem [10,11]. FG WC–Co material presenting tough bulk and hard surface exhibits superior mechanical properties. Inspired by the fabrication of FG WC–Co material, W–Ni–Fe base heavy alloy with gradient structure has been proposed.

In this study, the authors demonstrate that the gradient structures of W–Ni–Fe base heavy alloys can be induced by adding chemical element of molybdenum. Due to the chemical potential differential in various regions induced by diffusion of Mo atoms in the W–Ni–Fe system, the liquid phase migration occurs. Simultaneously, tungsten grain size varies in microstructure by the Mo concentration gradient. The purpose of the work aims at a better understanding of the diffusion behavior of molybdenum in W–Ni–Fe alloy.

## 2. Experimental

The characteristics of the elemental powders used in this study were shown in Table 1. Elemental powders of fine tungsten, nickel and iron were dry mixed according to the designed composition of 90W–7Ni–3Fe, and blended in a plastic jar by planetary mill (QM-2SP1) for 16 h, using tungsten balls. The mass ratio of ball to powder was 10:1 and the rotation speed was selected as 180 r/min. The powders were protected by Ar gas to avoid oxidation. Then, the mixture powders were compacted to cylinders of 12 mm in diameter and 10 mm in height with a pressure of 200 MPa. The measured green density of compacts was 12.34 g/cm$^3$ by the Archimedes' principle, whose relative density was 72%. The Mo powder was pressed separately on to thin slice with 12 mm in diameter and 1.5 mm in height. The 90W–7Ni–3Fe specimens with thin Mo compacts on the top of them (in Fig. 1a) were heated at 10 °C/min to the sintering temperature (1480 °C) for certain times, and cooled down to room temperature at 10 °C/min. The whole sintering cycle was done in hydrogen atmosphere.

The sintered specimens (in Fig. 1b) were cut into two homogeneous halves along the cross direction after removing the Mo thin compacts away, using wire electrical discharge machining, as seen in Fig. 1c. To avoid the influence of some other uncertain factors, only the cross section of the specimen was used for examination. The specimens were ground and polished to a depth of approximately 0.5 mm from

* Corresponding author.

0263-4368/$ – see front matter. 
http://dx.doi.org/10.1016/j.ijrmhm.2013.11.017

**Table 1**
Characteristics of the elemental powders used in this study.

| Powders | Purity (wt.%) | Mean particle size (μm) | Major impurities |
|---|---|---|---|
| W | 99.95 | 3 | O |
| Mo | 99.8 | 4 | Si, Fe |
| Ni | 99.8 | 3.5 | C, O, S |
| Fe | 97.8 | 3.5 | C, O, N |

the cross section. The polished specimens were etched slightly in Murakami's solution. Back-scattered electron images (BEI) of the etched specimens were examined by scanning electron microscope (SEM, Jeol-6360LV) at an accelerating voltage of 25 kV. Grain size in materials of liquid phase sintering is usually reported as the mean intercept length. The grain size was measured based on BEI images of the microstructures using linear intercept method. The composition of the sintered specimens in various regions was measured using EDS incorporated with SEM. The micro-hardness measurements of the matrix phase were carried out on the cross section at loads in the range 5 to 500 gf by Vickers' micro-hardness tester. The volume fraction of binding phase was calculated by the software of Phase Analysis (Leica MV).

## 3. Results and discussion

### 3.1. The variation of molybdenum content in W–Ni–Fe alloy

The total molybdenum content of the specimen is altered by the variation of diffusion time. In order to obtain a desired final Mo gradient in the specimen, an optimal sintering time must be determined. From the previous research [12], 2 h is optimum to obtain the designated gradient microstructure.

Fig. 2 shows molybdenum gradient of the sample for 2 h at the sintering temperature. The addition of molybdenum powders from the surface of specimen results in the diffusion behavior of molybdenum atoms. The Mo concentration decreases with the increasing distance from the surface for a certain holding time, forming Mo concentration gradient along the cross section. There exist three kinds of Mo diffusion process during liquid phase sintering as shown in Fig. 3. It occurs in the following steps:

(1) Mo diffuses from the Mo layer into the sample,
(2) The flux of Mo by liquid phase migration,
(3) Mo dissolves into W grains.

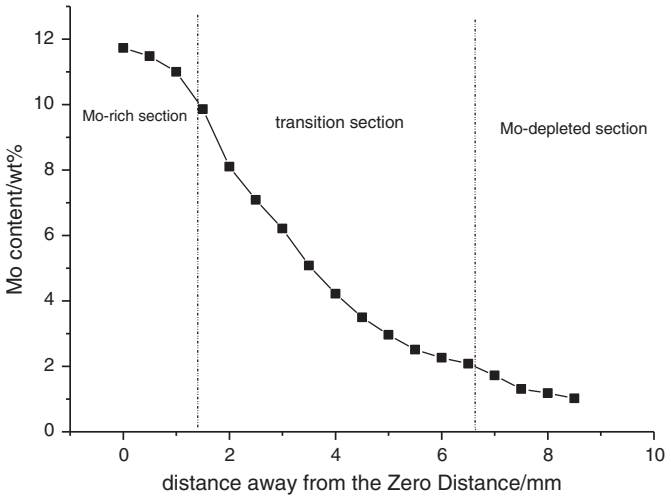


**Fig. 2.** The variation of Mo content along the cross direction after 2 h sintering.

The total diffusion flux of point A in the Fig. 2 can be expressed as

$$J_{Total} = J_{Diff} - J_{Mig} - J_{Dis} \quad (1)$$

where $J_{Total}$ is the total flux of Mo, $J_{Diff}$ is the flux of Mo diffusion, $J_{Mig}$ is the flux of Mo with the liquid phase migration, and $J_{Dis}$ is the mass of Mo dissolving into the W grains. The Mo diffusion process is only an uncomplicated process due to the Mo concentration gradient. Then, $J_{Diff}$ can be expressed as

$$J_{Diff} = \lambda D_1 \frac{dC}{dX} \quad (2)$$

where λ is a dimensionless constant and it is related to the volume fraction of liquid phase, by using the relation

$$\lambda = u^2 \quad (3)$$

where u is the volume fraction of liquid phase. D is the diffusion coefficient of Mo in the liquid phase (Ni–Fe phase) and is considered as constant, C is the Mo concentration, and X is the diffusion distance. The liquid migration can be determined by considering mass transport due to liquid flow. The flux of Mo by the liquid phase migration, $J_{Mig}$, can

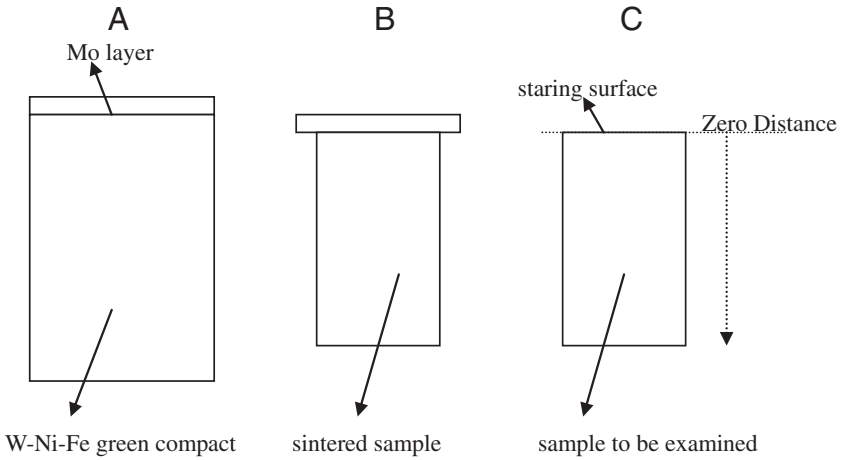


**Fig. 1.** Sketch of the sample in this research. A. W–Ni–Fe green compact by Mo layer placed on its top. B. The sample after 2 h' sintering at 1480 °C. C. The examined sample without Mo layer.