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A study of the manganese–tungsten binary phase diagram

Ossama Elsebaie, Kevin M. Jaansalu*

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, P.O. Box 17000, Station Forces, Kingston, Ontario K7K 7B4, Canada

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ABSTRACT

The current work investigated the manganese–tungsten binary system by studying the microstructure of a mechanical alloy of tungsten–35 at.% manganese, sintered at 1225, 1275, 1350, and 1425 °C. Consistency of the results is evaluated through thermodynamic modeling of the manganese–tungsten phase diagram. The microstructural constituents were characterized qualitatively and quantitatively in terms of the type of phases and the content of manganese in the tungsten rich-phase using X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDS). The XRD patterns revealed peaks associated with a tungsten-rich phase and manganese oxide (MnO) in the first set of samples while the patterns of the second set showed the strong peaks related to a manganese-rich phase and manganese dioxide (MnO_2). Backscattered images showed a distinct two phase microstructure in the first set of samples as compared to a three-phase microstructure in the second set of the samples. The maximum observed solubility of manganese in tungsten is 12 ± 3 at.% after sintering at 1350 °C for 90 min, compared to 9.3 at.% at 1268 °C based on a thermodynamic model. The maximum observed solubility of tungsten in manganese is about 10 at.% in the high temperature solid, compared to 7.4 at.% and 4.6 at.% in the solid and liquid phases respectively at the peritectic temperature of 1268 °C.

1. Introduction

Tungsten-based heavy alloys (WHAs) are not true alloys but are composite materials consisting of tungsten grains within a ductile metal matrix. WHAs are used instead of depleted uranium (DU) alloys in kinetic energy penetrators because of their environmentally friendly composition along with comparable density and corrosion resistance. However, a DU alloy offers superior penetration performance because of its susceptibility to adiabatic shearing during penetration and, in a sense, continually sharpens itself [1]. Efforts have been made to mimic this behaviour by improving the capability of WHAs to self-sharpen and consequently improve its penetration performance. One common approach in developing a new WHA is to examine the effect of alloying elements on the matrix which binds the tungsten particles. The elements are selected on the basis of their capability to result in adiabatic shear band formation by reducing both the thermal conductivity and the strain hardening rate, as well as increasing the thermal softening rate of the matrix. This should lead to an improvement in the WHA penetration capability to levels comparable to that of DU [2].

Extensive studies have been carried out using tungsten-nickel-iron and tungsten-nickel-copper alloys in kinetic energy projectiles [3]. Although the binder matrix in these alloys is a relatively low melting solid solution (Ni-Fe or Ni-Cu), the matrix exhibits high ductility which results in the expansion of the projectile head, known as mushrooming, that reduces the penetration efficiency of these projectiles [4,5]. In other studies, where iron was replaced with manganese in the binder matrix, manganese reduced the overall thermal conductivity and refined the microstructure of the alloy, both of which may promote thermal softening and hence facilitate the formation of adiabatic shear bands [6–8].

No solubility of manganese in tungsten has been noted in these efforts. Very little data exists in the literature regarding the phase diagram of the tungsten-manganese binary alloy system [9] and these elements are believed to be completely immiscible. However, when investigating the manganese nickel tungsten ternary system, Slyusarenko et al. [10] reported manganese solubility in tungsten ranging from 0 to 8 at.% at 1225 K. Other indirect observations support the hypothesis that manganese should exhibit some solubility in tungsten:

a. Manganese and tungsten both have the same body centered crystal structure at high temperature.
b. Manganese is soluble in elements in the same group as tungsten in the periodic table: chromium (up to 71.4 at.% Mn) and molybdenum (up to ~34 at.% Mn) [11]. Manganese also forms intermetallic compounds with these two elements: α and σ phases with chromium and the σ phase with molybdenum.

* Corresponding author.
E-mail address: kevin.jaansalu@rmc.ca (K.M. Jaansalu).

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Thus, manganese should display some limited solubility in tungsten and may even form an intermetallic compound, although none has ever been reported. Further experimental work in the manganese–tungsten binary system is warranted.

The most problematic factors are that the melting point of tungsten is above the normal boiling point of manganese and that there is a large difference between their densities. To mitigate these factors, the method of mechanical alloying was pursued. Initial trials carried out by the authors had shown that mixing of the elements was good and that a tungsten–manganese alloy could be formed with a relatively fine microstructure. Another factor is the oxidation of manganese which is an obstacle in forming a sound alloy, as evident from the microstructure in initial experiments [12]. Previous studies reported that many methods can be used to reduce the oxidation of manganese when it was added as a minor alloying element to WHAs [13,14]. However, as the manganese is the main alloying element in the present approach, minimizing the oxidation problem will be more challenging and different methods may be needed rather those reported in these previous studies.

To better understand the chemistry of the manganese–tungsten alloy system, there is a need to establish some compositional and thermodynamic boundaries. In the present study, the binary manganese–tungsten phase diagram will be investigated experimentally through the preparation of a manganese–tungsten alloy by mechanical alloying, followed by a quantitative assessment of the microstructural constituents in terms of manganese content and tungsten content at different sintering temperatures and times. The results will be examined from a thermodynamic point-of-view, with the aim of thermodynamically modeling the binary phase diagram. FactSage has been widely used in modeling phase diagrams; in particular, those diagrams of importance in processing multicomponent alloy systems. The capability to produce a phase diagram is a useful tool in the design of new alloys with appropriate microstructures to obtain the mechanical properties that satisfy service requirements.

2. Experimental procedure

The preparation of the alloy was accomplished through mechanical milling followed by sintering at temperatures above and below the melting point of pure manganese. The microstructural constituents were then characterized qualitatively and quantitatively using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). FactSage version 6.4 was used to calculate the binary manganese–tungsten phase diagram.

2.1. Alloy preparation

In order to continue the research work reported in [12], two sets of tungsten–35 at.% manganese (W-14 wt% Mn) samples were prepared and sintered in different ways to reduce the oxidation of manganese. All alloy samples were first prepared by weighing the metal powders listed in Table 1 to obtain the required alloy composition. The powders were then mechanically mixed in in a tungsten carbide jar rotating with a milling speed of 400 rpm for 4 h and a ball-to-powder weight ratio of 10:1 using a planetary ball mill (Retsch PM 100) with tungsten carbide balls. Mechanically alloyed powders were consolidated into green discs, 1.27 cm in diameter, under a uniaxial pressure of ~457 MPa for 1 min. To obtain a solid structure, the compacted green discs were sintered in a LECO Corporation TF-1 tube furnace, under a controlled atmosphere of high purity argon, followed by high purity hydrogen gas, dried through a liquid nitrogen cold trap, in order to reduce any oxides as well as dissolved oxygen in the powders. The first set of samples was sintered in an alumina combustion crucible at 1225 °C for 60 min and at 1275 °C, 1350 °C, and 1425 °C for 30 min. The second set of samples was prepared using the same conditions, except that a paraffin wax was added at about 1 wt% of the charge to help reduce the oxygen contamination. They were covered with a thin layer of elemental manganese powder (< 1 mm thick) during sintering for two different times; 30 and 90 min at the same sintering temperatures. This will investigate the effect of sintering time on the microstructure and the possible formation of intermetallic compounds.

Table 1
Characteristics of metal powders used to prepare the alloys in the present study, as reported by the supplier.

Material	Purity	Size	Supplier
Tungsten	99.95%	1–1.5 μm	Inframat Advanced Chemicals
Manganese	99.6%	< 10 μm	Alfa Aesar

2.2. Microstructural characterization

XRD was employed to investigate the phases formed after sintering. The samples were scanned with a Philips (PANalytical) X'Pert Pro MPD diffractometer with an X'Celerator high speed strip detector. The scanning was carried out on samples rotated at 2 revolutions per second using Cu Kα radiation (Ni filtered), or Co Kα radiation (Fe filtered). All the samples were scanned from 20° to 35° with a counting time of 20 s at a step size of 0.02°. Also, a Scintag X-1 diffractometer was used with a scan rate of 5° per second with Scintag DMSNT software version 31.39B. The lattice parameter was determined using the Scintag lattice refinement program 3.00. The database used is the Powder Diffraction File PDF-2 Release 2011 published by International Centre for Diffraction Data.

A scanning electron microscope, Philips VP-30XL or FEI FEG-Nova NanoSem, was used to examine the microstructural features in terms of the type and morphology of the phases after sintering. An elemental spot analysis of these phases was carried out on the surface and vertical cross sections of the samples using energy dispersive X-ray spectrometer (EDS) with an EDAX Apollo detector and Genesis software or with a Bruker xFlash 6|60 detector and Quantax Esprit 2.0 software.

2.3. Phase diagram modeling

Since the monograph by Kaufman and Berstein [15], the thermodynamic modeling of phase diagrams by Gibbs energy minimization has become well established. The Gibbs energy of a solution phase consists of the contributions from the pure components, the ideal energy of mixing, and a term representing the excess from ideal mixing. The Gibbs energy, G, of a solution phase α is of the form:

$$G^{\alpha} = x^{\alpha}_{Mn} G^{\alpha}_{Mn} + x^{\alpha}_{W} G^{\alpha}_{W} + G^{id} + G^{xs} \quad (1)$$

where x^{α} is the mole fraction of the element in the α solution, G^{α} is the Gibbs energy expression of the pure element in the α form, G^{id} is the ideal energy of mixing, and G^{xs} is the excess energy of mixing. FactSage version 6.4 was employed to plot the phase diagram of the binary manganese–tungsten alloy system [16]. The data for the pure elements were taken from the work of Dinsdale [17], as provided in the FactSage database. This data includes the Gibbs energy expressions for the four different allotropic structures of manganese (increasing from room temperature, bcc_A12, cub_A13, fcc_A1, and bcc_A2, or α, β, γ, δ respectively) and two Gibbs energy expressions for tungsten (bcc_A2 and fcc_A1 which is metastable). The liquid and solid solutions were modeled as regular solutions. The expression for the excess energy of mixing then takes the form:

$$G^{xs} = k^{s,\,l} x_W \cdot x_{Mn} \quad (2)$$

where k is the coefficient for a solid or the liquid phase, independent of temperature, and x_{Mn}, x_W are the mole fractions of manganese and tungsten. In order to calculate the binary phase diagram, expressions for tungsten in the bcc_A12 (α) and cub_A13 (β) forms, and suitable values for the coefficients need to be determined for each solution.