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



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ARTICLE INFO

Article history:

Received 21 March 2014

Received in revised form

9 June 2014

Accepted 12 June 2014

Available online

Keywords:

A. High-entropy alloys

B. Phase stability

B. Thermodynamic properties

ABSTRACT

The extent to which configurational entropy can stabilise a single solid solution in an $\text{Al}_{0.5}\text{CrFeCoNiCu}$ 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 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 as-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 $\text{Al}_{0.5}\text{CrFeCoNiCu}$ was reported to have two solid state phase fields; *fcc* + *fcc* at temperatures above 700 °C and L_{12} + *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

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phase stability of these materials is critical for their future selection, manufacture and exploitation. Therefore, in this study, the phase stability of $\text{Al}_{0.5}\text{CrFeCoNiCu}$ 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 $\text{Al}_{0.5}\text{CrFeCoNiCu}$ was prepared via arc melting in an inert atmosphere from elemental metals with purity $\geq 99.95\%$. 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 ($\sim 500 \times 500 \mu\text{m}$) 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 $\text{CuK}\alpha$ 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 room temperature and 1400 °C under flowing argon using a Netzsch 404 high temperature calorimeter at a heating rate of $10^\circ\text{C min}^{-1}$.

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–Marquandt non-linear least squares algorithm in Wavemetrics Igor Pro. Each profile function was a summation of two Gaussian peaks, accounting for the contributions from $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ radiation. The relative position, intensity and width of the $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ peaks were constrained, in line with diffraction theory, such that each profile

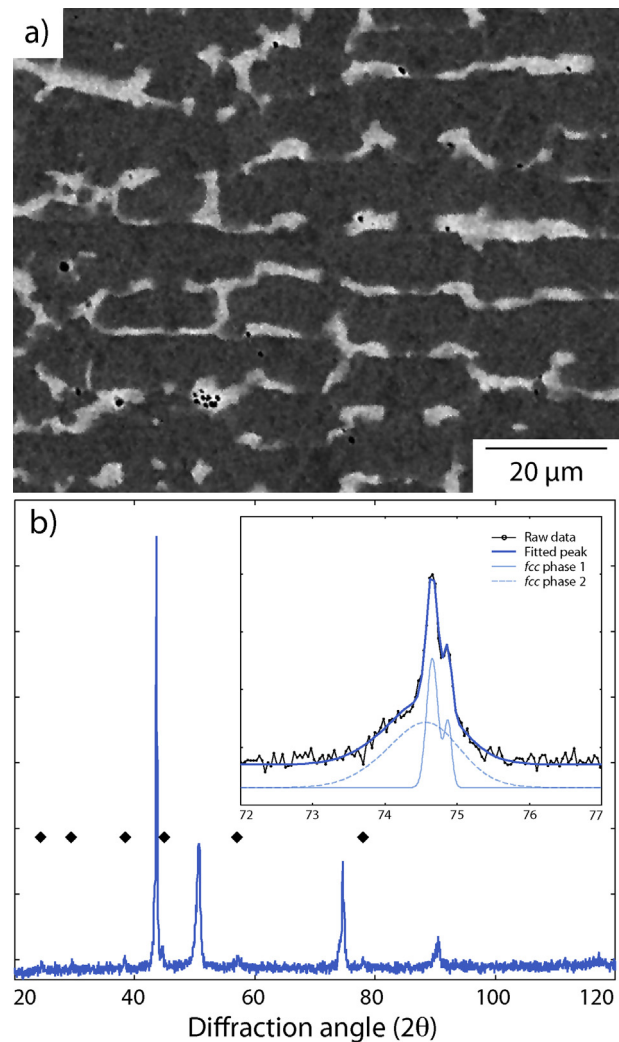


Fig. 1. As-cast $\text{Al}_{0.5}\text{CrFeCoNiCu}$; a) BSEI showing the two phase dendritic microstructure, and b) corresponding X-ray diffraction spectrum indicating an *fcc* structure, the diamond markers highlight the presence of another phase, and inset showing the fitted {220} peak, illustrating that both dendritic and interdendritic phases are *fcc*.

function had only three fitting variables. An example of fitted data is shown in the inset of Fig. 1b, along with the two constituent profile functions. The lattice parameters of the two phases were evaluated from the fitted Bragg angles of all *fcc* reflections through a non-linear least squares minimisation and were determined to be 3.595 and 3.602 Å respectively.

The microstructure observed following heat treatment for 1000 h at 1000 °C, Fig. 2a, was similar to that of the as-cast material, in agreement with the observations in Ref. [4]. However, in contrast to the as-cast material, the interfaces between the two phases were

Table 1

Summary of phase compositions (in at%) determined from five individual spot EDX analyses, the standard deviation of each measurement is less than 1%.

Condition	Phase	Al	Cr	Fe	Co	Ni	Cu
As-cast	Dendritic (grey)	6	23	23	21	18	9
	Interdendritic (white)	12	7	7	7	16	51
1000 °C 1000 h	Dendritic (grey)	7	23	23	20	19	8
	Interdendritic (white)	11	4	5	5	16	59

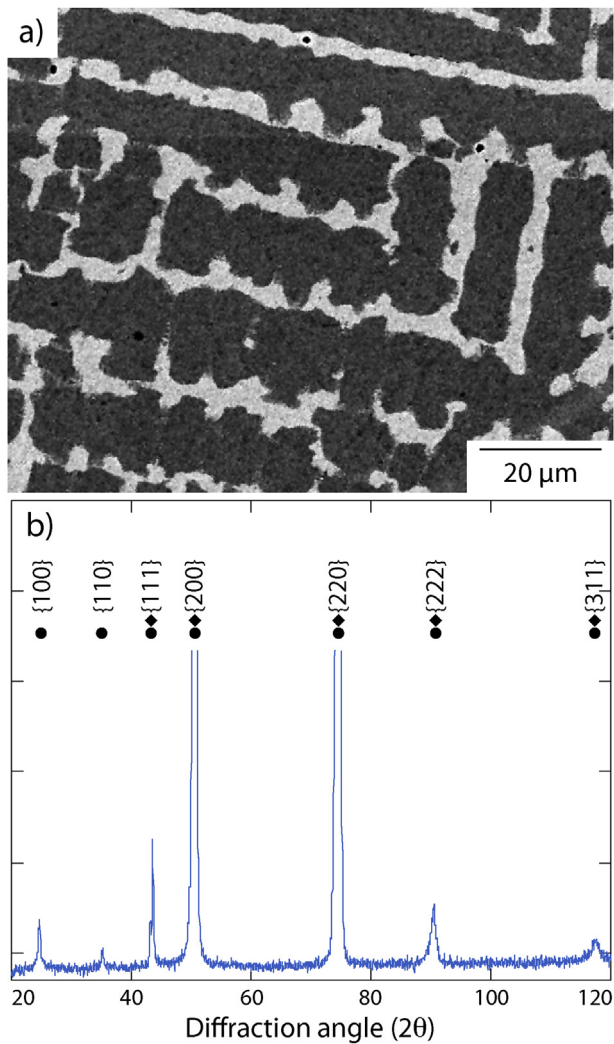


Fig. 2. $\text{Al}_{0.5}\text{CrFeCoNiCu}$ heat treated for 1000 h at 1000 °C; a) BSEI showing a two phase dendritic microstructure, similar to that of the as-cast, and b) the corresponding X-ray diffraction spectrum showing the presence of L_{12} superlattice reflections in addition to those of two fcc phases.

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 supports the assertion that the shouldering 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 L_{12} structure. Detailed investigation into the source of these reflections was conducted using transmission electron microscopy, Fig. 3 and Fig. 4, as a complete $fcc \rightarrow L_{12}$ 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 L_{12} superlattice structure. Dark field imaging from a superlattice reflection, Fig. 4, showed that the L_{12} 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 L_{12} 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 L_{12} 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 L_{12} dissolves in the as-cast sample may be attributed to compositional variations across cored dendrites and the corresponding changes in the L_{12} 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

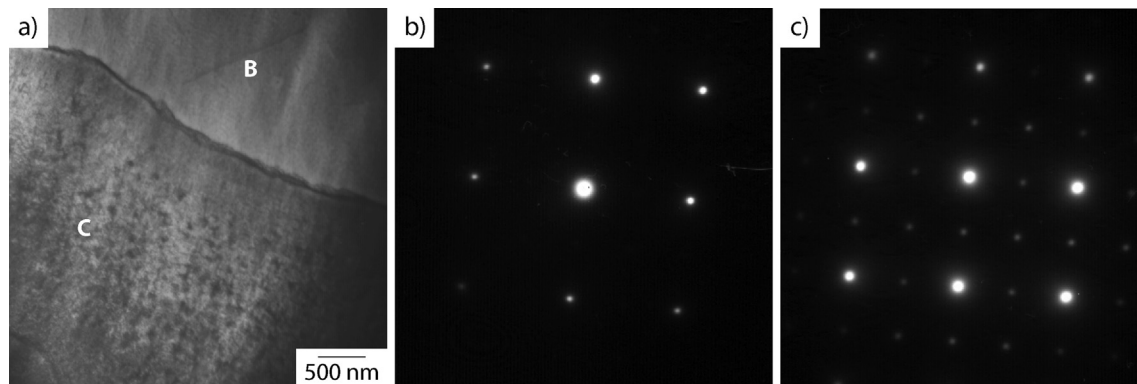


Fig. 3. a) Bright field TEM micrograph of a dendrite interface in $\text{Al}_{0.5}\text{CrFeCoNiCu}$ following 1000 h heat treatment at 1000 °C, b) [100] zone axis SADP from the interdendritic region (B) indicating an fcc structure, and c) [100] zone axis SADP from the within the dendrite (C) showing the presence of superlattice reflections consistent with the presence of L_{12} precipitates.

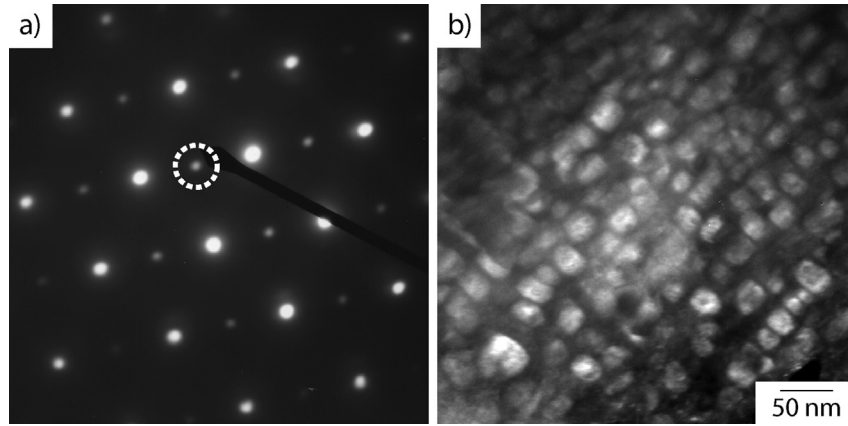


Fig. 4. a) [110] zone axis SADP from within a dendrite, indicating the superlattice reflection used to form the dark field image, and b) dark field image showing the cuboidal morphology of the L_{12} precipitates.

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 micro-segregation. 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 L_{12} 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 L_{12} 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 $Al_{0.5}CrFeCoNiCu$ when rapidly cooled from a liquid state is given below. This pathway differs to those proposed in Refs. [3] and [4], with the L_{12} phase precipitating within *fcc*₁ during cooling, rather than forming by complete ordering of *fcc*₁ [3],¹ or as a solidification product [4].

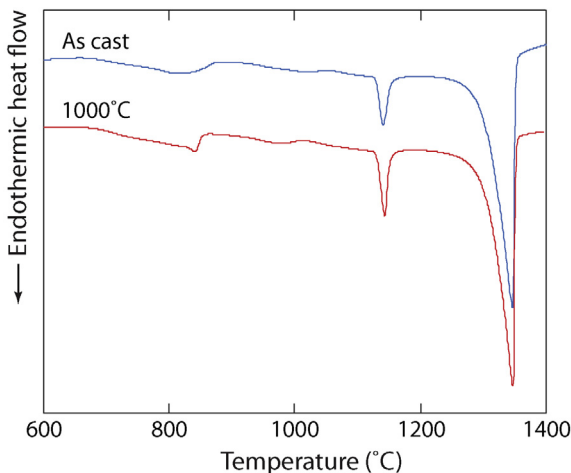
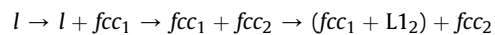


Fig. 5. DSC thermogram of $Al_{0.5}CrFeCoNiCu$ during heating and remelting from the as-cast and 1000 °C annealed conditions.

The evidence gathered in this study indicates that, at temperatures above 1000 °C, $Al_{0.5}CrFeCoNiCu$ 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 L_{12} precipitation in *fcc*₁ is reported in the text of reference [3]. However, the proposed phase diagram in the same work indicated an ordering transformation.

enthalpic term. However, the present work has shown that between 1000 °C and the solidus temperature, $\text{Al}_{0.5}\text{CrFeCoNiCu}$ exists 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 [27–29]. 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 $\text{Al}_{0.5}\text{CrFeCoNiCu}$ 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 entropic 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 stability, increasing their susceptibility to further phase decomposition.

5. Conclusions

The phase stability of an $\text{Al}_{0.5}\text{CrFeCoNiCu}$ 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 L_{12} 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.

Acknowledgements

The authors would like acknowledge K.A. Roberts, K.A. Christofidou and A. J. Knowles for their assistance, W.J. Clegg for his insightful comments, and the EPSRC/Rolls-Royce Strategic Partnership for funding (NGJ, AB and HJS under EP/H500375/1, JWA and BDC under EP/H022309/1).

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