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Effect of Al/Ni ratio, heat treatment on phase transformations and microstructure of $Al_xFeCoCrNi_{2-x}$ ($x = 0.3, 1$) high entropy alloys

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ABSTRACT

Laser-aided direct metal deposition, an additive manufacturing technique, was successfully used to fabricate thin walled high entropy alloy components. In this study, the ratio of aluminum to nickel in the AlFeCoCrNi system was decreased to observe the transition of the solid solution from a body centered cubic to a face centered cubic structure. Aluminum concentration was found to cause ordering and spinodal decomposition concomitantly in two of the compositions. The lattice parameter increased from 0.288 nm to 0.357 nm and the hardness decreased from 670 Hv to 149 Hv respectively. Differential thermal analysis was used to track the solidification paths of each of the compositions. Annealing at high temperature led to σ phase transformation in some of the compositions which along with solid solution strengthening accounted for the high softening resistance of these alloys. The optimization of the Al/Ni ratio in these alloys for better mechanical properties has been discussed with the help of an additional alloy composition as an example.

1. Introduction

Contrary to traditional metallurgical principles, multicomponent high entropy alloys solidify into simple solid solutions in preference to complex intermetallics [1,2]. Although entropy is important, is not a sufficient condition for solid solution formation [3–5].

The CoFeCrNi system has been reported to possess an FCC structure [6]. When aluminum was added to this system, the AlFeCoCrNi alloy system has been reported to solidify into BCC and FCC crystal structures. This duplex crystal structure was later reported to predominantly adopt a BCC structure as the Al atomic ratio was increased [7–9]. Increasing the Ni content is understood to promote the FCC [10]. Aluminum forms binary and ternary ordered compounds with all of the individual constituent elements of this system. Interesting findings were reported about the effect of aluminum on this alloy system like spinodal decomposition and high temperature hardness [11,12]. The effect of heat treatment should be investigated for better understanding of the underlying reasons for the occurrence of these findings. Impressive work hardening ability has been reported during homogenization and deformation studies of these alloys [13,14]. The diffusion of constituent elements in high entropy alloy systems was found to be slow owing to low diffusion coefficients and high activation energies [15,16]. This along with solute strengthening makes these materials retain their superior mechanical properties even at high temperatures. Aerospace, which is believed to be a possible area of application of these alloys, requires stability at extended exposure to high temperatures. In this work, the Al/Ni ratio was changed to witness the change in the crystal structure from BCC to FCC and also record the change in the microstructure and properties during this transition. The effect of extended heat treatment at elevated temperatures has been investigated. An effort has been made to suggest an Al/Ni ratio which could result in the optimal properties in this material.

Direct metal deposition using a high powered laser as the energy source is an additive manufacturing technique which could be used to produce metallic components with high efficiency. Laser deposited metallic components have been shown to possess better mechanical and thermal properties among other salient advantages as a result of rapid solidification which suppresses segregation and helps retain the homogeneity of the melt [17–19]. The present work employs this process for depositing high entropy alloy components of predetermined composition.

2. Experimental

In this work, the setup for the direct metal deposition (DMD) process consisted of a 1 kW fiber laser, coaxial powder feeder

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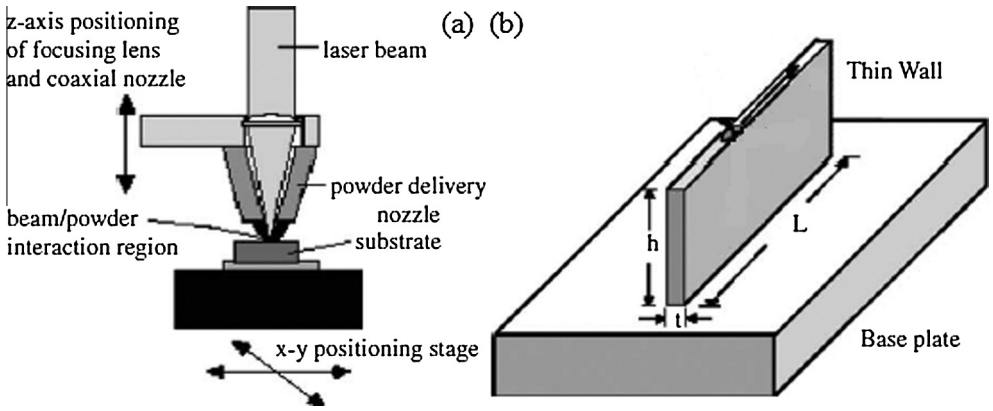

Fig. 2.1. Schematic diagrams of DMD process setup. (a) Front view of the deposition system and (b) orientation of thin wall [20].

system, photodiode and a pyrometer [Fig. 2.1(a)]. The depositions were made in the shape of a thin wall which was the target shape for all the deposition experiments [Fig. 2.1(b)]. Thin walls were built of size approximately 60 mm ∗ 30 mm ∗ 5 mm by scanning the laser along a single row and building upwards layer by layer in the z direction on 316 L stainless steel substrates.

Additionally to the normal or continuous mode (CW), the lasers was also used in the pulsed mode (PW) at a frequency of 500 Hz. The spot diameter was reduced to 0.25 mm and a scan speed of 600 mm/min was used. The pulse overlap was about 92%. This was an attempt to decrease the intermixing between clad layers and achieve higher cooling rates. Elemental powders which were predominantly spherical of the constituent elements with 99.9% purity, of −100 μm mesh size were mixed proportionately for different compositions and blended in a Turbula T2F tabletop shaker/mixer. The atomic fraction for the high aluminum and high nickel content alloys was estimated on the basis of previous work where it was reported that when the atomic fraction of Al ⩽ 0.3, the alloy would solidify primarily into a FCC solid solution [5–8]. Therefore, for better comparison, the Nickel content was adjusted proportionately.

Crystal structure and lattice parameters of the rapid solidification products were obtained from the corresponding XRD patterns. The XRD was done on a Philips MRD machine with an X-ray wavelength of 1.54 Å. The depth of penetration for the X-rays in this case was around 1 mm. The diffraction patterns were collected in the 2θ region of 0–90 °C. The diffraction patterns obtained from the test were then matched with those in the JCPDS database for phase identification. The solidification microstructure was analyzed by optical microscopy, SEM and EDS analysis, in a Helios 600 nanolab SEM. The sectioned samples were first mounted in Bakelite, ground with silicon carbide abrasive of varying grit sizes from 120 to 1200. They were polished with 9 μm, 3 μm and 1 μm diamond suspension on suitable polishing cloth. Finally the samples were vibratory polished for 30 min before being etched. The samples were kept inside stainless steel bags to limit the supply of oxygen during the heat treatment process. Firstly, the samples were soaked at 1273 K quenched in water referred to as quenched samples from here on. Secondly, the samples were annealed at 1273 K for 100 h referred to as annealed samples from here on. Differential thermal analysis (DTA) was used to track the phase transformation in these alloys from room temperature to 1573 K, which is close to their melting points. The samples were heated at a rate of 283 K/min in an inert atmosphere. Al_2O_3 was used as reference.

3. Results

The results of the XRD, microstructure, DTA and hardness have been tabulated in [Table 3.1] for ease of comparison and summary. While depositing the high aluminum content alloy, a cracking noise was heard at multiple instances. The deposits, both continuous and pulsed samples had fractured into small pieces right after deposition. The surface of the deposits was partially oxidized and had a gray color. The equiatomic alloy did not fracture and withstood the process. However, macro cracks could be seen at the substrate/deposit interface [Fig. 3.1]. These are a result of coherency stresses and thermal stresses caused by thermal expansion differences between the deposit and substrate. The total extent of the cracking could not be determined as subsequent deposition filled up prior crack. During sectioning, this alloy broke from substrate revealing the brittle tendency. The high nickel content alloy on the other hand was more ductile when compared to both the equiatomic and high aluminum content alloy compositions. There were no cracks observed and no cracking noises heard during or after the deposition process. The material was ductile enough for a thin bar to be bent by hand. These deposits did not fracture from the substrate any time after the processing.

3.1. XRD

The high entropy alloys studied solidified predominantly into BCC and FCC solid solutions [Fig. 3.2]. The predominant BCC solid solution in the high aluminum content alloy $Al_{1.7}FeCoCrNi_{0.3}$ had a = 0.288 nm. The peaks at 31° and the peak at 73.5° are forbidden peaks of a BCC lattice which indicate chemical ordering and Al-rich sub lattice in the alloy due to the higher composition. This partially ordered BCC structure is similar to a B2 intermetallic phase. These superlattice peaks do not appear in the PW samples due to the higher cooling rate which significantly reduces the diffusion of elements and grain size as evidenced by the broader peaks in the XRD of PW samples. The [1 1 0] and [2 1 1] peaks split upon heat treatment indicating the presence of two BCC phases of slightly different composition. The three peaks at 31° 2θ, 55° 2θ, 73° 2θ in the quenched sample of the PW deposit confirms that one of the BCC phase underwent ordering to a B2 phase during solidification.

The equiatomic AlFeCoCrNi composition solidified into a mixture of both BCC and FCC phases [Fig. 3.2]. The XRD pattern of the sample deposited in the CW mode shows peak splitting, lower angle peak corresponds to a BCC phase with a = 0.288 nm and the higher to a FCC phase with a = 0.357 nm. Superlattice peaks at similar diffraction angles as the high aluminum content alloy indicate the presence of a similar B2 structure. However, both the peak splitting and the presence of the superlattice peaks is very faint in the XRD patterns of the PW samples which indicates a dependance of the amount of BCC or FCC phases on cooling rate. This can be validated empirically by approximating the volume fraction of FCC (a) and BCC (1-a) phases in this alloy by taking the hardness