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Materials Science & Engineering A



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

Mechanical properties of low-density, refractory multi-principal element alloys of the Cr–Nb–Ti–V–Zr system

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ARTICLE INFO

Article history: Received 21 September 2012 Received in revised form 20 November 2012 Accepted 6 December 2012 Available online 13 December 2012

Keywords: Refractory alloys Crystal structure Microstructure Mechanical properties

ABSTRACT

Room temperature and elevated temperature mechanical properties of four multi-principal element alloys, NbTiVZr, NbTiV₂Zr, CrNbTiZr and CrNbTiVZr, are reported. The alloys were prepared by vacuum arc melting followed by hot isostatic pressing and homogenization. Disordered BCC solid solution phases are the major phases in these alloys. The Cr-containing alloys additionally contain an ordered FCC Laves phase. The NbTiVZr and NbTiV₂Zr alloys showed good compressive ductility at all studied temperatures while the Cr-containing alloys showed brittle-to-ductile transition occurring somewhere between 298 and 873 K. Strong work hardening was observed in the NbTiVZr and NbTiV₂Zr alloys during deformation at room temperature. The alloys had yield strengths of 1105 MPa and 918 MPa, respectively, and their strength continuously increased, exceeding 2000 MPa after \sim 40% compression strain. The CrNbTiZr and CrNbTiVZr alloys showed high yield strength (1260 MPa and 1298 MPa, respectively) but low ductility (6% and 3% compression strain) at room temperature. Strain softening and steady state flow were typical during compression deformation of these alloys at temperatures above 873 K. In these conditions, the alloys survived 50% compression strain without fracture and their yield strength continuously decreased with an increase in temperature. During deformation at 1273 K, the NbTiVZr, NbTiV₂Zr, CrNbTiZr, and CrNbTiVZr alloys showed yield strengths of 58 MPa, 72 MPa, 115 MPa and 259 MPa, respectively.

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1. Introduction

Aerospace and aircraft industries demand new metallic alloys for high-temperature load-bearing structures and thermal protection systems. These alloys should have a balance of high-temperature properties, including reduced density, superior to existing Ni-base superalloys or refractory alloys. Recently a high entropy alloying approach proposed by Yeh et al. [1–3] has been applied to produce several new refractory alloys with promising combinations of room temperature and elevated temperature mechanical properties and oxidation resistance [4–9]. These are MoNbTaW, MoNbTaVW, [4,5], HfNbTaTiZr [6,7], and CrMo_{0.5}NbTa_{0.5}TiZr [8,9]. The first three alloys are single-phase with a BCC crystal structure, probably due to high entropy of mixing and similar atomic radii of the alloying elements. The last alloy, which includes the addition of Cr, forms an additional minor Laves phase with the FCC crystal structure [8]. The design strategies used to predict stable high entropy alloys suggest [10,11] that this is the result of adding an element, Cr, which has a much smaller atomic radius than the other alloying elements.

0921-5093/\$-see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.msea.2012.12.018 These refractory alloys have rather high densities, in the range from 8.2 g/cm³ for the CrMo_{0.5}NbTa_{0.5}TiZr alloy to 13.8 g/cm³ for the MoNbTaW alloy.

New refractory high entropy alloys (HEAs) with densities below 7.0 g/cm³ have recently been produced by alloying Nb $(\rho_{\rm Nb}=8.57 \text{ g/cm}^3)$ with four low density refractory elements, V $(\rho_V = 6.11 \text{ g/cm}^3)$, Zr $(\rho_{Zr} = 6.51 \text{ g/cm}^3)$, Cr $(\rho_{Cr} = 7.14 \text{ g/cm}^3)$, and Ti ($\rho_{Ti}=4.51 \text{ g/cm}^3$) at near equiatomic concentrations. The microstructures and phase compositions of these alloys have been reported elsewhere [12]. These are NbTiVZr, NbTiV₂Zr, CrNbTiZr, and CrNbTiVZr alloys, which have the densities of 6.52 g/cm³, 6.34 g/cm³, 6.67 g/cm³, and 6.57 g/cm³, respectively. The NbTiVZr alloy consists of a disordered body centered cubic (BCC) matrix (the volume fraction is \sim 95%) and sub-micron sized particles of a second phase precipitated along dislocations and subgrain boundaries. The NbTiV₂Zr alloy consists of a mixture of three disordered BCC phases, with volume fractions of \sim 52%, 28%, and 20%, respectively. The CrNbTiZr and CrNbTiVZr alloys consist of a disordered BCC phase and ordered FCC Laves phase, with the volume fraction of the latter of 35% and 61%, respectively.

The aim of the present work was to study the deformation behavior of these low density refractory alloys in a wide temperature range and compare the properties of these alloys with the properties of other high entropy alloys and Ni superalloys.

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2. Experimental procedures

The Cr–Nb–Ti–V–Zr alloys were prepared by vacuum arc melting of the nominal mixtures of the corresponding elements, hot isostatically pressed (HIPd) at 1473 K and 207 MPa for 2 h and then annealed at 1473 K for 24 h in a high-purity argon. The processing details are reported in [12]. The alloy compositions are given in Table 1.

Rectangular cuboid specimens for compression testing were electric-discharge machined from the homogenized alloys. The specimen compression axis was perpendicular to the alloy surface, which was in contact with the copper plate during arc melting. The specimen surfaces were mechanically polished while maintaining parallel compression faces. During high temperature testing these faces were lubricated with boron nitride. The specimen's dimensions were \sim 4.7 mm \times 4.7 mm \times 7.7 mm. Compression tests were conducted at 298 K, 873 K, 1073 K and 1273 K in a computer-controlled Instron (Instron, Norwood, MA) mechanical testing machine outfitted with a Brew vacuum furnace and silicon carbide dies. Prior to each test, the furnace chamber was evacuated to $\sim 10^{-4} \text{ N/m}^2$. The test specimen was then heated to the test temperature at a heating rate of \sim 20 K/min, soaked at the test temperature for 15 min under 5 N controlled load, and then compressed to a 50% height reduction or to fracture, whichever happened first. A constant ramp speed that

Table 1 Chemical compositions (in at%) and density, ρ of the alloys studied in this work.

Alloy	Cr	Nb	Ti	V	Zr	$\rho~(\rm g/cm^3)$
NbTiVZr NbTiV ₂ Zr CrNbTiZr CrNbTiVZr	- 24.6 20.2	28.3 22.6 26.7 20.0	24.5 19.4 23.9 19.9	23.0 37.2 - 19.6	24.2 20.8 24.8 20.3	6.52 6.34 6.67 6.57

corresponded to an initial strain rate of 10^{-3} s⁻¹ was used. Room temperature tests were conducted at the same strain rate conditions in air, using a servo-hydraulic MTS testing machine, and thin Teflon foil was used between the compression faces and silicon carbide dies to reduce friction. The deformation of all specimens was video-recorded and image correlation software Vic-Gauge (Correlated Solutions, Inc.) was used to measure strains.

Vickers microhardness was measured on the polished crosssection surfaces of non-deformed and deformed specimens using a 136° Vickers diamond pyramid under 500 g load applied for 20 s. The microstructure was analyzed with the use of a scanning electron microscope (SEM) Quanta 600F (FEI, North America NanoPort, Hillsboro, Oregon, USA) equipped with a backscatter electron (BSE), energy-dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD) detectors.

3. Results

3.1. Compression properties

The engineering stress vs. engineering strain curves of the studied alloys at T=298 K, 873 K, 1073 K and 1273 K are given in Fig. 1 and the typical properties of the alloys are given in Table 2. During compression testing at room temperature (RT, 298 K), the NbTiVZr and NbTiV₂Zr alloys showed plastic yielding at $\sigma_{0.2} = 1105$ MPa and 918 MPa, respectively, after which a continuous increase in their strengths occurred with an increase in the compression strain (Fig. 1a and Fig. 1b). For example, the strengths of the NbTiVZr and NbTiV₂Zr alloys increased to $\sigma_{20}=1732$ MPa and 1635 MPa, respectively, after compression by 20% at RT. No macroscopic fracture was observed in these alloys after 50% compression strain. The RT compression behavior of CrNbTiZr and CrNbTiVZr alloys (Fig. 1c and Fig. 1d) was different from that described above. The samples showed plastic



Fig. 1. Engineering stress vs. engineering strain curves of (a) NbTiVZr, (b) NbTiV₂Zr, (c) CrNbTiZr and (d) CrNbTiVZr alloy samples deformed by compression at T=298 K, 873 K, 1073 K and 1273 K. The strain rate is \dot{e} = 10⁻³ s⁻¹.

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