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**Secondary phases in Al_xCoCrFeNi high-entropy alloys: an in-situ TEM
heating study and thermodynamic appraisal**

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Abstract

Secondary phases, either introduced by alloying or heat treatment, are commonly present in most high-entropy alloys (HEAs). Understanding the formation of secondary phases at high temperatures, and their effect on mechanical properties, is a critical issue that is undertaken in the present study, using the $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.3, 0.5, \text{ and } 0.7$) as a model alloy. The in-situ transmission-electron-microscopy (TEM) heating observation, an atom-probe-tomography (APT) study for the reference starting materials ($\text{Al}_{0.3}$ and $\text{Al}_{0.5}$ alloys), and thermodynamic calculations for all three alloys, are performed to investigate (1) the aluminum effect on the secondary-phase fractions, (2) the annealing-twinning formation in the face-centered-cubic (FCC) matrix, (3) the strengthening effect of the secondary ordered body-centered-cubic (B2) phase, and (4) the nucleation path of the σ secondary phase thoroughly. The present work will substantially optimize the alloy design of HEAs and facilitate applications of HEAs to a wide temperature range.

Keywords: high-entropy alloy, secondary phases, in-situ heating TEM, atom-probe-tomography, and thermodynamic calculations.

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1. Introduction

In recent years, high-entropy alloys (HEAs) have attracted considerable research interests. A rather novel concept in the alloy design was proposed by Cantor and Yeh et al. [1-11]. Up to now, several HEA systems were reported to have promising properties, such as high hardness, large work-hardening capacity, excellent high-temperature strength, good wear, oxidation, corrosion, fatigue, and fracture resistance [6, 12-26].

By definition, HEAs have a set of multi-elements, which are in equal, or near-equal, atomic ratios. HEAs tend to form a simple solid-solution structure, such as face-centered-cubic (FCC), body-centered-cubic (BCC), and/or hexagonal-close-packed (HCP) structures [4, 27-32]. This tendency is due to the high entropy of mixing of the solution phases. Thermodynamically, a system reaches the equilibrium, when the Gibbs energy of the system approaches its global minimum at a constant temperature and pressure [33, 34]. The crystallinity of HEAs is commonly simple, even though they are comprised of five or more than five elements. The simple crystal lattices exhibit both the individual characteristics of their constituents and collective features [35].

A literature survey indicates that most publications to date are focused on understanding and controlling the structure within as-cast and/or homogenized HEAs, especially at room temperature (RT). Certain publications reported on the microstructures after oxidation or heat treatment, e.g., mostly annealing, at elevated temperatures, like Al-Co-Cr-Ni-(Fe or Si) in air at 1,050 °C [36], $\text{Al}_x\text{CoCrFeNi}$ in air at

68 900 °C and 1,100 °C, and, then, quenched in water [37], AlCrCuFeMnTi in air at 590 –
69 1,100 °C [38], and FeCoNiCrCu_{0.5} in argon at 350 – 1,250 °C [39].

70 Unfortunately, these research results are mostly associated with the post-mortem
71 work. There are few reports about the in-situ structural changes of HEAs at elevated
72 temperatures. For example, in-situ research work has been published about the fast
73 electron irradiation in a transmission electron microscope (TEM) from 20 to 500 °C of
74 CoCrCuFeNi HEAs [40], the damage tolerance of CoCrFeMnNi HEAs [41], and the
75 stress-strain behavior on a macroscopic scale [42]. Therefore, the real mechanism of the
76 microstructural evolution of the multi-elements in HEAs at elevated temperatures, and
77 whether the solid solution can still hold at high temperatures during service or not, are
78 still not understood and documented in detail. Furthermore, it is critical to investigate
79 the dominant mechanism of the microstructural evolution for multicomponent HEAs at
80 elevated temperatures. In order to address these pertinent questions, an in-situ TEM
81 study is performed to study the dynamic microstructural changes of HEAs at 500 °C
82 and 900 °C, respectively.

83 The present research aims at an in-situ TEM-heating study of the microstructural
84 evolution of HEAs at elevated temperatures by heating and holding samples for some
85 time and, then, immediately cooling them down to RT in vacuum inside TEM. This
86 in-situ study facilitates the observation process for immobilizing the sample area, which
87 would be beneficial to monitor the subtle microstructure evolution. The results will be

confronted to thermodynamic calculations and compared with those at RT to provide the insight into the relationship among the microstructures, mechanical, and physical properties of HEAs at elevated temperatures. The $\text{Al}_x\text{CoCrFeNi}$ HEA systems have been used to elucidate their mechanical, anticorrosive, and thermal-expansive properties [4, 15, 16, 37, 43-46].

The research efforts, including the formation path and detailed existing characteristics of the σ phase, the direct evidence of the strengthening effect of the B2 phase, and the annealing-twinning formation in HEAs, can assess their capability and significantly facilitate the application of HEAs as future high-temperature materials. At the same time, the study could deepen our fundamental understanding on the phase stability and deformation mechanisms of both single-phase and multi-phase HEAs at high temperatures through the integration of experimental and theoretical approaches.

2. Materials and Methods

2.1 Sample preparation.

Ingots with nominal compositions of $\text{Al}_x\text{CoCrFeNi}$ (x values in molar ratios, x = 0.3, 0.5, and 0.7, denoted by $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$, respectively) alloys were prepared by arc-melting pure elements with a purity higher than 99.95 weight percent under a high-purity argon atmosphere on a water-cooled Cu hearth. The alloys were re-melted three times in order to obtain homogeneity. Then three as-cast buttons were heated to 1,250 °C in 2 hours, and completed with homogenization in a vacuum furnace for 50

hours, followed by furnace cooling on the way down. Homogenized buttons were canned in a carbon steel to avoid surface oxidation. The tubing was flattened and, then, welded shut with the button inside. Then the whole button was upset forged without the restriction of four sides to achieve a 50 % reduction at 1,250 °C. The needed reduction was calculated, and stops of carbon steels were placed on the platen to limit the reduction to 50 %. The final forged portions were ~ 5 mm thick.

2.2 Microstructural characterizations.

Samples for the electron-backscatter-diffraction (EBSD) observation and hardness measurements were cut from the center of the bulk material. The surface morphology of the polished specimens was studied by EBSD (XL-30 FEG FEI Philips) equipped with an EDS system for the chemical-composition analysis. The EBSD data were obtained by the Orientation Imaging Microscopy (OIM) hardware and Data Collection 7 software and analyzed by the TSL OIM Analysis 7.2 software (EDAX, Inc., Mahwah, NJ, USA) with the grain-tolerance angle of 5 degrees. To optimize the EDS analyses for both light and heavy elements, an acceleration voltage of 20 kV was used with K lines of Al, Co, Cr, Fe, and Ni.

Thin foils were prepared from the middle of the bulk materials and were observed through the selected-area-electron-diffraction (SAED) analysis and high-resolution TEM (HRTEM) observations operated at 400 kV, using the JEM 4000 EXII (JEOL Ltd., Tokyo, Japan). A double-tilt heating holder with a tantalum furnace (Model 652, Gatan,

Inc., Pleasanton, CA, USA) was used for the in-situ observation, and the smart mode was employed for heating to the preset temperatures and the subsequent holding for certain time before specimens were cooled down to RT in vacuum inside TEM. The temperatures were set at 500 °C, 700 °C, and 900 °C, respectively.

For the APT observation, a FEI Nova 200 dual-beam focused-ion-beam (FIB) instrument was utilized to perform lift-outs and annular milling to fabricate the needle-shaped APT specimens. APT was conducted with a local electrode atom probe (CAMECA LEAP 4000X HR) in a laser mode at a base temperature of - 243 °C and a 25 pJ laser energy. The data sets were reconstructed and analyzed, using the IVAS 3.6.12 software (CAMECA Instruments). A manual peak-decomposition routine was performed for the proximity histograms using known isotopic abundancies to account for peak overlaps, such as the Al⁺, Fe⁺⁺, and Cr⁺⁺ overlap at 27 Da.

2.3 Thermodynamic calculations.

Using the calculation of phase diagrams (CALPHAD) approach, thermodynamic properties of multicomponent HEAs are able to be predicted by two-step methods. In the first step, the parameters of thermodynamic models for the Gibbs energies of the constituent phases in the lower order systems, binaries and ternaries, will be obtained, in terms of known thermodynamic and phase equilibrium data (see Eqs. 1 and 2). In the second step, the Gibbs energies of multicomponent alloy phases will be obtained via an extrapolation method [47]. Related criteria are shown below.

If A and B form an ideal FCC solid solution, the Gibbs energy of the FCC phase is represented by,

$$G^{fcc} = x_A G_A^{fcc} + x_B G_B^{fcc} + RT(x_A \ln x_A + x_B \ln x_B) \quad (1)$$

If A and B form a sub-regular solution, the Gibbs energy will be described by,

$$G^{fcc} = x_A G_A^{fcc} + x_B G_B^{fcc} + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex,fcc} \quad (2)$$

where x_A and x_B are the at. % of A and B in the solid solution, respectively. G_A and G_B are the Gibbs energies of pure A and B. G^{ex} is the extra Gibbs energy caused by a sub-regular phase.

Thus, the Gibbs energy does reach its minimum at the composition of unequal amounts of A and B. The existence of other more stable phases will also affect the minimum Gibbs-energy position. The real alloy systems, which comprise many phases, can be much more complicated.

2.4 Neutron scattering.

Neutron-diffraction experiments were performed at the ORNL Spallation Neutron Source (SNS) using instruments (NOMAD, Nanoscale-ordered Materials Diffractometer) at RT with an aerodynamic levitator [5, 48]. This levitator provides a containerless environment, in which small samples (2-mm-diameter spheres) suspended above a conical nozzle with the flowing argon gas.

2.5 Tensile tests.

A computer-controlled Material Test System (MTS) servohydraulic-testing machine was employed for tension experiments on samples of Al_{0.3}, Al_{0.5}, and Al_{0.7} HEAs to characterize the mechanical behavior of the alloys. The flat dog-bone tension-sample geometry is shown in Figure 4e. The gauge length is 10 mm, while the width and thickness are 3.15 mm and 1 mm, respectively. The strain rate is $2 \times 10^{-4} \text{ s}^{-1}$.

3. Results

The morphologies, phase constitutions, and phase fractions of both FCC and BCC/B2 phases in Al_{0.3}, Al_{0.5}, and Al_{0.7} (shortening for Al_{0.3}CoCrFeNi, Al_{0.5}CoCrFeNi, and Al_{0.7}CoCrFeNi, respectively) samples were obtained through EBSD mapping, equipped with energy-dispersive X-ray spectroscopy (EDS), TEM, and atom-probe-tomography (APT) techniques.

3.1 EBSD characterizations at RT.

The EBSD-phase map results (Figures 1a and 1d) of the Al_{0.3} sample show that Al_{0.3} is almost a single solid-solution FCC phase. The mean grain size is larger than 600 μm . The Al_{0.5} sample (Figures 1b and 1e) consists of an approximately 98 volume-percent (vol. %) FCC phase and about 2 vol. % BCC/B2 phases. The mean grain size of FCC grains decreased to around 40 μm . The BCC/B2 phases exist in both grains and along grain boundaries. The Al_{0.7} sample (Figures 1c and 1f) consists of the 64 vol. % dendritic FCC (red color in Figure 1c) and 36 vol. % interdendritic BCC/B2 phases (green color in Figure 1c), with a mean grain size of 25 - 30 μm .

Mutual-misorientation plots revealed that no preferential orientation relationship between the dendritic FCC and interdendritic BCC/B2 grains exists. Note that the EBSD cannot differentiate BCC and B2 (an ordered BCC) phases.

3.2 Neutron-diffraction studies at RT.

Neutron profiles of Al_{0.3}, Al_{0.5}, and Al_{0.7} samples are performed at the ambient temperature, using aerodynamic levitation [5, 48] (Figure 1g). The data were fit to the solid-solution FCC and BCC/B2 structures, too, denoted by circles and squares, respectively. For Al_{0.3}, the only phase is FCC, while both FCC and BCC/B2 phases are present at RT for the Al_{0.5} and Al_{0.7} alloys. The lattice parameters derived from neutron-diffraction patterns are $a_{\text{FCC}} = 0.35808, 0.35958, \text{ and } 0.36048 \text{ nm}$ for Al_{0.3}, Al_{0.5}, and Al_{0.7}, and $a_{\text{BCC/B2}} = 0.28985 \text{ and } 0.28905 \text{ nm}$ for Al_{0.5} and Al_{0.7} HEAs, respectively. Neutron-diffraction patterns provide the information regarding the superlattice, i.e., the 100 peak, for Al_{0.7}, which indicates that the main phases in Al_{0.7} are the FCC and B2 (an ordered BCC) phases, not the BCC phase.

3.3 Morphology of twins in all three alloys at RT.

There are many $\Sigma 3$ ($60^\circ @ \langle 111 \rangle$) twins in the FCC phase, detected by EBSD, in all three alloys, Al_{0.3}, Al_{0.5}, and Al_{0.7} (Figures 1d, 1e, and 1f, respectively). The parent and daughter twins are shown in blue and red colors, respectively, on the maps. The untwinned area (white) is less than 10 vol. % in both Al_{0.3} and Al_{0.7} samples, while less than 3 vol. % in the Al_{0.5} sample. Figure 1h summarized the phase fractions, grain sizes,

and twin-area percentages of both parent and daughter twins in all three alloys, $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$ from EBSD results (Figure 1).

The crystallography information obtained through the EBSD and chemistry by the EDS analyses is combined in Figure 2, where the different maps of the same area of the $\text{Al}_{0.7}$ sample are displayed. The [001] inverse-pole-figure map (Figure 2a) is shown together with the twin parent/daughter map for the FCC phase (Figure 2b) and local average misorientation map in BCC grains (Figure 2c). The analysis is completed with five elemental distribution maps for all elements presented in the specimen. Al and Ni are rich in the BCC/B2 region, while Cr and Fe are rich in the FCC region.

3.4 TEM characterizations at RT.

The detailed microstructural analysis performed at RT by in-situ TEM. For $\text{Al}_{0.5}$ and $\text{Al}_{0.7}$, the matrix is an FCC phase. The grain size of the FCC phase is much larger than that of the BCC phase. The BCC phase looks like a long rod shape and distribute along grain boundaries on TEM images. Figure 3 gives the typical TEM micrographs of HEAs at RT. A rod-like BCC phase is clearly observed in $\text{Al}_{0.7}\text{CoCrFeNi}$, as shown in Figure 3a, while dislocations in the FCC region of $\text{Al}_{0.7}\text{CoCrFeNi}$ in Figure 3b (see also [33, 44, 49, 50]). The TEM morphologies of $\text{Al}_{0.5}$ and $\text{Al}_{0.7}$ are consistent with the EBSD results (Figures 1 and 2). Twins are easily observed in $\text{Al}_{0.5}$ at RT, as clearly shown in Figure 3c. Figure 3d gives the corresponding electron-diffraction pattern (EDP) of the twins, showing clearly the twinning relationship. Slip bands are also observed by

an optical-microscopic (OM) observation after indentation with a 100 gf force for 10 seconds. Figures 4a, 4b, and 4c show the slip bands near the indent of Al_{0.3}, Al_{0.5}, and Al_{0.7} samples at RT, respectively. HEAs deform in a jerky way, which was approved by both experiments and modelling [42].

3.5 APT characterizations at RT.

The elemental distribution and the chemical composition within different phases of Al_{0.3} and Al_{0.5} were obtained from APT. Figure 5a displays the individual atomic positions of Al, Co, Cr, Fe, and Ni in an analyzed volume of $46 \times 46 \times 180 \text{ nm}^3$. A one-dimensional (1D) line profile taken along the black arrow of all alloying elements is shown in Figure 5b. Average solute concentrations of Al, Co, Cr, Fe, and Ni are calculated to be 4.5, 23.4, 23.3, 25.7, and 23.5 atomic percents (at. %), respectively.

A frequency-distribution histogram [51] of the atom-probe data was performed within a $15 \times 15 \times 15 \text{ nm}$ cube that was carefully selected within the APT volume to avoid regions that could contain artifacts arising from crystallography, such as a crystallographic pole, to test if there is any association or clustering of the elements for Al_{0.3} (shown in Figure 5c). To accomplish the process, 100 ion bins were used to generate a compositional distribution of the experimental data, which is compared to the binomial distribution, $f(n)$ [52]. The deviation between the experimentally-measured distribution from the binomial distribution can be quantified, using χ^2 statistics [52]. A p test was performed to statistically verify the hypothesis that the experimental APT data

can be described by a random distribution of elements with a specific significance level [53]. The p value is the probability that the compositional fluctuations within the measured APT sub-volumes can be measured from a homogenous distribution described by the binomial distribution. A significance level of 0.05 was chosen, meaning that p values below 0.05 would reject the hypothesis that the elemental distributions are homogenous. The p values for Al, Co, Cr, Fe, and Ni were found to be 0.944, 0.180, 0.518, 0.464, and 0.284, respectively. These values confirm that the Al, Co, Cr, Fe, and Ni distributions are indeed homogenous.

Figures 5d and 5f present microstructures of both the FCC and B2 phases in $\text{Al}_{0.5}$ with the sub-nm resolution using APT, respectively. The NiAl-rich nanoprecipitates (Figure 5d) (which will be referred to the L1_2 phase) are found in the FCC region for $\text{Al}_{0.5}$. Related atomic concentrations across the FCC-nanoprecipitated interface, defined by a 15 at. % Al isosurface, are shown in Figure 5e. In the B2 region, the Cr-rich nanoprecipitate (Figure 5f) is present, and its composition matches that of the BCC phase, identified using CALPHAD (Table 1). A proximity histogram of the B2/BCC interface, defined by a 10 at. % Cr isosurface, is shown in Figure 5g. The B2 phase, measured by the atom probe, is NiAl rich, which correlates to the composition calculated by CALPHAD (Table 1). This trend indicates that the BCC phase detected by EBSD (Figures 1b and 1e) is most likely a B2 phase (an ordered BCC phase) in $\text{Al}_{0.5}$. Thus, APT is an efficient method that can reveal the nanostructures within the FCC and

B2 phases in Al_{0.5}. The Cr-rich BCC precipitate is the origin of the σ phase, which will be elucidated in Discussion.

3.6 In-situ TEM characterizations.

To obtain the dynamic structural information of Al_xCoCrFeNi HEAs, in-situ TEM characterizations are conducted during in-situ TEM heating from RT to 900 °C, followed by cooling down back to RT. As illustrated by the bright-field (BF) images of Al_{0.3} in Figure 6, no secondary phases are observed at RT (Figure 6a), then secondary phases are presented firstly at 500 °C (Figures 6b and 6c). As the temperature increases to 700 °C (Figure 6d) and 900 °C (Figure 6e), the amount of secondary phases increases qualitatively. Compared with Figures 6e and 6f, we can learn that the quantity of secondary phases decreases, when the temperature cooled down from 900 °C back to RT. However, there are still some secondary phases in Figure 6f, which means the formation of secondary phases is partially reversible.

3.6.1 In-situ TEM characterizations at 500 °C.

The BF TEM micrographs of the same area in HEAs at RT before and after annealing at 500 °C for 10 min. are shown in Figure 7. Figures 7a and 7b are of Al_{0.3}, 7c and 7d of Al_{0.5}, 7e and 7f of Al_{0.7}, respectively. For example, in Al_{0.3}, the FCC solid solution filled with dislocations is present at RT, before annealing (Figure 7a). During heating, at about 400 °C, some additional weak contrasts associated with the precipitation of secondary phases from the FCC-solution structure begin to appear.

After annealing at 500 °C for 10 min. and cooling back down to RT, the precipitates (marked by red arrows) become more apparent (Figure 7b), and the dislocation density has decreased considerably. The same results have been observed by the in-situ TEM, when these three HEAs were annealed at 900 °C for 10 min.

3.6.2 TEM microstructures at 900 °C.

The BF-TEM micrographs of the same Al_{0.7} area acquired at RT before and after annealing at 900 °C for 10 min. are shown in Figure 8. Before annealing, the grains are smooth without the presence of precipitates (Figure 8a), and the nano-sized BCC phase is homogenously distributed in the FCC matrix, which can be proven from the EDP shown in Figure 8b. The BCC and FCC phases have a perfect crystallographic-orientation relationship, $(110)_{\text{BCC}} // (200)_{\text{FCC}}$, $[001]_{\text{BCC}} // [001]_{\text{FCC}}$, which matches the result of other researchers [27]. While after annealing at 900 °C for 10 min. and cooling down to RT, many precipitates formed from the matrix, as shown in Figure 8c. There are two types of precipitates, i.e., equiaxial and rod-like phases, as identified by EDPs results. Figure 8d is the EDP of the rod-like phase, which is the Al-rich θ phase. The θ phase belongs to the monoclinic system with a space group of C2/m (12) and parameters of $a = 2.519$ nm, $b = 0.7574$ nm, $c = 1.094$ nm, and $\beta = 128.71^\circ$. Figure 8e is the EDP of the equiaxial phase, which is assigned as the Cr-rich σ phase. The σ phase belongs to a tetragonal system with a space group of P4₂/mm (136) and parameters of $a = 0.8799$ nm and $c = 0.4544$ nm. The parameters derived from

EDPs are $a = 0.8654$ nm and $c = 0.4540$ nm for the Cr-rich σ phase, and $a = 2.5159$ nm, $b = 0.7799$ nm, and $c = 1.0519$ nm for the Al-rich θ phase in the present study. All the experimental parameters are just somewhat smaller than pure CrFe and $\text{Al}_{45}\text{Cr}_7$ phases in the Joint Committee on Powder Diffraction Standards (JCPDS) [54] cards except for the b parameter of the Al-rich θ phase, which is increased by 3 %. Anyway, although there are slight discrepancies, the experimental data in the present study matches the result on the JCPDS cards. While there is not an orientation relationship observed between the σ -CrFe phase and the solid-solution matrix, there is crystallographic-orientation relationship found between the θ - $\text{Al}_{45}\text{Cr}_7$ phase and FCC solid-solution matrix, as illustrated on the TEM micrographs displayed in Figure 7d. As is clear from the pictures, the orientation relationship is $(-1\ 1\ 1)_{\text{Al}_{45}\text{Cr}_7} // (1\ 1\ -1)_{\text{FCC}}$, $[101]_{\text{Al}_{45}\text{Cr}_7} // [101]_{\text{FCC}}$.

The matrix lacks Cr, Fe, and Al, while it is rich in Ni. The EDS results proved that the isolated precipitate is an FCC phase (Figure 8f). Some satellite spots are also visible from main spots due to the other smaller-sized precipitates around it. This feature proves that the residual matrix can form the Ni-rich solid solution. The elemental constitutions of the isolated precipitate by the EDS analysis are 0.78, 6.67, 20.71, 29.84, and 42.01 (at. %) for Al, Co, Cr, Fe, and Ni, respectively. The lattice parameter is calculated to be $a = 0.3625$ nm within the Ni-rich FCC solid solution derived from EDPs, which is 0.56 % larger than that (0.36048 nm) before heating and annealing.

They can also be considered as having the same values within the system error.

Previous studies have shown the deviation from a homogeneous solid solution in the atomic distribution for HEAs [5, 29].

3.7 Properties.

The Vickers microhardness was measured with a load of 10 gf and holding time of 15 s. Each sample was measured at three random areas of each phase for the average and standard-deviation values. The Vickers hardness for the FCC (HV_{FCC}) and BCC/B2 phases (HV_{BCC}) of the $Al_{0.3}$, $Al_{0.5}$, and $Al_{0.7}$ alloys in the forged condition are listed in Figure 4d. Overall, the HV_{BCC} is higher than the HV_{FCC} (see also [1, 13]). For example, the value of HV_{BCC} in the forged $Al_{0.5}$ alloy is as high as 513, while the value of HV_{FCC} is only 279. Compared to hardness, tensile tests are sensitive to detect the embrittlement. Shown in Figure 4e, for $Al_{0.3}$, the values of the yield stress, ultimate tension stress, and ductility are 210 MPa, 500 MPa, and 97 %, respectively. For $Al_{0.5}$, the values of the yield stress, ultimate tension stress, and ductility are 550 MPa, 725 MPa, and 56 %, respectively. For $Al_{0.7}$, the values of the yield stress, ultimate tension stress, and ductility are 600 MPa, 740 MPa, and 8 %, respectively.

3.8 Thermodynamic calculations.

On the basis of our experience, the CALPHAD approach plays a more and more important role in the design and development of HEAs [47, 55-59]. For better understanding the stable phases and their fractions as well as the distribution of each

alloying element within different phases of all three alloys ($Al_{0.3}$, $Al_{0.5}$, and $Al_{0.7}$), equilibrium calculations are carried out on them within the temperature range from 200 to 1,500 °C (as shown in Figure 9). Six different phases, FCC, BCC, $L1_2$, B2, σ , and θ phases, are present in the three studied alloys ($Al_{0.3}$, $Al_{0.5}$, and $Al_{0.7}$), and their relative fractions and phase compositions at three experiment-related temperatures are listed in Table 1.

In $Al_{0.3}$, for 1,026 °C < T < 1,402 °C, only one FCC phase is present and stable. As the temperature decreases, the ordered B2 phase forms at 1,026 °C and disappears at 550 °C. The σ phase forms at temperatures below 720 °C and disappears at 350 °C, and the ordered $L1_2$ forms below 600 °C. Two kinds of disordered BCC phases will be present at even lower temperatures.

In $Al_{0.5}$, the ordered B2 phase will form in a larger temperature range, from 200 °C to 1,350 °C, which explains the presence of the B2 phase at RT. The σ phase begins to develop at a temperature of 820 °C, and disappears at 350 °C. Also, the ordered $L1_2$ and disordered BCC phases can form in the temperature range of 400 to 600 °C. The disordered BCC phase will separate into two different BCC phases when the temperature decreases below 400 °C.

In $Al_{0.7}$, the ordered B2 phases also form within a large temperature range (200 °C to 1,350 °C) and encompass a larger volume fraction, compared to $Al_{0.5}$. At temperatures between 900 °C and 1,350 °C, the BCC phase is present at an

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2 365 approximately 5 vol. %. The start temperature of the σ phase is increased to 900 °C. The
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5 366 σ phase disappears at approximately 350 °C, which is similar to that in Al_{0.3} and Al_{0.5}.
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8 367 The formation of L1₂ and two disordered BCC phases are also similar to those that form
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10 368 in Al_{0.3} and Al_{0.5}. More detailed information, e.g., chemical compositions of each phase,
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13 369 from our thermodynamic calculations is listed in Table 1, which indicates that the
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16 370 ordered B2 phase is NiAl rich, and the σ phase is Cr rich.
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4. Discussion

4.1 Effect of Al addition

Excessive alloying of the Al element results in the change of both microstructural and mechanical properties in $\text{Al}_x\text{CoCrFeNi}$ HEAs. There are mainly three structural features in $\text{Al}_x\text{CoCrFeNi}$: (1) the morphology, (2) the volume fractions of the six phases, and (3) existing temperatures of all six phases. As the aluminum ratio increases from 0.3 to 0.7, the morphology changes from large-sized equiaxed grains ($\sim 600 \mu\text{m}$) for $\text{Al}_{0.3}$, to small-size equiaxed ($\sim 60 \mu\text{m}$) for $\text{Al}_{0.5}$, and finally to dendrite/interdendrite structures for $\text{Al}_{0.7}$. The B2 phase initializes in both intragranular and intergranular sites, as the aluminum content increases. From $\text{Al}_{0.3}$ to $\text{Al}_{0.7}$, the volume fraction of the B2 phase increases from 0 % to 36 %, which indicates that the aluminum content is a critical factor for the FCC/B2 phase ratio, and which is also found in $\text{Al}_x\text{CoCrCuFeNi}$ [1, 60] and $\text{Al}_x\text{CoCrFeMnNi}$ [61]. The aluminum content expands the existing temperatures and increases the volume fraction of the B2 phase in $\text{Al}_x\text{CoCrFeNi}$, because Al acts as a strong NiAl-rich B2-phase stabilizer [62]. The increasing volume fractions of the B2 and σ phases explain the increase of the yield strength and the decrease of the elongation in $\text{Al}_x\text{CoCrFeNi}$ HEAs.

4.2 Deformation mechanisms of both FCC and BCC phases

Different deformation mechanisms could be clearly detected in the FCC and BCC phases (shown in Figure 2), which is illustrated in Figure 10a. Under the same plastic

deformation, annealing twins are present only in the FCC phase, while the BCC/B2 phases are highly deformed. The FCC phase is full of annealing $\Sigma 3$ twins ($60^\circ @ \langle 111 \rangle$), shown as yellow lines in all maps depicted in Figure 1 for all alloys investigated and in Figure 2 for the $\text{Al}_{0.7}$ sample. The existence of twins is unaffected, to the variation of the aluminum content. However, the untwinned area and both the parent and daughter twinned areas become finer, after increasing the aluminum content. On the other side, the BCC phase is characterized by large highly-deformed grains. The map of local average misorientations, indicating the high local deformation through dislocation glide and climb mechanisms are shown in Figure 2c. Therefore, as illustrated in Figure 9a, under the same high plastic deformation, originated from the 50 % forging in the last step of sample preparation, the BCC/B2 phases are highly deformed, while annealing twins are only present in the FCC phase.

4.3 Formation of intermetallic Cr-rich (both BCC and σ phase) precipitations

The globular Cr-rich σ phase precipitates are identified by both in-situ TEM experimental techniques together with EDP results (Figure 8), after annealing at 900 °C for 10 min. and cooling down to RT, as well as CALPHAD calculations (Figure 9c) for $\text{Al}_{0.7}$. Nano-scaled Cr-rich precipitates, identified by APT and thermodynamic calculations, are present in the B2 phase in $\text{Al}_{0.5}$ (Figure 5f). In $\text{Al}_{0.3}$, precipitates initiation were identified, using the in-situ heating TEM observation (Figure 7b), in which they are too small to obtain the crystal structure, employing conventional

diffraction methods. Therefore, through the detailed thermodynamic calculations (Figure 9), the σ phase appears to be stable at intermediate temperatures, between 350 °C and 720 °C for Al_{0.3}, between 350 °C and 810 °C for Al_{0.5}, and between 350 °C and 900 °C for Al_{0.7}, respectively. The σ phase is present in all three HEAs, because (1) Cr is known as a strong σ phase former, and the σ phase has also been shown to form in binary systems of the Cr-Co, Cr-Fe, and Cr-Ni. (2) more substitutional elements (Al, Co, Cr, Fe, and Ni), having similar atomic radii, do not make the σ phase unstable for HEAs. The Cr-rich phases were only found in the B2 region for Al_{0.5} by APT (Figure 5f), which may be rationalized as follows: (1) The Cr-rich phase is a second phase of a rich substitutional element. The diffusion of the substitutional element is very slow in the FCC phase [3]. Thus, the nucleation of the Cr-rich phase in the FCC phase is difficult. (2) The interface between the Cr-rich and FCC phases is incoherent [63] to prevent the formation of the Cr-rich structure in the FCC phase.

The APT and thermodynamic-calculation results for Al_{0.5} show that the σ -phase precipitation can be described as occurring in three steps (shown in Case 1 of Figure 10b) : (1) The Cr-rich BCC phase nucleates in the B2 region, resulting from the coherent interfaces and driven by the concentration profiles; (2) The σ phase nucleates at the BCC/B2 interface and rapidly grows within the BCC phase, attributed to the Cr-concentration profiles (partitioning of alloying elements); and (3) the eutectoid decomposition of the remaining BCC phase is around 600 °C (shown in Figure 9).

According to presented TEM experimental results, the CALPHAD-based analysis, and results reported in literatures [5, 28, 64-66], the σ phase at higher temperatures in $\text{Al}_{0.7}$ can also form directly from the FCC matrix (illustrated in Case 2 of Figure 10b). The evidence is that the σ phase is globular in shape inside the FCC matrix and has no relationship with the FCC matrix (Figures 8c and 8e).

The Cr-rich phases are also found in other HEAs [5, 27, 28, 65, 66], and stainless steels [63]. The hardness of the alloys increases with increasing the content of the σ phase in Fe-based composites [67]. The Cr-rich phase is referred to as the σ phase, which has been verified by EDS mapping in the scanning-electron microscopy (SEM) and selected-area diffraction (SAD) in the TEM to be present at the grain boundary after a 700 °C annealing for 1,000 hours [65] and 500 days [66] in CoCrFeMnNi , respectively. In mechanochemically-synthesized Cr-Fe-Co-Ni-Al-Ti alloys [68], σ phases are identified by X-ray diffraction (XRD) at even higher temperatures, 850 °C and 1,200 °C, respectively. The Cr-rich phase is referred to as the BCC phase in $\text{Al}_{1.3}\text{CoCrFeNi}$ [5] and Al-Co-Cr-Fe-Ni alloys, containing approximately a 15 to 23 atomic percent (at. %) Al [64]. Also, the Cr-rich phase was observed in the as-cast $\text{Al}_{0.44}\text{CoCrFeNi}$ alloy by Z-contrast imaging in a scanning TEM (STEM) [36]. However, the crystal structure of this Cr-rich phase was not identified. Thus, the precipitation of the Cr-rich phase, including the σ and BCC phases, is often observed in various HEAs, and the understanding of the Cr-rich precipitation will allow for some control over the

properties of HEAs in the future. By comparing the calculated existing temperature of the σ phase in $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$ (shown by orange curves in Figures 8a, 8b, and 8c, respectively), it shows that the σ phase can stand for higher temperatures, as the Al ratio increases, which is correlated with an increase in hardness (Figure 4d) and a decrease in elongation (Figure 4e) in HEAs, as the Al ratio increases.

4.4 Comparison between thermodynamic calculations and experimental results

The thermodynamically-calculated results help us better understand the experimental results. It facilitates the identification of the BCC/B2 phases (Figures 1b and 1c) as the B2 phase in $\text{Al}_{0.5}$ and $\text{Al}_{0.7}$. The calculations also effectively verify the structures of the NiAl-rich phase (Figures 5d and 5e) and nanoscaled Cr-rich phase (Figures 5f and 5g) in $\text{Al}_{0.5}$ as L_{12} and BCC phases, respectively. There are great agreements of the phase fractions between the measured and calculated values for $\text{Al}_{0.3}$ and $\text{Al}_{0.5}$, as described below. However, discrepancies are present. The experimental results show that the FCC phase fractions after homogenization at 1,250 °C for 50 hours are ~ 100, 98, and 64 % for $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$, respectively, while our calculated results are ~ 100, 96, and 80 %, accordingly. The discrepancy for the $\text{Al}_{0.7}$ alloy may be due to the inaccuracy of the current thermodynamic database. Nevertheless, furnace cooling rather than water quenching was used in the present work. The relatively-slow cooling rate could result in the formation of precipitates, such as the B2 phase (~ 0.1 vol. %) within the $\text{Al}_{0.3}$ alloy. Discrepancies are also expected at lower temperatures,

such as 500 and 900 °C. The reason for discrepancies is that the phase diagram represents the phase-equilibrium information, while the phase transformation in the solid state is the diffusion-controlled process, and it will take much longer time to reach the equilibrium state. The in-situ TEM work held the sample at different temperatures for only 10 min. Thus, the experimentally-observed microstructures are not in equilibrium.

5. Conclusions

By the novel integrated approach, combining the in-situ TEM observation, APT characterization, EBSD, neutron diffraction, and detailed thermodynamic calculations, (1) the aluminum effect on the phase fraction, (2) the annealing-twinning formation, (3) the nucleation of secondary phases, and (4) the effect of secondary phases on mechanical properties in $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.3, 0.5, \text{ and } 0.7$) HEAs have been discussed thoroughly. The following conclusions can be drawn.

a. The main phase constitution in the forged $\text{Al}_x\text{CoCrFeNi}$ HEAs is the mixture of the FCC and B2 phases. The fraction of the B2 phase increases with increasing the Al content. The volume fractions of the FCC phases are 99 %, 98 %, and 36 % for $\text{Al}_{0.3}\text{CoCrFeNi}$, $\text{Al}_{0.5}\text{CoCrFeNi}$, and $\text{Al}_{0.7}\text{CoCrFeNi}$, respectively.

b. Excessive alloying of the Al element results in the change of both microstructural and mechanical properties in $\text{Al}_x\text{CoCrFeNi}$ HEAs. As the aluminum ratio increases from 0.3 to 0.7, the morphology changes from large-sized equiaxed

grains, to small-sized equiaxed grains, and finally to dendrite/interdendrite grains. The aluminum contents expand the existing temperature and increase the volume fraction of the B2 phase in $\text{Al}_x\text{CoCrFeNi}$, as Al acts as a strong NiAl-rich B2-phase stabilizer.

c. Using the in-situ TEM study, there are predominantly two types of precipitates, a Cr-rich σ phase (a CrFe type) and an Al-rich θ phase (an $\text{Al}_{45}\text{Cr}_7$ type), observed and characterized by experimental efforts after annealing for 10 min. at 900 °C for $\text{Al}_{0.7}\text{CoCrFeNi}$. Thermodynamic calculations and APT results show that the σ phase is also present in $\text{Al}_{0.3}$ and $\text{Al}_{0.5}$. The nucleation path of the σ phase in both $\text{Al}_{0.5}$ and $\text{Al}_{0.7}$ is illustrated in two cases. The σ phase forms either in a three-step formation (a Cr-rich BCC phase nucleates in the B2 region $\rightarrow$ the σ phase nucleates at the BCC/B2 interface $\rightarrow$ the remaining BCC phase decomposes), or directly from the FCC matrix.

d. Twins are present only in the FCC regions for all three alloys, due to the low stacking fault energy [3]. The local average disorientation in the B2 region of $\text{Al}_{0.7}\text{CoCrFeNi}$ proves the strengthening effect of the B2 phase directly. Thus, the increasing volume fractions of the B2 and nano-sized σ phases explain the increase in the yield strength and decrease in the elongation of $\text{Al}_x\text{CoCrFeNi}$ HEAs.

e. The research efforts, including (1) the formation path and detailed existing characteristics of the σ phase, (2) the direct evidence of the strengthening effect of the BCC phase by EBSD, and (3) the annealing-twin formation only in FCC regions of HEAs, assess the capability of HEAs as future high-temperature materials thoroughly.

Above all, the study could provide our fundamental understanding on the phase stability and deformation mechanisms of both single-phase and multi-phase HEAs at elevated temperatures through the novel integration of experimental and theoretical approaches.

Above all, the present research could provide the basic understanding of the phase stability and deformation behavior of both single-phase and dual-phase HEAs, thus facilitating the application of HEAs at elevated temperatures.

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Author contributions

J. C. Rao, P. K. Liaw, V. Ocelik, D. I. Vainchtein, and J. Th. M. De Hosson designed the research; J. C. Rao and H. Y. Diao were the lead experimental scientists of the investigation; C. Zhang conducted thermodynamic calculations of the study; C. Kuo and Z. Tang synthesized the sample; W. Guo and J. D. Poplawsky analyzed the APT experimental results; and J. C. Rao, H. Y. Diao, and J. Th. M. De Hosson wrote the paper. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare that they have no competing interests.

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1 **Table 1 Stable phases, phase fractions, and phase-chemical compositions of all**
2 **three alloys at three experiment-related temperatures**

Para- meters Alloys	T (°C)	Stable Phase	Fraction (%)	Phase Composition (at. %)				
				Al	Co	Cr	Fe	Ni
Al _{0.3}	1,250	FCC	100	6.976	23.256	23.256	23.256	23.256
	900	FCC	94.15	5.057	24.079	54.499	24.450	21.915
		B2	5.85	37.864	10.000	3.263	4.041	44.832
	500	BCC	31.34	0.276	40.480	8.466	47.902	2.876
		L1 ₂	31.07	22.160	3.632	0.689	4.414	69.106
		σ	37.59	0.016	25.112	54.240	18.277	0.236
Al _{0.5}	1,250	FCC B2	95.56 4.04	10.001 37.282	22.678 11.388	22.880 6.591	22.955 4.813	21.477 39.926
	900	FCC	80.74	4.468	24.832	26.702	26.607	17.391
		B2	19.26	38.960	11.283	3.443	3.841	42.473
	500	BCC	28.515	0.297	38.982	8.649	49.198	2.874
		B2	18.022	39.903	9.485	0.409	2.537	47.667
		L1 ₂	17.290	22.150	3.373	0.668	4.589	69.220
		σ	36.173	0.015	24.365	54.091	19.193	2.334
Al _{0.7}	1,250	FCC	80.09	9.758	23.307	24.229	24.850	17.857
		BCC	1.65	8.231	18.760	37.590	27.616	7.804
		B2	18.26	38.019	12.600	6.856	5.034	37.490
	900	FCC	69.61	4.039	24.975	28.822	28.880	13.284
		BCC	0.32	4.575	18.807	44.466	27.421	4.730
		B2	30.07	40.128	12.742	3.566	3.610	39.953
	500	BCC	26.049	0.318	37.549	8.837	50.417	2.878
		B2	34.590	39.926	9.007	0.402	2.678	47.988
		L1 ₂	4.499	22.126	3.137	0.652	4.766	69.32
		σ	34.862	0.015	23.632	53.944	20.086	2.323

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(h)

Structures Materials	Phase (vol. %)		Grain Size (μm)		Twinned FCC Grains (vol. %)		
	FCC	BCC	FCC	BCC	Untwinned	Parent	Daughter
Al _{0.3} CoCrFeNi	99.9	0.1	> 600	-	9.5	54.5	36.0
Al _{0.5} CoCrFeNi	98.0	2.0	40.4	7.5	2.3	62.8	34.9
Al _{0.7} CoCrFeNi	64.0	36.0	26.6	19.2	9.7	52.5	37.8

Figure 1 Phase-constitution characteristics of Al_{0.3}CoCrFeNi, Al_{0.5}CoCrFeNi, and Al_{0.7}CoCrFeNi at RT, obtained by EBSD and neutron-diffraction measurements.

The FCC phase (red) are almost 100 %, 98 %, and 64 % and the BCC phase (green) 0 %, 2 %, and 36 % in Al_{0.3} (a), Al_{0.5} (b), and Al_{0.7} (c) samples, respectively. Black lines represent grain boundaries, and yellow lines denote 60°@<111> twins in the FCC phase.

60°@<111> twins in the FCC phase detected by the EBSD results in Al_{0.3}CoCrFeNi (**d**), Al_{0.5}CoCrFeNi (**e**), and Al_{0.7}CoCrFeNi (**f**) samples. The white area represents the untwinned fraction, blue and red colors denote the parent and daughter twin areas, respectively. Black pixels belong to the BCC phase. (**g**) Neutron-diffraction profiles of Al_{0.3}CoCrFeNi, Al_{0.5}CoCrFeNi, and Al_{0.7}CoCrFeNi samples at RT. Data were fit to the FCC and BCC/B2 structures, and the corresponding peaks are denoted by circles and squares, respectively. The primary phase is, therefore, identified as an FCC solid solution in all three alloys. However, except Al_{0.3}CoCrFeNi, both Al_{0.5}CoCrFeNi and Al_{0.7}CoCrFeNi contain a BCC phase. (**h**) is the summarized phase fractions, average grain diameters, and twin fractions in the FCC phase of Al_{0.3}CoCrFeNi, Al_{0.5}CoCrFeNi, and Al_{0.7}CoCrFeNi alloys

Figure 2 Microstructural characteristics of the $\text{Al}_{0.7}\text{CoCrFeNi}$ alloy after the forging process (hot plastic deformation), studied by the combination of EBSD and EDS mapping of about 1M points with step of $0.4\ \mu\text{m}$.

(a) [001] inverse-pole-figure map;

(b) Twin parent/daughter map of $\Sigma 3$ twins in the FCC phase;

(c) Local average misorientation map in the BCC phase (blue 0° , red 3°).

Rest: Co, Al, Ni, Cr and Fe EDS maps showing Al, Ni-rich BCC and Cr, Fe-rich FCC phases. Grain boundaries ($> 5^\circ$ in black) and $\Sigma 3$ twins (yellow) in the FCC phase are also shown.

Figure 3 Typical TEM micrographs showing general microstructures in HEAs at RT: (a) a narrow rod-like BCC phase along the FCC grain boundary in $\text{Al}_{0.7}\text{CoCrFeNi}$, (b) dislocations in the FCC phase of $\text{Al}_{0.7}\text{CoCrFeNi}$, (c) twins in $\text{Al}_{0.5}\text{CoCrFeNi}$, and (d) the corresponding EDP showing the twinning relationship.

(d)

Materials	HV (FCC)	HV (BCC)
Al_{0.3}CoCrFeNi	233 ± 6	-
Al_{0.5}CoCrFeNi	279 ± 11	513 ± 21
Al_{0.7}CoCrFeNi	312 ± 17	428 ± 13

(e)

Figure 4 Hardness and tensile properties of $\text{Al}_{0.3}\text{CoCrFeNi}$, $\text{Al}_{0.5}\text{CoCrFeNi}$, and $\text{Al}_{0.7}\text{CoCrFeNi}$. SEM micrographs of slip bands after indentation at RT with a 100 g force for 10 seconds: (a) $\text{Al}_{0.3}\text{CoCrFeNi}$, (b) $\text{Al}_{0.5}\text{CoCrFeNi}$, (c) $\text{Al}_{0.7}\text{CoCrFeNi}$, with a', b', c' magnifications accordingly. (d) The Vickers microhardness measured with a load of 10 gf and a load time of 15 s. Each sample was measured at three random areas of each phase for the average and standard deviation values. (e) Tensile engineering stress-strain curves of $\text{Al}_x\text{CoCrFeNi}$ alloys ($x = 0.3, 0.5, \text{ and } 0.7$). The gauge length is 10 mm, while the width and thickness are 3.15 mm and 1 mm, respectively. The strain rate is $2 \times 10^{-4} \text{ s}^{-1}$.

Figure 5 APT data of $\text{Al}_{0.3}\text{CoCrFeNi}$ and $\text{Al}_{0.5}\text{CoCrFeNi}$ at room temperature (RT). (a) Individual elemental maps, including Al, Co, Cr, Fe, and Ni, respectively, displaying the overall distribution of atoms in $\text{Al}_{0.3}\text{CoCrFeNi}$; (b) The concentration profile of all alloying elements taken along the black arrow in $\text{Al}_{0.3}\text{CoCrFeNi}$; Solute concentrations of Al, Co, Cr, Fe, and Ni are calculated to be 4.5, 23.4, 23.3, 25.7, and 23.5 at. %, respectively. (c) solute-frequency distribution histograms of all alloying elements with a block size of 100 atoms. The bold lines are the theoretical binomial distribution, while dots are the experimental data. (d) RT microstructures on the atomic level of the $\text{Al}_{0.5}\text{CoCrFeNi}$ alloy in the FCC region, showing that the FCC phase contains NiAl rich L_{12} nanoprecipitates, and (e) the proximity histogram, presenting atomic concentrations across the FCC- L_{12} interface. (f) An atom map from the B2 region, showing the atomic distribution within the B2 phase, which contains the Cr-rich BCC phase, and (g) the proximity histogram, presenting atomic concentrations across the B2/BCC interface.

Figure 6 TEM bright field images of Al_{0.3}CoCrFeNi alloy during in-situ TEM heating. (a) starting at RT, (b) reaching at 500 °C, (c) 500 °C for 30 s, (d) reaching at 700 °C, (e) reaching at 900 °C, (f) cooled down back to RT.

Figure 7 Snapshots at RT of in-situ heating TEM micrographs of HEAs before and after annealing at 500 °C for 10 min. (a, b) Al_{0.3}CoCrFeNi, (c, d) Al_{0.5}CoCrFeNi, and (e, f) Al_{0.7}CoCrFeNi. Newly-formed precipitates are indicated by red arrows for example.

$\text{Al}_{0.7}\text{CoCrFeNi}$ Before annealing

Figure 8 TEM micrographs of $\text{Al}_{0.7}\text{CoCrFeNi}$ at RT before and after annealing at 900 °C for 10 min. (a) A BF image before heating, (b) EDP of the matrix before heating, (c) A BF image after annealing, (d) EDP of the rod-like θ phase ($\text{Al}_{45}\text{Cr}_7$), (e) EDP of the σ phase (CrFe) showing the crystallographic-orientation relationship with the FCC matrix, and (f) EDP from an isolated precipitate, which proved that the precipitate is an FCC phase. Some side spots are also visible from main spots due to the other smaller-sized precipitates around it.

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Figure 9 CALPHAD diagram showing the relationship between the fractions of various phases and temperatures for (a) $\text{Al}_{0.3}\text{CoCrFeNi}$, (b) $\text{Al}_{0.5}\text{CoCrFeNi}$, and (c) $\text{Al}_{0.7}\text{CoCrFeNi}$, respectively.

Figure 10 (a) Schematic representation of difference responses of FCC and B2 phases after the same forging process. $\Sigma 3$ twins form in the FCC region, while high local deformation, characterized by the local average misorientation map, is present in the B2 region. **(b) The proposed formation path of the σ phase in two cases.** Case 1 is a three-step formation, based on APT results and thermodynamic calculations. Step 1: The Cr-rich BCC phase nucleates in the B2 region, resulting from the coherent interfaces and driven by the concentration profiles; Step 2: The σ phase nucleates at the BCC/B2 interface and rapidly grows within the B2 phase, attributed to Cr-concentration profiles (partitioning of alloying elements); and Step 3: the eutectoid decomposition of the remaining BCC phase is around 600 °C. Case 2 is that the σ phase at higher temperatures in $Al_{0.7}$ can form directly from the FCC matrix.

Secondary phases in Al_xCoCrFeNi High-entropy Alloys