On the entropic stabilisation of an Al$_{0.5}$CrFeCoNiCu high entropy alloy

N.G. Jones*, J.W. Aveson, A. Bhowmik, B.D. Conduit, H.J. Stone

Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, UK

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ABSTRACT

The extent to which configurational entropy can stabilise a single solid solution in an Al$_{0.5}$CrFeCoNiCu high entropy alloy has been assessed through characterisation of samples following casting and heat treatment at 1000 °C. At temperatures between 1000 °C and the onset of melting, the alloy was shown to be within a two phase field and these phases were stable following prolonged exposure at elevated temperature. X-ray and transmission electron diffraction indicated that both constituent phases had an fcc structure. Therefore, these phases share a Gibbs energy curve that must contain two local minima at the solidus temperature, rather than the single minimum required for a continuous solid solution. These observations indicate that there is no temperature at which this material is in a stable, solid state single phase field and that therefore, the configurational complexity is insufficient to stabilise a single solid solution phase against enthalpic effects.

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1. Introduction

High entropy alloys (HEAs) are a relatively new class of metallic materials that have no primary element, but are instead based on approximately equiatomic additions of five or more individual elements [1,2]. Traditionally, such mixtures would be expected to contain multiple intermetallic phases. However, X-ray and electron diffraction data from these materials has often revealed only a limited number of simple crystal structures, such as fcc or bcc and their related superlattice structures. It has been suggested that the apparent stability of these phases results from a high configurational entropy that outweighs the enthalpy of formation of intermetallic phases [2].

AlCrFeCoNiCu was one of the first reported high entropy alloys and initial work indicated that, with Al ratios less than 0.65, the cast microstructure contained only a single fcc phase. Higher Al contents promoted the formation of a bcc based phase [2]. Since then, a phase diagram for the system has been proposed, in which Al$_{0.5}$CrFeCoNiCu was reported to have two solid state phase fields; fcc + fcc at temperatures above 700 °C and L1$_2$ + fcc below 700 °C [3]. More recent studies of the same alloy have suggested there is equilibrium between two fcc phases and an ordered fcc phase at temperatures immediately below the solidus [4] and that precipitation of additional intermetallic phases occurs at intermediate temperatures [4,5]. These observations are in direct contrast to the phase equilibria proposed in Ref. [3]. Complementary thermodynamic predictions suggested that these intermetallic phases should indeed form. However, whilst broadly similar, none of the predicted phase assemblies in Ref. [4] match those found experimentally. This disparity is perhaps unsurprising as the compositions considered are well outside the assessed compositional space of the underlying databases.

Several studies on other high entropy alloys have reported that their solid solutions are stable with respect to heat treatment, albeit segregation has been observed to form other entropically stabilised phases [6–9]. Interestingly, there have also been reports of microstructural evolution through both age hardening [5,10–12] and precipitation [5,12–15] following exposure at elevated temperatures. These contrasting results illustrate the complexity of the phase equilibria in this class of alloys and the need to determine phase stability on a system by system basis. This need is further highlighted by a recent study that considered phase stability by systematically replacing each element in an equiatomic, five component alloy [16]. Whilst the base alloy formed a single solid solution, the microstructures of all the substitutional variants contained intermetallic phases, indicating that configurational entropy was not dominating the phase equilibria.

Despite the lack of agreement surrounding the phase stability of these materials, their reported mechanical and environmental properties are promising, both at ambient and elevated temperatures, leading to significant interest in their use for a wide range of applications [1–3,17–19]. However, resolving the uncertainty of the
phase stability of these materials is critical for their future selection, manufacture and exploitation. Therefore, in this study, the phase stability of Al$_0.5$CrFeCoNiCu has been studied following long term heat treatment directly from the as-cast state. The results obtained contradict all the previously proposed phase equilibria of this alloy and demonstrate, for the first time, that a solid state single phase field does not exist at any temperature.

2. Experimental

A 40 g ingot of Al$_0.5$CrFeCoNiCu was prepared via arc melting in an inert atmosphere from elemental metals with purity ≥99.95%. To achieve homogeneity, the ingot was inverted and remelted five times. A short section, ~10 mm long, was cut from the as-cast ingot, encapsulated in an evacuated, argon backfilled quartz ampoule and heat treated for 1000 h at 1000 °C, followed by an immediate water quench. Microstructural characterisation was carried out using backscattered electron imaging (BSEI) in a JEOL 5800 Scanning Electron Microscope. Compositional data was obtained in the same microscope using an Oxford Instruments energy dispersive X-ray (EDX) spectroscopy system. Individual phase compositions were determined by averaging five point analyses, and the bulk composition assessed from five, large area (~500 × 500 μm) scans. The bulk analyses indicated that each of the elemental components was within 1 at% of the nominal concentration. Higher magnification images of ion milled thin foils were acquired using a JEOL 200CX Transmission Electron Microscope (TEM) and selected area diffraction patterns (SADP) taken from different regions of interest. Macroscopic crystallographic information was obtained via X-ray diffraction using a Philips PW1050 diffractometer in Bragg–Brentano geometry with CuK$_\alpha$ radiation, a 0.64 mm divergence slit, a 0.2 mm receiving slit and 0.04° steps in 2θ with 20 s count times. Differential Scanning Calorimetry (DSC) was performed between netzsch 404 high temperature calorimeter at a heating rate of 10 °C min$^{-1}$.

3. Results

The as-cast material, Fig. 1a, exhibited a dendritic microstructure with Fe, Co, Cr rich dendrites and Cu, Al rich interdendritic material. EDX determined phase compositions are given in Table 1. Casting-induced porosity was also observed in the interdendritic regions. X-ray diffraction from this material, Fig. 1b, revealed peaks corresponding to an fcc structure, consistent with previous reports [2]. In addition, several low intensity peaks were also present in the spectra, as identified by diamond markers, indicating that a small volume fraction of at least one other structure existed within the material in this condition. However, the area of these smaller peaks was inconsistent with the volume fraction of interdendritic material observed in Fig. 1a.

Closer examination of the fcc peaks revealed a distinct shouldering on the low 2θ side. The observation of two phases in the microstructure, Fig. 1a, and the absence of diffraction peaks of sufficient intensity to account for the second phase suggested that both phases had the fcc structure and that the distinct shouldering arose as a result of the difference in the lattice parameters of these two phases, rather than solidification-induced microsegregation of the dendrites. To account for this, each diffraction peak was fitted with two profile functions using a Levenberg–Marquardt non-linear least squares algorithm in Wavemetrics Igor Pro. Each profile function was a summation of two Gaussian peaks, accounting for the contributions from CuK$_\alpha_1$ and CuK$_\alpha_2$ radiation. The relative position, intensity and width of the CuK$_\alpha_1$ and CuK$_\alpha_2$ peaks were constrained, in line with diffraction theory, such that each profile

![Fig. 1. As-cast Al$_0.5$CrFeCoNiCu; a) BSEI showing the two phase dendritic microstructure, and b) corresponding X-ray diffraction spectrum indicating an fcc structure, the diamond markers highlight the presence of another phase, and inset showing the fitted (220) peak, illustrating that both dendritic and interdendritic phases are fcc.](image)

Table 1

<table>
<thead>
<tr>
<th>Condition</th>
<th>Phase</th>
<th>Al</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>Dendritic (grey)</td>
<td>6</td>
<td>23</td>
<td>23</td>
<td>21</td>
<td>18</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Interdendritic (white)</td>
<td>12</td>
<td>7</td>
<td>7</td>
<td>16</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>1000 °C 1000 h</td>
<td>Dendritic (grey)</td>
<td>7</td>
<td>23</td>
<td>23</td>
<td>20</td>
<td>19</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Interdendritic (white)</td>
<td>11</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>16</td>
<td>59</td>
</tr>
</tbody>
</table>
sharper, suggesting homogenisation had occurred during thermal exposure. Indeed, evidence of this was observed in the phase compositions given in Table 1, which indicated small variations in the elemental partitioning between the two phases in the as-cast and heat treated states.

The corresponding X-ray diffraction spectrum of the annealed sample, Fig. 2b, showed two sets of overlapping fcc reflections, similar to Fig. 1b, with average lattice parameters of 3.597 and 3.632 Å. The similarity between this diffraction pattern and that obtained from the as-cast sample suggests that the shoulder in the as-cast state arose as a result of two overlaid fcc diffraction patterns, rather than as a result of any microsegregation. However, following annealing, the intensity and definition of the low angle peaks were significantly enhanced and could be indexed with the L12 structure. Detailed investigation into the source of these reflections was conducted using transmission electron microscopy, Fig. 3 and Fig. 4, as a complete fcc → L12 ordering transformation has previously been suggested [3]. A bright field image of a dendrite interface is shown in Fig. 3a, with the interdendritic and dendritic material labelled as regions B and C respectively. The SADP from the interdendritic material, Fig. 3b, showed reflections corresponding to an fcc structure, whilst the SADP from the dendrites, Fig. 3c, showed diffraction spots consistent with the presence of an L12 superlattice structure. Dark field imaging from a superlattice reflection, Fig. 4, showed that the L12 phase formed as small, ~25 nm, cuboidal precipitates within the fcc matrix, akin to gamma prime in Ni-base superalloys.

DSC thermograms measured during the heating and remelting of as-cast and annealed material are shown in Fig. 5. Both traces show a pronounced, sigmoidal deviation at ~850 °C, which was sharper in the annealed material, and two large, endothermic events at ~1150 and ~1350 °C.

Sigmoidal deviations are commonly observed in the thermograms of Ni-base superalloys and correspond to the gamma prime solvus temperature [20]. As fine L12 precipitates were observed in the fcc dendrites, the deviation at ~850 °C can be attributed to the dissolution of this phase. The occurrence of the sigmoidal feature in both thermograms suggests that the L12 precipitates were also present in the as-cast microstructure, and this structure accounted for the majority of the low intensity peaks in Fig. 1b. The wider temperature range over which the L12 dissolves in the as-cast sample may be attributed to compositional variations across cored dendrites and the corresponding changes in the L12 solvus temperature. The smaller endothermic peak at ~1150 °C is typical of the incipient melting of an interdendritic constituent, whilst the larger peak at ~1350 °C is consistent with the bulk melting of a...
compositionally graded dendrite. These two melting temperatures are in good agreement with those reported in Ref. [3]. In addition, small deviations can be seen above 1000 °C in both thermograms. However, no microstructural feature has been identified that may account for these deviations.

4. Discussion

Metastable solidification phases would decompose during long duration thermal exposures and evidence of that transformation would be seen in both the differential thermal analysis and the corresponding microstructures. The consistency between the microstructures, phase compositions and thermograms of the as-cast and 1000 °C annealed samples indicates that the solidification phases are not simply a result of solute segregation and kinetic limitations. Further, no phase transformations were observed between 1000 °C and the onset of melting in the thermograms, nor was there any evidence of phase evolution between Figs. 1 and 2, beyond the elimination of solidification induced microsegregation. Therefore, it can be concluded that the two phases formed during solidification are thermodynamically stable above 1000 °C. This conclusion is in agreement with the predictions of Tong et al. [3] and in contrast to the results of Ng et al. [4], who suggested two fcc phases and an ordered fcc phase were stable immediately below the solidus temperature. The differential thermal analysis data, Fig. 5, suggests that the L12 phase precipitated on cooling through a solvus at ~850 °C, rather than being present at higher temperatures. This interpretation is also consistent with the fine scale of the L12 precipitates observed in Fig. 4. If these precipitates had been present during the extended annealing treatment, then significant coarsening would have occurred. Conversely, fine scale particles, such as those observed here, would be expected if the solid state transformation occurred during cooling, where nucleation rates would be high and growth limited. Such behaviour is consistent with the metallurgy of Ni-base superalloys, where the solid state precipitation of the gamma prime phase occurs even at extremely high cooling rates and may lead to gamma prime precipitates of similar size and morphology to those seen here [21–26].

Based on these observations, a summary of the transformation pathway of Al0.5CrFeCoNiCu when rapidly cooled from a liquid state is given below. This pathway differs to those proposed in Refs. [3] and [4], with the L12 phase precipitating within fcc1 during cooling, rather than forming by complete ordering of fcc1 [3],1 or as a solidification product [4].

$$I \rightarrow I + fcc_1 \rightarrow fcc_1 + fcc_2 \rightarrow (fcc_1 + L12) + fcc_2$$

The evidence gathered in this study indicates that, at temperatures above 1000 °C, Al0.5CrFeCoNiCu is in a two phase field in which both constituent phases have an identical crystal structure and similar lattice parameters. Whilst this has been previously identified [3], its significance to the thermodynamics of this alloy and the concept of entropic stabilisation, has not been discussed.

Classical thermodynamics states that for two components to exhibit complete solid solubility in each other they must be extremely similar in terms of atomic size, electronic configuration and must crystallise in the same structure [27,28]. The Gibbs energy curve that describes this behaviour has a single minimum and is strongly dependent on the entropy of mixing. A similar Gibbs energy curve, with a single minimum, would be expected in multi-component alloys if, as suggested in Ref. [2], the configurational complexity of the alloy enabled the entropic term to dominate the

1 It should be noted that L12 precipitation in fcc1 is reported in the text of reference [3]. However, the proposed phase diagram in the same work indicated an ordering transformation.
entropic term. However, the present work has shown that between 1000 °C and the solidus temperature, Al0.5CrFeCoNiCu as two fcc structures, which cannot be described by a Gibbs energy curve of this form.

The Gibbs energy curve for any given crystal structure extends continuously across compositional space. Therefore, two phases that have the same crystal structure must also have a common Gibbs energy curve. In addition to the case of complete solubility described above, as temperature decreases, the enthalpic term can begin to dominate the entropic term, leading to the Gibbs energy curve developing two local minima [27]. This leads to partial solubility between the two elements and the occurrence of a miscibility gap between the two solid solutions. If the Gibbs energy curve develops two minima above the solidus temperature, then the phase diagram will be either eutectic or peritectic, for example, the Cu–Ag [30] or Pt–Ag [31] binary systems respectively. In contrast, if the Gibbs energy curve develops two minima below the solidus temperature, then a continuous solid state single phase field will exist at higher temperatures, giving way to a miscibility gap and phase separation at lower temperatures, for example the Au–Ni system [32]. These principles also apply in higher order systems, and the necessity for continuous Gibbs energy curves is elegantly demonstrated by considering the Cu–Ag–Au ternary system. The fcc Cu and fcc Ag phases in the Cu–Ag binary system show only limited solubility in each other, with no continuous solid state single phase field across the composition range. However, complete solid solubility, and a single fcc phase field, can be achieved by sufficient additions of Au, for instance, concentrations greater than 30 at% at 750 °C [33]. This situation cannot be described unless the Gibbs energy curve is continuous across the entire ternary composition space.

The observation that Al0.5CrFeCoNiCu solidified as two compositionally distinct fcc structures, rather than a cored single phase of continuously varying composition, requires the corresponding Gibbs energy curve to contain two local minima at the temperature at which the final stage of solidification occurred. Microstructural examination has shown that these two phases are stable with respect to prolonged aging at both 1000 °C in the present work and at 1100 °C in Refs. [4], indicating the existence of a two phase equilibrium phase field in this temperature range. Thus, if an entropically stabilised single solid solution phase was to exist, it could only do so between 1100 °C and the onset of melting at 1150 °C. No evidence of a transformation was observed in the DSC thermograms between these temperatures and as the extent of entropically stabilisation will decrease at lower temperatures, it can be concluded that there is no a single solid solution phase field in this material. Furthermore, the elemental partitioning associated with the formation of the two phases will significantly reduce their entropic instability, increasing their susceptibility to further phase decomposition.

5. Conclusions

The phase stability of an Al0.5CrFeCoNiCu alloy has been assessed following casting and 1000 h heat treatment at 1000 °C. The alloy solidified as two compositionally distinct fcc phases, which were observed to be stable following heat treatment at 1000 °C. An L12 phase was also present in the as-cast and 1000 °C annealed microstructures. However, in contradiction to previous reports, this phase was shown to precipitate during cooling and had a solvus temperature of ~850 °C. The two fcc structures are therefore the thermodynamically stable equilibrium phases at high temperature and, as they possess the same crystal structure, share a Gibbs energy curve. Correspondingly, this Gibbs energy curve must contain two local minima, as opposed to one for a continuous solid solution. Therefore, enthalpic terms dominate the behaviour of this alloy and a single, stable, solid state phase field does not exist in this material.

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