Cu assisted stabilization and nucleation of L1₂ precipitates in Al_{0.3}CuFeCrNi₂ fcc-based high entropy alloy

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Abstract

A detailed investigation of precipitation of the ordered L1₂ (γ') phase in a Al_{0.3}CrCuFeNi₂ high entropy alloy (HEA), more generally referred to as a complex concentrated alloy (CCA), reveals the role of copper (Cu) on stabilization and precipitation of the ordered L1₂ (γ') phase. Detailed characterization via coupling of scanning and transmission electron microscopy, and atom probe tomography revealed novel insights into Cu clustering within the face-centered cubic matrix of this HEA, leading to heterogeneous nucleation sites for the γ' precipitates. The subsequent partitioning of Cu into the γ' precipitates indicates their stabilization is due to Cu addition. The γ' order-disorder transition temperature was determined to be ~930°C in this alloy, based on synchrotron diffraction experiments, involving *in situ* annealing. The growth and high temperature stability of the γ' precipitates was also confirmed via systematic scanning electron microscopy investigations of samples annealed at temperatures in the range of 700 - 900°C. The role of Cu revealed by this study can be employed in the design of precipitation strengthened HEAs, as well as in a more general sense applied to other types of superalloys, with the objective of potentially enhancing their mechanical properties at room and elevated temperatures.

Keywords

High entropy alloys, synchrotron X-Ray Diffraction, atom probe tomography, L1₂

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Introduction

In pursuit of new alloy development, High Entropy Alloys (HEAs) have attracted a lot of attention in the last decade. The HEA term was coined by considering the fact that even on alloying five different elements with unlike crystal structures the product was a single phase uni-crystal structure, largely stabilized by the high configurational entropy [1]. Since then there has been an explosion in this field and quite a few promising single-phase HEAs have been identified, such as face-centered cubic (*fcc*) alloys; $\text{Al}_{0.1}\text{CoCrFeNi}$ [1] and CrCoFeMnNi [2] , and body-centered cubic (*bcc*) alloys; NbMoTaW [3], NbMoTaVW [4], NbTiMoVA10.5 [5] and HfNbTaTiZr [6]. HEAs have not only interested researchers due to their simple crystal structures but also due to the exceptionally high tensile or/and compression strength exhibited by some of these alloys. Fracture strengths reaching ~ 4 GPa [7] and yield strengths of ~ 2.5 GPa [8, 9] have been reported. The *bcc* based HEAs comprising refractory elements VNbMoTaW [10] and ordered HEA systems primarily containing the B2 phase, such as AlCoCrFeNi [11], have shown a 0.2% yield stress of ~ 1250 MPa at ambient temperatures. Single phase CoCrFeMnNi has also been reported to exhibit fracture-toughness values higher than $200 \text{ MPa}\cdot\text{m}^{1/2}$ [12]. HEAs have also been referred to as multi-principal element alloys, since they do not have a single base element, as well as complex concentrated alloys (CCAs).

While there has been a strong focus by researchers to identify HEAs exhibiting a single-phase solid solution based microstructure, more recently, it has been acknowledged that these multi-principal element systems often exhibit phase separation (including spinodal decomposition) as well as ordering tendencies leading to the formation of ordered second-phase precipitates [13-18]. Such second-phase decomposition products are often the result of the competition between

high configurational entropy of mixing, usually dominant at higher temperatures, versus the enthalpies of mixing, usually dominant at lower temperatures. Therefore, in many cases the same HEA could potentially exhibit a single-phase solid solution at a higher temperature but decompose to form one or more second phases at lower temperature. The resulting microstructures can often be very complex and hierarchal, spanning over multiple length scales [19, 20]. Understanding the evolution of such microstructures with competing influences of entropy and enthalpy is key for the future development of HEAs or more broadly CCAs.

While the quest for finding more single solid solution high entropy alloys continues [6], the previously reported HEA's (CrFeMnCoNi , $\text{Al}_{0.1}\text{FeCrCoNi}$, HfNbTaTiZr etc.) are being investigated at various levels of detail in order to mature them for real engineering applications. Thermo-mechanical treatments, friction stir processing, severe plastic deformation by rolling, forging and torsion etc. [21, 22, 23 & 24] have been some methods employed to refine the microstructures and improve the mechanical properties. Addition of minor elements for solid solution strengthening, or a precipitate former for precipitation strengthening, have been other approaches that have been recently employed for designing new HEAs with enhanced properties [25].

One of the first single-phase high entropy alloys reported was $\text{Al}_{0.1}\text{CoCrFeNi}$ by Yeh et al. [1]. Since then many results have been published on the $\text{Al}_x\text{CoCrFeNi}$ system [26, 27 & 28]. Experimental results have shown that Co is not necessarily essential for obtaining a single solid solution and since Co is expensive, it can be readily substituted by Ni to maintain similar level of *fcc* formers in the HEA composition [29, 30]. The present study is based on a previously reported $\text{Al}_x\text{CrCuFeNi}_2$ graded HEA alloy, where an increase in Al content was found to cause a

transition in the principal solidification phase from *fcc* to *bcc* [31]. At low Al content (Al=0-0.4) it has been reported to contain a *fcc* matrix and interdendritic Cu-rich *fcc* phase. Subsequently, in a more recent study the authors have further investigated a specific composition, $\text{Al}_{0.3}\text{CrCuFeNi}_2$, by casting this alloy followed by rolling it at ambient temperature and solutionizing the dendritic structure to obtain a uniform microstructure consisting of single-phase equiaxed *fcc* grains. Annealing the $\text{Al}_{0.3}\text{CrCuFeNi}_2$ alloy at temperatures in the range of 550-700°C, resulted in the precipitation of the ordered L1_2 (γ') phase [30].

In the present paper, a systematic investigation was conducted on the formation and evolution of ordered L1_2 precipitates at different aging temperatures in the *fcc* based HEA ($\text{Al}_{0.3}\text{CuFeCrNi}_2$) specifically focusing on the following aspects:

1. Synchrotron diffraction experiments during *in situ* heating and cooling experiments to capture the order-disorder transition in this system in real time. Validation of the stability of the ordered L1_2 (γ') precipitates, based on scanning electron microscopy (SEM) investigation of the growth and coarsening of L1_2 (γ') precipitates as a function of temperature in the range 700°C-900°C.
2. Detailed transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) studies to characterize the mechanism of L1_2 (γ') precipitation, focusing on their nucleation sites within the *fcc* matrix.
3. Detailed Atom Probe Tomography (APT) experiments to determine Cu clustering within the *fcc* matrix, and its subsequent influence on L1_2 (γ') precipitation, as a function of temperature.

Experimental

The alloy was cast in a conventional arc melting furnace by mixing constituent elements, with purity greater than 99.9%, on a water-cooled hearth made of copper in a controlled atmosphere of pure argon. Repeated melting was carried out for five times and the ingot was inverted before every re-melt to ensure chemical homogeneity of the alloy. The cast ingot was ~10 mm in diameter and ~30 mm in length and was cut into thin slices for characterization.

Macroscopic microstructural characterization and the composition of the arc melted materials was examined by using an FEI Nova-NanoSEM 230™ scanning electron microscope (SEM). The SEM was fitted with an energy dispersive X-ray (EDS) detector (EDAX, Model: Apollo X), and a pure Ni standard was used to calibrate it. Alloy samples were scanned several regions in areas of 1x1 mm² to ensure the composition and homogeneity and EDAX's Genesis Spectrum version 6.0 software was used to process the raw data. The as-cast samples were cold rolled (CR) by giving a 20 % reduction in thickness and subsequently solution annealed (SA) at 1000°C for 3h. The SA samples were isothermally annealed at 550°C for 150h (CR-SA-550), 700°C for 50h (CR-SA-700), 800°C for 20h (CR-SA-800), and 900°C for 20h (CR-SA-900). The current alloy composition has been reported to have copper segregation at inter-dendritic regions in the as-cast condition [31]. Hence cold rolling and solutionization was done to obtain a micro-structurally and compositionally homogenous structure. The further annealing treatments were done to study the precipitation behavior in this alloy. The precipitate evolution at various temperatures was characterized by SEM.

Conventional Transmission electron microscopy (TEM) studies were carried out with a FEI Tecnai G2 TF20™ operating at 200 kV. Precipitate characterization was done using conventional and high angle annular dark field- scanning TEM (HAADF-STEM) modes. To measure the composition, energy dispersive spectroscopy (Super-X system) equipped on an FEI-TITAN G2 TEM microscope was used in the HAADF STEM mode operating at 300 kV and the results were analyzed with FEI's ES vision software version 6. TEM foils were prepared by an FEI Nova Nanolab 200 dual-beam focused ion beam (FIB) instrument using a Ga ion beam for milling. The ion beam thinning of the samples was done in multiple steps starting from 30 kV ions and finishing with 5 kV ions to reduce the surface damage caused by higher energy ions. Samples for *in situ* synchrotron studies were prepared with dimensions of 5 mm × 5 mm × 0.5 mm (thickness). The experiment was carried out at the 11-IDC beam-line (111 keV, $\lambda = 0.117418 \text{ \AA}$) of the Advanced Photon Source (APS) at Argonne National laboratory (ANL). A CeO₂ standard (NIST diffraction intensity standard set: 674a) was utilized to calibrate the distance between sample and the 2D detector, the position of the beam center and the detector tilt angle. The scattered radiation was collected on a Perkin Elmer 2D detector system. The Fit-2D software was used to radially integrate the 2D diffraction data to produce 1D intensity vs. two-theta (2θ) plots. Further details about the experimental procedure can be found elsewhere [32]. The resulting 1D diffraction data were analyzed using the Pawley method [33], as embodied in the TOPAS software package (Bruker), to obtain accurate measurements of the lattice parameters for the two phases as a function of temperature.

Results and Discussion

Coarser scale $LI_2(\gamma')$ precipitation in as-cast versus thermo-mechanically processed conditions

The back-scattered SEM results from the as-cast and CR-SA conditions are shown in Fig. 1. As reported earlier for Cu containing HEAs [13, 31, 34, 35 & 36] Cu segregates to the inter-dendritic regions in the as-cast structure as shown in Fig. 1(a). The compositions of the two regions in the microstructure, based on SEM-EDS are - grey matrix phase: Al: 4 at.%, Cr: 21 at.%, Fe: 23 at.% Ni: 40 at.% and Cu: 12 at.% and white phase: Al: 6 at.%, Cr: 6 at.%, Fe: 6 at.% Ni: 22 at.% and Cu: 58 at.% . The Cu EDS map, shown as an inset in Fig. 1(a), clearly reveals inter-dendritic segregation of Cu. The as-cast sample was annealed at 700°C for 50h and a preferential precipitation of cuboidal second phase precipitates was observed, as shown in Fig. 1(b). The number density and volume fraction of these second phase precipitates appears to be higher in the Cu rich inter-dendritic regions as shown in the higher magnification view in Fig. 1(b) inset. While the identity of these cuboidal second phase precipitates cannot be determined from these SEM images, they are likely to be $L1_2$ ordered γ' precipitates, based on similar observations presented previously [30]. The as-cast alloy was rolled and solution annealed at 1000°C for 3 h to obtain an equiaxed grain microstructure. The destruction of the dendritic microstructure resulted in the subsequent homogenization of the macro-scale Cu segregation, which is not observed in the SEM images from the CR-SA condition, shown in Fig. 1(c). **Figs. 1(d), (e) and (f) show backscatter SEM images from the CR-SA- 700, CR-SA-800 and CR-SA-900 samples, after isothermal annealing respectively at 700°C, 800°C, and 900°C, where homogenously distributed precipitates, exhibiting a dark contrast, are observed throughout the microstructure. With an increase in the annealing temperature from 700°C to 900°C, there is a substantial increase in the size scale of the precipitates. After annealing at all the temperatures 700°C, 800°C, and 900°C, precipitates exhibiting two types of morphologies are clearly visible, both equiaxed-like morphology as well as long needle-**

shaped precipitates (refer Figs. 1(d), 1(e) and 1(f)). These two types of precipitates could potentially be ordered γ' precipitates as well as Cu-rich precipitates, but conclusive identification of these two types of precipitates requires more detailed analysis. ImageJ software was used to analyze these backscatter images to generate data regarding the distribution of these darker contrast regions/precipitates. A total of 5 images for each condition were utilized in the analysis. A summary of various observations from these images is presented in Table 1. The average size of the darker contrast regions/precipitates (average area of each precipitate) substantially increased from $0.005 \mu\text{m}^2$ at 700°C to $0.025 \mu\text{m}^2$ at 800°C to $0.19 \mu\text{m}^2$ at 900°C .

Order-disorder transition

The results of synchrotron diffraction experiments carried out during *in situ* heating and cooling, have been summarized in the XRD plots shown in Fig. 2. The starting condition employed for these *in situ* heating-cooling synchrotron experiments was a CR-SA-700 sample which contained well-developed L1_2 (γ') precipitates prior to the initiation of the heating cycle at the synchrotron. The X-ray beam had a square cross-section of $500 \times 500 \mu\text{m}^2$ and the thickness of the sample was about $1000 \mu\text{m}$. The high energy of the synchrotron beam permitted carrying out the XRD experiments in transmission mode through relatively thick samples, leading to averaging over substantial sample volumes. Furthermore, the samples were rocked through an angle of $\pm 5^\circ$ to provide better statistical averaging over grains of multiple orientation. The right inset in Fig. 2 shows a magnified view clearly revealing the L1_2 peaks at various temperatures. The $\{100\}$ L1_2 peak is highlighted by the red box and it is observed that the peak starts to disappear above 900°C .

These *in situ* XRD experiments clearly indicate an order to disorder transition at high temperature ($>900^{\circ}\text{C}$) and subsequent re-ordering during cooling. The rate of heating and cooling was 0.5°C/s . X-ray diffraction datasets were collected during the whole experiment after intervals of 18 s (corresponding to $\sim 9^{\circ}\text{C}$ temperature intervals). Lattice constants were determined from selected data points along the heating and cooling cycles, and have been plotted against temperature in Fig. 3. At the early stages of the heating cycle, the lattice expanded linearly due to thermal expansion but above $\sim 930^{\circ}\text{C}$, there is a change in the slope with the rate of expansion increasing substantially. Similarly, while cooling down, prior to the reordering of matrix, leading to lattice contraction, a change in slope can be observed. The current observation of lattice expansion on disordering has also been reported earlier in Ni-based superalloys [32, 37 & 38]. The change in the slope or the change in the rate of expansion while heating (disorder) and while cooling (re-order) can be attributed to the order-disorder transition in this alloy, as clearly pointed out in the figure (Fig. 3). **However, it is difficult to conclude that the order-disorder transformation temperature in this alloy is exactly 930°C , based solely on the change in the slope of the lattice parameter versus temperature plot. This is particularly pertinent considering the fact that the synchrotron x-ray diffraction results shown in Fig. 2 exhibit L_{12} superlattice peaks at 950°C . It is possible that these superlattice peaks are remnant from partially dissolved L_{12} precipitates, that did not completely dissolve during the 0.5°C/s heating rate. Additionally, to ascertain the complete dissolution of L_{12} phase above 930°C , a long-term annealing treatments were carried out at $935^{\circ}\text{C}/20\text{hrs}$ and the high angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image from this condition is shown in Fig. 4 (a). The sample clearly exhibit two**

phases (bright contrast phase and a dark contrast phase). The elemental distribution map (STEM-EDS map) showed that the bright contrast phase was rich in Cu and lean in all other elements whereas the matrix phase is seen to be rich in Ni, Cr and Fe. Al did not show much partitioning. Cu and Ni maps are shown in Fig. 4 (b) and (c) respectively. The selected area diffraction patterns (SADP) from [011] zone axes of Cu rich phase and the matrix are shown Fig (d-e) respectively, which did not show presence of any extra super-lattice spot hence it can be concluded that ordering of fcc is not prevalent at 935°C.

Copper clustering in solution treated and quenched condition

Selected area electron diffraction (SAD) patterns from the CR-SA sample are shown in Fig. 5, where (a), (b), and (c) correspond to the [001], [112], and [011] zone axes (ZA) of an *fcc* phase respectively. The principal reflections visible in all these diffraction patterns are the fundamental *fcc* spots. Additionally, there are possibly some very faint reflections visible at the {011} positions in [001] and [112] zone axes diffraction patterns. While these additional spots are very faint and also diffuse, they indicate the possibility of early stages of long-range ordering (LRO) within the *fcc* matrix. Hence the possibility of ordering within the *fcc* matrix in the solution treated and quenched sample cannot be ruled out. Fig. 5 shows the atom probe APT results from the CR-SA sample. The ion maps for the different elements have been shown in Figs. 6(a to f), and correspondingly labeled. A clear inhomogeneity can be seen in the Cu ion map shown in Fig. 6(f). This compositional inhomogeneity has been quantified by plotting the 1-D compositional profile, averaged along a cylindrical cross-section (radius = 20 nm, length = 120 nm), along the direction shown in Fig. 6(a). This 1-D profile is shown in Fig. 6(g), and clearly exhibits fluctuations in the Cu composition with an average

wavelength of approximately 20 nm. These fluctuations are present in the solution treated and water quenched condition of this alloy, and the Cu content in some regions is as high as ~80at% (refer Fig. 6(g)). These compositional fluctuations can be attributed to a phase separation within the *fcc* matrix. However, it should be noted that these compositional fluctuations occur over a length scale (~ 20nm) that is substantially more refined (by about three orders of magnitude) as compared to the phase separation (~ 10-20 μ m) resulting in Cu-rich inter-dendritic regions in the as-cast alloy (refer to Fig. 1(a)). Such macroscopic Cu segregation is not observed in the CR-SA condition of this alloy, shown in the backscatter SEM image in Fig. 1(c). Therefore, it can be deduced that the dendritic segregation was completely obviated and the alloy was compositionally homogenized in the CR-SA condition at the solution treatment temperature of 1000°C. During the subsequent quench from 1000°C to room temperature, the alloy phase separates into Cu-rich and Cu-depleted regions as shown in Fig. 6, presumably via a rapid spinodal decomposition process.

A 45at% Cu iso-concentration surface (also referred to as iso-surface) has been used to delineate the Cu-rich regions and the corresponding interfaces have been shown in the reconstruction in Fig. 7 (a). Composition profiles across these interfaces have been calculated in the form of a proximity histogram shown in Fig. 7(b). The Cu rich phase consists of ~80 at% Cu, ~ 16 at% Ni and ~4 at% Al. Referring back to the raw ion map for Al shown in Fig. 6(d), a weak clustering tendency is observed in the case of this element too. However, the exact location of this Al clustering is difficult to identify. Fig. 7(c) shows a 5 nm slice of the raw ion map showing Cu (red) and Al (black) ions. The highlighted region (yellow box) in Fig. 7(c) has been magnified in Fig. 7(d) and the corresponding Cu-rich and Al-rich regions have been highlighted via iso-

surfaces; 45 at% Cu (red) and 8 at% Al (black). Fig. 7(d) clearly reveals that the Al-rich regions lie adjacent to the Cu-rich regions, or more specifically at the interface between the Cu-rich regions and the surrounding matrix. A proximity histogram averaging fifty randomly selected Al-rich interfaces is shown in Fig. 7(e). Al enrichment up to ~14 at% is observed in these regions. It is important to note that while the Cu and Al clustering is clearly visible in the APT reconstructions and the corresponding compositional analysis of the CR-SA sample, there is no indication of the formation a Cu-rich phase in the electron or synchrotron X-ray diffraction patterns. This clearly indicates two things; firstly the lattice parameters of the primary *fcc* matrix and the Cu-rich phase are very similar, and secondly, the Cu-rich phase is disordered. **Additionally, it should also be noted that the possible presence of weak and diffuse superlattice reflections at the {011} positions in the [001] and [112] *fcc* zone axes (ZA) SAD patterns from this CR-SA condition (shown in Figs. 5(a) and (b)), indicates the possibility of long-range ordering within the Al-rich regions adjacent to the Cu-rich regions. However, based on the results presented in this study it is rather difficult to conclusively prove ordering within the Al-rich regions.**

The strong tendency for Cu-clustering in this system, leading to the formation of Cu-rich regions even in the solution treated and quenched condition (CR-SA), can be rationalized based on the relative interaction parameters for the various binary combinations involving Cu. Thus, the principal binary interaction parameters are Cu-Ni, Cu-Fe, Cu-Cr, and Cu-Al. While Cu-Ni is well known as an isomorphous system, it should be noted that complete solid-state miscibility is seen only above ~500°C. At lower temperatures, there is a miscibility gap in this system, indicative of positive enthalpy of mixing or a positive interaction parameter [39,40]. Both Cu-Fe

and Cu-Cr largely exhibit solid-state immiscibility at lower temperatures ($< 300^{\circ}\text{C}$), and have large positive enthalpies of mixing. Cu-Al is the only binary system involving Cu that has a negative enthalpy of mixing, but with the mole fraction of Al in this alloy being only 0.3 atomic fraction, this interaction is likely to have a relatively weaker influence. Therefore, comparing these binary interaction parameters, it can be rationalized that Cu will have a strong tendency to cluster in this alloy. Furthermore, Cu clustering has been previously reported to occur in other HEAs [41, 42].

Early stages of $L1_2$ (γ') precipitation

Figs. 8 (a, b & c) show the SAD patterns from [001], [011] and [112] zone axes from the CR-SA-550 sample. The super-lattice reflections at $\{001\}$ and $\{011\}$ locations in all three SAD patterns confirms the presence of $L1_2$ ordering. These $L1_2$ precipitates have been highlighted in the dark-field TEM image shown in Fig. 8(d), which were recorded by selecting a super-lattice reflection from the [001] SAD pattern. This dark-field image indicated a homogenous distribution of very fine scale (~ 5 nm) precipitates within the fcc matrix after annealing at 550°C for 150h.

Fig. 9 shows the STEM results from the CR-SA-550 condition. Fig. 9(a) shows a high angle annular dark-field (HAADF) STEM image exhibiting a uniform distribution of fine scale precipitates of a brighter contrast. This second phase is clear in the magnified image shown in the lower part of Fig. 9(a). Compositional profiles for the different elements, along the yellow arrow marked in Fig. 9(a), are plotted in Fig. 9(b). The composition profile for Cu exhibits relatively high amplitude fluctuations. Furthermore, the composition profiles for Ni, Fe, and Cr, appear to be synchronized with enrichments and depletions at the same location, and out of phase

with the Cu fluctuations. The STEM-EDS elemental maps for the different elements are shown in Figs. 9(c to g) with each correspondingly labeled. Fig. 9(c) clearly shows the Cu-rich precipitates. Some Al enrichment is also visible in Fig. 9(e) but the signal to noise ratio is not sufficiently high to delineate Al-rich precipitates. While the dark-field TEM image in Fig. 8(d) clearly showed the presence of $L1_2$ ordered precipitates within the *fcc* matrix, and the STEM-EDS results showed Cu clustering, the relationship between these two observations and their spatial correlation cannot be conclusively established solely based on these experimental observations. Therefore, detailed APT investigations were carried out to further investigate the relationship between the Cu-rich precipitates and the $L1_2$ ordered precipitates.

Fig. 10 shows the 3D APT reconstructions of ion maps for various elements from the CR-SA-550 sample. Fig. 10 (a) shows all the ions, and at least three compositionally different phases are clearly visible. The Cu-rich phase is dominated by red, the Ni and Al rich γ' phase is dominated by black, while the matrix is dominated by blue. The composition of the three phases was calculated by extracting spheres of 5 nm diameter from each phase as marked by 1, 2 and 3 and generating the bulk composition of these spheres. Sphere 1 which is from the Cu-rich phases has ~94 at% Cu and rest is mostly Ni as shown in Table 2. Sphere 2 corresponds to the γ' phase (as shown in Fig. 10(e)) which is ~ 56 at% Ni, ~17 at% Cu and 24 at% Al. As the $L1_2$ phase has a stoichiometry of 3:1 for the ratio of Ni sites to Al sites, it appears that the Cu atoms preferentially occupy the Ni sites resulting in a γ' phase stoichiometry of $(\text{Ni,Cu})_3\text{Al}$. Since partition towards the γ' phase it can be concluded that Cu stabilizes this ordered $L1_2$ phase in this HEA. The 3D reconstructions of the ionic maps shown in Fig. 10 clearly reveal a relationship between the *fcc* Cu and the $L1_2$ (γ') ordered phases, with precipitates of both phases associated to

each other (refer to Fig. 10(a)). Furthermore, lattice planes are also clearly visible within the $L1_2$ (γ') ordered precipitates, in both Figs. 10(a) and (e). Unit cells for *fcc* Cu and the $L1_2$ ordered phase with $(\text{Ni/Cu})_3\text{Al}$ stoichiometry are shown in Fig. 11 (a). Fig. 11 (b) shows a higher magnification (15 nm x 10 nm x 5 nm) view of the reconstruction showing only Cu (red) and Al (black) ions. The region of the 3D reconstruction was selected near a [001] pole, to reveal the {001} lattice planes corresponding to the *fcc* Cu and $L1_2$ (γ') phases. The lattice planes in both phases are parallel and appear to display a cube-on-cube orientation relationship. To depict the lattice planes more clearly and measure the interplanar spacing, spatial distribution maps (SDM) have been constructed from these phases and are shown in Figs. 11(c) and (d). Fig. 11(c) shows the Cu-Cu SDM for the Cu-rich precipitate while Fig. 11(d) shows the Al-Al SDM for the $L1_2$ (γ') ordered precipitate. A derivative of the radial distribution function, the SDM is usually utilized to determine the distribution of solute atoms in the z-direction as well as to create a 2D map to locate atomic positions in the x-y lateral plane [43, 44]. Fig. 11(c) shows the yz-SDM corresponding to self-interaction of Cu-Cu. The SDM, plotted on the plane defined by the y- and z-axes, were created from a region of interest (ROI), placed at the center of the pole (most probably {001}) and the angular offset between the ROI and the actual lattice planes in the reconstructions was carefully minimized so that the highest spatial resolution could be obtained in the SDM. The yz-SDM for Cu-Cu interactions reveals that the minimum separation between the Cu atoms is 0.18 nm in the z-direction. While the yz-SDM for Al-Al interactions shown in Fig 11(d) reveals that the minimum separation between Al-Al atoms is 0.37 nm.

The Cu rich phase exhibits an interplanar spacing of ~0.18 nm which can be attributed to the {002} planes of *fcc* Cu rich phase. A similar SDM from the γ' phase showed a d spacing of

~0.37 nm. These planes are likely to be the {001} planes of the ordered phase. It has been reported earlier by Meher et al. [45, 46] that in ordered precipitates like γ' the resolution to detect the {002} is affected by the offset of the precipitate from zone axis and temperature of evaporation. The bonding on the Ni-Ni planes is mostly metallic and hence weaker than the covalent/ionic bonding due to hybridization $p_{\text{Al}}-d_{\text{Ni}}$ orbitals on mixed Ni-Al planes [45, 46]. The evaporation of the pure Ni rich planes is much easier as compared to more strongly bond Ni-Al planes and hence during the field evaporation process in the atom probe, the pure nickel planes merge with the mixed Ni-Al planes, resulting in only a single set of {001} planes appearing in the reconstruction [45, 46]. This makes the detection of the {002} planes very difficult, if not impossible, until the offset of the precipitates from the [001] direction is minimized and evaporation temperatures are reduced to as low as 20 K. However, from the viewpoint of the present paper, the near parallel alignment of the {002} planes of *fcc* Cu and the {001} planes of the ordered $L1_2$ (γ') precipitate, is sufficient evidence to establish the cube-on-cube orientation relationship between these two phases.

Fig. 12(a) shows a 20 nm x 50 nm x 10 nm slice of the reconstruction from the larger view APT reconstruction from the CR-SA550 condition, shown in Fig. 10. The Cu-rich precipitate and the $L1_2$ (γ') precipitate are encapsulated by a Cu-isosurface (red) and an Al-isosurface (grey). The γ' precipitates are seen to grow on the orthogonal edges of the Cu phase maintaining the orientation relationship. 1-D compositional profiles for the different elements have been plotted along the axis of the cylinder, aligned across a *fcc* Cu/ $L1_2$ (γ') interface, shown in Fig. 12(a), and these profiles have been shown in Fig. 12(b). The Cu-rich phase, which is >95 % (at.) Cu and nearly pure Cu, appears to be directly attached to the $L1_2$ (γ') precipitate with an average composition

of 60at% Ni, 15at% Cu, and 25at% Al. Based on the detailed APT-based experimental observations presented in Figs. 10, 11, and 12, and the corresponding quantitative analysis, the following insights can be obtained;

1. The *fcc* Cu-rich precipitates within the *fcc* matrix of the HEA are associated with the Al-rich ordered $L1_2$ (γ') precipitates.
2. The {002} planes of the *fcc* Cu-rich precipitates are aligned parallel to the {001} planes of the ordered $L1_2$ (γ') precipitates, suggesting a cube-on-cube orientation relationship between these two phases.
3. Cu partitions to the ordered $L1_2$ (γ') precipitates indicating that the ordered precipitates are stabilized by Cu, and assuming a stoichiometry of Ni_3Al in this ordered phase, the Cu atoms appear to occupy the Ni sites.
4. There are two possible mechanisms leading to the formation of spatially associated Cu-rich and Al-rich $L1_2$ (γ') precipitates: spinodal decomposition within the *fcc* matrix of the HEA, leading to phase separation into Cu-rich and Al-rich regions in close proximity, followed by ordering within the Al-rich regions to form $L1_2$ (γ') precipitates, or, initial Cu-clustering within the *fcc* matrix of the HEA, followed by these Cu-rich clusters acting as heterogeneous nucleation sites for the Al-rich $L1_2$ (γ') precipitates.

Advanced stages of $L1_2$ (γ') precipitation

Similar studies were carried out on CR-SA-700 condition as shown in Figs. 13 and 14. Fig. 13 shows the TEM results where (a) shows the [011] ZA SAD pattern and (b) shows a dark-field TEM image made from {001} superlattice spot highlighted (yellow circle) in the SAD pattern

shown in Fig. 13(a). The size scale of γ' has increased from ~ 5 nm in CR-SA-550 to ~ 75 nm in case of CR-SA-700. Figs. 13(c-e) show the elemental maps obtained by STEM-EDS mapping from this sample. Figs. 13(c) and (d) show the Al and Cu maps respectively. Fig. 13(c) shows the $L1_2$ (γ') precipitates while Fig. 13(d) shows the Cu-rich precipitates within the *fcc* matrix of the HEA. Fig. 13(e) shows an overall STEM-EDS map where the signals from all the constituent elements of this HEA have been superimposed. This STEM-EDS map clearly substantiates that the Cu-rich precipitates act as heterogeneous nucleation sites for the (γ') precipitates. The compositions of the three phases, based on the STEM-EDS analysis, are listed in Table 3. The γ' precipitates contain Ni = 52 at%, Cu = 31 at%, Al = 11.5 at% Fe = 4 at% and Cr = 1.5 at%, the Cu-rich precipitates adjacent to the $L1_2$ precipitates contain ~ 86 at% Cu and γ matrix composition is Ni = 43 at%, Al = 2 at. %, Cu = 15 at%, Cr = 18 at. % and Fe = 22 at%. As discussed in the previous case for the CR-SA-550 sample, in the present case too, partition of Cu into the $L1_2$ precipitates substantiates that the Cu-rich precipitates not only nucleate the $L1_2$ precipitates but also stabilize it. There could be dilution of compositions of fine precipitates (γ' and Cu-rich phase) in STEM-EDS due to beam interactions and over lapping of these phases in TEM foil. Hence a better estimate of elemental partitioning in γ' - γ is provided by APT results.

Fig. 14 shows the APT reconstruction from CR-SA-700 condition. Due to larger size scale of the phases in this condition, only the $L1_2$ (γ') and matrix phases were captured in the reconstruction. A proximity histogram was generated from the interface marked as 2 in the figure. The partitioning of the elements are found to very similar to that observed in case of the CR-SA-550 condition with Ni, Cu and Al partitioning towards γ' . The composition of γ matrix and γ' were extracted using a 5 nm diameter sphere as explained earlier and the APT compositions for the

two phases are listed in Table 4. The γ' precipitates contain Ni = 56.5 at%, Cu = 16.5 at%, Al = 21 at% Fe = 2 at% and Cr = 4 at% where the γ matrix composition is Ni = 45 at%, Cu = 6 at%, Al = 2.5 at%, Fe = 19.5 at% and Cr = 25 at %.

Isothermal annealing at even higher temperatures of 900°C, corresponding to the CR-SA-900 sample, exhibited a rather interesting change in the microstructure. The backscatter SEM image from this sample, shown in Fig. 1(f) shows needle-shaped precipitates with a dark contrast, indicating that these needles are enriched in the lighter elements, e.g. Al in this alloy system. Since, the darker contrast phase in case of the CR-SA-700 sample (Fig. 1(d)) is the ordered $L1_2(\gamma')$ phase, it would appear the dark needle-shaped precipitates in Fig. 1(f) belong to the $L1_2(\gamma')$ phase. More detailed TEM results from this condition are shown in Fig. 15. The bright-field image in Fig. 15(a) shows multiple needle-shaped precipitates, aligned perpendicular to each other. A [001] zone axis electron diffraction pattern from only the *fcc* matrix is shown in Fig. 15(b). Figs. 15(c) and (d) show [001] and [011] zone axes diffraction patterns from regions containing both the *fcc* matrix and the precipitates. The presence of {001} and {011} superlattice reflections in these diffraction patterns, clearly establishes the presence of $L1_2$ ordering within the needle-shaped precipitates. A dark-field TEM image, recorded from the specific {011} superlattice reflection marked with a circle in Fig. 15(d), is shown in Fig. 15(e). Interestingly, this dark-field image highlights nanoscale γ' precipitates within the needle-shaped region, rather than the entire needle being highlighted. This indicates that the needle-shaped regions themselves are composed of two distinct phases, a disordered *fcc* matrix with a highly refined uniform dispersion of γ' precipitates. A HAADF-STEM image of the intersection of two perpendicularly aligned needle-shaped regions is shown in Fig. 15(f) together with the

corresponding STEM-EDS maps for Al, Cu and Fe shown in Figs. 15(f) insets on left and right respectively. The needle-shaped regions have an overall higher Cu content as compared to the surrounding matrix. Al partitioning is not very strong but it appears high in the needle-shaped regions. APT results from this sample are shown in Fig. 16. Site-specific samples were prepared using the dual-beam FIB from regions containing the needle-shaped regions, as shown in Fig. 16(a) and (b). While it was rather challenging to capture all three regions of interest within the same APT reconstruction, one example of such a case is shown in Figs. 16(d) and (e). The approximate region from which this APT sample was extracted has been illustrated in Fig. 16(c), where a dark-field TEM image is shown together with a schematic of the APT sample. The actual APT reconstruction in Fig. 16(d) shows a small section of a γ' precipitate at the top, a small section of the Cu-rich channel below the precipitate (γ_1), and then a large region of the *fcc* matrix below. The composition profiles for the relevant elements, averaged along a cylinder a diameter 3 nm along the axis of the reconstruction (marked by an arrow in Fig. 16(d)), have been plotted in Fig. 16(e). The Al+Ni rich marks the γ' precipitate, with the Cu-rich region to its right, and the *fcc* matrix further to the right is enriched in Fe, Ni, and Cr. While it is rather difficult to get quantitative information for the γ' precipitate from this APT reconstruction, since only a very small section of the precipitate was captured, the overall trends in the composition profiles are well reflected for all three regions. Based on the SEM, TEM and APT results from the CR-SA-900 sample, it can be concluded that after 900°C/20hrs annealing there is a phase separation within the *fcc* matrix leading to the formation of Cu-rich needle-shaped regions and γ' precipitation is largely confined to within these needle-shaped phase separated regions. This is unlike the CR-SA-550 and CR-SA-700 conditions, where conjoint or coupled γ' /Cu-rich precipitates are uniformly distributed within the *fcc* (γ) matrix. The details of the mechanism

leading to the phase separation into needle-shaped Cu-rich regions and γ' precipitation within these Cu-rich regions, requires further investigation. Interestingly, the SEM results from the 960°C/20hrs annealed condition, shown in Fig. 4(a), exhibits brighter contrast Cu-rich needle-shaped regions since the γ' precipitates within these regions have dissolved (temperature is higher than the order-disorder transformation temperature).

Summary and Conclusion

The role of Cu in HEAs, such as $\text{Al}_{0.3}\text{CuCrFeNi}_2$ has been investigated in detail in the present study. While Cu has a strong tendency to segregate into the inter-dendritic regions in the as-cast condition, a homogeneous distribution of Cu, at the macroscopic length scale, can be obtained by deforming and recrystallizing the as cast alloy. Subsequently, the role of Cu on stabilization and precipitation of the ordered L1_2 (γ') precipitates can be summarized as follows:

- 1. The order-disorder transition associated with the formation of the L1_2 (γ') phase in this HEA has been investigated via *in situ* synchrotron XRD annealing experiments and while the exact order-disorder transition temperature could not be determined, this temperature was determined to lie within the range 930°C-960°C for this alloy.**
2. Cu has a strong clustering tendency in this HEA system and consequently phase separation is clearly observed in the solution-treated and quenched condition of the alloy, revealed by APT. Cu-rich clusters containing as high as 80at% Cu are observed. A small degree of Al enrichment is also observed adjacent to the Cu-rich regions.
- 3. There are two possible mechanisms leading to the formation of spatially associated Cu-rich and Al-rich L1_2 (γ') precipitates within the microstructure: spinodal decomposition within the *fcc* matrix of the HEA, leading to phase separation into**

Cu-rich and Al-rich regions in close proximity, followed by ordering within the Al-rich regions to form $L1_2$ (γ') precipitates, or, initial Cu-clustering within the *fcc* matrix of the HEA, followed by these Cu-rich clusters acting as heterogeneous nucleation sites for the Al-rich $L1_2$ (γ') precipitates. This leads to uniformly distributed conjoint/coupled $L1_2$ (γ')/Cu-rich precipitates within the *fcc* matrix of the HEA.

4. Based on APT results, Cu partitions to the $L1_2$ (γ') phase, indicating the stabilization of this ordered phase by Cu. Furthermore, assuming a stoichiometry of Ni_3Al for the γ' phase, the Cu atoms appear to occupy the Ni sites in the ordered $L1_2$ structure.
5. Higher temperature (800-900°C) isothermal decomposition of this alloy occurs via a macroscopic phase separation leading to the formation of Cu-rich needle-shaped regions, with the γ' precipitation being largely confined to within these needle-shaped regions.

The γ' order-disorder transformation temperature for this alloy lies in the range 930°C-960°C, which is much higher than that observed in case of the $Al_{0.3}CrFeCoNi$ HEA reported previously [24], where γ' dissolved below 700°C. The clustering of Cu in this HEA can be harnessed to develop a more homogeneous distribution of fine scale γ' precipitates for enhanced precipitation strengthening both at room as well as at elevated temperatures. The results presented in this paper lead to some fundamental insights into the mechanism of Cu clustering in high entropy alloys and its consequent influence on precipitation and stabilization of ordered phases. This approach can be effectively employed in other precipitation-hardened HEAs or in general other alloy systems.

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References

- [1] Yeh, J.W, S-K. Chen, S-J. Lin, J-Y. Gan, T-S. Chin, T-T. Shun, C-H. Tsau, and S-Y. Chang. "Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes." *Advanced Engineering Materials* 6, no. 5 (2004): 299-303.
- [2] Cantor, Brain, I. T. H. Chang, P. Knight, and A. J. B. Vincent. "Microstructural development in equiatomic multicomponent alloys." *Materials Science and Engineering: A* 375 (2004): 213-218.
- [3] Zou, Y., Maiti, S., Steurer, W. and Spolenak, R., 2014. Size-dependent plasticity in an Nb 25 Mo 25 Ta 25 W 25 refractory high-entropy alloy. *Acta Materialia*, 65, pp.85-97.
- [4] Senkov, O. N., Wilks, G. B., Miracle, D. B., Chuang, C. P., & Liaw, P. K. (2010). Refractory high-entropy alloys. *Intermetallics*, 18(9), 1758-1765.
- [5] Chen, S. Y., Yang, X., Dahmen, K. A., Liaw, P. K., & Zhang, Y. (2014). Microstructures and crackling noise of AlxNbTiMoV high entropy alloys. *Entropy*, 16(2), 870-884.
- [6] Gao, M. C., & Alman, D. E. (2013). Searching for next single-phase high-entropy alloy compositions. *Entropy*, 15(10), 4504-4519.
- [7] Zhang, Y., X. Yang, and P. K. Liaw. "Alloy design and properties optimization of high-entropy alloys." *Jom* 64, no. 7 (2012): 830-838.
- [8] Zhu, J. M., H. M. Fu, H. F. Zhang, A. M. Wang, H. Li, and Z. Q. Hu. "Microstructures and compressive properties of multicomponent AlCoCrFeNiMo x alloys." *Materials Science and Engineering: A* 527, no. 26 (2010): 6975-6979.
- [9] Zhou, Y. J., Y. Zhang, Y. L. Wang, and G. L. Chen. "Solid solution alloys of AlCoCrFeNiTix with excellent room-temperature mechanical properties." *Applied physics letters* 90, no. 18 (2007): 1904.
- [10] Senkov, O. N., Wilks, G. B. & Scott, J. M. & Miracle, D.B. Mechanical properties of Nb25Mo25Ta25W25 and V20Nb20Mo20Ta20W20 refractory high entropy alloys. *Intermetallics* 19, 698–706 (2011).
- [11] Wang, Y. P., Li, B. S., Ren, M. X., Yang, C. & Fu, H. Z. Microstructure and compressive properties of AlCrFeCoNi high entropy alloys. *Mat. Sci. Engng* 491, 154–158 (2008).
- [12] Gludovatz, Bernd, Anton Hohenwarter, Dhiraj Catoor, Edwin H. Chang, Easo P. George, and Robert O. Ritchie. "A fracture-resistant high-entropy alloy for cryogenic applications." *Science* 345, no. 6201 (2014): 1153-1158.
- [13] Jones, N. G., J. W. Aveson, A. Bhowmik, B. D. Conduit, and H. J. Stone. "On the entropic stabilisation of an Al 0.5 CrFeCoNiCu high entropy alloy." *Intermetallics* 54 (2014): 148-153.
- [14] Otto, Frederik, Ying Yang, Hongbin Bei, and Easo P. George. "Relative effects of enthalpy and entropy on the phase stability of equiatomic high-entropy alloys." *Acta Materialia* 61, no. 7 (2013): 2628-2638.
- [15] Chuang, Ming-Hao, Ming-Hung Tsai, Woei-Ren Wang, Su-Jien Lin, and Jien-Wei Yeh. "Microstructure and wear behavior of AlxCo 1.5 CrFeNi 1.5 Tiy high-entropy alloys." *Acta Materialia* 59, no. 16 (2011): 6308-6317.
- [16] Singh, S., N. Wanderka, K. Kiefer, K. Siemensmeyer, and J. Banhart. "Effect of decomposition of the Cr–Fe–Co rich phase of AlCoCrCuFeNi high entropy alloy on magnetic properties." *Ultramicroscopy* 111, no. 6 (2011): 619-622.
- [17] Pradeep, K. G., N. Wanderka, P. Choi, J. Banhart, B. S. Murty, and D. Raabe. "Atomic-scale compositional characterization of a nanocrystalline AlCrCuFeNiZn high-entropy alloy using atom probe tomography." *Acta Materialia* 61, no. 12 (2013): 4696-4706.

- [18] Manzoni, A., H. Daoud, R. Völkl, U. Glatzel, and N. Wanderka. "Phase separation in equiatomic AlCoCrFeNi high-entropy alloy." *Ultramicroscopy* 132 (2013): 212-215.
- [19] Borkar, T., B. Gwalani, D. Choudhuri, T. Alam, A. S. Mantri, M. A. Gibson, and R. Banerjee. "Hierarchical multi-scale microstructural evolution in an as-cast Al₂CuCrFeNi₂ complex concentrated alloy." *Intermetallics* 71 (2016): 31-42.
- [20] Guo, Sheng, Chun Ng, and C. T. Liu. "Sunflower-like solidification microstructure in a near-eutectic high-entropy alloy." *Materials Research Letters* 1.4 (2013): 228-232.
- [21] Otto, Frederik, Nikki L. Hanold, and Easo P. George. "Microstructural evolution after thermomechanical processing in an equiatomic, single-phase CoCrFeMnNi high-entropy alloy with special focus on twin boundaries." *Intermetallics* 54 (2014): 39-48.
- [22] Kumar, N., Komarasamy, M., Nelaturu, P., Tang, Z., Liaw, P. K., & Mishra, R. S. (2015). Friction stir processing of a high entropy alloy Al_{0.1}CoCrFeNi. *JOM*, 67(5), 1007-1013.
- [23] Schuh, B., Mendez-Martin, F., Völker, B., George, E. P., Clemens, H., Pippan, R., & Hohenwarter, A. (2015). Mechanical properties, microstructure and thermal stability of a nanocrystalline CoCrFeMnNi high-entropy alloy after severe plastic deformation. *Acta Materialia*, 96, 258-268.
- [24] Tang, Q. H., Huang, Y., Huang, Y. Y., Liao, X. Z., Langdon, T. G., & Dai, P. Q. (2015). Hardening of an Al_{0.3}CoCrFeNi high entropy alloy via high-pressure torsion and thermal annealing. *Materials Letters*, 151, 126-129.
- [25] He, J. Y., H. Wang, H. L. Huang, X. D. Xu, M. W. Chen, Y. Wu, X. J. Liu, T. G. Nieh, K. An, and Z. P. Lu. "A precipitation-hardened high-entropy alloy with outstanding tensile properties." *Acta Materialia* 102 (2016): 187-196.
- [26] Kao, Y. F., Chen, T. J., Chen, S. K., & Yeh, J. W. (2009). Microstructure and mechanical property of as-cast, homogenized, and deformed Al_xCoCrFeNi (0 ≤ x ≤ 2) high-entropy alloys. *Journal of Alloys and Compounds*, 488(1), 57-64. [16]
- [27] Shun, T. T., & Du, Y. C. (2009). Microstructure and tensile behaviors of FCC Al_{0.3}CoCrFeNi high entropy alloy. *Journal of Alloys and Compounds*, 479(1), 157-160.
- [28] Shun, T. T., Hung, C. H., & Lee, C. F. (2010). The effects of secondary elemental Mo or Ti addition in Al_{0.3}CoCrFeNi high-entropy alloy on age hardening at 700 °C. *Journal of Alloys and Compounds*, 495(1), 55-58.
- [29] Ng, C., Guo, S., Luan, J., Wang, Q., Lu, J., Shi, S., & Liu, C. T. (2014). Phase stability and tensile properties of Co-free Al_{0.5}CrCuFeNi₂ high-entropy alloys. *Journal of Alloys and Compounds*, 584, 530-537.
- [30] B. Gwalani, V. Soni, D. Choudhuri, M. Lee, J.Y. Hwang, S.J. Nam, H. Ryu, S.H. Hong, R. Banerjee, Stability of ordered L1₂ and B₂ precipitates in face centered cubic based high entropy alloys - Al_{0.3}CoFeCrNi and Al_{0.3}CuFeCrNi₂, *Scripta Materialia*, 123 (2016) 130-134.
- [31] Borkar, T., B. Gwalani, D. Choudhuri, C. V. Mikler, C. J. Yannetta, X. Chen, R. V. Ramanujan, M. J. Styles, M. A. Gibson, and R. Banerjee. "A combinatorial assessment of Al_xCrCuFeNi₂ (0 < x < 1.5) complex concentrated alloys: Microstructure, micro, and magnetic properties." *Acta Materialia* 116 (2016): 63-76.
- [32] B. Gwalani, T. Alam, C. Miller, T. Rojhirunsakool, Y. S. Kim, S. S. Kim, M. J. Kaufman, Yang Ren, and R. Banerjee. "Experimental investigation of the ordering pathway in a Ni-33 at. % Cr alloy." *Acta Materialia* 115 (2016): 372-384.
- [33] Pawley, G. S. "Unit-cell refinement from powder diffraction scans." *Journal of Applied Crystallography* 14.6 (1981): 357-361.

- [34] Guo, S., Ng, C., Lu, J., & Liu, C. T. (2011). Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys. *Journal of applied physics*, 109(10), 103505.
- [35] Guo, Sheng, Chun Ng, and Chain Tsuan Liu. "Anomalous solidification microstructures in Co-free Al_xCrCuFeNi 2 high-entropy alloys." *Journal of Alloys and Compounds* 557 (2013): 77-81.
- [36] Tung, C. C., Yeh, J. W., Shun, T. T., Chen, S. K., Huang, Y. S., & Chen, H. C. (2007). On the elemental effect of AlCoCrCuFeNi high-entropy alloy system. *Materials letters*, 61(1), 1-5.
- [37] Marucco, Alessandra, and Birendra Nath. "Effects of ordering on the properties of Ni-Cr alloys." *Journal of materials science* 23.6 (1988): 2107-2114.
- [38] Gialanella, Stefano, Simon B. Newcomb, and Robert W. Cahn. "Order Parameter and Lattice Parameter in L12 Ordered Alloys, with Special Reference to Ni₃Al-Based Alloys." *Ordering and disordering in alloys*. Springer Netherlands, 1992. 67-78.
- [39] Takeuchi, Akira, and Akihisa Inoue. "Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element." *Materials Transactions* 46, no. 12 (2005): 2817-2829.
- [40] an Mey, Sabine. "Thermodynamic re-evaluation of the Cu₃Ni system." *Calphad* 16, no. 3 (1992): 255-260.
- [41] Tong, Chung-Jin, Yu-Liang Chen, Jien-Wei Yeh, Su-Jien Lin, Swe-Kai Chen, Tao-Tsung Shun, Chun-Huei Tsau, and Shou-Yi Chang. "Microstructure characterization of Al_xCoCrCuFeNi high-entropy alloy system with multiprincipal elements." *Metallurgical and Materials Transactions A* 36, no. 4 (2005): 881-893.
- [42] Yeh, J-W., S-K. Chen, S-J. Lin, J-Y. Gan, T-S. Chin, T-T. Shun, C-H. Tsau, and S-Y. Chang. "Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes." *Advanced Engineering Materials* 6, no. 5 (2004): 299-303.
- [43] Moody, Michael P., Baptiste Gault, Leigh T. Stephenson, Ross KW Marceau, Rebecca C. Powles, Anna V. Ceguerra, Andrew J. Breen, and Simon P. Ringer. "Lattice rectification in atom probe tomography: Toward true three-dimensional atomic microscopy." *Microscopy and Microanalysis* 17, no. 02 (2011): 226-239.
- [44] Geiser, Brian P., Thomas F. Kelly, David J. Larson, Jason Schneir, and Jay P. Roberts. "Spatial distribution maps for atom probe tomography." *Microscopy and Microanalysis* 13, no. 06 (2007): 437-447.
- [45] Meher, Subhashish, Tanaporn Rojhirunsakool, Peeyush Nandwana, Jamie Tiley, and Rajarshi Banerjee. "Determination of solute site occupancies within γ' precipitates in nickel-base superalloys via orientation-specific atom probe tomography." *Ultramicroscopy* 159 (2015): 272-277.
- [46] Meher, S., P. Nandwana, T. Rojhirunsakool, J. Tiley, and R. Banerjee. "Probing the crystallography of ordered Phases by coupling of orientation microscopy with atom probe tomography." *Ultramicroscopy* 148 (2015): 67-74.

Tables

Table 1. ImageJ analysis of three sample conditions showing the distribution of darker contrast regions/precipitates in the matrix

	CR-SA-700	CR-SA-800	CR-SA-900
Precipitate density	210 particles / μm^2	35 particles / μm^2	1.3 particles / μm^2
Area fraction	10.1%	22.8%	23.03%
Average size	0.005 μm^2	0.025 μm^2	0.19 μm^2

Table 2. CR-SA-550 condition: Composition of Cu-rich phase, γ' (L12 precipitate) & γ (matrix) by atom probe tomography (APT)

Location	1 (Cu)		2 (γ')		3(γ)	
Ions	At. Percent (%)	Sigma (%)	At. Percent (%)	Sigma (%)	At. Percent (%)	Sigma (%)
Al	0.79	0.17	24.01	1.47	1.14	0.25
Ni	4.80	0.42	56.20	2.52	39.76	1.70
Cu	94.23	2.56	17.19	1.21	0.82	0.21
Cr	0.00	0.00	1.16	0.29	28.47	1.38
Fe	0.18	0.08	1.44	0.32	29.81	1.42

Table 3. CR-SA-700 condition: Composition of Cu-rich phase, γ' (L12 precipitate) & γ (matrix) by STEM EDS

Ions	1 (Cu)	2 (γ')	3(γ)
Al	2.60	11.47	2.31
Ni	8.89	51.70	42.55
Cu	85.71	31.28	15.38
Cr	0.72	1.39	17.86
Fe	2.08	4.16	21.9

Table 4. CR-SA-700 condition: Composition of γ' (L12 precipitate) & γ (matrix) by atom probe tomography (APT)

Location	γ		γ'	
Ions	At. Percent (%)	Sigma (%)	At. Percent (%)	Sigma (%)
Al	4.70	0.18	21.10	0.45
Ni	44.91	0.65	56.62	0.83
Cu	5.74	0.20	16.56	0.39
Cr	19.64	0.39	1.73	0.12
Fe	25.02	0.45	3.99	0.18

Figure captions

Figure 1. *Back scattered SEM:* (a) As-cast microstructure showing the segregation of Cu-rich phase in the inter-dendritic regions. (Inset- shows the elemental EDS map of Cu) (b) As-cast and annealed at 700°C for 50 h. The γ' is observed to preferentially form in the inter-dendritic region. The inset shows the higher magnification image with higher density of cuboidal precipitates in the interdendritic region. (c) cold rolled (20%) and solutioned (1000°C for 3 h) CR-SA condition, (d) CR-SA followed by subsequent annealing at 700°C for 50 h, CR-SA-700 (e) CR-SA followed by annealing at 800°C for 20 h, CR-SA-800 (f) CR-SA followed by annealing at 900 ° C for 20 h, CR-SA-900 . No second phase is observed in CR-SA whereas the size of second phase increases with temperature as we go from 700°C to 900°C

Figure 2. *Synchrotron XRD traces from an insitu experiment done on CR-SA-700.* Inset on right shows the magnified view where the γ' ($L1_2$ -Space Group = P_{mmm}) peaks can be clearly identified.

Figure 3. The plot of lattice parameter of *fcc* phase vs temperature. The change in slope while heating and cooling denotes the order-disordered transformation reaction. Lattice expansion is observed when the matrix is dis-ordered.

Figure 4. High Angle Annular Dark Field -Scanning Transmission electron microscopy (HAADF-STEM): (a) shows the HAADF-STEM image from the CR-SA-935 condition.(b-c) STEM-EDX: Elemental distribution map showing the elements with the color coding: Cu-red, Ni-blue (d-e) Selected area diffraction patterns (SADP) from [011] zone axes of Cu rich phase and the matrix respectively

Figure 5. *Transmission electron microscopy (TEM) on CR-SA condition:* (a, b & c) selected area diffraction patterns (SADP) from (a) [001], (b) [112], and (c) [011] zone axes (ZA) of the CR-SA sample respectively.

Figure 6. *Atom probe tomography (APT) on CR-SA condition:* (a) reconstruction showing all ions, (b), (c), (d), (e) and (f) show the ion map of various elements as labeled (g) 1-D compositional profiles along the arrow shown in (a).

Figure 7. *Atom probe tomography (APT) on CR-SA condition:* (a) reconstruction showing 45% Cu iso-concentration surface (b) proximity histogram across the selected interface between the Cu-rich regions and matrix showing compositional partitioning (c) 5 nm slice of the raw ion map showing Cu (red) and Al (black) ions (d) region marked with yellow box in (c) has been magnified and Cu rich and Al rich regions have been highlighted using 45 at% Cu (red) and 8 at% Al (black) iso-concentration surfaces. (e) Proximity histogram averaging fifty randomly selected Al-rich interfaces showing compositional partitioning between inside and outside Al rich regions.

Figure 8. *Transmission electron microscopy (TEM) on CR-SA-550 condition:* (a) SADP from [001] ZA (b) [011] ZA (c) [112] ZA showing the super-lattice spot at {001} and {011} positions marked in yellow color. (d) dark field (DF) TEM image obtained from the super-lattice spot encircled in yellow in (b) SADP [011] ZA showing the super-lattice spot at {001} position The γ' to precipitates are lighted up in the DFTEM image.

Figure 9. High Angle Annular Dark Field -Scanning Transmission electron microscopy (HAADF-STEM) on CR-SA-550 condition: (a) shows the HAADF-STEM image, the lower portion shows high magnification image. (b) EDX - compositional line profiles for various elements along the yellow arrow shown in (a), spikes in Cu concentration can be clearly seen. (c - g) EDX- elemental distribution maps showing various elements as labeled in the figure.

Figure 10. Atom probe tomography (APT) on CR-SA-550 condition: (a) reconstruction showing all ions, (b), (c), (d), (e) and (f) show the ion map of various elements as labeled.

Figure 11. Atom probe tomography (APT) on CR-SA-550 condition: (a) Unit cells for fcc Cu and the γ' ordered phase (with $(\text{Ni/Cu})_3\text{Al}$ stoichiometry (b) high magnification (15 nm x 10 nm x 5 nm) view of the reconstruction showing only Cu (red) and Al (black) ions (c) and (d) spatial distribution maps (SDM) from Cu-rich phase and γ' .

Figure 12. Atom probe tomography (APT) on CR-SA-550 condition: (a) 20 nm x 50 nm x 10 nm slice which the Cu-rich precipitate & γ' being encapsulated by a Cu-isosurface (red) and an Al-isosurface (grey). (b) 1-D compositional profiles for the different elements have been plotted along the axis of the cylinder in the figure by red arrow.

Figure 13. Transmission electron microscopy (TEM) on CR-SA-700 condition: (a, b & c) show the SADP $ZA=[112]_{\text{fcc}}$, $[110]_{\text{fcc}}$ and DFTEM from the selected extra superlattice spot respectively. The γ' precipitates are lighted up in the DFTEM image in (c). (d through h) show elemental distribution maps for Fe, Cr, Al, Ni & Cu respectively (g) overall STEM-EDS map where the signals from all the constituent elements of this HEA have been superimposed.

Figure 14. Atom probe tomography (APT) on CR-SA-700 condition: reconstruction showing all ions, (b) proximity histogram showing compositional partitioning across the interface γ - γ' interface.

Figure 15 Transmission electron microscope (TEM): (a) BFTEM image from CR-SA-900 showing needle-shaped precipitates (b) [001] zone axis electron diffraction pattern from only the fcc matrix (c)&(d) [001]& [011] zone axis electron diffraction pattern from region containing precipitate and the matrix respectively. (e) dark-field TEM image, recorded from the specific {011} superlattice reflection marked with a circle in (d). (f) HAADF-STEM image of the intersection of two perpendicularly aligned needle-shaped regions together with the corresponding STEM-EDS maps for Al, Cu and Fe shown as insets as labeled

Figure 16 Atom probe tomography (APT) on CRSA-900 condition: (a) SEM image showing the region used for site-specific sample prepared using the dual-beam FIB (b) SEM image of the needle prepared for atom probe tomography showing the alignment of precipitates (c) TEM dark field image showing the approximate region captured in the APT reconstruction highlighted with white trapezium shape (d) APT reconstruction capturing the 3 phases - $L1_2$, Cu rich fcc phase and the fcc matrix from top to bottom (e) A cylindrical 1-D compositional profile along the direction shown by the arrow in (d) presenting the partitioning of various elements in different phases along this direction.

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