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Compositional variation effects on the microstructure and properties of a refractory high-entropy superalloy $AlMo_{0.5}NbTa_{0.5}TiZr$

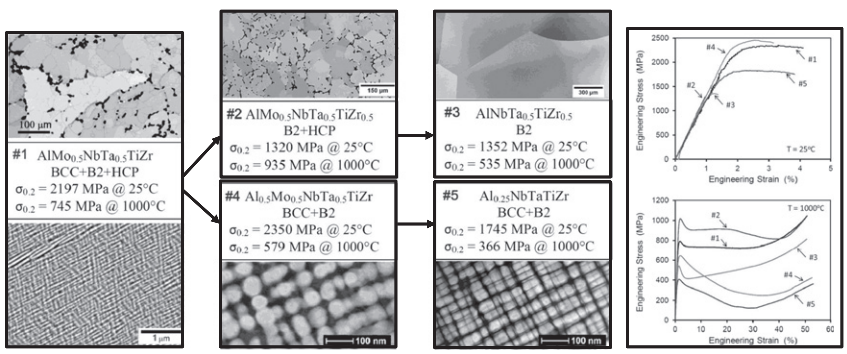
O.N. Senkov [a,*], J.K. Jensen [b], A.L. Pilchak [a], D.B. Miracle [a], H.L. Fraser [b]

[a] *Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433, United States*
[b] *Center for the Accelerated Maturation of Materials, Department of Materials Science and Engineering, The Ohio State University, 1305 Kinnear Rd., Columbus, OH 43212, United States*

HIGHLIGHTS

- A BCC-based analog to superalloy microstructures is sought with a ductile BCC matrix and coherent ordered B2 nano-precipitates.
- $AlMo_{0.5}NbTa_{0.5}TiZr$ has a brittle B2 matrix, coherent BCC nano-precipitates and coarse HCP particles at grain boundaries.
- Sequential composition changes removed BCC and HCP phases in some alloys but the B2 phase remained continuous.
- Deformation inverted the microstructure into a continuous BCC matrix and discrete B2 precipitates.

GRAPHICAL ABSTRACT



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ABSTRACT

An $AlMo_{0.5}NbTa_{0.5}TiZr$ baseline alloy was shown earlier to have good high temperature strength but poor ductility below 600 °C due to coarse intermetallic grain boundary particles and a continuous ordered B2 matrix phase. Systematic composition changes intended to remove the deleterious microstructural features and to improve mechanical properties were explored in the present work. The baseline alloy and the new alloys studied here, $AlMo_{0.5}NbTa_{0.5}TiZr_{0.5}$, $AlNbTa_{0.5}TiZr_{0.5}$, $Al_{0.5}Mo_{0.5}NbTa_{0.5}TiZr$ and $Al_{0.25}NbTaTiZr$, all had an ordered B2 matrix crystal structure. Additionally, coherent BCC nanoscale precipitates were present at a high volume fraction inside the B2 matrix grains in $AlMo_{0.5}NbTa_{0.5}TiZr$, $Al_{0.5}Mo_{0.5}NbTa_{0.5}TiZr$ and $Al_{0.25}NbTaTiZr$, and/or coarse, grain-boundary particles existed in $AlMo_{0.5}NbTa_{0.5}TiZr$ and $AlMo_{0.5}NbTa_{0.5}TiZr_{0.5}$. The mechanical properties were assessed with microhardness and compression testing at 25 °C and 1000 °C. $Al_{0.5}Mo_{0.5}NbTa_{0.5}TiZr$ showed the highest hardness (Hv = 6.4 GPa) and strength ($\sigma_{0.2}$ = 2350 MPa) at 25 °C and modest strength ($\sigma_{0.2}$ = 579 MPa) at 1000 °C. $AlMo_{0.5}NbTa_{0.5}TiZr_{0.5}$ had the highest strength ($\sigma_{0.2}$ = 935 MPa) at 1000 °C, but was brittle at 25 °C. High-temperature deformation produced a desirable microstructure in $Al_{0.5}Mo_{0.5}NbTa_{0.5}TiZr$ and $Al_{0.25}NbTaTiZr$ alloys consisting of a continuous BCC phase and discontinuous B2 nano-precipitates. The relationships between the composition, microstructure, and properties were identified and discussed.

1. Introduction

High entropy alloys (HEAs) are one of the most recent developments in material science, which open a vast, unexplored area of alloy compositions and the potential to influence solid solution phase stability

* Corresponding author.
E-mail address: oleg.senkov.ctr@us.af.mil (O.N. Senkov).

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through control of configurational entropy [1–3]. Using the HEA concept, several refractory high entropy alloys (RHEAs) have recently been reported as promising alternatives to Ni-based superalloys [4–11]. RHEAs with a low density and high strength are among the most promising recent achievements in this field [10–17]. The reported densities of these new RHEAs are in the range of 5.9 to 8.4 g/cm^3 and their specific strengths are often superior to Ni-based superalloys [11–14]. Some of these alloys consist of very fine, nano-scale mixtures of disordered BCC and ordered B2 phases with similar lattice parameters [11,18,19], which may be responsible for their high strengths. Among these RHEAs, $AlMo_{0.5}NbTa_{0.5}TiZr$ has impressive yield strength of 745 MPa and good compressive ductility (>50% height reduction) at 1000 °C. Detailed analysis of the microstructure and crystal structure of this alloy using advanced transmission electron microscopy (TEM) and atom probe tomography (APT) techniques revealed a nano-scale, modulated mixture of an ordered B2 matrix and coherent, cuboidal precipitates of a disordered BCC phase [18,19]. Based on these microstructural features, which are typical to superalloys, complex composition and the high strength at temperatures from 25 °C to 1200 °C, this two-phase alloy was named a "refractory high entropy superalloy" [19].

Despite showing exceptionally good high-temperature properties, the $AlMo_{0.5}NbTa_{0.5}TiZr$ superalloy has very limited ductility at temperatures ≤600 °C, which has been explained by the presence of brittle, coarse intermetallic precipitates at grain boundaries [19,20]. It was found that these grain-boundary (GB) precipitates have a hexagonal (P63/mcm) crystal structure and are predominantly composed of Al and Zr with an overall composition (in at.%) of ~$Al_{37}Mo_2Nb_8Ta_2Ti_9Zr_{42}$ [20]. Based on model γ/γ′ superalloys, an 'ideal' microstructure of refractory superalloys would consist of two nanometer-scale, ordered/disordered coherent phases, one of which is a disordered BCC matrix and another is ordered B2 precipitates, while the deleterious hexagonal intermetallic grain-boundary phase is completely removed. In some cases, heat treatment and/or hot working processing are used to remove intermetallic particles from grain boundaries, but annealing at 1000–1400 °C and water quenching of $AlMo_{0.5}NbTa_{0.5}TiZr$ revealed this phase to be stable over a large range of temperatures [20].

In this work, an attempt has been made to remove the coarse, GB intermetallic phase, while maintaining the equiaxed grain microstructure comprised of the nano-scale interpenetrating phases, by adjusting the composition of the base $AlMo_{0.5}NbTa_{0.5}TiZr$ superalloy. Based on the large number of intermetallic phases that form in the Al-Zr binary system and the large electronegativity difference compared to other constituent elements in the HEA composition, the effects of reducing Al and Zr on the HEA microstructure were first investigated and characterized. In addition, the effect of removing Mo on the alloy phase composition, strength and ductility was also explored.

2. Experimental procedures

HEA ingots with the compositions $AlMo_{0.5}NbTa_{0.5}TiZr$ (base composition, alloy #1), $AlMo_{0.5}NbTa_{0.5}TiZr_{0.5}$ (reduction of Zr by ½ molar ratio, alloy #2), $AlNbTa_{0.5}TiZr_{0.5}$ (reduction of Zr by ½ molar ratio and removal of Mo, alloy #3), $Al_{0.5}Mo_{0.5}NbTa_{0.5}TiZr$ (reduction of Al by ½ molar ratio, alloy #4), and $Al_{0.25}NbTaTiZr$ (reduction of Al by ¾ molar ratio and replacement of Mo with Ta, alloy #5) were prepared by vacuum arc melting in an inert gas atmosphere. The samples were then hot isostatic pressed (HIP'd) for 2 h at 1400 °C and 207 MPa to remove any porosity and annealed in a flowing argon furnace at 1400 °C for 6 h followed by a furnace cool to room temperature with the initial cooling rate of 20 °C/min.

A Bruker D2 Phaser X-ray diffractometer, at Cu Kα radiation, was used to identify the crystal structure of main phases in the alloys. The microstructure was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. SEM was equipped with backscattered electron (BSE) and electron backscatter diffraction (EBSD) detectors. BSE and EBSD image processing and analysis was performed using the Materials Image Processing and Automated Reconstruction (MIPAR) software package [21].

Samples for TEM analysis were extracted at site specific locations from the bulk sample using an FEI Helios NanoLab 600 Dual-Beam focused ion beam (DB-FIB) instrument. The FIB lift-out and thinning procedures are described elsewhere [18]. The thinned FIB lamellae were characterized using conventional bright-field (BF) and dark-field (DF) TEM imaging in an FEI CM200. Scanning transmission electron microscopy (STEM) high-angle annular dark-field (HAADF) micrographs were taken with an FEI Probe-Corrected Titan 80-300 STEM operating

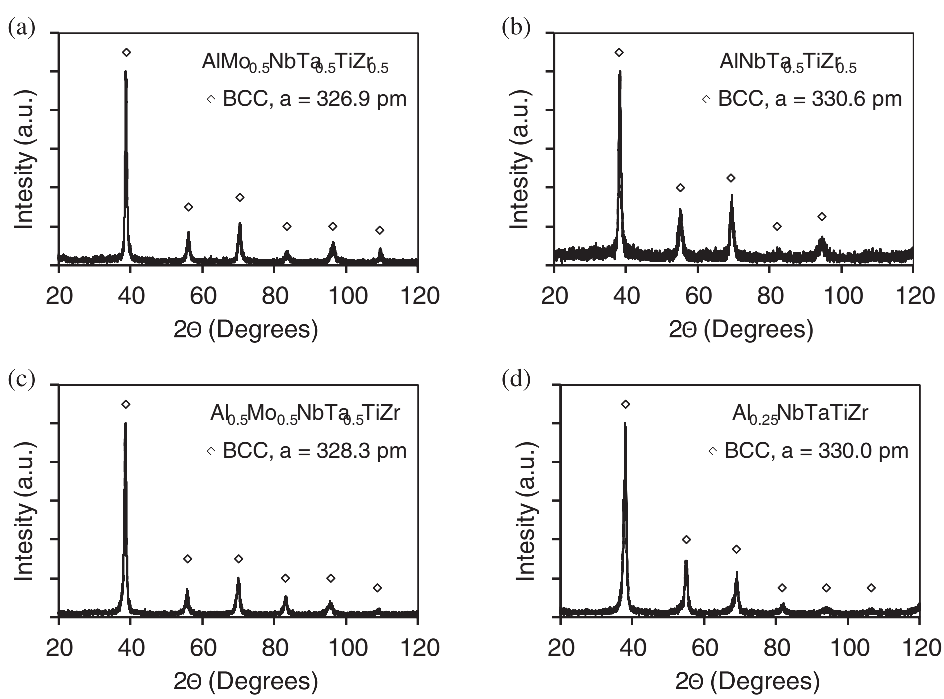

Fig. 1. X-ray diffraction patterns of (a) $AlMo_{0.5}NbTa_{0.5}TiZr_{0.5}$, (b) $AlNbTa_{0.5}TiZr_{0.5}$, (c) $Al_{0.5}Mo_{0.5}NbTa_{0.5}TiZr$, and (d) $Al_{0.25}NbTaTiZr$.