Heat treatments' effects on the microstructure and mechanical properties of an equiatomic Al-Cr-Fe-Mn-Ni high entropy alloy

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ABSTRACT

The microstructure and properties of an equiatomic AlCrFeMnNi high entropy alloys (HEA) in the as-cast and heat treated conditions are presented. Using a variety of advanced characterization methods, it is shown that the AlCrFeMnNi solidified dendritically with Cr, Fe and Mn rich dendrite cores (DC) and Al and Ni rich interdendritic (ID) regions. Upon cooling, during solidification, AlCrFeMnNi alloy underwent spinodal decomposition. The DC area decomposed to a mixture of B2 and FCC matrix with nano cuboid BCC precipitates, while the ID region decomposed to a BCC matrix with B2 precipitates. The combination of relatively soft DC surrounded by hard ID regions resulted in high compressive strength combined with large compressive ductility and can be regarded as a "macro" composite material. The cracks initiate and propagate in the harder and more brittle ID regions. Heat treatments increased the amount of the FCC phase and enhanced microstructural coarsening. The undesirable σ phase was not detected after any heat treatment.

1. Introduction

High Entropy Alloys (HEA), also known as multi-principal element alloys or compositionally complex concentrated alloys, frequently comprise of simple solid solutions (FCC, BCC and HCP) instead of complex intermetallic compounds and, in some cases, yield unique combinations of high strengths [1–4], superior resistance to thermal softening [4–6], outstanding resistance to wear [7–9] and corrosion [10,11]. These alloys have generated considerable interest in the materials science community due to their potential industrial applications as tools, molds, dies as well as mechanical and furnace parts [12–14]. Many of the HEAs of interest are easily produced using conventional casting equipment, i.e. arc melting and induction melting, making mass production a possibility [13]. Therefore, correlations between the processing parameters and mechanical properties are essential for future structural applications involving HEAs [15]. In this regard, numerous studies were performed on the influence of thermo-mechanical processes (for example: heavily cold rolling followed by annealing [16,17], friction stir-processing [18] and different manufacturing processes such as laser fabrication [19]) on the mechanical properties and the microstructure of HEAs [20–22]. One of the advantages of HEAs is the wide range of properties adjustable via variations in manufacturing methods [23–26] and/or composition

[27].

These alloys might provide unusual combinations of strength and ductility which can be foreseen if the ratio between the FCC/BCC phases (of which these alloys are comprised) is controlled. In general, the hardness of the FCC phase is between 1.0 and 2.0 GPa [3]. HEAs having only the FCC phase (for example: CoCrCuFeNi) exhibit ductilities between 20% and 60%, and usually exhibit significant work hardening [28]. One way to improve the strength of these HEAs is by adding Al to the alloys. It was found, that additions of Al to CoCrCuFeNi results in hardness increase from 1.33 to 6.55 GPa [3], due to the formation of the harder BCC phase. With sufficient Al, the precipitation of nano-sized B2 precipitates also leads to increased hardness values. However, these alloys become more brittle and microcracks at the corners of microhardness indents are observed in some alloys [3]. Microstructure of alloys with relatively high Al contents (x > 1) composed of a BCC matrix with B2 precipitates, with hardness values varying typically between 5.00 and 6.00 GPa, while the ductility decreases to less than 5% [28]. Similar results were obtained in $Al_xCoCrFeNi$ [29,30] alloys (i.e. without Cu). The phase content of these alloys changes as a function of Al concentration and it can be summarized as follows. First, when x is less than 0.3 the alloy is 100% FCC. As the value of x is increased past 0.3, a BCC phase is observed. If the Al concentration is increased above 0.9, the alloy consists of the

BCC phase only. The hardness of these alloys also changes accordingly from around 1.0 GPa to above 5.0 GPa.

It was reported that equiatomic CoCrFeMnNi HEA possesses single FCC solid solution which solidifies dendritically [12], exhibiting relatively low strength and large tensile strain [31,32]. In current research, it was decided to replace the Co in the CoCrFeMnNi by Al. There are several reasons for that: first, Co does not play a central role in promoting a BCC matrix or B2 precipitates [33] while Al, as it was mentioned earlier, is known to transform the soft FCC phase to the harder BCC phase in other HEA systems [29,34–36]. Second, maintaining Cr in the alloy was considered desirable since Cr is known as a BCC stabilizer and for its impact on prompting passivity and improving oxidation resistance. For example adding 6 at% Cr to $Fe_{30}Ni_{20}Mn_{35}Al_{15}$ (at%) alloy induced the formation of protective oxide scales on the surface [37,38] and reduced susceptibility to H embrittlement [39]. Moreover, Cr lowers the yield strength and, therefore, contributes to the improved ductility, possibly by easing dislocation cross-slip in the deformed FCC phase where most of the Cr resides [37,38].

Following the logic of Al addition presented earlier, AlCrFeMnNi HEA seemed promising with regard to its potentially-desirable mechanical properties. Thus, the goals of the present work were to characterize the cast structure and to study the influence of different heat treatments on the microstructure and mechanical properties of the equiatomic AlCrFeMnNi alloy and to understand the impact of Co replacement by Al on the mechanical properties of the AlCrFeMnNi alloy.

2. Experimental procedures

2.1. Arc melting

A nominally equiatomic AlCrFeMnNi alloy was prepared by non-consumable electrode arc melting under a Ti-gettered, high-purity argon atmosphere on a water-cooled copper hearth. Approximately 50 g of raw materials, with purities higher than 99.5%, were melted for ~30 s at least 5 times to ensure that all raw materials were well mixed in liquid prior to solidification. The buttons were flipped over between each melting cycle in order to improve chemical homogeneity. The nominal and actual compositions of the AlCrFeMnNi alloys are summarized in Table 1. The actual composition was checked using EDS in the SEM in at least 25 different locations and all fell within the measured compositions presented in Table 1. The dimensions of the button after melting were ~37 mm diameter and maximum height of ~13 mm. After arc melting, the buttons were cross-sectioned into 4 mm-wide strips. The middle of the 4 mm strips was sliced into rectangles with $4{\times}4$ mm^2 cross-section and a height of 8–13 mm. Then, the height of the rectangles was abraded from both sides to 6 mm as this was the desired length for compression tests. The rest of the specimens were used for microstructure and microhardness analyses.

The metallographic specimens were mounted in phenolic, abraded on SiC papers up to 4000 grit and then polished with the final polish on a Buehler Vibromet using 0.05 μm colloidal silica for 16–20 h. The colloidal silica is a slightly alkaline solution in these HE alloys. Therefore, no additional etchant was applied prior to examination by

Table 1
Nominal and measured compositions (in at%) of the HEA used in this investigation.

Element	AlCrFeMnNi alloy	
	Nominal	Measured
Al	20	19.3
Cr	20	20.5
Fe	20	21.5
Mn	20	17.9
Ni	20	20.8

Field-Emission Scanning Electron Microscopy (FESEM) equipped with Energy Dispersive Spectroscopy (EDS) capabilities. For the EDS measurements, the raw intensity data were ZAF corrected to an accuracy of ± 0.4 at% for the elements studied [40].

2.2. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) (DTA-NETZSCH Thermal Analysis DSC 404 cell) was conducted on small rectangular pieces that were cut to fit into the small alumina crucibles used for DTA. Each piece weighed between 130 to 170 mg. The scans were made from room temperature to 1500 °C at rates of 20 °C/min. Each specimen was heated and cooled 3 times under essentially identical conditions.

2.3. Heat treatments

Based on the DTA results and taking into account information available on similar HEA systems the following heat treatments were performed: 400, 600, 850, 1040 and 1200 °C for 4 h and water quenched. It turn out that [41] the 1100 °C temperature that was chosen by Kao et al. [36] for homogenization of similar alloy is too low while 1200 °C (used here) is better for homogenization. Following Kao et al. [36] and according to our experience, 4 h is sufficient for creating the majority of microstructural changes in the specimen. Heat treatments were performed in air. Up to 1040 °C the oxidation was minimal. The homogenization at 1200 °C was performed under Ar protective environment.

2.4. X-ray diffraction (XRD) analysis

XRD patterns of polished and unetched samples were recorded on a Rigaku RINT 2100 diffractometer with Cu K_{α} radiation (λ=0.15406 nm). Data were acquired from 20 to 100° 2θ with a step size of 0.02° and step time of 15 s/step.

2.5. Transmission Electron Microscopy (TEM) analysis

For transmission electron microscopy (TEM), slices were cut from the as-cast or heat treated samples and abraded to a thickness of about 150 μm, from which 3 mm diameter disks were drilled out with an abrasive hole saw that utilizes fine SiC particles. Final thinning was performed in a Fischione twin-jet electropolisher using a solution of 10% $HClO_4$ +90% CH_3OH at approximately −30 °C. When necessary, a Gatan Duo-Mill argon ion mill was used to further thin the specimens using 5 kV Ar ions at an angle of 5 ° for 0.5–2 h.

2.6. Compressive tests

For compressive testing, the rectangular specimen dimensions were $4{\times}4$ mm^2 in cross section and 6 mm in height. The long dimension was perpendicular to the bottom of the ingot. The samples were compressed using a strain rate of $5{\times}10^{-3}$ mm/s. At least three different specimens were tested.

3. Results

3.1. Differential thermal analysis (DTA) results

DTA scans for the AlCrFeMnNi alloy are shown in Fig. 1. Three thermal cycles were performed and exhibited essentially identical results. Consequently, only the third cycle data are shown in Fig. 1. For clarity, the derivative curves that were used to determine the inflection points and the corresponding peak temperatures, are not shown here. As can be seen, the cooling curve for the AlCrFeMnNi alloy contains only two exothermic peaks at 1300 and 1345 °C. Lower temperature peaks corresponding to solid-state reactions were not