Contents lists available at ScienceDirect

# Materialia

journal homepage: www.elsevier.com/locate/mtla

# Full Length Article

# Insight into the kinetic stabilization of Al0.3CoCrFeNi high-entropy alloys

Elaf A. Anber<sup>a,b</sup>, Andrew C Lang<sup>b</sup>, Eric A. Lass<sup>c</sup>, Pranav Kumar Suri<sup>b</sup>, James L Hart<sup>a,b</sup>, Daniel Scotto D'Antuono<sup>b</sup>, Haoyan Diao<sup>c</sup>, Rui Feng<sup>c</sup>, Roger Doherty<sup>b</sup>, Peter K Liaw<sup>c</sup>, Mitra L Taheri<sup>a,b,\*</sup>

<sup>a</sup> Department of Materials Science & Engineering, Johns Hopkins University, 3400 N. Charles Street, Baltimore, MD 21218, United States

<sup>b</sup> Department of Materials Science and Engineering, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, United States

#### ARTICLE INFO

Keywords: High entropy alloys In-situ TEM heating Intermediate phase evolution Kinetic stabilization Thermodynamic calculations

# ABSTRACT

The Al<sub>x</sub>CoCrFeNi family of high entropy alloys (HEAs) has received considerable attention due to its promising thermal, mechanical, and corrosion-resistant properties which make it widely suited for aerospace and marine applications. While the formation of secondary phases has been studied at various annealing temperatures, the results have focused on the late stages of precipitation, highlighting the need for the analysis of the intermediate stage precipitation. Here we use in-situ heating in the transmission electron microscope (TEM) complemented by ex-situ characterization of bulk annealed specimens, thermodynamic calculations, and precipitation simulations to study the phase evolution of  $Al_{0.3}$  CoCrFeNi. Due to the high density of nucleation sites in the thin film, *in-situ* TEM reveals the formation of an additional intermediate phase, Co-B2 at 550 °C, where hundreds of hours are predicted for this phase to be shown during ex-situ experiments. At higher annealing temperatures between 700 and 900 °C, in-situ TEM shows the formation of Cr-rich precipitates as the first intermediate phase, followed by NiAl precipitates that form co-precipitates. The formation of these precipitates occurs concurrently, contrary to the findings of previous studies. In conjunction with the *in-situ* and *ex-situ* TEM studies, thermodynamic calculations and precipitation simulations have been performed to predict the formation of these phases and are found to support the experimental results. The present work provides new insight into the microstructural evolution of HEAs and reveals the importance of intermediate stages of thermal evolution, enabling an enhanced predictive view of phase evaluation in this class of alloys.

# 1. Introduction

Recently, a new class of materials, termed high-entropy alloys (HEAs), has become the subject of emerging interest due to their unique physical and structural properties [1-17]. Their unconventional alloy design contains multiple principal elements in equal atomic concentrations [18-20]. HEAs tend to crystallize into single or dual phase solid solutions, and most have either face-centered- cubic (FCC), body-centered-cubic (BCC), or mixed FCC/BCC structures [1-20]. HEAs and their phase evolution are thought to be governed by high configurational entropy, sluggish diffusion, and severe lattice distortion [21-36]. It has been widely suggested that HEAs are potential candidates for high-temperature applications. A key challenge in the advancement of HEAs is phase stability, which affects not only the thermodynamic equilibrium of the alloy system, but also its mechanical and corrosion resistance properties. Recent studies have shown that the corrosion resistance of

a dual phase Al<sub>x</sub>CoCrFeNi alloy deteriorates due to localized corrosion formed along NiAl B2/ FCC interfaces [37-40] and Cr-rich precipitates within dendrite regions [41]. Interestingly, the B2 phase is known to enhance the mechanical properties of Al<sub>0.3</sub>CoCrFeNi [36], contributing to strength and ductility [1].

Aluminum-containing HEAs (i.e. Al<sub>x</sub>CoCrFeNi), where Al is added in order to lower alloy density and enhance corrosion resistance, has been widely studied in terms of phase stability due to their suitability for aerospace and marine applications [24,28,29,30,36]. Despite the fact that many of these investigations focused on phase evolution during prolonged annealing, there remains many open questions regarding the formation of intermediate phases during annealing. A mechanistic study of thermal evolution and precipitate stability is vital to creating a predictive understanding of the HEA microstructure, leading to the ability to tailor specific alloys for targeted applications.

\* Corresponding author. E-mail address: mtaheri4@jhu.edu (M.L. Taheri).

https://doi.org/10.1016/j.mtla.2020.100872 Received 3 August 2020; Accepted 13 August 2020 Available online 19 August 2020 2589-1529/© 2020 Acta Materialia Inc. Published by Elsevier B.V. All rights reserved.







<sup>&</sup>lt;sup>c</sup> Department of Materials Science and Engineering, University of Tennessee Knoxville, 1508 Middle Drive, Knoxville, TN 37996, United States

To date, a consensus has not been reached regarding the temperature dependence of stable secondary phases formed in Al<sub>0.3</sub>CoCrFeNi [24,28-30,36]. According to previous experimental observations [28], Al<sub>0.3</sub>CoCrFeNi exists as a single solid solution (a disordered FCC) phase after aging at 900 °C based on data collected using x-ray diffraction. Others have investigated the phase stability of this alloy after heating at various annealing temperatures and longer heating periods, showing that the disordered FCC phase exists up to 700 °C and precipitates B2 (Ni-Al) phase at temperature between 700 °C -1000 °C [29]. Additionally, the formation of the L12 phase at 550 °C [32], 700 °C [36], and 850 °C [30], and the presence of the B2 phase in as-received and homogenized alloys at 1100 °C [24], have been reported from ex-situ studies. More recent investigations have utilized in-situ TEM heating techniques to monitor the phase evolution of  $Al_x$ CoCrFeNi (x = 0.3-0.7) at temperatures between 500 and 900 °C [26]. When x = 0.3, the authors reported the precipitation of secondary phases out of the disordered FCC phase at around 400 °C and forming more readily with an increase in temperature to 900 °C[26]. While these results mark a step forward in the understanding of the secondary phase formation, they lack chemical and structural data necessary for the secondary phases reported for Al<sub>0.3</sub>CoCrFeNi.

The discrepancies among studies in terms of phase evolution and stability highlight the need for continued work towards understanding the thermal evolution of this class of HEAs. In the present work, we build a more robust understanding of phase stability windows in the Al0.3CoCrFeNi alloy system through direct observation and computational analysis, combining both bulk and in-situ annealing techniques, high-resolution and analytical TEM, thermodynamic calculations, and precipitation simulation. We experimentally identify the phase separation of the single FCC Al<sub>0.3</sub>CoCrFeNi HEAs during ex-situ and in-situ TEM heating, at intermediate and high annealing temperatures. The information that we gather from ex-situ experiments (potential phases and temperature range where secondary phases formed) are used to further understand the stability of Al0.3 CoCrFeNi HEAs in a real-time observation using in-situ heating in TEM and tracking the early, intermediate, and final stages of intermediate phase formation. Using in-situ TEM heating, we accelerate the formation of secondary phases by means of high density surface nucleation sites in the thin foil, we are able to track the formation of additional intermediate phases, for which formation during ex-situ heating experiments currently remains unknown. It is important to note, however, that similar behavior is expected during ex-situ experiments if annealing extends for a long period of time or if the density of nucleation sites is enhanced (such as in the case of a nanostructured alloy). The results are compared with thermodynamic calculations using TCHEA1 and a precipitation simulation using the TC Prisma module of Thermocalc to predict equilibrium phases, volume fraction, and chemical composition as a function of temperature in Al0.3CoCrFeNi.

Designing a study concentrating on heterogeneous precipitation events, we have uncovered key findings in HEA phase formation pertaining Co-rich, Cr-BCC and B2 precipitation, revealing that the formation of these precipitates can happen concurrently, adding new insight to previous studies [24,29,30,36].

#### 2. Methods

#### 2.1. Thermodynamic calculations and precipitation simulations

Thermocalc software, version 2017a [42] was used in conjunction with the Thermocalc TCHEA1 [43] thermodynamic databases to perform the equilibrium phase diagram calculations for the quinary Al-Co-Cr-Fe-Ni system. Phase equilibria were predicted for the Al<sub>0.3</sub>CoCrFeNi alloy at temperatures of 550 °C, 700 °C, and 900 °C, including expected equilibrium phases and their respective phase fractions (as mole fractions) and compositions. The thermodynamic calculations were performed twice. First all phases in the database were included, which predicted the  $\sigma$  phase in equilibrium at temperatures below about 800 °C. Because the formation of the  $\sigma$  phase is known to be extremely sluggish in many alloys (e.g., requiring thousands of hours at elevated temperatures in stainless steel [44,45]), it was suspended, and the thermodynamic calculations were performed again excluding the  $\sigma$ -phase.

In order to uncover the dynamic role of nucleation site density on intermediate phase formation between various heating conditions, the Thermocalc TC Prisma module was used to simulate the precipitation behavior in the Al<sub>0.3</sub>CoCrFeNi alloy, again using the TCHEA1 thermodynamic database along the Ni-based superalloy mobility database developed by Campbell et al. [46]. The simulations were performed at 550 °C and 700 °C using two different nucleation site density assumptions. Secondary phase formation in the ex-situ experiments was observed primarily on grain boundaries, therefore the grain boundary nucleation was assumed to predict the precipitation in the ex-situ experiments. The default grain size of 100  $\mu$ m was assumed, yielding calculated grain boundary nucleation site density of  $6.5 \times 10^{23}$  m<sup>-3</sup>. For the *in-situ* TEM experiments, nucleation was observed experimentally to occur in all areas of the sample, not just along grain boundaries. This is almost certainly a result of surface-dominated nucleation in the thin TEM specimens and causes the intermediate phases to form much faster than in the bulk, ex-situ experiments. To simulate the precipitation behavior in the in-situ experiments, homogeneous, bulk nucleation was assumed, where the nucleation site density was on the order of atomic density,  $8.6 \times 10^{28}$  $m^{-3}$ , five orders of magnitude greater than for the grain boundary nucleation.

For simplicity, a spherical precipitate morphology was assumed for both BCC and B2 phases . Following the reported values of Chen et al. [47], the interfacial free energies were estimated as 25 mJ/m<sup>2</sup> and 250 mJ/m<sup>2</sup> for the FCC-BCC and FCC-B2 interfaces, respectively. Additionally, due to the short-comings in the thermodynamic database, the Gibbs free energy of the Cr-BCC phase was modified by adding -300 J/mol to increase its stability so that it precipitated from the FCC matrix at 700 °C. Precipitation simulation could not be performed at 900 °C due to these same short comings.

#### 2.2. Sample preparation and microstructural analysis

Ingots of Al<sub>0.3</sub>CoCrFeNi were produced via vacuum-induction melting. The ingots then underwent hot isostatic pressing at 1204 °C and 103 MPa for four hours. To ensure chemical homogeneity, the alloys were subsequently heat treated at 1250 °C for two hours in a vacuum furnace. As-homogenized ingots were sliced into 300  $\mu$ m thick samples by electrical discharge machining, followed by the traditional metallographic and related electropolish preparation for TEM. Samples were *in-situ* heat treated in a JEOL 2100 LaB<sub>6</sub> TEM, equipped with a highresolution pole piece, using a Gatan heating holder at a ramp rate of 0.5°/s up to 550, 700, 900 °C, and held there for 10, 60, and 120 min, respectively.

For *ex-situ* TEM observation, the as-homogenized samples were heat treated up to  $550 \degree C$  for 100 hrs, 700  $\degree C$  for 72 and 500 hrs and at 900  $\degree C$  for 72 hrs in a vacuum furnace. Focused ion beam (FIB) was performed in a FEI Strata DB 235, which was used to prepare TEM lamella from areas of interest. The sample was prepared via a typical FIB *in-situ* liftout procedure using 30 kV Ga-ions and was thinned to electron transparency at 5 kV.

Microstructural analysis was carried out on as-homogenized and annealed samples using energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) in the Scanning-TEM (STEM) mode on a JEOL 2100 field emission TEM, equipped with a highresolution pole piece. EELS analyses were performed using direct detection EELS (DD-EELS) system that offers great improvements in combined energy resolution and energy field of view [48]. The precipitate measurements were held using ImageJ software in conjunction with AdobePS<sup>TM</sup> across many areas and samples to assure a reasonable level of statistical significance.



Fig. 1. a) Calculated phase diagram of Al<sub>x</sub>CoCrFeNi showing the phase variation with temperature and Al fraction, and b) the same phase diagram with excluding the  $\sigma$  phase from the calculations.

# 3. Results

# 3.1. Thermodynamic calculations and precipitation simulation

Phase equilibria in the Al<sub>x</sub>CoCrFeNi alloy system was calculated using the Thermocalc software and the TCHEA1 high entropy alloy database [42,43], including the equilibrium phase diagrams, equilibrium phase fractions, and the composition of each phase at the three temperatures of interest, 550, 700, and 900 °C. Fig. 1 presents two isopleth sections of the Al-Co-Cr-Fe-Ni equilibrium phase diagram for equimolar amounts of Co, Cr, Fe, and Ni, as a function of mole fraction of the Al. Fig. 1a shows the calculated equilibrium phase diagram, where the  $\sigma$  phase (rich in Cr and Co) is present at temperatures below about 600 °C. Formation of the  $\sigma$  phase can be extremely sluggish in many alloys, and often is not observed experimentally during the investigation of the microstructural evolution. Therefore, Fig. 1b presents the same isopleth except that the  $\sigma$  phase has been excluded from the calculations. The calculated equilibrium phases and their predicted compositions (without the  $\sigma$  phase) are found in Table 1 and compared to the measured compositions of the experimentally-observed phases found in the Al<sub>0.3</sub>CoCrFeNi alloy after annealing at 550 °C, 700 °C, and 900 °C for the different times. At temperatures above about 600 °C, two large phase fields exist, a single-phase FCC region, and a two-phase FCC+B2#1 region. The boundary between these two regions increased with increasing the Al content from 0 atomic percent (at%) Al around 550 °C to 10 at% Al around 1300 °C, very near the solidus. Below about 650 °C, a Crrich BCC phase and a second B2-phase became stable, B2#2. The low-temperature B2#2-phase is ferromagnetic, related to the B2 in the binary Co-Fe; while the B2#1-phase is paramagnetic, more closely related to the NiAl-B2 phase. At still lower temperatures and high Al-contents, the Ni<sub>3</sub>Al-based L1<sub>2</sub> phase appeared, though the maximum temperature of its existence was only about 500 °C.

To further our understanding of concepts related to nucleation site density effects on the formation of secondary phases, precipitation simulations were performed using the TC Prisma module of Thermocalc. Employing the bulk nucleation to approximate the high density of surface nucleation sites in the thin foil during in-situ TEM investigation, the simulations demonstrate that at 550 °C, (see Fig. 2a), it took tens of minutes for the Cr-BCC phase to nucleate, and more than hour for the Co-rich B2#2 phases to nucleate. If GB-nucleation is used instead, as observed in the ex-situ experiments, the simulations predict that only the Cr-BCC phase will form for times up to > 100 h, as shown in Fig. 2b. At 700 °C, where Cr-BCC is less stable, relative to B2 than at 550 °C, both BCC and NiAl-B2#1 are predicted to form in < 1 hour, Fig. 2c. However, because of the much larger driving force for the formation of NiAl-B2#1, compared to Cr-BCC at 700 °C, the former dominated the precipitation behavior at longer times. For GB nucleation, Fig. 2d, Cr-BCC was the first intermediate phase to form, in tens of hours. NiAl-B2#1 then began to form after 100 hour, while the volume fraction of Cr-BCC decreased with increasing time. The simulation predicted that the Cr-BCC phase would completely dissolve by 1000 hrs, indicating that it is metastable at 700  $^\circ\text{C}$  in the thermodynamic database, even with - 300 kJ/mol added to the phase's free energy. Precipitation simulations could not be performed at 900 °C due to the limitation of the thermodynamic database (the Cr-BCC phase is unstable above about 700 °C).

TC Prisma is not capable of addressing co-precipitation, but the simulation results presented here serve as a qualitative interpretation of the expected precipitation behavior in Al<sub>0.3</sub>CoCrFeNi during both in-situ TEM observation and ex-situ experiments. In summary, the TC Prisma simulations demonstrate that the greatly increased nucleation site density in the in-situ experiments allows precipitation of secondary phases to occur one to two orders of magnitude faster than possible using exsitu experiments. It should also be noted that while the attractiveness of calculations based on Thermocalc databases lies in the ability to predict the multicomponent alloy phase equilibria using thermodynamic descriptions built from binary and ternary systems, the accuracy of such calculations relies on the availability of the experimental data. For conventional alloys, based on a single principal element, the experimental data are typically widely available, and calculated phase equilibria are reasonably accurate. HEAs, by definition, lie in the middle of the multicomponent compositional space, where experimental data of ternary and higher-order systems are often sparse or nonexistent. Therefore, the extrapolation of such databases, even those designed for HEAs like TCHEA1, can provide valuable qualitative information about phase equilibria and microstructural evolution in these alloys, however, quantitative prediction of phase boundaries, compositions, and kinetics may be limited.

#### 3.2. Phase evolution of Al<sub>0.3</sub>CoCrFeNi

#### 3.2.1. As-homogenized state

Figs. 3(a-b) contain the representative STEM-high-angle annular dark-field (HAADF) images, EDS analysis, and selected-area diffrac-

#### Table 1

 $Phase and chemical composition of Al_{0.3} CoCrFeNi as obtained by EDS and equilibrium thermodynamic calculations.$ 

	Heating conditions			Chemical Composition (at.%)				
	T(°C)	Time	Phase	Al	Со	Cr	Fe	Ni
Thermodynamic	550		FCC-A1	0.60	23.90	26.50	18.30	30.60
Calculations			BCC-B2	12.30	28.90	7.90	29.50	21.30
(excluding $\sigma$ phase)			BCC-A2	0.00	2.90	93.70	3.30	0.10
	700		FCC-A1	1.00	24.60	30.00	25.00	19.40
			BCC-B2	21.90	24.00	8.700	18.90	26.60
	900		FCC-A1	3.20	24.90	27.20	24.80	20.00
			BCC-B2	24.90	22.30	8.20	16.20	28.30
As Homogenized	1250	2 hr.	FCC-A1	7.47	22.98	24.05	23.76	21.74
In-situ TEM	550	1 hr.	FCC-A1	7.32	22.58	24.78	23.15	22.17
		2hr	FCC-A1	6.17	24.39	23.82	22.40	23.22
			BCC-B2	8.00	28.77	19.58	20.72	22.93
			BCC-A2	6.97	17.56	28.06	21.92	25.49
	700	10 min.	FCC-A1	8.15	22.42	23.86	22.68	22.89
			BCC-A2	5.92	18.73	33.88	19.62	21.85
		1	FCC-A1	6.23	23.43	24.71	23.00	22.63
		hr.	BCC-A2	0.45	18.95	48.17	15.85	16.58
		2	FCC-A1	6.37	24.61	23.77	23.59	21.66
		hr.	BCC-A2	3.60	7.08	74.17	10.24	4.91
			BCC-B2	32.36	16.48	6.18	14.13	30.85
	900	10 min.	FCC-A1	5.35	24.94	20.93	24.11	24.67
			BCC-A2	0.00	19.71	48.41	15.12	16.76
		1	FCC-A1	2.91	27.27	24.46	23.84	21.52
		hr.	BCC-A2	3.52	3.14	86.04	4.09	3.21
			BCC-B2	27.94	11.50	2.25	13.60	44.71
Ex-situ TEM	550	100	FCC-A1	6.45	23.20	25.51	22.79	22.05
		hr.	BCC-A2	5.73	23.05	27.52	21.91	21.79
	700	72	FCC-A1	5.68	23.06	25.99	23.68	21.59
		hr.	BCC-B2	20.87	17.42	14.20	17.22	30.29
		500	FCC-A1	3.19	24.19	24.57	25.37	22.68
		hr.	BCC-A2	0.00	0.00	93.83	0.00	6.17
			BCC-B2	33.01	12.81	4.18	8.82	41.18
	900	72	FCC-A1	4.12	24.42	27.16	24.62	19.68
		hr.	BCC-B2	29.86	15.17	5.57	10.35	39.05

tion patterns (SADPs) of the as-homogenized  $Al_{0.3}$ CoCrFeNi. The results show that the material is chemically and structurally homogeneous, and there is no evidence of chemical segregation or phase separation. The EDS-measured chemical composition of the as-homogenized  $Al_{0.3}$ CoCrFeNi is listed in Table 1. The corresponding SADP from the [013] zone axis shows only FCC reflections. Our results are consistent with those reported in the literature [26,32], in which  $Al_{0.3}$ CoCrFeNi is revealed to be a single FCC phase after the homogenization treatment.

## 3.2.2. Ex-situ tem heating

To examine the stability of as-homogenized single phase  $Al_{0.3}$ CoCrFeNi, ex-situ TEM heating experiments were performed at temperatures between 550 and 900 °C. Figs. 3c-e show the representative STEM-HAADF and STEM-EDS elemental maps of the  $Al_{0.3}$ CoCrFeNi annealed *ex-situ* at 550 °C for 100 hrs. Nanoscale precipitates formed exclusively along grain boundaries (GBs) with an average size of 135 nm. Based on the STEM-EDS analysis, these precipitates are primarily enriched with Cr. The SADPs from the Cr-rich precipitates show the reflection of the [113] BCC from the precipitates, indicating the disordered BCC structure of Cr-rich precipitates.

Figs. 3f-h present the STEM-HAADF and STEM-EDS analysis of  $Al_{0.3}$ CoCrFeNi *ex-situ* annealed at 700 °C for 72 hrs. As shown in the STEM-HAADF image (Fig. 3f), micro-sized precipitates were formed along GBs. These precipitates are plate-like with an average length of 1.2 µm. The SADPs (Figs. 3p-q) taken from the precipitates show the [ $\bar{1}12$ ] BCC within the [ $\bar{1}13$ ] FCC<sub>matrix</sub> reflections. The precipitates were further analyzed via STEM-EDS and found to be enriched with mainly Ni-Al, indicating the formation of the NiAl-B2 phase.

The STEM-HAADF and STEM-EDS analyses of  $Al_{0.3}$ CoCrFeNi *ex-situ* annealed at 700 °C for 500 hrs are presented in Figs. 3i-k. Phase separation was detected along GBs. Specifically, two distinct types of precipitates formed along GBs: NiAl-B2 and Cr-rich BCC precipitates. The

average size of NiAl precipitates increased significantly in comparison to the 700 °C 72 hrs annealing treatment, reaching sizes of up to 2.4  $\mu$ m. Chemical analysis of the Cr-rich phase shows that these precipitates consist almost completely of Cr (~94 at% Cr), and are encased with the B2 (NiAl) precipitates. The morphology of these precipitates are both spherical and blocky, with an average size of 300 nm.

The STEM-HAADF and STEM-EDS analyses of Al<sub>0.3</sub>CoCrFeNi *ex-situ* annealed at 900 °C for 72 hrs are shown in Figs. 3l-n. In a similar fashion to that which was found in the 700 °C annealing conditions, NiAl-B2 phases formed along the GBs, with an average size of 2.7  $\mu$ m.

Thus, based on the experimental analysis, we find that the  $Al_{0.3}$ CoCrFeNi alloy beyond 500 °C degrades by forming multiple secondary phases (Cr-BCC, NiAl-B2, and Co-B2). The summary details of the phase evolution regarding the precipitates structure, preferred location and size over different annealing conditions are listed in Table 2.

### 3.2.3. In-situ tem heating

*In-situ* TEM heating was performed in order to characterize dynamicprecipitation events in Al<sub>0.3</sub>CoCrFeNi at temperatures ranging between 550 and 900 °C. As shown in Figs. 4a-b, the alloy annealed at 550 °C for 1 hour and exhibits a similar microstructure to that found in the as-homogenized state, in which only a single FCC phase was observed. When held at 550 °C for 2 hrs, however, secondary phases were observed. Figs. 4c-g show STEM-HAADF, and EDS analysis of Al<sub>0.3</sub>CoCrFeNi annealed at 550 °C for 2 hrs. As evident in Figs. 4c and 4e, the Al<sub>0.3</sub>CoCrFeNi alloy is no longer a single phase, and nanoscale secondary phases have begun to form within the grain interior. Based on the EDS and EELS analysis, and unlike the *ex-situ* analysis, two different types of precipitates formed: Co-rich, and Cr-rich precipitates. The Cr-rich and Co-rich precipitates possess a blocky and /or spherical morphology with an average size of ~ 25 nm and ~ 18 nm, respectively.

Table 2



**Fig. 2.** Precipitation simulations using the TC Prisma module of Thermocalc for  $Al_{0.3}$ CoCrFeNi at 550 °C for (a) bulk nucleation and (b) grain boundary nucleation; and at 700 °C for (c) bulk nucleation and (d) grain boundary nucleation. The in-situ experiments were approximated by bulk nucleation (thin film surface nucleation); while the ex-situ experiments used grain boundary (GB) nucleation as observed in the experiments.

Summary of precipitate type, location, and size for <i>ex-situ</i> and <i>in-situ</i> TEM-heated samples.								
Heating conditions	Temp (°C)	Time	Precipitate Type	Precipitates locations	Precipitates diameter(nm)			
Ex-situ TEM	550	100 hr	Cr-BCC	GBs	134.142			
	700	72 hr	NiAl-B2	GBs	1191.00			
		500 hr	Cr-BCC	NiAl-B2	2400.00(co-precipitates)			
			NiAl-B2	GBs				
	900	72 hr	NiAl-B2	GBs	2739.00			
In-situ TEM	550	1hr	No separation					
		2 hr	Cr-BCC	Grain interior (matrix)	24.268			
			Co-rich(B2)	Grain interior (matrix)	18.462			
	700	10min	Cr-BCC	Grain interior (matrix)	36.00			
		1 hr	Cr-BCC	Grain interior (matrix)	159.460			
		2 hr	Cr-BCC	B2 phase	286.820 (co-precipitate)			
			NiAl-B2	Grain interior (matrix)				
	900	10min	Cr-BCC	Grain interior (matrix)	142.770			
		1 hr	Cr-BCC	B2 phase	1151.530 (co-precipitate)			
			NiAl-B2	Grain interior (matrix)				



Fig. 3. Microstructures of Al<sub>0.3</sub>CoCrFeNi after homogenization and ex-situ TEM annealing. Representative HAADF image of the as-homogenized Al<sub>0.3</sub>CoCrFeNi and EDS elemental maps showing the distribution of Al, Ni, Cr, Co, and Fe (a), SADPs presenting the reflection of the FCC phase of the as-homogenized state. STEM-HAADF image of the annealed sample at 550 °C for 100 hr (c). The EDS elemental maps showing the distribution of Cr (d), Co (e). STEM-HAADF image of the annealed sample at 700 °C for 72 hr (f). The EDS elemental maps presenting the distribution of Ni (g), Al (h). STEM-HAADF image of the annealed sample at 700 °C for 500 hr (i), EDS elemental maps showing the distribution of Ni and Al (j and k, respectively). STEM-HAADF image of the annealed sample at 900 °C for 72 hr (l), and EDS elemental maps exhibit the distribution of Ni (m) and Al (n). SADP shows the FCC refection from the matrix (o). SADP of Ni-Al precipitates presents the BCC reflection (p). SADP of Cr-rich precipitates shows the BCC reflection (q).

Figs. 5a-f show the representative STEM-HAADF images and EDS maps of the  $Al_{0.3}$ CoCrFeNi at 700 °C for 10 min, 1 hour, and 2 hrs. After annealing at 700 °C for 10 min, nanoscale secondary phases are seen in the grain interior (Fig. 5a). These precipitates are globular, enriched with Cr and Co, with an average size of ~ 36 nm. Increasing the annealing time to 1 hour (Fig. 5b), the average size of Cr-rich precipitates increased significantly to around 160 nm. The chemical composition of

these precipitates was very similar to those that were observed in the 700  $^\circ\text{C-10}$  min condition.

In order to study the effects of long-period annealing on phase decomposition, the alloy was further annealed for 2 hrs at 700 °C (Fig. 5d). Similar to the previous heat treatments, several precipitates formed. Based on the STEM-EDS analysis (Figs. 5e-f), the precipitates can be classified into: a phase rich in Ni and Al, and a Cr-rich phase. The av-



**Fig. 4.** Microstructures of Al<sub>0.3</sub>CoCrFeNi after *in-situ* TEM heating at 550 °C. Representative STEM-HAADF images of the annealed sample at 550 °C for 1 hr (a) and SADP showing the reflection of the FCC phase (b). STEM-ADF image of the annealed sample-area1 at 550 °C for 2 hr (c) and EELS elemental mapping of Co(d). STEM-ADF(Annular Dark Field) images of the annealed sample-area2 at 550 °C for 2 hr, EELS elemental mapping of Co(f) and Cr(g).

erage size of the co-precipitates was around 286 nm. These precipitates were further analyzed, using SAED, and Figs. 5m-o show the reflections of [001] FCC matrix and [011] BCC from Cr-rich precipitates, which are comparable to the crystal structure of the precipitates observed at 550 °C (2 hrs), 700 °C after 10 min, and 700 °C after 1 hour, and [111] BCC from NiAl precipitates.

Figs. 5g-l show STEM-HAADF of the  $Al_{0.3}$ CoCrFeNi after *in-situ* TEM annealing at 900 °C for 10 min (g-i), and 1 hour (j-l). The microstructure of the alloy in this condition was indistinguishable to the 700 °C state, where Cr-BCC and B2 phases were formed.

At 900 °C after 10 min, secondary phases with the average grain size of ~142 nm formed in the grain interior. Figs. 5g-i show a bright-field TEM image of precipitates, and present a STEM-HAADF image of individual precipitates, respectively. These precipitates are plate-like, and enriched mainly with Cr and Fe, indicating the formation of Cr-BCC phase. Figs. 5j-l present STEM-HAADF and EDS analysis of the Al<sub>0.3</sub>CoCrFeNi after annealing at 900 °C for 1 hour. Similar to 700 °C-2 hrs, co-precipitates with Cr-rich BCC and NiAl-B2 phases formed in the grain interior. The average size of the co-precipitates increased significantly in comparison with 700 °C-2 hrs to around 1.15  $\mu$ m.

#### 4. Discussion

# 4.1. Phase evolution of $Al_{0.3}$ CoCrFeNi: the role of heterogeneous nucleation site density on precipitation events of intermediate phases

The thermodynamic calculations and precipitation simulations show excellent qualitative agreement with the experimental results where Co-B2, Cr-BCC, and NiAl phases are predicted to form. While the phase equilibria calculations predict multiple phases to be in equilibrium at intermediate temperatures, the precipitation simulations, in conjunction with the experimental results, uncover the role of heterogeneous nucleation site density on precipitation events of intermediate phases.

Considering the short annealing time, the thermodynamic calculations correspond very well to our three observed phases after 2 hrs at 550 °C, the FCC matrix, and two BCC phases one slightly rich in Cr and one rich in Co. An equally good agreement between experiments and calculations is observed at 900 °C, where FCC and B2 phases are both predicted and observed experimentally (except for a small amount of the Cr-rich BCC phase observed during the *in-situ* experiment after 1 hour). After 72 hrs at 900 °C, where kinetics are sufficiently fast, the microstructural evolution may approach equilibrium and the measured and calculated compositions of the two phases are also in good agreement.

The calculations and experiments differ slightly at 700 °C. Experimentally, the FCC and B2 phases are observed after annealing for 72 hrs at 700 °C, while a third phase, the Cr-rich BCC structure is found after annealing for 500 hrs, as well as after 2 hrs during the *in-situ* experiment. The calculated phase equilibrium consists of two-phase FCC and B2 structures, while Cr-rich BCC phase is predicted to be unstable. However, it should be noted that the predicted BCC solvus temperature is quite close to 700 °C, (685 °C for the as-homogenized composition). This trend suggests that the Cr-rich BCC phase is nearly stable, assuming that kinetics are not favorable for the  $\sigma$ -phase formation. Small deviations in the composition or temperature, or shortcomings in the thermodynamic database, may be cause for this discrepancy. This trend also explains the need to add - 300 J/mol to the free energy of the Cr-BCC phase in order to perform the precipitation simulations at 700 °C, and the inability to



Fig. 5. Microstructures of Al<sub>0.3</sub>CoCrFeNi after in-situ TEM annealing at 700 °C and 900 °C. STEM-HAADF images of annealed samples at  $700\,^\circ\!\mathrm{C}$  for 10 min., 1hr (a and b, respectively), EDS elemental map showing the distribution of Cr (c). Representative STEM-HAADF image of the annealed  $\mathrm{Al}_{0.3}\mathrm{CoCrFeNi}$  at 700 °C for 2 hr (d), and EDS elemental maps presenting the distribution of Cr (e)and Ni (f). Representative STEM-HAADF image for the annealed sample at 900 °C for 10 min (g), STEM-HAADF image from Cr-rich precipitates(h), and EDS elemental maps exhibiting the distribution of Cr (i). STEM-HAADF image for the annealed sample at 900 °C for 1 hr (j), EDS elemental maps showing the distribution of Ni(k) and Cr(l). The SADP of the matrix after annealing at 700 °C for 2 hr (m). SADPs of the Cr-rich BCC and NiAl B2 precipitates show the reflections of the BCC structure (n, o, respectively).

simulation precipitation at 900  $^\circ$ C because of the instability of the phase even with the addition of - 300 J/mol to its free energy.

The precipitation simulations also show excellent qualitative agreement with the experimental results at 550 and 700 °C, where Co-B2, NiAl, and Cr-BCC are predicted to form. Using homogeneous nucleation to simulate the in-situ TEM experiments at 550 °C, where a high density of surface nucleation sites in the thin film are available, the Co-rich B2 phase along with the Cr-BCC phase are predicted to form after 1 hour of heating, which is consistent with *in-situ* TEM results. If GB nucleation is assumed instead, as observed experimentally in ex-situ TEM experiments, Cr-BCC phase is predicted to form in a few hours, while the precipitation of Co-B2 phase is expected to require several hundred hours at 550 °C. This explains the absence of the Co-B2 phase observed in ex-situ TEM experiments after 100 hrs, where only the Cr-BCC phase formed. Similar agreement is demonstrated at 700 °C, where Cr-BCC and NiAl phases are predicted. However, due to the much larger driving force for the formation of NiAl-B2#1, compared to Cr-BCC, the former dominates the GB precipitation behavior for longer times, consistent with ex-situ experimental observations.

We found that the combination of *in-situ* heating in the transmission electron microscope (TEM) complemented by *ex-situ* characterization of bulk annealed specimens, thermodynamic calculations, and precipitation simulations facilitates the study of phase evolution of multicomponent HEAs and effectively monitors the early stages of the intermediate phase formation. Our finding that is supported in literature is that the single FCC phase  $Al_{0.3}$ CoCrFeNi alloy is unstable at a temperature beyond 500 °C [26,32]. However, our results are inconsistent with other previous studies [24,28,29,30,36] concerning the temperature dependent.

dence and structure of stable secondary phases where we see that the formation of these features is governed by a complex diffusion mechanism, indicating the importance of monitoring the diffusivity measurements for these alloys in a real-time observation.

Phase separation is known to be controlled by several factors, such as atomic size, free energy of mixing (enthalpy and entropy), and electronegativity [49,50]. Here we interpret the formation of secondary phases and their chronological sequence based on thermodynamic barriers and diffusion kinetics. While *in-situ* TEM enables tracking the evolution of Co-B2 phase because of the high density of heterogeneous nucleation sites, we found that the sequence of co-precipitates (Cr-BCC, NiAl-B2) is governed by diffusion kinetics.

Specifically, our experimental results report the formation of coprecipitates (NiAl-B2 and Cr-BCC) in both ex-situ TEM (700 °C-500 hrs) and in-situ TEM (700 °C-2 h and 900 °C-1hour), however, the chronological order of the Cr-BCC and the NiAl-B2 phases was inconsistent. During in-situ TEM, the Cr-rich BCC phase was the only secondary phase that separated out of the disordered FCC phase after 10 min and 1 hour exposure at 700 °C and 10 min at 900 °C, while the longer annealing time was required for the NiAl-B2 phase to form at 700 °C (2 h) and formed more readily with increasing the heating temperature to 900 °C (1hour). Ex-situ TEM heated microstructure, by comparison, showed the formation of the NiAl-B2 phase as the first secondary phase, followed by the Cr-BCC phase after 500 hrs at 700 °C. If various heterogeneous nucleation sites were to be characterized in terms of nucleation barrier for precipitation, the sequence from lowest to highest is typically: free surfaces, grain boundaries/interfaces, stalking faults, dislocations, and vacancies [51]. Therefore, in the case of ex-situ experiments where grain boundaries are the main nucleation sites and annealing times are significantly longer, the phase with the greatest thermodynamic stability, in the present case B2, will dominate the observed precipitation behavior regardless of other nucleation-related barriers such as interfacial energy or the relative diffusivities of the various elements. The calculated thermodynamic driving forces for precipitation of Cr-BCC and NiAl-B2 (at 550 °C) phases from the homogenized  $Al_{0.3}$ CoCrFeNi alloy investigated here are 2.1 kJ/mol and 7.7 kJ/mol, respectively, indicating NiAl-B2 should dominate precipitation after long periods of time in the ex-situ experiments.

Conversely, the short times of the in-situ TEM experiments favor the phase that nucleates most easily, i.e. lowest nucleation barrier. The nucleation barrier for precipitation is affected by the precipitate/matrix interfacial energy and the diffusivity of the elements required for the phase to form and grow. From reference [47], the Cr-BCC interfacial energy is likely lower than that of NiAl-B2, consistent with the observation of the precipitation sequence in the in-situ TEM experiments. However, the Ni<sub>3</sub>Al-L1<sub>2</sub> phase, which is also metastable relative to the homogenized Al<sub>0.3</sub>CoCrFeNi alloy, has a low interfacial energy because of its related FCC crystal structure. It also has a similar precipitation driving force, 2.6 kJ/mol (at 550 °C), compared to the Cr-BCC phase, but was not observed in any of the present experiments. Consequently, the main factor controlling the formation and the sequence of co-precipitates here must be the diffusion kinetics, where the phase containing elements with the highest diffusivity will form first. Dabrowa et al. [16] studied the diffusion of the single FCC AlCoCrFeNi HEAs, combining experiments using diffusion couples and simulations applying the Darken Manning approach. The authors reported that Cr has the highest diffusivity, followed by Fe, Co, and Ni (which said to have the lowest diffusivity). This trend is consistent with the current in-situ TEM results where the Cr-rich BCC phase is formed as the first intermediate phase within the FCC matrix and NiAl-B2 as the second phase, while Ni3Al-L1 $_2$  does not form at all in the present investigation because of its low driving force and requirement for Fe, Co, and Ni diffusion.

The major influence of using the *in-situ* heating technique we report here is the formation of the Co-rich B2 phase at 550 °C, where the *in-situ* TEM accelerates its formation due to the aid of high density of nucleation sites in the thin film. We anticipate that the phase transfor-

mation we reported will have noticeable impact on the mechanical and corrosion properties of the  $\mathrm{Al}_{0.3}\mathrm{CoCrFeNi}.$  For example, it has been reported that BCC structure phases exhibit higher strength than the FCC phases. Therefore, at the low annealing temperature of 550 °C, the formation of Co-rich B2 phase along with the Cr-BCC phase is expected to exhibit a remarkable influence on the overall strength of HEAs. Additionally, the co-precipitation of phases (NiAl and Cr-BCC) was reported to further enhance the mechanical properties of the aged alloy, since these co-precipitates provide a complex obstacle to dislocation movement [52,53]. Unlike the mechanical properties, the formation of Al, and Cr rich phases may negatively impact the formation of the protective oxide layers and thus, deteriorate the corrosion properties when the alloy is exposed to a corrosive environment. Specifically, a severe degradation in the corrosion properties, and particularly the pitting resistance [39] in both NaCl and H<sub>2</sub>So<sub>4</sub> solutions, have been reported when the B2 (NiAl) phase is presented in the Al-based HEAs, contrary to the Butler et al.[54]. study suggesting that the formation of the B2 (NiAl) phase near the alloy surface may work as a reservoir for Al, promoting the formation of Al<sub>2</sub>O<sub>3</sub> oxide layers.

#### 4.2. Structure and chemical composition of intermediate phases

In the literature, there are three possible phases reported in  $Al_{0.3}$ CoCrFeNi including FCC, NiAl-B2, and NiAl-L12 phases [25]. Our experimental results demonstrate, in addition to FCC and NiAl-B2, the formation of Cr-BCC and Co-rich (B2) phases. Fig. 6 shows a correlation between *in-situ* TEM heating, *ex-situ* TEM heating, thermodynamic calculations, and the literature in terms of stable phases.

The Cr-BCC phase (*red box in Fig.* 6) is observed experimentally in all heating conditions (except *ex-situ* 900 °C-72-hours condition). It is important to mention that the Cr-rich phase has not previously been reported experimentally to form in  $Al_{0.3}$ CoCrFeNi after ageing at intermediate and high annealing temperatures, which is clearly observed in our *ex-situ* and *in-situ* TEM experiments.

The Cr-rich phases in HEAs have been reported as two different structures: the Cr-BCC phase, and Cr-rich  $\sigma$  phase. The Cr-rich BCC phase was recently reported in AlCuCoCrFeNi [55], Al<sub>1.5</sub>CoCrFeNi [56], and CoCrFeNi [57], and were labeled as an A2 structure with a lattice parameter of a = 0.2884 nm [25]. In AlCuCoCrFeNi [55], the Cr-BCC phase is mainly enriched with Cr-Co, which is similar to the precipitates that formed during our 700 °C-10 min, and 700 °C-1 hour experiments. Also, the Cr-rich BCC phase that was reported in Al<sub>1.5</sub>CoCrFeNi [56] contains Cr and Fe as principal elements, which is consistent with our Cr-Fe precipitates that formed at 700 °C-2 hrs, 900 °C-10 min, and 900 °C-1 hour. Additionally, our chemical analysis of Cr-rich BCC precipitates (the heating condition: 900 °C-1 hour) nearly matches the precipitates observed in CoCrFeNiMn after the 500 days exposure at 500 °C, where Cr content was about 86 at% [57].

The other reported structure of Cr-rich precipitates is the tetragonal P4<sub>2</sub>mnm structure (referred to the Cr-rich  $\sigma$  phase), lattice parameters, a = 0.360 nm and c = 0.45582 nm [57], where previously reported in Al<sub>0.7</sub>CoCrFeNi [26] and CoCrFeMnNi [57]. In the study of CoCrFeNiMn [57], the authors reported the formation of Cr-rich  $\sigma$  phase after *exsitu* TEM heating at 700 °C for 500 days, where the Cr content of these phases is about 46 at%. Rao et al. [26] reported the formation of Cr-rich  $\sigma$  phase in Al<sub>0.7</sub>CoCrFeNi after *in-situ* TEM heating at 900 °C for 10 min, where the precipitates were identified using SADPs.

Similar to Cr-rich phases, there are two different crystalline phases reported for Ni-rich phases: ordered BCC-B2 phase, and ordered FCC-L1<sub>2</sub> phase. For the B2 phase, our results are consistent with previous studies where the B2 phase formed at relatively higher annealing temperatures (700–900 °C) during *in-situ* and *ex-situ* TEM heating. Shun et al. [36] reported the formation of the B2 phase in Al<sub>0.3</sub>CoCrFeNi after *ex-situ* TEM heating at 900 °C for 72 h with a chemical composition similar to our B2 phase. A more recent study [29] investigated the thermal stability of this alloy after prolonged annealing at 700 °C for 100, 200, and 500 hrs.



**Fig. 6.** Schematic diagram comparing *in-situ* TEM, *ex-situ* TEM, thermodynamic calculations, and literature in terms of the phase stability. Cr-rich BCC phase, which is not reported experimentally in the literature of Al<sub>0.3</sub>CoCrFeNi, is present during the *in-situ* and *ex-situ* TEM heating (except *ex-situ* 900 °C), and thermodynamic calculations (below 700 °C).

The study reveals that the B2 phase formed after ageing at 700 °C for 200 and 500 hrs. However, no phase separation has been reported after annealing at 700 °C for 100 hrs, which is clearly seen in our *ex-situ* TEM 700 °C 72 hour condition.

In the case of the ordered FCC-L1<sub>2</sub> phase, Gwalani et al. [32] reported the formation of nanosized L1<sub>2</sub> precipitates after *ex-situ* TEM heating at 550 °C for 150 hrs of the thermomechanical-processed Al<sub>0.3</sub>CoCrFeNi (20% rolling + heating at 1200 C for 30 min), where the average size of the precipitate was around 5 nm. The chemical analysis using Atom Probe Tomography showed that the precipitates were mainly enriched in Ni and Cr. In comparison, using a similar temperature regime, we did not observe the formation of the L1<sub>2</sub> phase for both *ex-situ* and *in-situ* TEM experiments. The L1<sub>2</sub> phase may require longer exposure time at 550 °C, highlighting the role of the diffusion mechanism discussed in Section 4.1.

Unlike previous studies of  $Al_{0.3}$ CoCrFeNi, we detected the formation of the Co-rich (B2) ordered BCC phase formed at 550 °C during *in-situ* TEM annealing. Recently, Otto et al. [57] reported the formation of Corich B2 phase in CoCrFeNiMn after *ex-situ* TEM ageing at 500 °C for 500 hrs along with the NiMn-L1<sub>0</sub> and Cr-rich BCC phases. They further investigated the precipitates using Scanning Electron Microscopy-EDS, where the Co content of the Co-rich B2 phase was about 46 at%, relatively higher than the content of Co in our B2 phase (~ 28 at%), which may be attributed to the extended ageing regime essential for chemical homogeneity.

It is not surprising to mention that the size of the secondary phases increased continuously by increasing the heating temperature and the time for both heating conditions (see online supplementary S1and S2), where precipitates tend to coarsen into a larger size and lower density to reduce the total interfacial energy of the system [51].

Fig. 7 illustrates the influence of *in-situ* TEM conditions (heating temperature and time) on the Cr content of the Cr-BCC phase. As shown in the figure, the Cr concentration increased from around 30 at% at 550 °C



**Fig. 7.** Effect of in-situ TEM heating conditions on the Cr content of the Cr-BCC precipitates. The Cr content in precipitates increases with annealing time and temperature.

to about 48 at% at 900 °C-10 min. Increasing the exposure time from 10 min to 2 hrs at 700 °C, the content of Cr increased from 35 at% to 74 at%, and a similar trend was seen for the 900 °C condition (the Cr concentration increased from 48 to 85 at% for 10-minutes and 1-hour exposure times, respectively). This can be attributed to the nucleation of NiAl-B2 (poor-Cr phase) along Cr-BCC interphase, where Cr is rejected towards Cr-rich areas, enhancing the Cr content of Cr-rich precipitates.

In addition, in regard to the B2 phase, we observed a slight increase in the concentrations of Ni and Al by increasing the heating temperature and time, achieving 30 at% for the Al and 40 at% for the Ni. This trend is another indication of the dynamic role of diffusion kinetics on the stability window of these alloys.

## 5. Conclusion

We have evaluated the stability of the  $Al_{0.3}$ CoCrFeNi system via designing a study concentrating on heterogeneous precipitation events and directly comparing the role of nucleation site density on the formation of intermediate phases using *in-situ* and *ex-situ* TEM, coupled with precipitation simulations and thermodynamic calculations. *In-situ* TEM allows us to reveal the formation of an additional intermediate phase (Co-B2 phase) after 2 hrs heating at 550 °C due to the aid of high density surface nucleation sites in the thin foil. We would expect this process to take hundreds of hours (based on our precipitation simulation) for this phase to form during *ex-situ* TEM experiment, explaining its absence after 100 hrs annealing at 550 °C.

Contrary to previous studies, the *in-situ* TEM results confirmed the formation of co-precipitates (Cr-BCC and NiAl-B2 phases) where the Cr-BCC phase formed prior to the NiAl-B2 phase. The B2 phase took a longer time to form and was observed exclusively together with Cr-rich precipitates during *in-situ* TEM heating, which may have been attributed to the preexisting Cr-rich phase interphase. Moreover, the content of Cr in Cr-rich precipitates increased significantly by increasing the heating temperature and time, while the contents of Ni and Al in the B2 phase were slightly increased. The technique provides a more detailed view of mechanisms behind phase separation, particularly the role of diffusion and thermodynamics on the formation and stability of secondary phases.

The experimental results compared well with thermodynamic calculations in terms of the precipitation temperature and composition of secondary phases excluding the  $\sigma$  phase. However, the Cr-BCC phase was not predicted at temperatures beyond the 700 °C condition while it was clearly observed in ex-situ and in-situ TEM experiments, suggesting the importance of modifying the methods to consider the diffusion kinetics of these alloys. (i.e., the Multi-Cell Monte Carlo Relaxation method [58]). Additionally, the precipitation simulations show an excellent agreement with experimental results, revealing the importance of employing various nucleation sites on intermediate phase formation. When bulk nucleation (approximated by in-situ TEM) is employed, the precipitation time of Co-B2 phase was minimized from hundreds of hours (if ex-situ TEM experiment is used) to only 1 hour, and a similar agreement is demonstrated at 700 °C in which Cr-BCC and NiAl-B2 phases are predicted. The results of this study imply that much care should be taken when investigating and predicting potential intermediate phase formation in other HEAs, especially when considering different annealing times during heat treatment. Intimate knowledge of the particularities of the intermediate phases (i.e. Cr-rich and/or Al-rich) plays a vital role in fundamentally understanding the high-temperature performance of HEAs.

#### **Declaration of Competing Interest**

None

## Acknowledgment

The authors gratefully acknowledge funding in part from the National Science Foundation MRI program (award #1429661) and in part from the Office of Naval Research through the Multidisciplinary University Research Initiative (MURI) program (award # N00014–20–1– 2368). The authors are thankful to Dr. Michel Gao of the National Energy Technology Laboratory (Albany, Oregon) for the time taken to engage us in many useful discussions. PKL acknowledges support from (1) the Army Office Projects (W911NF-13–1–0438 and W911NF-19–2–0049) program managers, Drs. Michael P. Bakas, David M. Stepp, and S. Mathaudhu and (2) the National Science Foundation (DMR-1611180 and 1809640) program directors, Judith Yang, Gary Shiflet, and Diana Farkas.

#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mtla.2020.100872.

#### References

- [1] D. Li, C. Li, T. Feng, Y. Zhang, G. Sha, J.J. Lewandowski, P.K. Liaw, Y. Zhang, High-entropy Al<sub>0.3</sub>CoCrFeNi alloy fibers with high tensile strength and ductility at ambient and cryogenic temperatures, Acta Mater 123 (2017) 285–294, doi:10.1016/j.actamat.2016.10.038.
- [2] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Microstructural development in equiatomic multicomponent alloys, Mater. Sci. Eng. A. 375–377 (2004) 213–218, doi:10.1016/j.msea.2003.10.257.
- [3] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, Adv. Eng. Mater. 6 (2004) 299–303 +274, doi:10.1002/adem.200300567.
- [4] E.A. Anber, A.C. Lang, E.A. Lass, P.K. Suri, D.S. D'Antuono, H. Diao, P.K. Liaw, M.L. Taheri, Thermal Stability of High Entropy Alloys during in Situ TEM Heating, Microsc. Microanal. 24 (2018) 1928–1929, doi:10.1017/S1431927618010127.
- [5] J.J. Licavoli, M.C. Gao, J.S. Sears, P.D. Jablonski, J.A. Hawk, Microstructure and Mechanical Behavior of High-Entropy Alloys, J. Mater. Eng. Perform. 24 (2015) 3685– 3698, doi:10.1007/s11665-015-1679-7.
- [6] F. Otto, Y. Yang, H. Bei, E.P. George, Relative effects of enthalpy and entropy on the phase stability of equiatomic high-entropy alloys, Acta Mater. 61 (2013) 2628–2638, doi:10.1016/j.actamat.2013.01.042.
- [7] P.F. Yu, H. Cheng, L.J. Zhang, H. Zhang, Q. Jing, M.Z. Ma, P.K. Liaw, G. Li, R.P. Liu, Effects of high pressure torsion on microstructures and properties of an Al0.1CoCrFeNi high-entropy alloy, Mater. Sci. Eng. A. 655 (2016) 283–291, doi:10.1016/j.msea.2015.12.085.
- [8] T.T. Shun, C.H. Hung, C.F. Lee, Formation of ordered/disordered nanoparticles in FCC high entropy alloys, J. Alloys Compd. 493 (2010) 105–109, doi:10.1016/j.jallcom.2009.12.071.
- [9] Z. Tang, T. Yuan, C.W. Tsai, J.W. Yeh, C.D. Lundin, P.K. Liaw, Fatigue behavior of a wrought Al<sub>0.5</sub>CoCrCuFeNi two-phase high-entropy alloy, Acta Mater. 99 (2015) 247–258, doi:10.1016/j.actamat.2015.07.004.
- [10] X. Gao, Y. Lu, B. Zhang, N. Liang, G. Wu, G. Sha, J. Liu, Y. Zhao, Microstructural origins of high strength and high ductility in an AlCoCrFeNi2. 1 eutectic high-entropy alloy, Acta Mater. 141 (2017) 59–66, doi:10.1016/j.actamat.2017.07.041.
- [11] F. Otto, A. Dlouhý, C. Somsen, H. Bei, G. Eggeler, E.P. George, The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy, Acta Mater. 61 (2013) 5743–5755, doi:10.1016/j.actamat.2013.06.018.
- [12] F. He, Z. Wang, Q. Wu, J. Li, J. Wang, C.T. Liu, Phase separation of metastable CoCrFeNi high entropy alloy at intermediate temperatures, Scr. Mater. 126 (2017) 15–19, doi:10.1016/j.scriptamat.2016.08.008.
- [13] J.Y. He, H. Wang, H.L. Huang, X.D. Xu, M.W. Chen, Y. Wu, X.J. Liu, T.G. Nieh, K. An, Z.P. Lu, A precipitation-hardened high-entropy alloy with outstanding tensile properties, Acta Mater. 102 (2016) 187–196, doi:10.1016/j.actamat.2015.08.076.
- [14] B. Schuh, F. Mendez-Martin, B. Volker, E.P. George, H. Clemens, R. Pippan, A. Hohenwarter, Mechanical properties, microstructure and thermal stability of a nanocrystalline CoCrFeMnNi high-entropy alloy after severe plastic deformation, Acta Mater. 96 (2015) 258–268, doi:10.1016/j.actamat.2015.06.025.
- [15] G. Laplanche, A. Kostka, C. Reinhart, J. Hunfeld, G. Eggeler, E.P. George, Reasons for the superior mechanical properties of medium-entropy CrCoNi compared to high-entropy CrMnFeCoNi, Acta Mater. 128 (2017) 292–303, doi:10.1016/j.actamat.2017.02.036.
- [16] J. Dabrowa, W. Kucza, G. Cieslak, T. Kulik, M. Danielewski, J.W. Yeh, Interdiffusion in the FCC-structured Al-Co-Cr-Fe-Ni high entropy alloys: experimental studies and numerical simulations, J. Alloys Compd. 674 (2016) 455–462, doi:10.1016/j.jallcom.2016.03.046.
- [17] G. Bracq, M. Laurent-Brocq, L. Perrière, R. Pirès, J.M. Joubert, I. Guillot, The fcc solid solution stability in the Co-Cr-Fe-Mn-Ni multi-component system, Acta Mater. 128 (2017) 327–336, doi:10.1016/j.actamat.2017.02.017.
- [18] S.K. Chen, P.H. Lee, C.H. Lin, AlCoCrFeNiTi and its equal-molar five-component alloys in a metal mixological enthalpy-entropy plane, Q. Phys. Rev. 3 (2017) 1–28.
- [19] Y. Ma, B. Jiang, C. Li, Q. Wang, C. Dong, P.K. Liaw, F. Xu, L. Sun, The BCC/B2 Morphologies in AlxNiCoFeCr High-Entropy Alloys, Metals (Basel) 7 (2017) 57, doi:10.3390/met7020057.
- [20] S. Xia, M.C. Gao, T. Yang, P.K. Liaw, Y. Zhang, Phase stability and microstructures of high entropy alloys ion irradiated to high doses, J. Nucl. Mater. 480 (2016) 100–108, doi:10.1016/j.jnucmat.2016.08.017.
- [21] V. Dolique, A.L. Thomann, P. Brault, Y. Tessier, P. Gillon, Thermal stability of Al-CoCrCuFeNi high entropy alloy thin films studied by in-situ XRD analysis, Surf. Coatings Technol. 204 (2010) 1989–1992, doi:10.1016/j.surfcoat.2009.12.006.

- [22] Y. Zhang, T.T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Z.P. Lu, Microstructures and properties of high-entropy alloys, Prog. Mater. Sci. 61 (2014) 1–93, doi:10.1016/j.pmatsci.2013.10.001.
- [23] K.K. Alaneme, M.O. Bodunrin, S.R. Oke, Processing, alloy composition and phase transition effect on the mechanical and corrosion properties of high entropy alloys: a review, J. Mater. Res. Technol. 5 (2016) 384–393, doi:10.1016/j.jmrt.2016.03.004.
- [24] Y.F. Kao, T.J. Chen, S.K. Chen, J.W. Yeh, Microstructure and mechanical property of as-cast, homogenized, and deformed AlxCoCrFeNi (0 ≤ x ≤ 2) high-entropy alloys, J. Alloys Compd. 488 (2009) 57–64, doi:10.1016/j.jallcom.2009.08.090.
- [25] D.B. Miracle, O.N. Senkov, A critical review of high entropy alloys and related concepts, Acta Mater. 122 (2017) 448–511, doi:10.1016/j.actamat.2016.08.081.
- [26] J.C. Rao, H.Y. Diao, V. Ocelík, D. Vainchtein, C. Zhang, C. Kuo, Z. Tang, W. Guo, J.D. Poplawsky, Y. Zhou, P.K. Liaw, J.T.M. De Hosson, Secondary phases in Alx-CoCrFeNi high-entropy alloys: an in-situ TEM heating study and thermodynamic appraisal, Acta Mater. 131 (2017) 206–220, doi:10.1016/j.actamat.2017.03.066.
- [27] Q. Wang, Y. Ma, B. Jiang, X. Li, Y. Shi, C. Dong, P.K. Liaw, A cuboidal B2 nanoprecipitation-enhanced body-centered-cubic alloy Al0.7CoCrFe2Ni with prominent tensile properties, Scr. Mater. 120 (2016) 85–89, doi:10.1016/j.scriptamat.2016.04.014.
- [28] W.R. Wang, W.L. Wang, J.W. Yeh, Phases, microstructure and mechanical properties of AlxCoCrFeNi high-entropy alloys at elevated temperatures, J. Alloys Compd. 589 (2014) 143–152, doi:10.1016/j.jallcom.2013.11.084.
- [29] C. Zhang, F. Zhang, H. Diao, M.C. Gao, Z. Tang, J.D. Poplawsky, P.K. Liaw, Understanding phase stability of Al-Co-Cr-Fe-Ni high entropy alloys, Mater. Des. 109 (2016) 425–433, doi:10.1016/j.matdes.2016.07.073.
- [30] Q. Tang, Y. Huang, H. Cheng, X. Liao, T.G. Langdon, P. Dai, The effect of grain size on the annealing-induced phase transformation in an Al0•3CoCrFeNi high entropy alloy, Mater. Des. 105 (2016) 381–385, doi:10.1016/j.matdes.2016.05.079.
- [31] W.P. Wang, W.L. Wang, S.C. Wang, Y.C. Tsai, C.H. Lai, J.-.W. Yeh, Effects of Al addition on the microstructure and mechanical property of AlxCoCrFeNi high-entropy alloys, Intermetallics 26 (2012) 44–51, doi:10.1016/j.intermet.2012.03.005.
- [32] 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 - Al0.3CoFeCrNi and Al0.3CuFeCrNi2, Scr. Mater. 123 (2016) 130–134, doi:10.1016/j.scriptamat.2016.06.019.
- [33] Y.L. Zhao, T. Yang, Y. Tong, J. Wang, J.H. Luan, Z.B. Jiao, D. Chen, Y. Yang, A. Hu, C.T. Liu, J.J. Kai, Heterogeneous precipitation behavior and stacking-fault-mediated deformation in a CoCrNi-based medium-entropy alloy, Acta Mater. 138 (2017) 72– 82, doi:10.1016/j.actamat.2017.07.029.
- [34] K.Y. Tsai, M.H. Tsai, J.W. Yeh, Sluggish diffusion in Co-Cr-Fe-Mn-Ni high-entropy alloys, Acta Mater. 61 (2013) 4887–4897, doi:10.1016/j.actamat.2013.04.058.
- [35] M. Vaidya, S. Trubel, B.S. Murty, G. Wilde, S.V. Divinski, Ni tracer diffusion in CoCr-FeNi and CoCrFeMnNi high entropy alloys, J. Alloys Compd. 688 (2016) 994–1001, doi:10.1016/j.jallcom.2016.07.239.
- [36] T.T. Shun, Y.C. Du, Microstructure and tensile behaviors of FCC Al0.3CoCrFeNi high entropy alloy, J. Alloys Compd. 479 (2009) 157–160, doi:10.1016/j.jallcom.2008.12.088.
- [37] M.-.H. Tsai, J.-.W. Yeh, High-Entropy Alloys: a Critical Review, Mater. Res. Lett. 2 (2014) 107–123, doi:10.1080/21663831.2014.912690.
- [38] Y. Shi, L. Collins, N. Balke, P.K. Liaw, B. Yang, In-situ electrochemical-AFM study of localized corrosion of AlxCoCrFeNi high-entropy alloys in chloride solution, Appl. Surf. Sci. 439 (2018) 533–544, doi:10.1016/j.apsusc.2018.01.047.
- [39] Y. Qiu, S. Thomas, M.A. Gibson, H.L. Fraser, N. Birbilis, Corrosion of high entropy alloys, Npj Mater. Degrad. 1 (2017) 15, doi:10.1038/s41529-017-0009-y.

- [40] Y. Kao, T. Lee, S. Chen, Y. Chang, Electrochemical passive properties of AlxCoCrFeNi (x= 0, 0.25, 0.50, 1.00) alloys in sulfuric acids, Corros. Sci. 52 (2010) 1026–1034.
- [41] Li, Q.H., Yue, T.M., Guo, Z.N. & Lin, X. Microstructure and Corrosion Properties of AlCoCrFeNi High Entropy Alloy Coatings Deposited on AISI 1045 Steel by the Electrospark Process. 44, 1767–1778 (2013).
- [42] Thermocalc 2017a, Themo-Calc Software AB, Sweden, 2017.
- [43] TCHEA1 High Entropy Alloy database, Themo-Calc Software AB, Stockholm, Sweden, 2015.
- [44] A. Perron, C. Toffolon-Masclet, X. Ledoux, F. Buy, T. Guilbert, S. Urvoy, S. Bosonnet, B. Marini, F. Cortial, G. Texier, C. Harder, V. Vignal, P. Petit, J. Farré, E. Suzon, Understanding sigma-phase precipitation in a stabilized austenitic stainless steel (316Nb) through complementary CALPHAD-based and experimental investigations, Acta Mater. 79 (2014) 16–29, doi:10.1016/j.actamat.2014.06.066.
- [45] M. Schwind, J. Kallqvist, J.O. Nilsson, J. Ågren, H.O. Andren, Sigma-Phase Precipitation in Stabilized Austenitic Stainless Steels, Acta Mater. 48 (2000) 2473–2481, doi:10.1016/S1359-6454(00)00069-0.
- [46] C.E. Campbell, W.J. Boettinger, U.R. Kattner, Development of a diffusion mobility database for Ni-base superalloys, Acta Mater. (2002), doi:10.1016/S1359-6454(01)00383-4.
- [47] H. Chen, Y.Q. Si, D.G. McCartney, An analytical approach to the β-phase coarsening behaviour in a thermally sprayed CoNiCrAlY bond coat alloy, J. Alloys Compd. (2017), doi:10.1016/j.jallcom.2017.02.002.
- [48] J.L. Hart, A.C. Lang, A.C. Leff, P. Longo, C. Trevor, R.D. Twesten, M.L. Taheri, Direct detection electron energy-loss spectroscopy: a method to push the limits of resolution and sensitivity, Sci Rep 7 (1) (2017) 1–14.
- [49] Y. Zhou, D. Zhou, X. Jin, L. Zhang, X. Du, B. Li, Design of non-equiatomic mediumentropy alloys, Sci. Rep. 8 (2018), doi:10.1038/s41598-018-19449-0.
- [50] M. Widom, Modeling the structure and thermodynamics of high-entropy alloys, J. Mater. Res. (2018) 1–18, doi:10.1557/jmr.2018.222.
- [51] D.A. Porter, K... Easterling, Phase Transformation in Metals and Alloys, Chapman Hall, 2014, doi:10.1007/s13398-014-0173-7.2.
- [52] Z. Zhang, C.T. Liu, M.K. Miller, X.-L. Wang, Y. Wen, T. Fujita, A. Hirata, M. Chen, G. Chen, B.A. Chin, A nanoscale co-precipitation approach for property enhancement of Fe-base alloys, Sci. Rep. 3 (2013) 1327, doi:10.1038/srep01327.
- [53] Z.B. Jiao, J.H. Luan, M.K. Miller, Y.W. Chung, C.T. Liu, Co-precipitation of nanoscale particles in steels with ultra-high strength for a new era, Mater. Today 20 (2017) 142–154, doi:10.1016/j.mattod.2016.07.002.
- [54] T.M. Butler, J.P. Alfano, R.L. Martens, M.L. Weaver, High-Temperature Oxidation Behavior of Al-Co-Cr-Ni-(Fe or Si) Multicomponent High-Entropy Alloys, Jom 67 (2015) 246–259, doi:10.1007/s11837-014-1185-7.
- [55] L.J. Santodonato, Y. Zhang, M. Feygenson, C.M. Parish, M.C. Gao, R.J.K. Weber, J.C. Neuefeind, Z. Tang, P.K. Liaw, Deviation from high-entropy configurations in the atomic distributions of a multi-principal-element alloy, Nat. Commun. 6 (2015) 5964, doi:10.1038/ncomms6964.
- [56] T. Yang, S. Xia, S. Liu, C. Wang, S. Liu, Y. Zhang, J. Xue, S. Yan, Y. Wang, Effects of AL addition on microstructure and mechanical properties of AlxCoCrFeNi High-entropy alloy, Mater. Sci. Eng. A. 648 (2015) 15–22, doi:10.1016/j.msea.2015.09.034.
- [57] F. Otto, A. Dlouhý, K.G. Pradeep, M. Kuběnová, D. Raabe, G. Eggeler, E.P. George, Decomposition of the single-phase high-entropy alloy CrMnFeCoNi after prolonged anneals at intermediate temperatures, Acta Mater. 112 (2016) 40–52, doi:10.1016/j.actamat.2016.04.005.
- [58] C. Niu, W. Windl, M. Ghazisaeidi, Multi-Cell Monte Carlo Relaxation method for predicting phase stability of alloys, Scr. Mater. 132 (2017) 9–12, doi:10.1016/j.scriptamat.2017.01.001.