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Effect of aluminum on the microstructure and properties of two refractory high-entropy alloys

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Abstract

The microstructure, phase composition and mechanical properties of the $AlMo_{0.5}NbTa_{0.5}TiZr$ and $Al_{0.4}Hf_{0.6}NbTaTiZr$ high-entropy alloys are reported. The $AlMo_{0.5}NbTa_{0.5}TiZr$ alloy consists of two body-centered cubic (bcc) phases with very close lattice parameters, $a_1 = 326.8$ pm and $a_2 = 332.4$ pm. One phase was enriched with Mo, Nb and Ta and another phase was enriched with Al and Zr. The phases formed nano-lamellae modulated structure inside equiaxed grains. The alloy had a density of $\rho = 7.40$ g cm^{-3} and Vickers hardness $H_v = 5.8$ GPa. Its yield strength was 2000 MPa at 298 K and 745 MPa at 1273 K. The $Al_{0.4}Hf_{0.6}NbTaTiZr$ had a single-phase bcc structure, with the lattice parameter $a = 336.7$ pm. This alloy had a density $\rho = 9.05$ g cm^{-3}, Vickers microhardness $H_v = 4.9$ GPa, and its yield strength at 298 K and 1273 K was 1841 MPa and 298 MPa, respectively. The properties of these Al-containing alloys were compared with the properties of the parent $CrMo_{0.5}NbTa_{0.5}TiZr$ and HfNbTaTiZr alloys and the beneficial effects from the Al additions on the microstructure and properties were outlined. A thermodynamic calculation of the solidification and equilibrium phase diagrams was conducted for these alloys and the calculated results were compared with the experimental data.

Keywords: Refractory alloys; Phase composition; Crystal structure; Microstructure; Mechanical properties

1. Introduction

Multi-principal-element alloys, also known as high-entropy alloys (HEAs) because of their high entropy of mixing of alloying elements, have recently come to the attention of the scientific community due to some interesting and unexpected microstructures and properties [1–3]. The metallurgical strategy is to stabilize the disordered phase relative to impinging ordered intermetallics by maximizing the configurational entropy. One appealing aspect of this approach is that the reduction of the Gibbs free energy, by the entropy of formation, increases with an increase in temperature. Such an approach could be very useful in developing new high-temperature structural alloys, in an alloy composition space that has not been previously explored. While the HEA approach has produced some stable solid solution body-centered-cubic (bcc) and face-centered-cubic (fcc) alloys [1,4–9], recent studies have shown that intermetallic phases can form in HEAs. This often is associated with alloying with elements with large differences in atomic radius and large negative enthalpies of mixing [4,10,11].

Several high-entropy refractory alloys with promising combinations of room temperature and elevated temperature mechanical properties and oxidation resistance have recently been reported. These are MoNbTaW, MoNbTaVW [6,7], HfNbTaTiZr [8,9], $CrMo_{0.5}NbTa_{0.5}TiZr$ [12,13] and Cr_xNbTiV_yZr [14,15]. The high entropy of mixing and similar atomic radii (e.g. ~146 pm) of the alloying elements resulted in the formation of disordered bcc crystal structures in the alloys without Cr. However, the alloys

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with Cr, the atomic radius ($r_{Cr} = 128$ pm) of which is much smaller than the atomic radii of other elements, additionally contained a cubic Laves phase, resulting in a considerable decrease in ductility at temperatures below 800 °C [12,14,15].

In the present work, the compositions of two earlier reported refractory alloys, HfNbTaTiZr and $CrMo_{0.5}NbTa_{0.5}TiZr$, have been modified to produce the $Al_{0.4}Hf_{0.6}NbTaTiZr$ and $AlMo_{0.5}NbTa_{0.5}TiZr$ alloys. Here we study the effect of alloying with Al on the microstructure, composition and mechanical properties of these new refractory HEAs. Aluminum forms a number of binary and ternary intermetallic phases with bcc refractory elements. At the same time, the atomic radius of Al ($r_{Al} = 143$ pm) is very similar to the atomic radii of the refractory elements ($\langle r \rangle = 146$ pm), excluding Cr ($r_{Cr} = 128$ pm), which may affect the formation energy of the intermetallic phases in the HEAs. Furthermore, it has been well documented that additions of Al stabilize the bcc crystal structure in the $Al_xCoCrCuFeNi$ [1] and $Al_xCoCrFeMnNi$ [16] HEAs and gradually transform their crystal structure from fcc to bcc. It is also expected that alloying with Al will considerably reduce the density of the refractory HEAs.

2. Experimental procedures

The $AlMo_{0.5}NbTa_{0.5}TiZr$ and $Al_{0.4}Hf_{0.6}NbTaTiZr$ HEAs were prepared by vacuum arc melting of nominal mixtures of the corresponding elements. Titanium, zirconium and hafnium were in the form of 3.2 mm diameter slugs with purities of 99.98%, 99.95% and 99.9%, respectively. Niobium and tantalum were in the form of 1.0 and 2.0 mm wires, and their purities were 99.95% and 99.9%, respectively. Molybdenum was in the form of 1 mm thick sheet with a purity of 99.99%. Aluminum was in the form of 50–100 mm^3 buttons with a purity of 99.999%. Arc melting was conducted on a water-cooled copper plate. High-purity molten titanium was used as a getter for residual oxygen, nitrogen and hydrogen. To achieve a homogeneous distribution of elements in the alloys, each alloy was re-melted five times, was flipped for each melt, and was in a liquid state for ~5 min during each melting event. The prepared specimens were ~12 mm high, 30 mm wide and 100 mm long and had shiny surfaces, indicating minimal oxidation during vacuum arc melting. The actual alloy compositions, determined with inductively coupled plasma-optical emission spectroscopy, are given in Table 1. The $AlMo_{0.5}NbTa_{0.5}TiZr$ alloy was hot isostatically pressed (HIPed) at 1673 K and 207 MPa for 2 h and then annealed at 1673 K for 24 h in continuously flowing high-purity argon. The $Al_{0.4}Hf_{0.6}NbTaTiZr$ alloy was HIPed at 1473 K and 207 MPa for 2 h and then annealed at 1473 K for 24 h in continuously flowing high-purity argon. During HIP and annealing, the samples were covered with Ta foil to minimize oxidation. The cooling rate after annealing in both cases was 10 K min^{-1}. The crystal structure was identified with the use of an X-ray diffractometer, Cu Kα radiation and a 2Θ scattering range of 10–140°. The experimental error in the measurements of the lattice parameters was ±0.5 pm.

Alloy densities were measured with an AccuPyc 1330 V1.03 helium pycnometer. Vickers microhardness was measured on polished cross-section surfaces using a 136° Vickers diamond pyramid under 500 g load applied for 20 s. The microstructure was analyzed with a scanning electron microscope (SEM) Quanta 600F (FEI, North America NanoPort, Hillsboro, Oregon, USA) equipped with backscatter electron (BSE), energy-dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction detectors. The experimental error in the measurements of the chemical composition was ±0.3 at.%. The average grain/particle size and the volume fractions of the phases were determined in accordance with ASTM E112 and ASTM E562 standards, using the image analysis software Fovea Pro 4.0 by Reindeer Graphics, Inc.

Compression tests of rectangular specimens with the dimensions of ~4.7 mm × 4.7 mm × 7.7 mm were conducted at 298 K, 873 K, 1073 K, 1273 K and 1473 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 ~10^{-4} N m^{-2}. The test specimen was then heated to the test temperature at a heating rate of ~20 K min^{-1}, 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 corresponded to an initial strain rate of 10^{-3} s^{-1} was used. Room temperature tests were conducted at the same loading conditions but in air. The deformation of all specimens was video-recorded and image correlation software Vic-Gauge (Correlated Solutions, Inc.) was used to measure strains.

3. Results

3.1. Crystal structure, density and microhardness

X-ray diffraction patterns of the annealed cast alloys are shown in Fig. 1. Two phases, both with the bcc crystal structures, are identified in the $AlMo_{0.5}NbTa_{0.5}TiZr$ alloy

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

Alloy	Al	Hf	Mo	Nb	Ta	Ti	Zr
$AlMo_{0.5}NbTa_{0.5}TiZr$	20.4	–	10.5	22.4	10.1	17.8	18.8
$Al_{0.4}Hf_{0.6}NbTaTiZr$	7.9	12.8	–	23.0	16.8	18.9	20.6