Materials Science & Engineering A 733 (2018) 59–70

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Effect of hot isostatic pressing on the microstructure and mechanical properties of additive manufactured $Al_xCoCrFeNi$ high entropy alloys

Jithin Joseph[a,*], Peter Hodgson[a], Tom Jarvis[b], Xinhua Wu[b], Nicole Stanford[c], Daniel Mark Fabijanic[a]

[a] Institute for Frontier Materials, Deakin University, Waurn Ponds 3216, Australia
[b] Monash Centre for Additive Manufacturing, Monash University, Clayton 3168, Australia
[c] Future Industries Institute, University of South Australia, Mawson Lakes 5095, Australia

ARTICLE INFO

Keywords:
High entropy alloy
Direct laser fabrication
Hot isostatic pressing
Microstructure
Mechanical properties

ABSTRACT

Three high entropy alloys (HEAs), based on the $Al_xCoCrFeNi$ alloy system have been prepared by direct laser fabrication (DLF) with aluminium molar fractions (x) of 0.3, 0.6 and 0.85. These three alloys had FCC, duplex FCC + BCC, and BCC crystal structures, respectively. The effect of hot isostatic pressing (HIP) on alloy density, microstructure and mechanical properties of these DLF bulk high entropy alloys was studied for the first time. HIP was found to decrease the number of large pores (> 5 μm) in the as-deposited alloys, which equated to a marginal increase in density. HIP also induced microstructural coarsening, chemical homogenisation and resulted in a general improvement in the mechanical properties of FCC HEA (x = 0.3). HIP improved the compressive properties of the dual phase HEA (x = 0.6), however, degraded the tensile properties as a result of the coarsening of hard BCC grain boundary precipitates. The mechanical properties were compromised in the high aluminium (x = 0.85) HEA due to the formation of σ-phase at the phase and grain boundaries, which induced a brittle fracture in tension and compression. A cooling curve transformation diagram (CCT) for the σ-phase was determined by a dilatometric method and the critical cooling rate to inhibit σ-phase formation was found to be 1 K/s.

1. Introduction

An alloy design strategy has recently been developed which utilises a minimum of five principal elements, to produce what is known as HEAs. These have attracted wide scientific interest due to their ability to form solid solution structures with unusual properties [1–4]. HEAs showed a high probability of forming a single-phase random solid solution structure [5–7] due to the combined effects of the high configurational entropy of mixing, near-zero enthalpy of mixing and small atomic size differences of the constituent elements [8–10]. High entropy alloys are found to be excellent candidates for high-temperature structural applications and energy absorbing materials due to their high fracture strength and excellent strength retention over a wide range of temperatures [3,11]. The $Al_xCoCrFeNi$ HEA system is one of the most extensively studied HEA systems. Several publications in the literature have determined the effect of Al concentration on the microstructural evolution [12,13], phase stability [14], mechanical [15,16], electrical [17] and magnetic [18] properties of the $Al_xCoCrFeNi$ system. Due to these excellent combination of physical and mechanical properties, $Al_xCoCrFeNi$ HEA system was chosen for the present study.

DLF has been used in the current study to produce bulk cylinders of HEA specimens of the desired composition. DLF allows the in-situ mixing/melting of metal powders fed into the focal point of a laser beam to produce a homogeneous alloy deposit onto a pre-existing metallic substrate [19]. Previously, we have shown that as-deposited DLF HEAs have a coarse columnar structure and significant elemental segregation to grain boundaries and second phase precipitates [15], which deteriorated the mechanical properties [20,21]. Thus, microstructural and chemical homogeneity cannot be ensured in the as-deposited HEAs processed by DLF. Therefore, the measured mechanical properties in the as-deposited condition may not be a true indication of the mechanical properties of the fully homogenised state.

Post-processing treatments such as ageing [22], annealing [23,24], homogenising [25], cold deformation [26] and thermomechanical processing [27,28] are reported to have a positive influence on the microstructure and mechanical properties of various arc-melted high entropy alloys. HIP is an elevated temperature densification process where the component is subjected to isostatic pressure at elevated

* Correspondence to: Institute for Frontier Materials, Deakin University, Waurn Ponds Campus, 75 Pigdons Road, Victoria 3216, Australia.
E-mail address: jithin.joseph@deakin.edu.au (J. Joseph).

https://doi.org/10.1016/j.msea.2018.07.036
Received 15 May 2018; Received in revised form 9 July 2018; Accepted 10 July 2018

temperature. This process has been extensively used in superalloy castings, and additive manufactured metallic components to heal defects such as cavities, voids and hot cracking [29], in addition to homogenising the microstructure [30]. The high temperature softens the alloy, allowing the high isostatic pressure to reduce the size and number-density of closed porosity, without distorting the shape of the as-deposited component. Co-axial DLF using a blend of five elemental powders presents as a convenient synthesis technique for high entropy alloys, although the technique is new and there have been only limited studies [31–34]. Especially lacking is the effects of thermal post-processing. The present study aims to assess and understand the effect of HIP on the pore characteristics and microstructural changes of DLF HEAs and relate these changes to the tensile and compressive properties.

2. Materials and methods

Three alloys were fabricated using DLF and post-processed by HIP: $Al_{0.3}$CoCrFeNi, $Al_{0.6}$CoCrFeNi and $Al_{0.85}$CoCrFeNi, hereafter referred to as $Al_{0.3}$, $Al_{0.6}$, and $Al_{0.85}$. A TRUMPF TruLaser Cell 7040 was used for fabricating the Al_xCoCrFeNi HEAs from spherical gas-atomized powders of Co, Cr, Fe, Ni and Al (99.99% purity, 50–150 μm). Detailed DLF process parameters for producing the HEA billets (cross-section of $15 \times 15\,mm^2$ and 100 mm in length) are detailed in a previous publication [15]. The HIP of HEA samples was performed using an Avure QIH-9 Hot Isostatic Press. Samples were heated to a temperature of 1100 °C at a heating rate of 5 °C/min, and the pressure increase to 300 MPa over the same period. These conditions of temperature and pressure were maintained for two hours, followed by a linear decrease in temperature (at a cooling rate of 5 °C/min) and pressure to ambient conditions. To assess the effects of cooling rate on phase formation, HIP samples with a height of 10 mm and diameter of 5 mm were prepared by EDM for controlled cooling experiments in a TA instrument DIL 805 A/D dilatometer. The samples were reheated to HIP treatment temperatures (1100 °C) and cooled in a controlled argon atmosphere at numerous rates between 0.02 K/s and 2.5 K/s. Based on the dilatometry results, two cooling rates of interest were selected (25 K/s and 1.5 K/s) to conduct experiments on bulk deposits of $Al_{0.85}$ HEA. Samples were heated to 1100 °C, and the cooling rate was measured via thermocouples placed within the samples. Water quenching and air cooling were used to approximate the desired cooling rates of 25 K/s and 1.5 K/s, respectively.

The phase constituents of the alloy samples were determined by x-ray diffraction using a PANalytical X'PERT PRO X-ray diffractometer using monochromatic Cu Kα ($\lambda = 1.54$ Å) radiation at 40 kV and 30 mA. The XRD analysis was performed on polished sample surfaces oriented parallel to the direction of solidification, and the scans were performed over a scanning range of $20^\circ < 2\theta < 120^\circ$ with a 0.05° step size per second. A LECO GDS 850 A Glow Discharge Optical Emission Spectrometer (GDOES) operating at 700 V and 20 mA was used to determine the bulk chemical homogeneity at various positions along the deposition height. The microstructural characterisation, crystallographic texture orientation and local chemical composition of the samples were characterised using a Zeiss Supra 55VP scanning electron microscope equipped with OXFORD X-Max EDS detector and OXFORD Nordlys EBSD detector, at an operating voltage of 20 kV. TEM investigations were conducted for the microstructural analysis of deformed specimens using a JOEL 2100 LaB_6 transmission electron microscope at an operating voltage of 200 kV, coupled with a Gatan Orius SC100 high-resolution camera. Thin foils for TEM analysis were prepared from the bulk specimens by ion milling using GATAN precision ion polishing system. Tensile specimens with a gauge length, gauge width and thickness of 16 mm, 4 mm and 2 mm respectively and cylindrical compression test specimens of 8 mm diameter and 12 mm height were wire electrical discharge machined from the as-deposited and HIP-processed ingots around the z-axis (solidification axis). The alloy samples were tested in compression using a Servotest Thermo Mechanical Test Simulator (TMTS-500 kN) and tensile tested using an Instron 100 kN tensile machine at an initial strain rate of $10^{-3}\ s^{-1}$. Three sets of mechanical (compressive/tensile) tests were performed for each composition in as-deposited, and HIP-processed conditions and all mechanical tests were stopped at a true strain of 1.0 if the failure had not already occurred.

Table 1
Chemical composition of the as-deposited and HIP-processed (a) $Al_{0.3}$, (b) $Al_{0.6}$ and (c) $Al_{0.85}$ alloys determined by glow-discharge optical emission spectroscopy.

	Atomic % (+ 0.5)				
	Co	Cr	Fe	Ni	Al
(a) $Al_{0.3}$ alloy					
DLF	23.4	22.9	23.3	23.1	7.1
DLF/HIP	23.3	23.1	23.6	22.8	7.2
(b) $Al_{0.6}$ alloy					
DLF	21.4	20.9	22.8	21.6	13.3
DLF/HIP	21.7	21.1	21.9	21.8	13.5
(c) $Al_{0.85}$ alloy					
DLF	20.2	20.7	21.1	19.8	18.3
DLF/HIP	19.7	21.1	21.6	19.3	18.4

3. Results

3.1. Phase, microstructure and texture analysis

The bulk chemical composition of the as-deposited and HIP-processed HEA samples were quantified by glow-discharge optical emission spectroscopy, and this showed the composition to be consistent with the elemental composition of the starting powder mixture (Table 1).

The specimen porosity was measured by optical and scanning electron microscopy, and the results of this analysis are shown in Fig. 1. It was observed that there was a significant reduction in the number of larger diameter pores (> 5 μm) in the as-deposited $Al_{0.3}$ alloy samples (Fig. 1(a)) after HIP-processing as shown in Fig. 1(b). The direct laser fabricated $Al_{0.3}$ alloy samples in the as-deposited condition were 99.4% dense (porosity level of 0.6%, Fig. 1(c)). However, the population of small pores remained after HIP (porosity level of 0.5%, Fig. 1(d)) for $Al_{0.3}$ alloy. This trend was consistent for all three alloys.

The XRD pattern of as-deposited alloys was presented in a previous publication [15]. The HIP-processed samples of the $Al_{0.3}$ alloy showed a single phase FCC structure (Fig. 2) exhibiting a strong (200) peak, similar to the as-deposited alloy. The XRD pattern of HIP-processed $Al_{0.6}$ alloy samples showed the presence of a duplex (FCC + BCC) structure, Fig. 2. The XRD spectra of the HIP-processed $Al_{0.85}$ alloy showed a BCC structure with one peak corresponding to the ordered B2 phase (Fig. 2), similar to the as-deposited alloy [15]. Additionally, the XRD spectra of $Al_{0.85}$ alloy after HIP-processing exhibited the presence of peaks corresponding to the σ-phase. The σ-phase is commonly observed in stainless steels and has a body-centered tetragonal structure (space group: $P4_2/mnm$) [35].

A comparison of the as-deposited and HIP-processed alloys are shown in Figs. 3 and 4. Both the as-deposited (Fig. 3(a)) and HIP-processed $Al_{0.3}$ alloy (Fig. 3(d)) samples had a large and columnar grain structure, having an average size of 250 μm in the transverse direction and 1250 μm in the vertical (solidification) direction. The as-deposited $Al_{0.6}$ alloy had a dual phase structure (FCC + BCC) with the FCC phase having a Widmanstätten grain structure longitudinal to the direction of deposition, Fig. 3(b). However, the application of HIP induced a markedly different microstructure in the $Al_{0.6}$ alloy (Fig. 3(e)). In the case of $Al_{0.85}$ alloy, HIP-processing resulted in the transformation of columnar grain structure in the as-deposited condition (Fig. 3(c)) to