Journal of Alloys and Compounds 683 (2016) 221–230

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Heat treatment impacts the micro-structure and mechanical properties of AlCoCrFeNi high entropy alloy

A. Munitz [a,*], S. Salhov [a], S. Hayun [b], N. Frage [b]

[a] Nuclear Research Center-Negev, P.O. Box 9001, Beer-Sheva, 841900, Israel
[b] Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel

ARTICLE INFO

Article history:
Received 24 January 2016
Received in revised form
3 May 2016
Accepted 6 May 2016
Available online 10 May 2016

Keywords:
Crack propagation
High entropy alloys
Mechanical properties
Sigma phase
Spinodal decomposition

ABSTRACT

AlCoCrFeNi alloy was prepared by arc melting and examined as-cast and after various heat treatments using XRD, SEM, micro-hardness and compression tests. It was found that the alloy solidified dendritically with an Al- and Ni-rich dendrite core and inter-dendritic regions rich in Co, Cr, and Fe. The dendrite core of the as-cast material presented a relatively soft matrix with nano-sized precipitates, while the inter-dendritic regions consisted of a relatively hard matrix with nano-sized particles larger than those in the dendrite core. Heat treatment did not change the dendritic morphology, however, different phase transformations occurred, especially in the inter-dendritic regions. Heat treatment between 650 and 975 °C caused transformation of the BCC matrix in the inter-dendritic regions to the σ phase, leading to a further increase in hardness. Heat treatment at 1100 °C caused transformation of the σ phase in the inter-dendritic matrix to a BCC structure and softening of the alloy. Heat treatment at 1200 °C caused partial phase dissolving and homogenization, which in turn enabled the alloy to re-enter the miscibility gap and decomposition to a BCC matrix, with B2 precipitation in the dendrite core and inter-dendritic regions. The impact of these changes on morphology and phase composition upon heat treatment in terms of mechanical behavior was discussed.

1. Introduction

High entropy alloys (HEA) have drawn considerable interest from the materials community due to their industrial applications as tools, molds, dies, and mechanical and furnace parts [1–3]. These alloys are easily fabricated by using standard casting equipment, i.e. arc melting and induction melting furnaces, thus making mass production potentially easy [2]. These alloys usually comprise simple solid solutions (FCC, BCC and HCP) laid over more complex inter-metallic compounds, yielding alloys with high strengths [4–7], superior resistance to thermal softening [7–9], and outstanding resistance to wear [10–12] and corrosion [13,14].

One of the most extensively investigated HEA is Al_xCoCrCuFeNi [6,15–19], where x (the atomic ratio in the alloy) ranges from 0 to 3. These alloys exhibit excellent elevated temperature strength and good wear resistance [6]. In general, the hardness of the FCC phase is between 1.0 and 2.0 GPa [6]. Alloys having a sole FCC phase present ductility between 20 and 60%, and usually exhibit significant work hardening [17]. With addition of aluminum ($x = 0$ to 3), the hardness of the alloys increases from 1.33 to 6.55 GPa [6], mainly due to the increased fraction of a strong BCC phase and strengthening of the BCC and FCC phases by the dissolved aluminum atoms. The precipitation of a nano-sized AlNi (B2) phase also leads to increased hardness values. However, these alloys become brittle and micro-cracking at the corners of the micro-hardness imprints was observed [6]. For alloys with relatively high Al content ($x > 1$), the micro-structure is composed of BCC matrix with B2 precipitates, with hardness values typically between 5.00 and 6.00 GPa, while the ductility decreases to less than 5% [17]. Furthermore, Al_xCoCrCuFeNi alloys cannot be used at elevated temperatures due to Cu segregation in the inter-dendritic regions and grain boundaries, a scenario that is undesired as it compromises high temperature strength [2]. To overcome these drawbacks and to increase the softening resistance at high temperatures, Mo has been used instead of Cu, given its high melting point and elastic modulus [20,21]. Ti was added to improve the mechanical properties [22]. In other works, Ti [4,23] or Mn [9,24–26] replaced Cu.

Another manner to improve the high temperature mechanical

* Corresponding author.
E-mail address: munitza@yahoo.com (A. Munitz).

http://dx.doi.org/10.1016/j.jallcom.2016.05.034
0925-8388/

properties of the alloy is by fabrication without Cu, as in the case of $Al_xCoCrFeNi$ [27–34], where x (the atomic ratio in the alloy) ranges from 0 to 2. It was found [33,34] that the micro-structure and hardness of these alloys changed with increasing Al content in the alloy. For low Al concentration ($x < 0.3$), the micro-structure consisted of a soft FCC phase with hardness of about 1.0 GPa. Increasing the Al content between 0.3 and 0.9 caused the precipitation of a BCC phase along with the FCC structure. The fraction of the BCC phase increased with the Al alloy content, while hardness increased monotonically to 4.5 GPa. For Al concentrations above 0.9, only the hard BCC phase was stable, with hardness reaching 5.0 GPa [33,34]. The increased hardness was partly attributed to the spinodal decomposition of the BCC solid solution and the precipitation of NiAl nano-particles [2].

Recently numerous studies were performed on the influence of thermo-mechanical processes such as heavily cold rolling followed by annealing [35,36], friction stir-processing [37], and different manufacture process such as laser fabrication [38] on the mechanical and properties and the microstructure of AlCoCrFeNi system. Molecular dynamic simulation [39] and numerical simulations [40].

To close porosity in as-cast AlCoCrFeNi alloy, Tang et al. [41] performed hot isostatic pressing (HIP) for specimens at 1100 °C for 1 h at a pressure of 207 MPa. Following HIP, the AlCoCrFeNi samples were heated in argon to 1150 °C at 10 °C/min, held at 1150 °C for 50 h, and then cooled to $T = 50$ °C at 10 °C/min. Tensile tests were then performed at 700 °C for the as-cast and homogenized specimens. The ultimate tensile strength was virtually unaffected and was 396 MPa. However, homogenization produced a large increase in ductility from 1.0% in the as-cast condition to around 12% for the homogenized specimens. An interesting concept was introduced by Lu et al. [42], namely eutectic high-entropy alloys (EHEA), in which the micro-structure has an eutectic-like micro-structure composed of alternating soft FCC and hard BCC phases. They designed $AlCoCrFeNi_{2.1}$ (atomic portion) with an as-cast micro-structure comprising a fine lamellar FCC/B2 which showed an unprecedented combination of high tensile ductility and high fracture strength from room temperature up to 600 °C. The as-cast and heat-treated to 600 °C alloy had a σ_{UTS} of 944 and 806 MPa and, tensile elongations of 27 and 34%, respectively.

A striking property of the $Al_xCoCrFeNi$ alloy with $x = 1$ is its high ultimate compression strength, along with high elongation. It was found (unpublished work) that $Al_xCoCrCuFeNi$ ($x = 1$) alloy displayed compressive yield strength and ultimate compression strength of about 1500 and 1750 MPa, respectively, with a compressive elongation of only 4%. The AlCoCrFeNi alloy of equimolar composition with the same compressive yield strength value had an ultimate compressive strength of about 2800 MPa and elongation above 20% [2,4,43]. Accordingly, it would be important to broaden the work of Wang et al. [43] and investigate the impact of different heat treatment on the mechanical properties of the alloy.

The goals of the present work were: i) to impose different heat treatments to the AlCoCrFeNi alloy and analyze their influences on the mechanical properties of the alloy and correlate these with micro-structure and. ii) to understand the impact of Cu extraction from AlCoCrFeNi alloy on the markedly increased compression contraction in AlCoCrFeNi.

2. Experimental procedures

2.1. Arc melting

AlCoCrFeNi (denoted as HE63) alloy with an equi-atomic nominal composition was prepared by non-consumable electrode arc melting under a Ti-gettered, high-purity argon atmosphere on a water-cooled copper hearth. Fifty 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 their liquid state. The casts were turned upside down between each melting to improve chemical homogeneity. The nominal and actual compositions of the AlCoCrFeNi alloys are summarized in Table 1. The actual compositions of the buttons were checked at least at 20 different places and locations and all fell within the measured compositions provided in Table 1. The dimensions of the button after melting were 37 mm diameter and maximum height 11 mm. After arc melting, the casts were cross-sectioned into 4 mm-wide strips. The middle of the 4 mm strips was sliced into rectangles with dimensions of 4×4 mm^2 cross-section and a height of 8–11 mm. Then, the heights of the rectangles were abraded from both sides to 6 mm. The rest of the pieces were used as specimens for micro-structure and micro-hardness measurements.

2.2. Heat treatments

According to our experience with HEA alloy exhibiting formation of an σ phase at intermediate temperatures, BCC to σ transformation occurred at around 650 °C and transformation back to BCC occurred at around 950 °C. As XRD diffractograms until 600 °C were identical to the cast alloy, we, therefore, used the cast results to represent the alloy at temperatures lower than 600 °C. The 850 °C point was chosen as the middle temperature range for the existence of the σ phase [34]. As a residual σ phase still existed at 950 °C, we used 975 °C sample as representing the alloy after the σ was completely dissolved. The 1100 °C sample was chosen following Kao at al [32]. However, our results indicate that at 1100 °C, homogenization was not obtained and as such, we choose 1200 °C as the homogenization temperature. Nevertheless, when the heating was performed in air only, a minimal oxidation layer was observed above 1000 °C. Following Kao et al. [32] and according to our experience, 3 h was sufficient time for creating the majority of changes in the specimen.

2.3. Metallographic specimen preparation, SEM analysis and micro-hardness determination

The metallographic specimens were mounted in phenolic resin, abraded by SiC papers up to 4000 grit and polished on a Buehler Vibromet using 0.05 μm colloidal silica. Whereas etching was not generally needed to observe micro-structure, in the as-cast condition, the specimens were slightly etched with Aqua Regia etchant to expose macro-structure. Micro-structural examination was performed using a high-resolution scanning electron microscope (Micro FA SEM- Quanta 200) equipped with an EDAX energy dispersive spectroscopy (EDS) unit. The raw data were corrected with a ZAF computer program [44] with accuracy of ±0.4 at%. The same specimens were also used for Vickers micro-hardness tests. For micro-hardness measurements of the dendrite core and the inter-dendritic regions, a 100 g load was applied for 15 s [9]. At least five indentations in the same region were conducted and the

Table 1
Nominal and actual compositions (at. %) of the AlCoCrFeNi alloy used in this investigation as measured using EDS analysis from more than 20 different places and locations. The measurement accuracy is ±0.4 at. %.

Element	Al	Co	Cr	Fe	Ni
Nominal	20	20	20	20	20
Actual	20.8	19.8	19.7	20	19