



## Refractory high-entropy alloys

O.N. Senkov<sup>a,b,\*</sup>, G.B. Wilks<sup>a,c</sup>, D.B. Miracle<sup>a</sup>, C.P. Chuang<sup>d</sup>, P.K. Liaw<sup>d</sup>

<sup>a</sup> Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, OH 45433, USA

<sup>b</sup> UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432, USA

<sup>c</sup> General Dynamics, Corp., Dayton, OH 45431, USA

<sup>d</sup> Department of Material Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA

### ARTICLE INFO

#### Article history:

Received 20 April 2010

Received in revised form

26 May 2010

Accepted 31 May 2010

Available online 23 June 2010

#### Keywords:

B. Alloy design

B. Crystallography

C. Casting

D. Microstructure

F. Electron microscopy, scanning

### ABSTRACT

Two refractory high-entropy alloys with near-equiatomic concentrations, W–Nb–Mo–Ta and W–Nb–Mo–Ta–V, were produced by vacuum arc melting. Despite containing many constituents both alloys have a single-phase body-centered cubic (BCC) structure. The lattice parameters  $a = 3.2134(3)$  Å for the quaternary alloy and  $a = 3.1832(2)$  Å for the quinary alloy were determined with high-energy X-ray diffraction using a scattering vector length range from 0.7 to  $20 \text{ \AA}^{-1}$ . The alloy density and Vickers microhardness were  $\rho = 13.75 \text{ g/cm}^3$  and  $H_v = 4455 \text{ MPa}$  for the W–Nb–Mo–Ta alloy and  $\rho = 12.36 \text{ g/cm}^3$  and  $H_v = 5250 \text{ MPa}$  for the W–Nb–Mo–Ta–V alloy. The exceptional microhardness in these alloys is greater than any individual constituent, suggesting the operation of a solid-solution-like strengthening mechanism.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

Metallic alloys with superior mechanical and functional properties remain in high demand for the aerospace industry. Conventional alloys, especially for structural applications, are sometimes considered a relatively mature technology. Typically, such alloys have a base element that dominates the chemistry, accounting for ~80% (by weight) or more of the total formulation. Even superalloys, with as many as 12 elements in a single alloy, often contain over 50% of the base element. Only in comparatively rare cases, have superalloys with roughly 20% each of up to three transition metal elements (Fe, Ni, Co, and/or Cr) been developed. This limited scope of alloying strategy mainly stems from the fact that ternary or higher-order intermetallic compounds form unexpectedly in multi-component alloys, generally after long-term exposure at elevated operating temperatures. These new phases often have complex crystal structures that do not support plasticity, and scavenge desirable elements from the host phase. Formation of these complex intermetallics typically heralds a reduction in mechanical properties, corrosion resistance, and microstructure stability. This long-held experience provides a strong disincentive for unnecessarily complex alloy formulations.

Within the past several years, a fundamentally new alloying concept has been proposed [1–4]. Termed high-entropy alloys (HEAs), these new materials are formed by combining  $n$  elements of roughly equimolar concentrations. When  $n$  is large (typically  $n \geq 5$ ), the high entropy of mixing can stabilize solid-solution-like phases with relatively simple crystal structures rather than forming the conventionally expected complex intermetallic phases. Thus, while these alloys may be compositionally complex, they are microstructurally simple. Clearly, this concept offers a vast opportunity to explore, discover, and develop fundamentally new classes of alloys for structural and functional applications. Alloying element combinations previously perceived as objectionable due to microstructure instability may now be a possibility, suggesting completely new families of light metal alloys, high strength metals, and high-temperature metals.

To date, high-entropy alloy research seems to emphasize alloys based on the late transition metals such as Fe, Ni, Co and Cu. To the authors' knowledge, there have been no systematic efforts to explore HEAs based primarily on refractory element constituents. Since metallic alloys for high-temperature load-bearing structures and thermal protection remain in high demand for the aerospace industry, there is a clear rationale for exploring HEAs composed of constituents with high melting temperatures. Therefore, this work describes the development and characterization of two obvious compositions of HEAs based on refractory elements. The first alloy was chosen to contain equal concentrations of W, Nb, Mo, and Ta,

\* Corresponding author. UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432, USA. Tel.: +1 937 2551320.

E-mail address: [oleg.senkov@wpafb.af.mil](mailto:oleg.senkov@wpafb.af.mil) (O.N. Senkov).

while the second alloy was created by the addition of an equal atomic percent of V to the same constituents.

## 2. Experimental procedures

W–Nb–Mo–Ta and W–Nb–Mo–Ta–V alloys—referred to as Alloy 1 and Alloy 2, respectively—were prepared at Pittsburgh Materials Technology, Inc. (Jefferson Hills, PA) by vacuum arc melting of equimolar mixtures of the corresponding elements. High purity Ti was used as a getter for residual gases in the high vacuum chamber. W, Mo, and V were in the form of 45.7 mm diameter rods with a purity of 99.7%, 99.0%, and 99.9% (by weight), respectively, while Ta and Nb were in the form of chips and had a purity of 99.0% and 99.99%, respectively. The alloys were prepared in the form of buttons of ~10 mm thick and ~60–70 mm in diameter. To achieve a homogeneous distribution of elements in the alloys, the buttons were remelted four times, flipped for each melt, and had a total time of over 1 h in the liquid state. The buttons had lustrous surfaces indicating no oxidation occurred during vacuum arc melting. The final composition of the alloys, determined by inductively-coupled plasma-optical emission spectroscopy (ICP-OES), is reported in Table 1. It should be noted that the composition of each alloy is close to equiatomic. The microstructure and properties of the alloys were studied in the as-cast condition. The crystal structure was identified with the use of high-energy synchrotron X-ray diffraction (MAR345 Image Plate Detector, Advanced Photon Source, Argonne National Laboratory). The samples for X-ray diffraction were in the form of ~0.75 mm thick plates. The X-ray energy was 105 keV and the beam spot-size was  $0.05 \times 0.05$  mm. The scattering vector ranged from 0.7 to  $20 \text{ \AA}^{-1}$ .

The density of the alloys was measured with an AccuPyc 1330V1.03 pycnometer. The pycnometer cell volume was  $12.2284 \text{ cm}^3$ . The weight of the samples was from 10 to 15 g and was measured with an accuracy of  $\pm 0.0001$  g, while the volume of the samples was determined with an accuracy of  $\pm 0.0001 \text{ cm}^3$  by measuring the free volume of the loaded cell using He gas and ten purges.

Alloy microstructures were analyzed with the use of a scanning electron microscope (SEM) equipped with both backscatter electron (BSE) and energy dispersive spectroscopy (EDS) detectors. Electron probe micro-analysis (EPMA) was conducted using a Cameca SX100 micro-analyzer operating at an accelerating voltage of 15 keV. The effective excitation volume at the sample surface, from which the elemental composition was collected, was ~3  $\mu\text{m}$  in diameter and ~3  $\mu\text{m}$  deep. Vickers microhardness was measured on polished cross-section surfaces using a 136-degree Vickers diamond pyramid under 500 g load applied for 30 s.

## 3. Results and discussions

### 3.1. Crystal structure

X-ray diffraction patterns of the studied W–Nb–Mo–Ta and W–Nb–Mo–Ta–V alloys are reported in Fig. 1a and b, respectively. In these figures, the scattering vector length  $Q$  is plotted versus the scattered X-ray intensity. The inter-planar spacing  $d$  is related to  $Q$  by the relationship

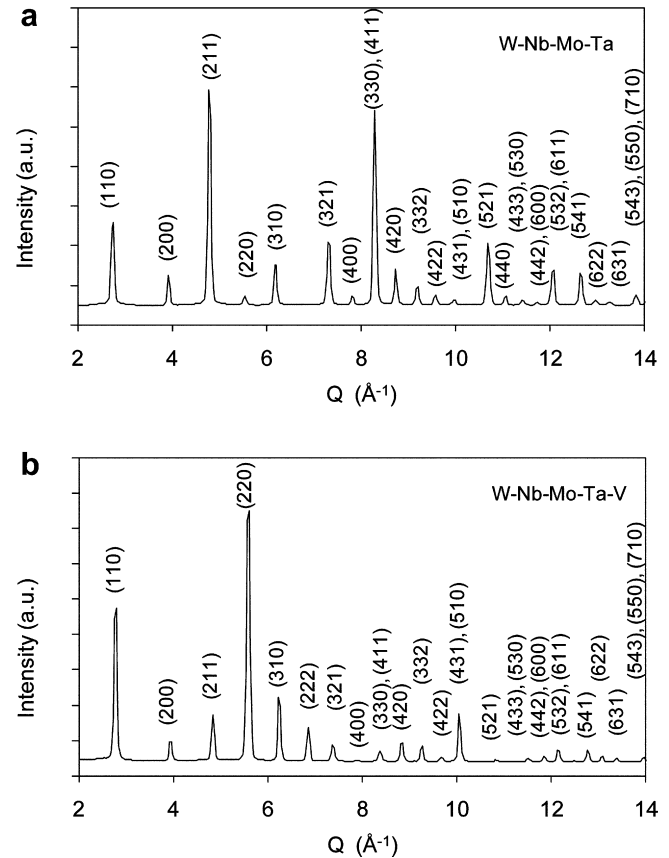


Fig. 1. X-ray diffraction patterns of the (a) W–Nb–Mo–Ta and (b) W–Nb–Mo–Ta–V alloys. All peaks in the patterns belong to the same BCC crystal lattice and their indexes are shown.

$$d = 2\pi/Q = \lambda/(2 \sin \theta) \quad (1)$$

where  $\lambda$  is the wavelength of the incident x-rays and  $\theta$  is half the scattering angle. All peaks on these X-ray patterns have been identified with appropriate indices and are congruent with a single BCC phase (Pearson symbol cI2). The large number of the X-ray peaks provided high accuracy in determining the lattice parameters, which were  $a_1 = 3.2134(3) \text{ \AA}$  for W–Nb–Mo–Ta (Alloy 1) and  $a_2 = 3.1832(2) \text{ \AA}$  for W–Nb–Mo–Ta–V (Alloy 2). The different relative intensities of the same peaks in the two alloys were most likely due to apparent texture effects caused by the small number of grains within the X-ray excited volume.

Formation of the BCC crystal structure in the two developmental alloys was expected, as all five elements used to produce these alloys have identical BCC crystal lattices. Moreover, these elements also have similar atomic radii (see Table 2) and similar valence numbers (6 for V, Nb and Ta and 5 for W and Mo) [5]. Following the Hume-Rothery rules, solid solutions are formed in binary systems of these metals over a whole range of the concentrations (although a TaV<sub>2</sub> phase forms in the Ta–V system below 1310 °C) [6]. The lattice parameters of pure elements, taken from Ref. [7], are given in Table 2. Using the rule-of-mixtures approach, a ‘theoretical’ crystal lattice parameter,  $a_{\text{mix}}$ , of an alloy can be estimated:

$$a_{\text{mix}} = \sum c_i a_i \quad (2)$$

where  $c_i$  and  $a_i$  are the atomic fraction and the lattice parameter of element  $i$ . The calculated  $a_{\text{mix}}$  for the studied alloys are given in Table 2. The  $a$  values, determined by X-ray diffraction are also given in this table. Within experimental error, the lattice parameter of

Table 1

Chemical composition (in wt./at.%) of two refractory alloys produced by vacuum arc melting.

Alloy ID/element	W	Nb	Mo	Ta	V
Alloy 1	36.0/27.3	15.2/22.7	17.8/25.6	31.7/24.4	0.0/0.0
Alloy 2	33.0/21.1	16.2/20.6	17.6/21.7	23.9/15.6	9.08/21.0

Download English Version:

<https://daneshyari.com/en/article/1601240>

Download Persian Version:

<https://daneshyari.com/article/1601240>

[Daneshyari.com](https://daneshyari.com)