

Experimental and Computational Investigation of High Entropy Alloys for Elevated-Temperature Applications

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ABSTRACT

To create and design novel structural materials with enhanced creep-resistance, fundamental studies have been conducted on high-entropy alloys (HEAs), using (1) thermodynamic calculations, (2) mechanical tests, (3) neutron diffraction, (4) characterization techniques, and (5) crystal-plasticity finite-element modeling (CPFEM), to explore future candidates for next-generation power plants.

All the constituent binary and ternary systems of the Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems were thermodynamically modeled within the whole composition range. Comparisons between the calculated phase diagrams and literature data are in good agreement. Seven types of HEAs were fabricated from Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems. The $\text{Al}_x\text{CrCuFeMnNi}$ HEAs have disordered [face-centered cubic (FCC) + body-centered cubic (BCC)] crystal structures, not FCC or BCC single structure. 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 constitute phases, and (3) existing temperatures of all six phases. After homogenization, the $\text{Al}_{0.3}\text{CoCrFeNi}$ material is a pure FCC solid solution. After aging at 700 °C for 500 hours, the optimal microstructure combinations, the FCC matrix, needle-like B2 phase within grains, and granular σ phase along grain boundary, is achieved for $\text{Al}_{0.3}\text{CoCrFeNi}$. The cold-rolling process is utilized to reduce the grain size of $\text{Al}_{0.1}\text{CoCrFeNi}$ and $\text{Al}_{0.3}\text{CoCrFeNi}$. The chemical elemental partitioning of FCC, BCC, B2, and σ phases at different temperatures, before and after mechanical tests, in Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems are quantitatively characterized by both synchrotron X-ray diffraction, neutron diffraction with levitation, scanning electron microscopy (SEM), advanced atom probe tomography (APT), and transmission electron microscopy (TEM). In-situ neutron diffraction experiments were conducted to study the strengthening effect of B2 phase on tensile properties of $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs directly. The results shows the creep behavior of $\text{Al}_{0.3}\text{CoCrFeNi}$ is superior to conventional alloys, and the heat treatment introduces secondary B2 phase into the FCC matrix, which increase the yielding strength, decrease the ductility, diminish the serrated flow during compression tests at high temperatures.

In summary, the outcomes of the development of the HEAs with creep resistance include: (1) Suitable candidates, for the application to boilers and steam and gas turbines at temperatures above 760 °C and a stress of 35 MPa. (2) Fundamental understanding on the precipitate stability and deformation mechanisms of both single-phase and precipitate-strengthened alloys at room and elevated temperatures, and (3) The demonstration of an integrated approach, coupling modeling [thermodynamic calculations and crystal-plasticity finite-element modeling (CPFEM)] and focused experiments, to identify HEAs that outperform conventional alloys for high-temperature applications, which will be applicable for the discovery and development of other high-temperature materials in the power-generating industry.

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EXECUTIVE SUMMARY

The creation and design of novel structural materials with enhanced creep resistance has always been the goal of many scientists and engineers. The high-entropy alloy (HEA) concept has revolutionized alloy-design approaches by employing the use of multi-principal elements in contrast to traditional alloys, based on one or two principal elements with small amounts of alloying elements to achieve desired properties. HEAs have shown to be suitable materials for elevated-temperature applications.

Fundamental studies have been conducted, using (1) thermodynamic calculations to quantify the phase compositions, phase fractions, and phase stability versus temperature and composition, (2) mechanical tests (hardness, tensile, compression, nanoindentation, and creep) for the ductility investigation and the creep-resistance examination, (3) neutron diffraction to reveal the deformation mechanisms of both single-phase and precipitate-strengthened HEAs, during plastic (tensile and creep) deformation, (4) characterization techniques (atomic-probe tomography, transmission-electron microscopy) to verify the predictions by thermodynamic calculations and study the creep deformation mechanisms, and (5) crystal-plasticity finite-element modeling (CPFEM) to further verify the lattice evolution of lattice strains during high-temperature deformation.

In the first task, all the constituent binary and ternary systems of the Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems were thermodynamically modeled within the whole composition range. Comparisons between the calculated phase diagrams and literature data are in good agreement. The multi-component thermodynamic database of the Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems were then obtained via extrapolation. The current Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni thermodynamic database enables us to carry out the calculations of phase diagrams, which can be used as useful guidelines to identify the Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni HEAs with desirable microstructures and creep properties.

In the second task, seven types of HEAs were fabricated from Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems. The $\text{Al}_x\text{CrCuFeMnNi}$ HEAs have disordered [face-centered-cubic (FCC) + body-centered-cubic (BCC)] crystal structures, not a FCC or BCC single structure. But the constituent phases vary for different aluminum concentrations. The $\text{Al}_{0.1}\text{CrCuFeMnNi}$ has two kinds of FCC phases and one kind of the BCC phase, while $\text{Al}_{0.8}\text{CrCuFeMnNi}$ has one kind of the FCC phase and two kinds of BCC phases. 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 constitute phases, and (3) existing temperatures of all six phases. After homogenization, the $\text{Al}_{0.3}\text{CoCrFeNi}$ material is a pure FCC solid solution. After aging at 700 °C for 500 hours, the optimum microstructure combinations, the FCC matrix, needle-like B2 phase within grains, and granular σ phase along grain boundaries, is achieved for $\text{Al}_{0.3}\text{CoCrFeNi}$. The cold-rolling process is utilized to reduce the grain size of $\text{Al}_{0.1}\text{CoCrFeNi}$ and $\text{Al}_{0.3}\text{CoCrFeNi}$.

In the third task, the chemical elemental partitioning of FCC, BCC, B2, and σ phases at different temperatures, before and after mechanical tests, in Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems are quantitatively characterized using both synchrotron X-ray diffraction, neutron diffraction with levitation, scanning electron microscopy (SEM), advanced atom probe tomography (APT), and transmission electron microscopy (TEM).

The physical metallurgy of HEAs, i.e., the structure-property relationship, coupled with alloy design in Task 1 and mechanical properties in Task 4, is investigated.

In the fourth task, the mechanical properties are studied by hardness, compression, and tensile tests. As the Al ratio increases, the yielding stress increases, while the ductility decreases in both Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems. In-situ neutron diffraction experiments were conducted to study the strengthening effect of B2 phase on tensile properties of $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs directly. The results shows that the creep behavior of $\text{Al}_{0.3}\text{CoCrFeNi}$ is superior to conventional alloys, and the heat treatment introduces secondary B2 phases into the FCC matrix, which increase the yielding strength, decrease the ductility, and diminish the serrated flow during compression tests at high temperatures.

In summary, the outcomes of the development of the HEAs with creep resistance include: (1) Suitable candidates, $\text{Al}_x\text{CrCuFeMnNi}$ and $\text{Al}_x\text{CoCrFeNi}$ HEA systems, for the application to oilers and steam and gas turbines at temperatures above 760 °C and a stress of 35 MPa. (2) Fundamental understanding on the precipitate stability and deformation mechanisms of both single-phase and precipitate-strengthened alloys at room and elevated temperatures, and (3) The demonstration of an integrated approach, coupling modeling [thermodynamic calculations and crystal-plasticity finite-element modeling (CPFEM)] and focused experiments, to identify HEAs that outperform conventional alloys for high-temperature applications, which will be applicable for the discovery and development of other elevated-temperature materials in the power-generating industry.

1. INTRODUCTION

Nowadays, most efficient fossil-energy power plants operate at the steam temperature of ~ 600 °C [1]. Nearly two dozens of power plants worldwide have been operated with the main steam temperatures of 580 °C to 600 °C and steam pressures of 24 to 35 MPa. Based on Ref. [1], the steam temperature is expected to increase another 50 °C to 100 °C in the next 20 or 30 years. In addition, extensive research has been performed in the United States with the goal of achieving the steam temperature of 760 °C and pressure of 35 MPa. To achieve proposed steam temperatures and pressures, new advanced high-temperature alloys, which can survive at the expected service temperature and pressure for a long period (~ 30 years), are needed.

Depending on the experienced temperature and stress, components in fossil-energy power plants are mainly based on ferritic heat-resistant steels, austenitic heat-resistant steels, or nickel-based superalloys. Ferritic steels are always preferred, compared with austenitic steels in fossil-energy power plants, especially for heavy-section components, because of their low thermal expansion coefficient, high thermal conductivity, and relative low cost. Austenitic steels are likely to suffer from thermal fatigue, and, then, cause problems in fossil-energy power plants [1]. On the other hand, nickel-based superalloys [2] have been employed in more severe conditions due to superior high-temperature strength. However, their cost is much higher than steels, and, thus, their applications are limited to certain critical parts. Creep resistances of these three sorts of materials are compared by the 10^5 h creep rupture strength at the temperature of 500 °C to 750 °C, shown in Figure 1. Although austenitic steels have better creep resistance than ferritic steels, newly-developed ferritic steels (T/P91, T/P92, and T/P911) can be used in the region, where austenitic steels dominated. To complementing existing fossil-energy materials, we aim at performing fundamental studies on the $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloy (HEA) system for use in boilers and steam and gas turbines at temperatures above 760 °C and a stress of 35 MPa, and develop an integrated approach, coupling thermodynamic calculations and focused experiments, to identify HEAs that outperform conventional alloys.

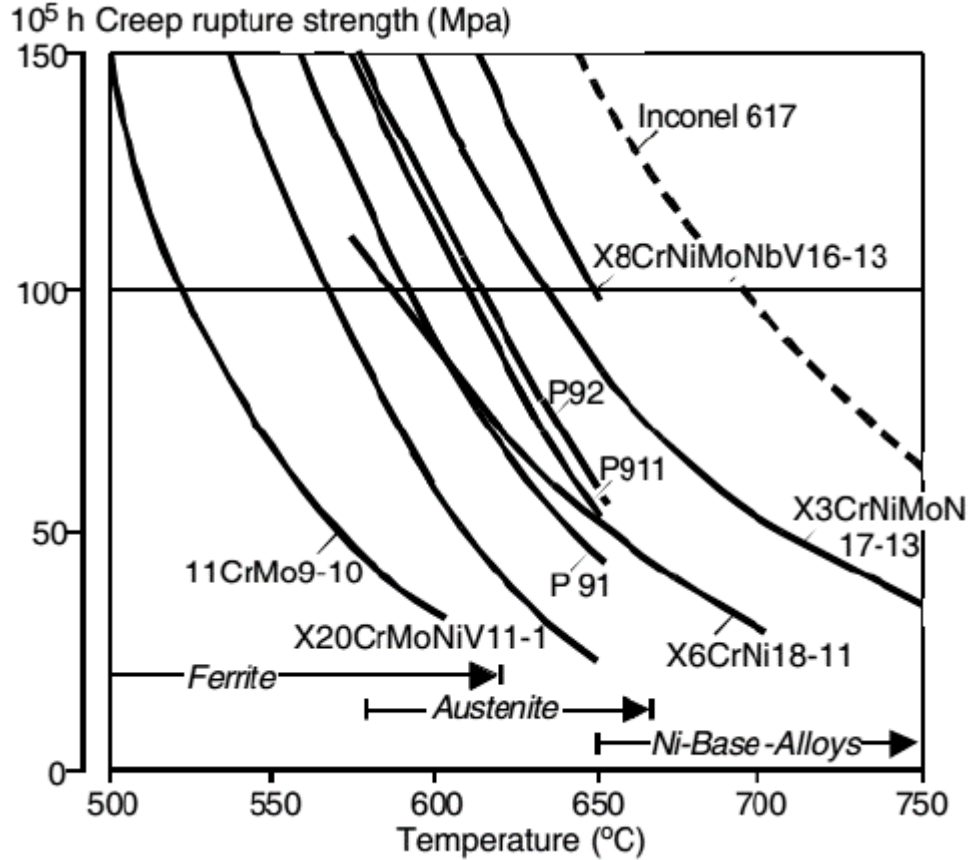


Figure 1. The comparison of the creep resistance of ferritic steels, austenitic steels, and nickel-based alloys [3].

1.1 Objective and Motivation

The objectives of this research are to (1) perform fundamental studies on the $\text{Al}_x\text{CrCuFeMnNi}$ and $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloy (HEA) systems for use in boilers and steam and gas turbines at temperatures above 760 °C and a stress of 35 MPa, (2) investigate the creep behavior and related deformation mechanisms of HEAs, (3) study the thermodynamics and kinetics of NiAl precipitates and their strengthening effect in the creep behavior of HEAs, and (4) develop an integrated approach, coupling modeling [thermodynamic calculations and crystal-plasticity finite-element modeling (CPFEM)] and focused experiments, to identify HEAs with excellent creep properties that outperform conventional alloys for high-temperature applications. The proposed work

will take advantage of the seamless integration of materials by design, materials mechanical properties, materials microstructural characterization, and theoretical modeling.

Novel structural materials are sought to extend the temperature and pressure of boilers, steam turbines, and gas turbines. The efficiency of the conventional fossil-power plant is a strong function of the steam temperature and pressure. By increasing the steam temperature from 593 °C to 700 °C, the efficiency will increase from 47 %, representing the current state-of-the-art plant to around 55 %. For example, ferritic steels are currently used only at temperatures below 620 °C due to their limited creep resistance at higher temperatures. Thus, new alloy systems are needed for advanced power plants. Recently, high-entropy alloys (HEAs) or multi-principal-element alloys, a new type of advanced materials, are nearly equiatomic and multi-element systems, which can crystallize as a single phase or multi-phases [4-6]. In other words, HEAs are considered as “Metal Buffet”, in which several metallic elements, e.g., Al, Co, Cr, Fe, Ni, Mn, Ti, Nb, Hf, Ta, Zr, are mixing together. HEAs attract great attention for their outstanding properties, such as the good strength and ductility [7-10], great fatigue [11-13], outstanding low-temperature fracture toughness [14], decent wear resistance [15-17], corrosion resistance [18], and elevated-temperature softening resistance [19-21], which make them as potential structural materials with many applications. For long-term applications, the creep properties of HEAs must be examined carefully. However, based on our knowledge, very limited studies have been conducted for HEAs on their long-term creep behavior. Only two papers using indentation tests [22, 23], one paper using stress-relaxation tests [24], and one paper using in-situ slow strain rate tensile tests [25] to study and estimate the creep behavior of HEAs have been reported. Thus, it becomes obvious for critical issues about HEAs: (1) how does the multi-principal elements affect the microstructures and their creep properties?; (2) how does the high-entropy configuration influence creep deformation mechanisms at high temperatures?; and (3) what is the specific fundamental contributing factors in controlling the creep properties of HEAs? These issues will be addressed by accomplishing the above project goal.

The research efforts include new material development and applications, mechanical behavior, deformation mechanisms, multiscale modeling, and microscopy science. A systematical study on mechanical properties at room and elevated temperatures (the ductility, fracture toughness, creep resistance, etc.) can assess the capability of HEAs as components in fossil-energy power plants with the steam temperature of 700 °C or even higher. At the same time, the study could deepen our fundamental understanding on the precipitate stability and deformation mechanisms of both single-phase and precipitate-strengthened alloys at room and elevated temperatures. The proposed research may result in a series of HEAs, which can strongly elevate the steam working temperatures and pressures, and thus, the efficiency of fossil-energy power plants in the future.

1.2 Framework

Based on the experience of our group with creep studies on ferritic steels, we hypothesize that HEAs with appropriate compositions will show superior creep resistance over traditional alloys due to (1) resulting high entropy of mixing to lower the free energy of solution phases at high temperatures; (2) accompanied sluggish diffusion due to the difficult cooperation among the migrations of different elements yields simple solid solutions at high temperatures; (3) a great tendency to form nanoscale deformation twins at high temperatures; and (4) highly-thermal resistant precipitation to induce required level of strength and creep properties at high temperatures. If the above hypothesis can be confirmed, it will greatly sharpen the basis understanding of the HEAs' creep behavior with high-entropy configurations, which empowers them with outstanding properties to surpass other conventional alloys at elevated temperatures for engineering applications.

To test the above hypothesis, a systematic research plan integrating experimental and computational efforts is proposed, including the alloy design, processing, prediction, and verification components. Figure 2 outlines the integrated experimental and computational framework. The present research mainly focuses on the creep behavior of HEAs from four fundamental aspects, including (1) Task 1: Thermodynamic Calculations to select the suitable HEAs; (2) Task 2: Alloy Fabrication; (3) Task 3: Microstructural Characterizations to experimentally verify predicted phases

and determine structures at elevated temperatures; (4) Task 4: Mechanical Characterizations to complete ex-situ and in-situ creep and mechanical behavior using neutron diffraction techniques. Crystal-plasticity finite-element modeling (CPFEM) is utilized to provide a basic understanding and prediction of creep/tension behavior.

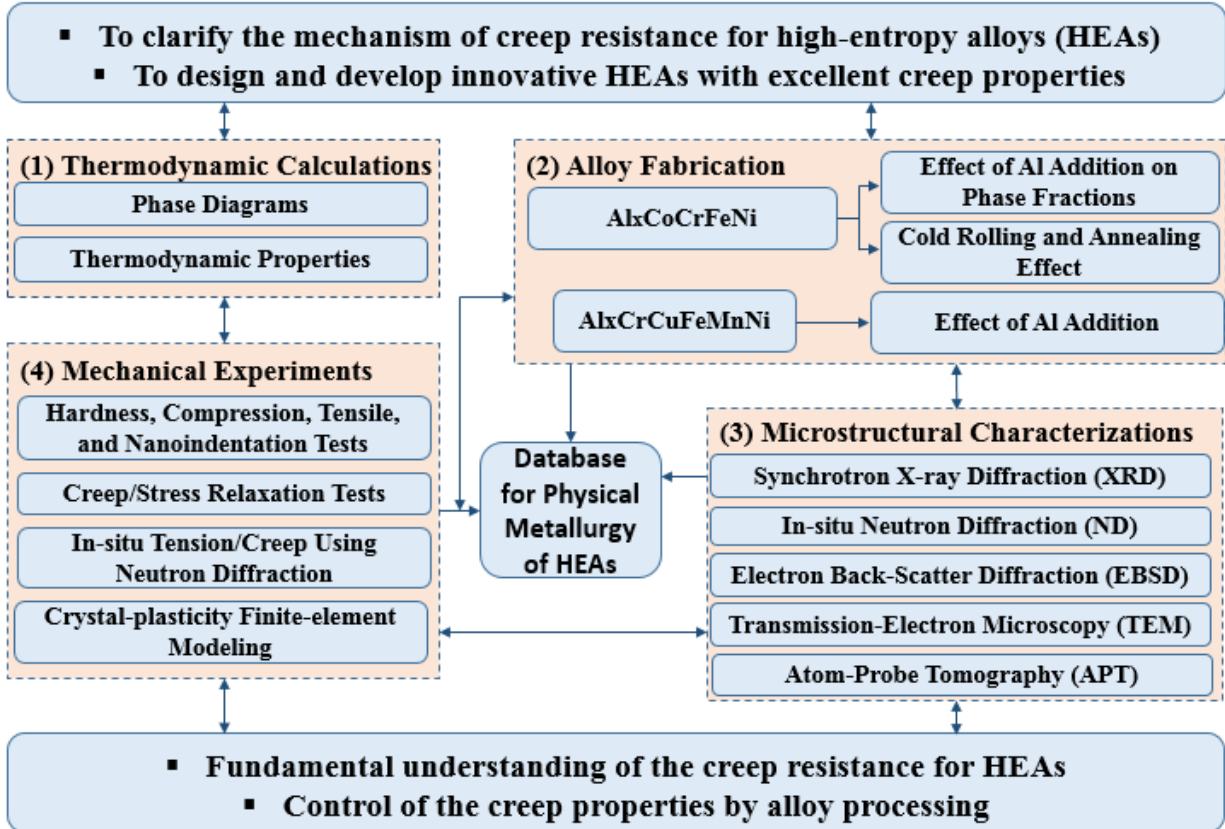


Figure 2 The framework of the present integrated experimental and computational work.

2 BACKGROUND

2.1 Unique Properties of High-Entropy Alloys

2.1.1 Formation of HEAs

Based on achieving a high configuration entropy of mixing among alloying elements, HEAs (also called multi-component alloys by Cantor *et al.* [4]) have been proposed [4-6, 26-28]. HEAs are solid-solution alloys containing more than five principal elements in equal or near-equal atomic percent (at.%) [6]. The mechanical behavior of many HEAs has been extensively studied, and shown to have excellent properties for use as structural alloys, particularly in high-temperature applications [11, 19, 29]. Until now, several investigated HEAs (containing at least four chemical compositions) are considered as single-phase solid solutions, which can be divided into four families for the first time, shown in Figure 3. The Type 1 is solid solutions of 3d-transition metals only (CoCrFeMnNi [4, 14, 30, 31], CoCrFeNi [30, 32, 33], CoFeMnNi [30], CoCrMnNi [30], and $\text{Co}_{0.25}\text{Cr}_{0.1}\text{Fe}_2\text{Mn}_{1.35}\text{Ni}_{1.3}$ [34]). The Type 2 is combinations of transition metals with Al ($\text{Al}_{0.3}\text{CoCrFeNi}$ [35, 36], $\text{Al}_{0.24}\text{CoCrFeMnNi}$ [37], $\text{Al}_{0.4}\text{CoCrFeNi}_2$ [38], and $\text{Al}_{0.4}\text{Hf}_{0.6}\text{TaTiZr}$ [39]). The Type 3 is based on refractory metals (NbMoTaW, NbMoTaVW, and HfNbTaTiZr [19, 40]). Few other alloy systems, such as CoCrFeNiPd and CoCrFeNiPd₂ [41], are found to be a single phase too.

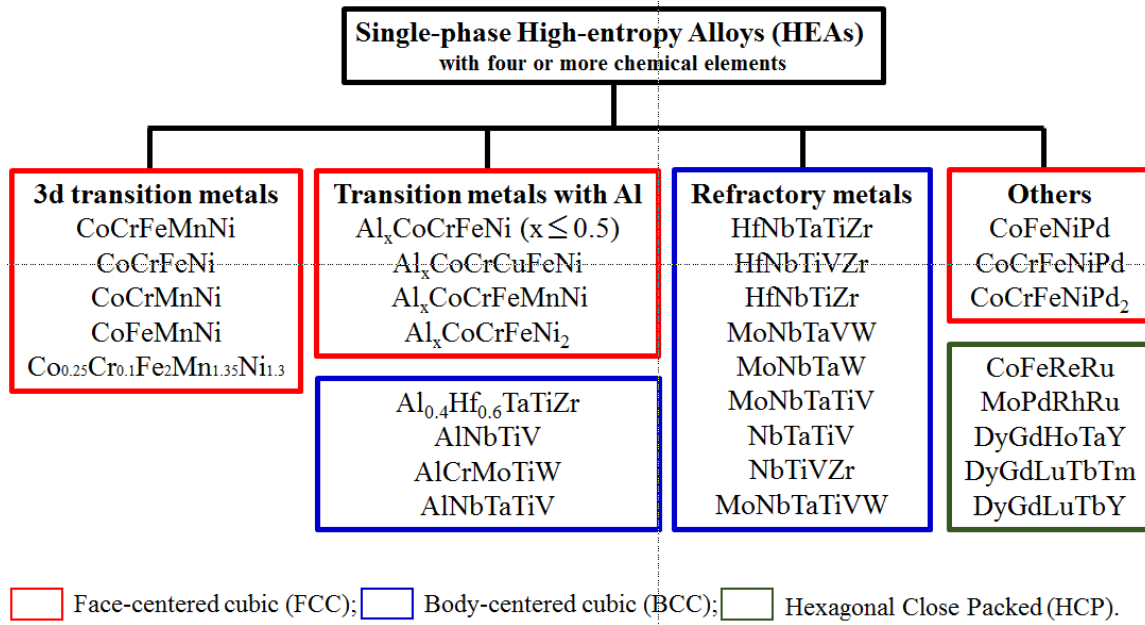


Figure 3 The classifications of single-phase high-entropy alloys (HEAs)

2.1.2 Structures of HEAs

High-entropy alloys (HEAs), a new class of solid-solution alloys, have attracted worldwide attention for their unique properties. Rules for predicting solid-solution formation of HEAs have been developed, by weighing both thermodynamics and geometry factors. It is found that solid solutions tend to form when several parameters, e.g., a mixing enthalpy parameter and an atomic-size difference parameter, fall within certain limits. Criteria for solid-solution formation in HEAs continue to be improved, for example, by including the effect of valence electron concentration. These thermodynamics- or geometry- based rules are useful for choosing compatible elements and compositional ranges, when creating or designing new creep-resistant HEAs.

Due to the size difference of multiple principal elements, the lattice of a face-centered cubic (FCC) or body-centered cubic (BCC) structure is highly distorted. This lattice distortion is important to the pinning effect on dislocation and reduction of stacking fault and grain boundary energy, which results in promising mechanical, thermal, and electrical properties. Different from minor alloy addition in conventional alloys, by changing the Al content in a wide range, while keeping other

principal elements in an equimolar ratio, the matrix-structures of HEAs change gradually from FCC to BCC solution phases. Actually, the microstructures evolution in $\text{Al}_x\text{CoCrFeNi}$ system, with respect to increasing the aluminum content, is actually more complicated than a simple switch from FCC to BCC solution phases. The BCC phase splits into ordered and disordered phases and the alloy microstructures undergo a series of changes, including the appearance needle-, droplet-, and wall-shaped structures. Moreover, nano-particles have been reported in HEAs. The formation and structure of matrix, ordered/disordered phase, and nano-particle perhaps greatly affect mechanical properties. The present work focuses on one of the earliest quinary high-entropy alloys (HEAs), $\text{Al}_{0.3}\text{CoCrFeNi}$. It belongs to the $\text{Al}_x\text{CoCrFeNi}$ system, which is one of the most well-developed and refined HEA systems [18, 22, 35, 36, 42-55].

Wang *et al.* [56] has studied the effect of Al addition on the microstructures of $\text{Al}_x\text{CoCrFeNi}$ HEAs. Figure 1 shows the crystal-structure evolution with the increase of the Al content. The dotted line shows the nominal atomic content of Al in the $\text{Al}_x\text{CoCrFeNi}$ alloys, and the actual Al content is exhibited by the black line. The figure indicates that when $x = 0.1 \sim 0.5$, the actual Al content of the face-centered cubic (FCC) phase is the same as the nominal one. Then the two lines separated due to the formation of the body-centered cubic (BCC) phase. Wang *et. al* [22, 56] concluded that the the maximum amount of Al atoms in the FCC solid solution of the $\text{Al}_x\text{CoCrFeNi}$ alloy system is 11.0 atomic percent (at.%), while the minimum Al content of the BCC phase is 18.4 at.%. With increasing the Al content, the crystal structure evolves from the FCC, to duplex (FCC + BCC), to pure BCC phases.

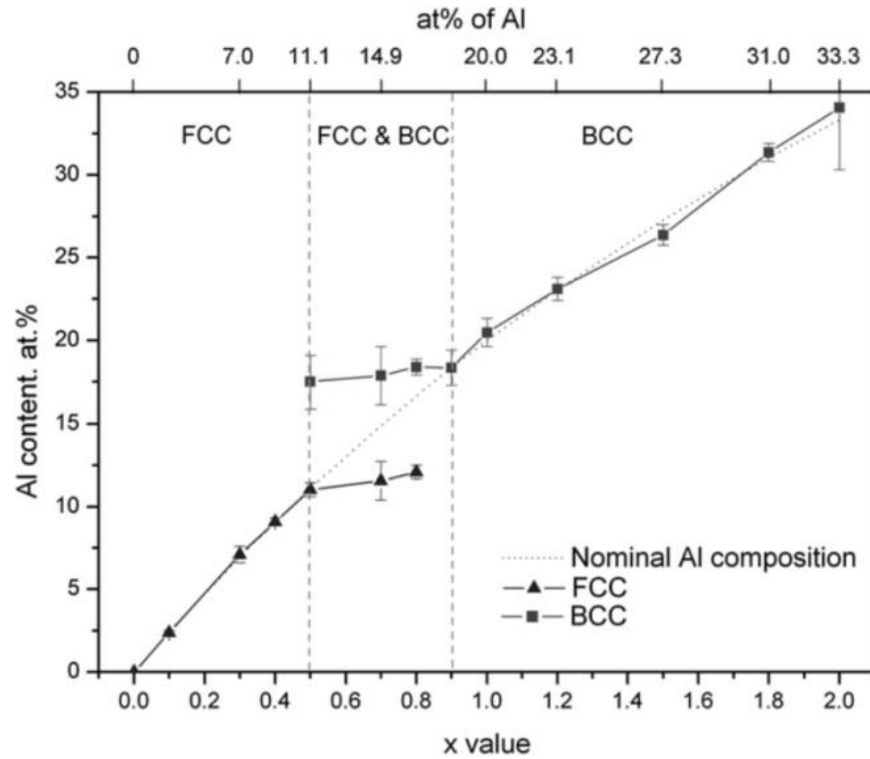


Figure 4 Actual Al content of the as-cast $\text{Al}_x\text{CoCrFeNi}$ alloys as a function of x value [56]

Figure 5 shows the optical micrographs of as-cast $\text{Al}_x\text{CoCrFeNi}$ HEAs. It is shown that the microstructure evolves with the increase of the Al content, starting from the columnar cellular structure ($x = 0.1 \sim 0.3$) to columnar dendrite ($x = 0.4 \sim 0.6$) (the increase of interdendritic regions with the addition of Al), equiaxed nondendritic grain ($x = 0.7 \sim 0.8$), equiaxed dendritic grain ($x = 0.9 \sim 1.5$), and finally non-quiaxed dendritic grain structures.

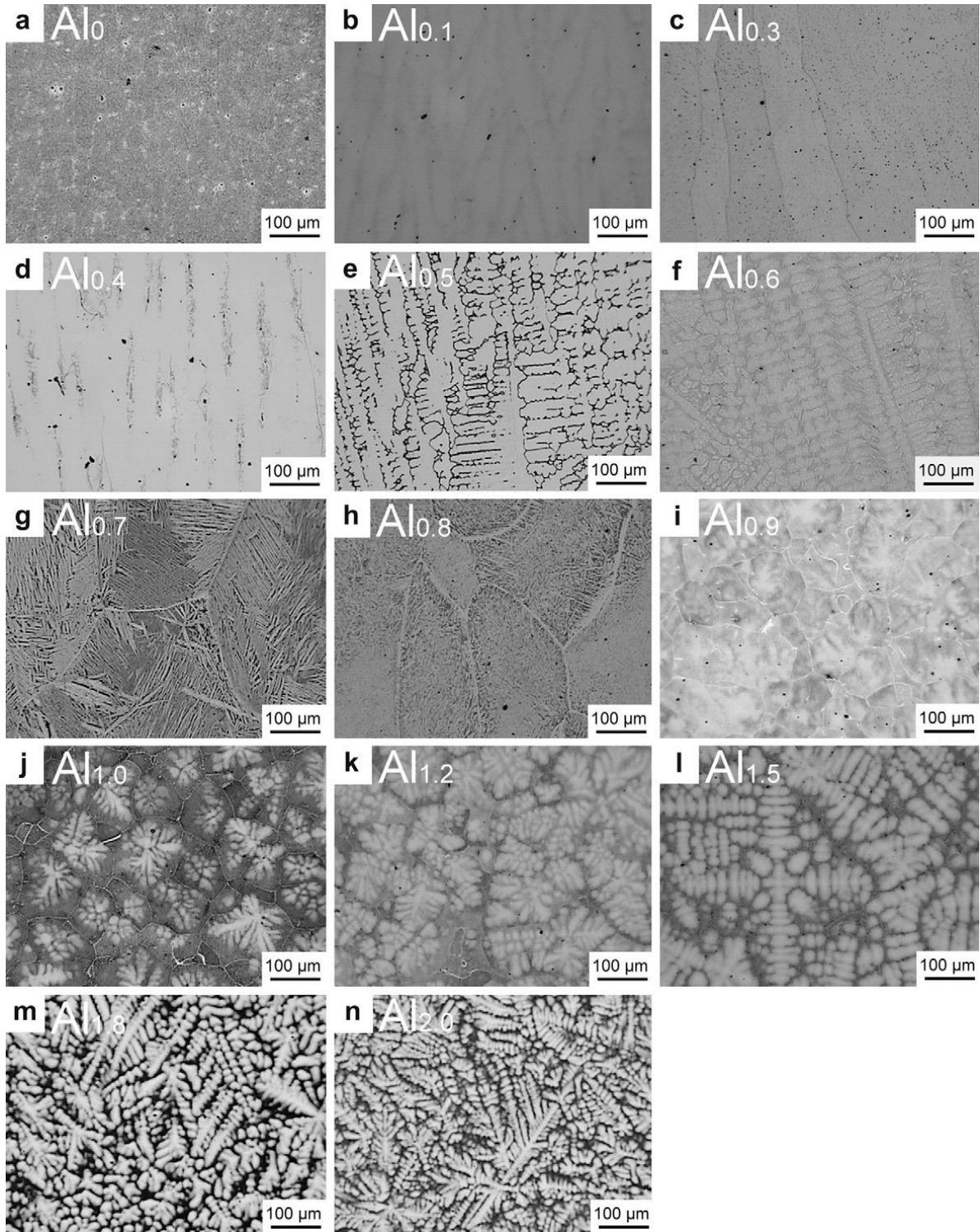


Figure 5 Optical micrographs of as-cast $\text{Al}_x\text{CoCrFeNi}$ HEAs ^[56].

2.1.3 Mechanical Properties of HEAs

Kao *et al.* [57] investigated the mechanical behavior of as-cast homogenized and deformed $\text{Al}_x\text{CoCrFeNi}$ HEAs. In terms of hardness, the hardness of the FCC phase was smaller than the BCC phase, while the values of hardness are consistent throughout BCC and FCC regions to some extent and showed the increase, as the volume fraction of the BCC increases in the BCC-FCC mix region. Also, by comparing as-deformed and as-homogenized samples, no stress-induced phase transformation was found during deformation. The as-deformed alloys exhibit higher hardness than the as-homogenized ones, while having the same microstructure. They also found that the hardening ability of the FCC phase was about twice that of BCC.

In Li *et al.*'s work on $\text{Al}_x\text{CoCrFeNi}$ HEAs [58], their results confirm that Al promotes the formation of the BCC phase, and the crystal lattice constant of the alloys increases, as x increases. They believed that the increase of the crystal lattice constant induces the increase of hardness.

The HEAs have been investigated mechanically, using hardness [4], compression [[5, 8, 27, 29, 59-72], tension [37, 73, 74], great fatigue [8-10], fracture [14], nanoindentation [75], and in-situ neutron-diffraction [31] techniques and calculations based on the density-functional theory (DFT) [76] to scientifically obtain the deformation mechanisms of HEAs. Above all, the mechanical properties of HEAs and related crystalline structures are summarized, using data from Refs. [9, 19, 29, 39, 73, 74, 77] and are schematically shown in Figure 6a. For the Type-1 HEAs, the CoCrFeMnNi is the representative face-centered-cubic (FCC) solid solution, which is suitable for studying the deformation mechanism of HEAs. The yield stress of Type 1 is relatively low, compared to Types 2 and 3. When a small amount of Al (< 0.5) is introduced into 3d-transition metals, the Type-2 HEAs have higher yield stresses than Type 1, which is the result of solid-

solution-strengthening mechanisms and related clustering-strengthening effect. However, at high temperatures above 800 °C, the yield stress decreases greatly. For Type 3, the yielding stresses of refractory HEAs decrease relatively slow when the temperature is above 1,000 °C. This phenomenon shows that refractory HEAs (Type 3) have great potential for high-temperature nuclear reactor applications. When Al is introduced into refractory metals, only one type of HEAs, $\text{Al}_{0.4}\text{Hf}_{0.6}\text{NbTaTiZr}$ [Type 2 (BCC)] is a single-phase HEA. Even though the yielding stress of $\text{Al}_{0.4}\text{Hf}_{0.6}\text{NbTaTiZr}$ at room temperature is very high, the yielding stress decreases much more than refractory HEAs (Type 3), as the temperature increases. The comparison between single-phase HEAs and conventional alloys are also shown in Figure 6a. The yielding stress of Type 1 HEAs is comparable to conventional alloys, Haynes 230 (Ni-Cr-W-Mo superalloy), Hastelloy X alloy (Ni-Cr-Fe-Mo superalloy), Inconel alloy 600 (Ni-Cr-Fe superalloy), and Type 304 stainless steel. When the temperature is below 527 °C, Types 2 and 3 HEAs have superior yielding stresses, compared to conventional alloys. When the temperature is beyond 727 °C, yielding stresses of Type 3 HEAs are generally 5 times more than that of conventional alloys. Thus, previous systematic studies of HEAs, shown in Figure 3, have identified HEAs as good candidates for high-temperature applications [9, 19, 29, 39, 73, 74, 77].

Composition, such as $\text{Al}_{0.5}\text{CoCrCuFeNi}$, shows promising fatigue resistance at room temperature, when compared to other conventional alloys and bulk metallic glasses (BMGs), shown in Figure 6b. With respect to the fatigue ratio of the stress range divided by the ultimate tensile strength (UTS), HEAs span from the lower bound, comparable to the INCONEL 625 superalloy, to the higher bound, surpassing all the other alloys. The present proposal draws upon results from these related HEA systems to develop a strategy for evaluating and optimizing the alloy mechanical properties for applications in coal-powered boilers, steam turbines, gas turbines, and related high-temperature and high-pressure systems.

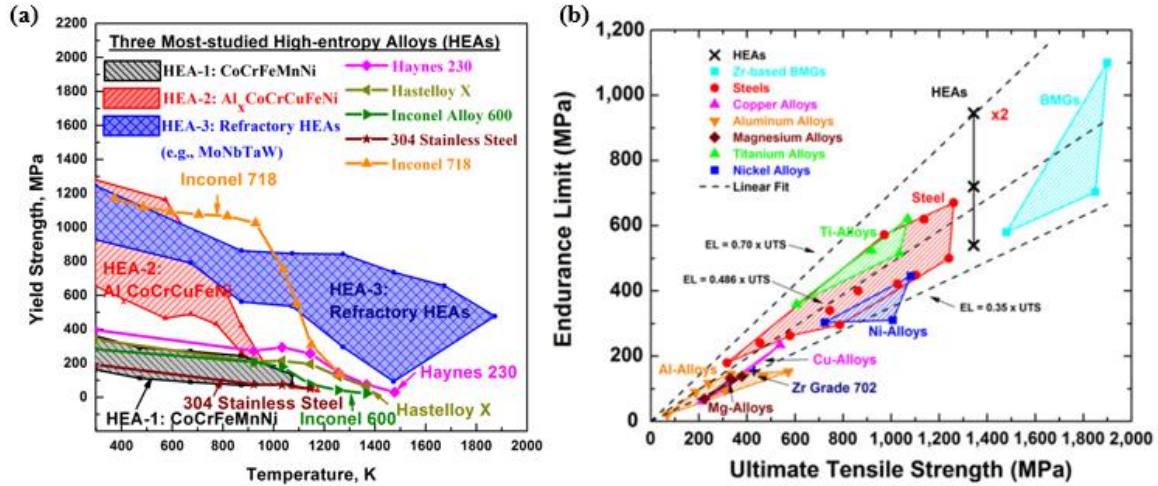


Figure 6 Superior mechanical properties of HEAs. (a) The yield strength of HEAs is comparable to commercial superalloys. (b) The fatigue-endurance limit of the Al_{0.5}CoCrCuFeNi HEA exceeds that of most metals, metallic alloys, and close to that of some bulk-metallic glasses.

Wang *et al.* also investigated the mechanical behavior of Al_xCoCrFeNi HEAs by hardness tests [56]. In their work, they agreed that the formation of the BCC phase played a vital role in the increase of hardness, as x increases. They confirmed the consistency between lattice constants and hardness. Besides, they found that the morphology also plays a role in the hardening behavior of the alloys. Thus, this trend explained the maximum hardness value of Al_{0.9}CoCrFeNi, since it has the finest spinodal structure.

Shun *et al.* investigated the tensile behavior of the Al_{0.3}CoCrFeNi alloy [78]. As shown in Figure 7, the as-cast sample exhibits the lowest yielding strength (around 170 MPa) and work-hardening rate. Both yielding strength and work hardening rate were increased by ageing and samples after ageing at 700 °C show the highest yielding strength. This trend suggests that heat-treatment can increase the yielding strength.

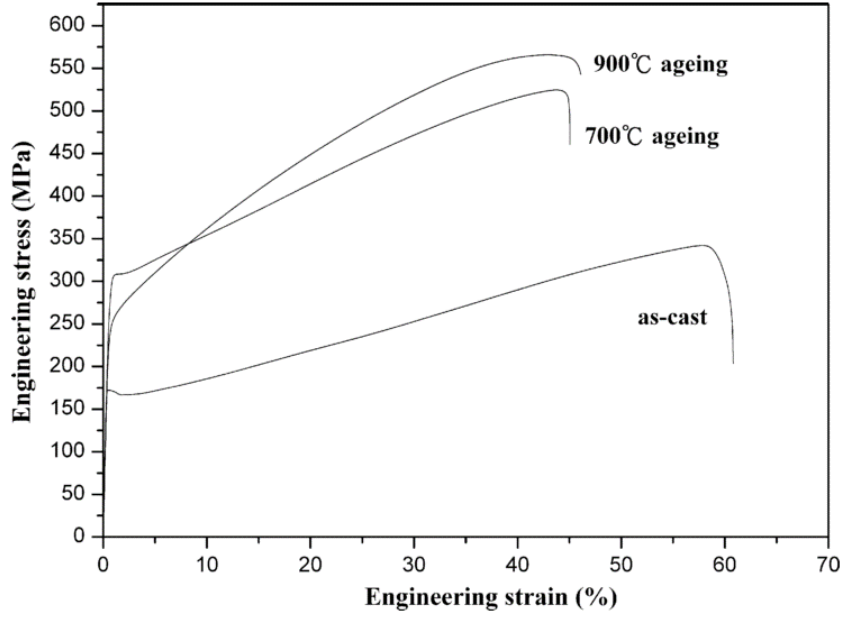


Figure 7 Engineering stress-strain curves for the as-cast, 700 °C-aged, and 900 °C-aged $\text{Al}_{0.3}\text{CoCrFeNi}$ alloys ^[78].

The polycrystalline CoCrFeMnNi and single-crystal CoCrFeNi HEAs own typical dislocation-dominated deformation characteristics of normal FCC metals during tensile tests at both room temperature and high temperatures. The initial plasticity, up to tensile strains of about 2 %, occurs exclusively by the planar glide of (110) dislocations on $\langle 111 \rangle$ planes, in the temperature range from - 196 °C to 600 °C. Both complete dislocation, $1/2 \langle 110 \rangle$, and partial dislocation, $1/6 \langle 112 \rangle$, associated with stacking faults, are observed. At higher strains, slip became more homogeneous and cell structures developed [74]. In single-crystal CoCrFeNi HEAs, slip traces for (001), (011) and (111) oriented surfaces under spherical microindentation, show that $\{111\}\langle 110 \rangle$ are primary slip systems [79]. However, at low temperature, - 196 °C, the polycrystalline CoCrFeMnNi deforms different, compared with normal FCC metals. The yielding stress and ductility are higher than those at high temperatures, which refer to nanoscale deformation twins formed at large strain (~ 20 % strain). More experimental data and evidences and clear mechanisms and theories are required for HEAs in the future.

3. TASK 1: ALLOY DESIGN

The objective of this task is to (1) quantify phase compositions, phase volume fractions, phase stability, and elemental distributions versus temperature and composition before fabrication, (2) simulate kinetic reactions for BCC, FCC, and NiAl B2 phases during solidification to direct subsequent heat treatment processes, and (3) understand physical metallurgy and optimize mechanical properties of HEAs from the predicted microstructure through the structure-property relationship.

3.1 The CALPHAD Approach

The CALPHAD (acronym of Calculation of Phase Diagrams) method could be important to obtain multicomponent phase diagrams not only for basic materials research in related areas, such as thermochemistry and solid state transformation, but also for alloy design and processing development efficiently.

Using the 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 [80]. 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.

3.2 Thermodynamic Database Development Overview

Thermodynamic database of the multi-component Al-Cr-Cu-Fe-Mn-Ni is under development. Table 1 lists the constituent binary and ternary systems of the Al-Cr-Cu-Fe-Mn-Ni system. There are 15 constituent binaries and 20 constituent ternaries. The (✓) shows the systems we are working on and reported here. The systems without any signs will be done in the future.

Table 1: Constituent binary and ternary systems in the Al-Cr-Cu-Fe-Mn-Ni System

Binary Systems				
Al-Cr (✓)	Al-Cu (✓)	Al-Fe (✓)	Al-Mn (✓)	Al-Ni (✓)
Cr-Cu (✓)	Cr-Fe (✓)	Cr-Mn (✓)	Cr-Ni (✓)	Cu-Fe (✓)
Cu-Mn (✓)	Cu-Ni (✓)	Fe-Mn (✓)	Fe-Ni (✓)	Mn-Ni (✓)
Ternary Systems				
Al-Cr-Cu (✓)	Al-Cr-Fe (✓)	Al-Cr-Mn (✓)	Al-Cr-Ni (✓)	Al-Cu-Fe (✓)
Al-Cu-Mn (✓)	Al-Cu-Ni (✓)	Al-Fe-Mn (✓)	Al-Fe-Ni (✓)	Al-Mn-Ni (✓)
Cr-Cu-Fe (✓)	Cr-Cu-Mn (✓)	Cr-Cu-Ni (✓)	Cr-Fe-Mn (✓)	Cr-Fe-Ni (✓)
Cr-Mn-Ni (✓)	Cu-Fe-Mn (✓)	Cu-Fe-Ni (✓)	Cu-Mn-Ni (✓)	Fe-Mn-Ni (✓)

3.3 Results and Discussion

3.3.1 Thermodynamic Database Validation

Up to now, all the constituent binary systems of the Al-Cr-Cu-Fe-Mn-Ni system have been thermodynamically modeled on the basis of our previous work. Thermodynamic descriptions of five binary systems with Mn are newly obtained. The calculated phase diagrams of these binary systems using our current thermodynamic database are given below.

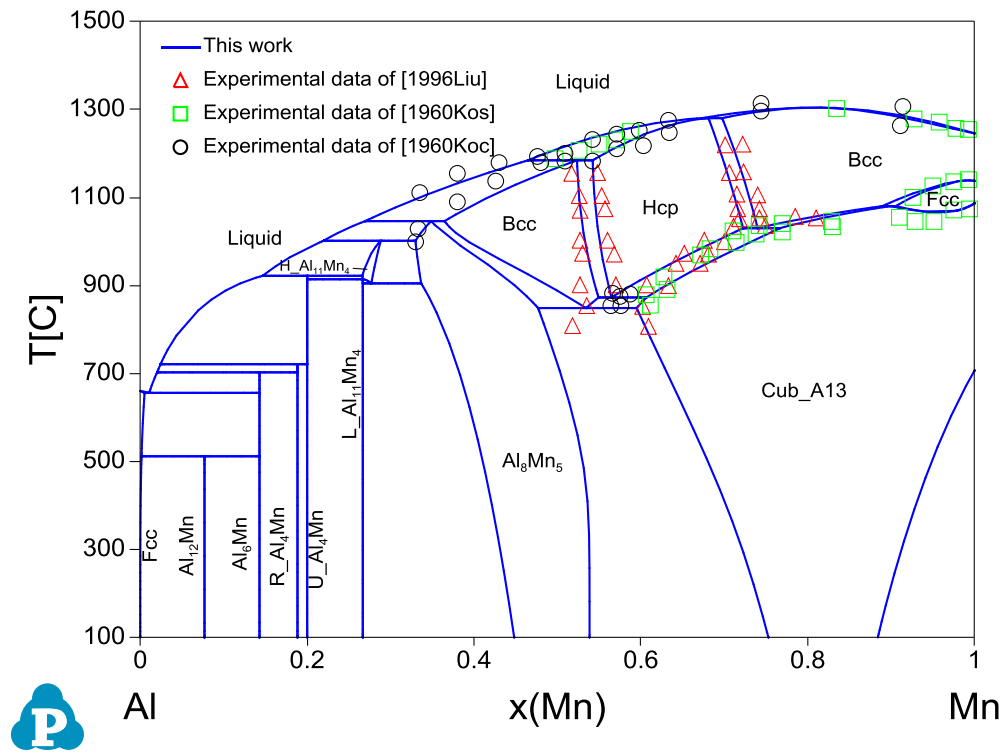


Figure 8 Calculated Al-Mn binary phase diagram

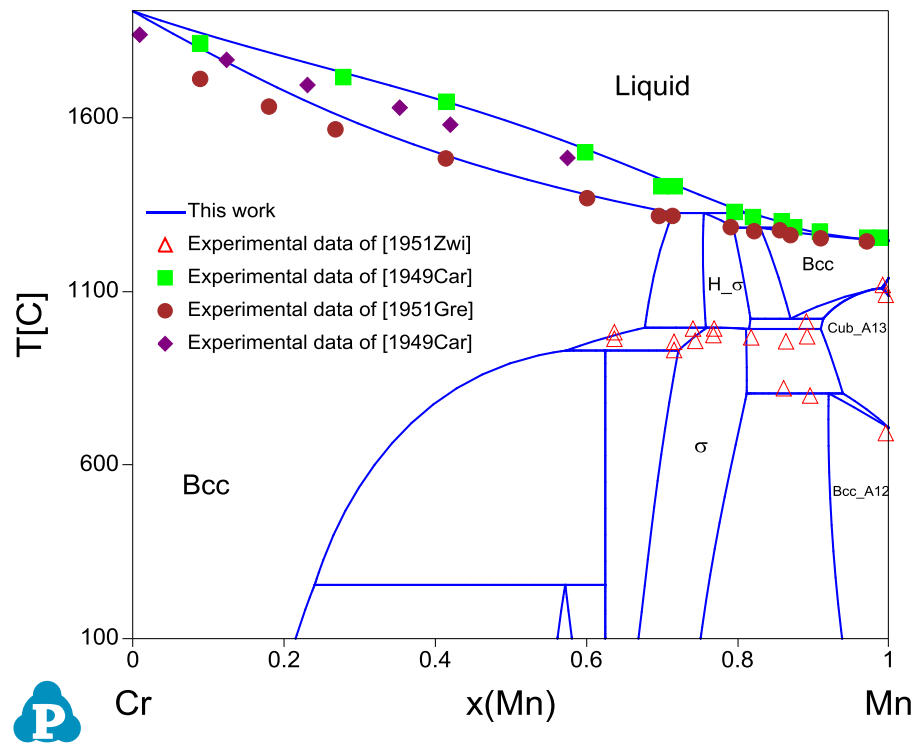


Figure 9 Calculated Cr-Mn binary phase diagram

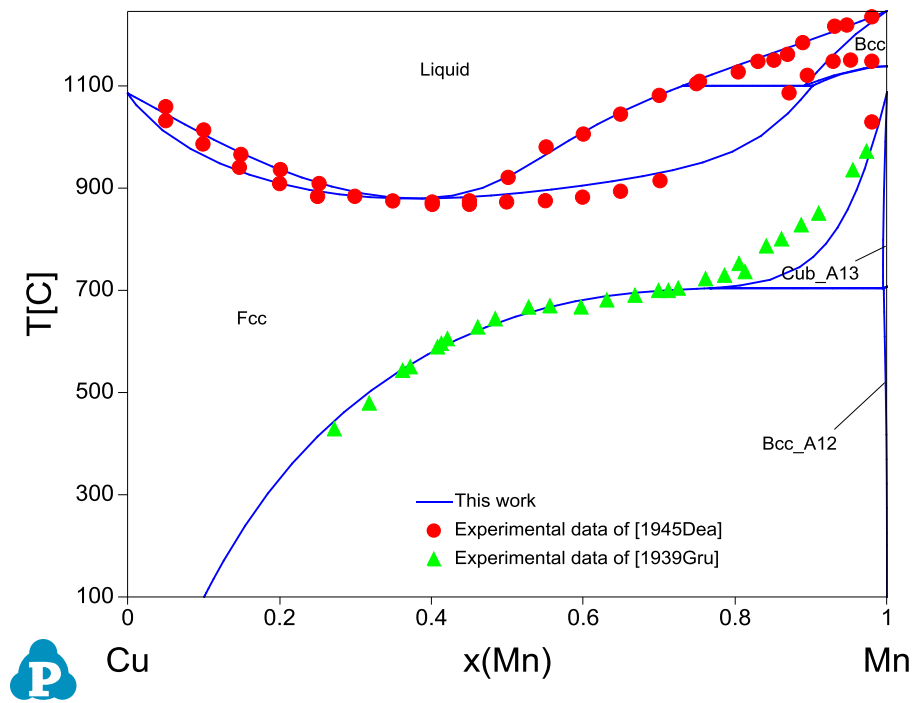


Figure 10 Calculated Cu-Mn binary phase diagram

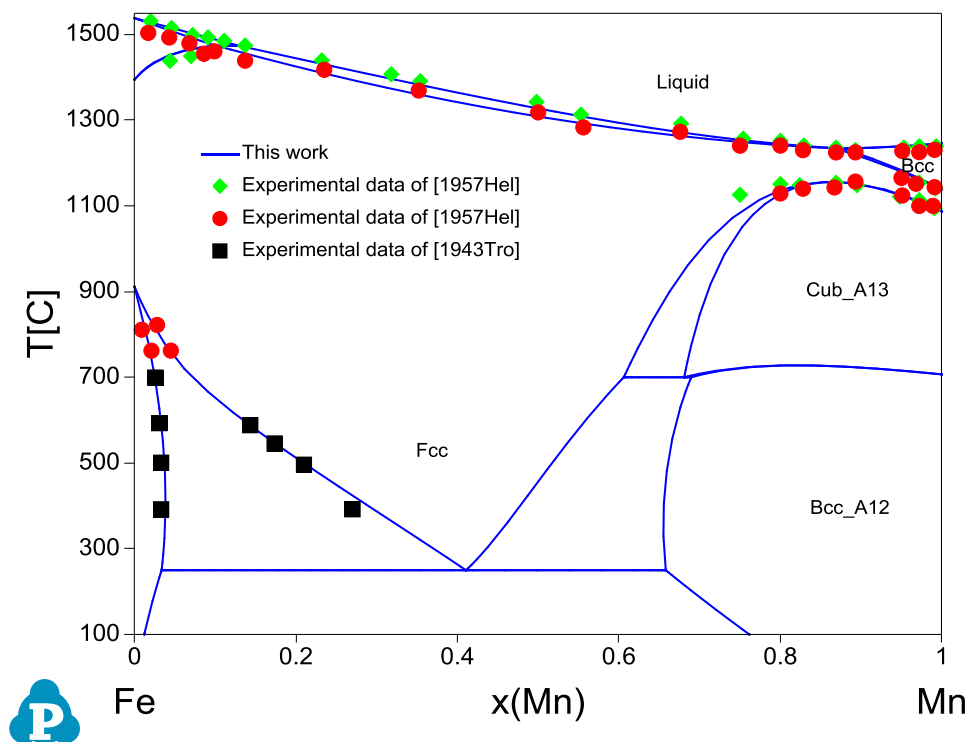


Figure 11 Calculated Fe-Mn binary phase diagram

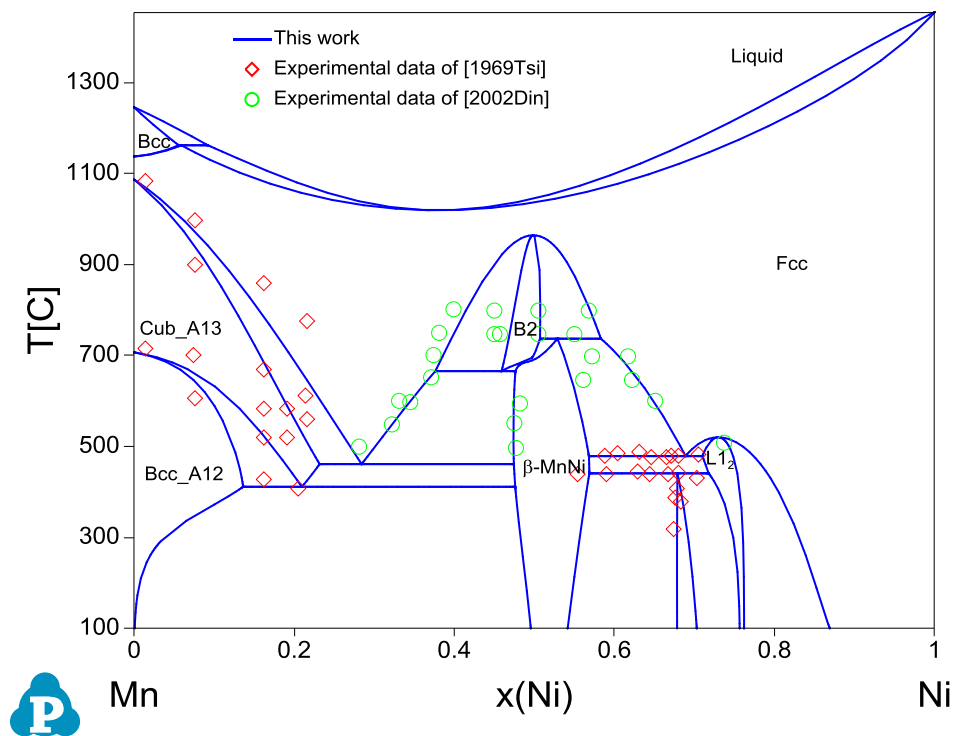
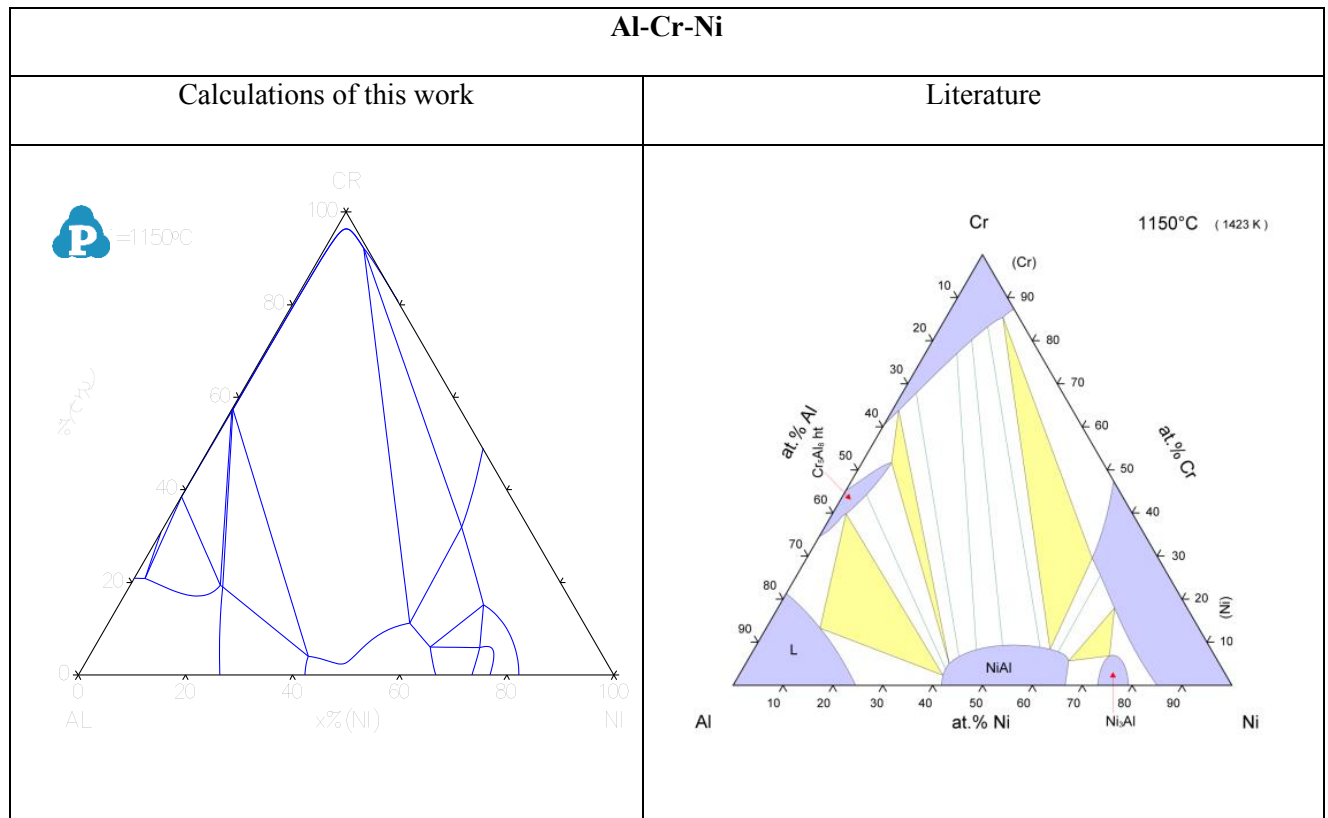
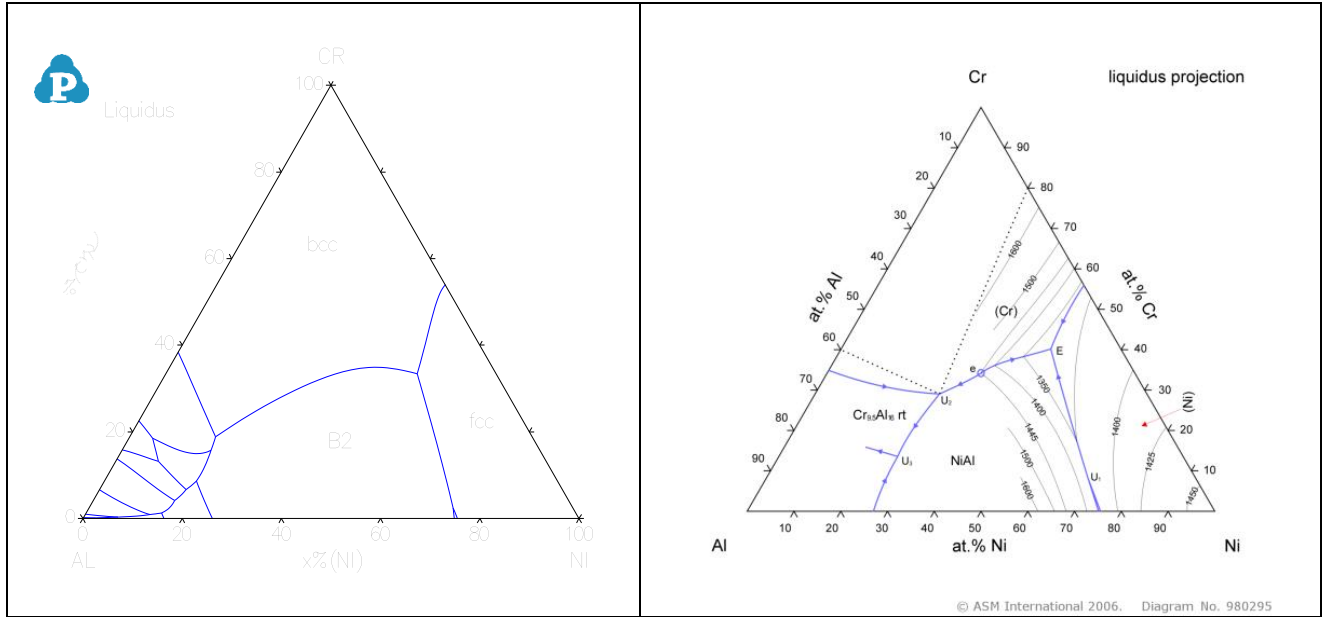


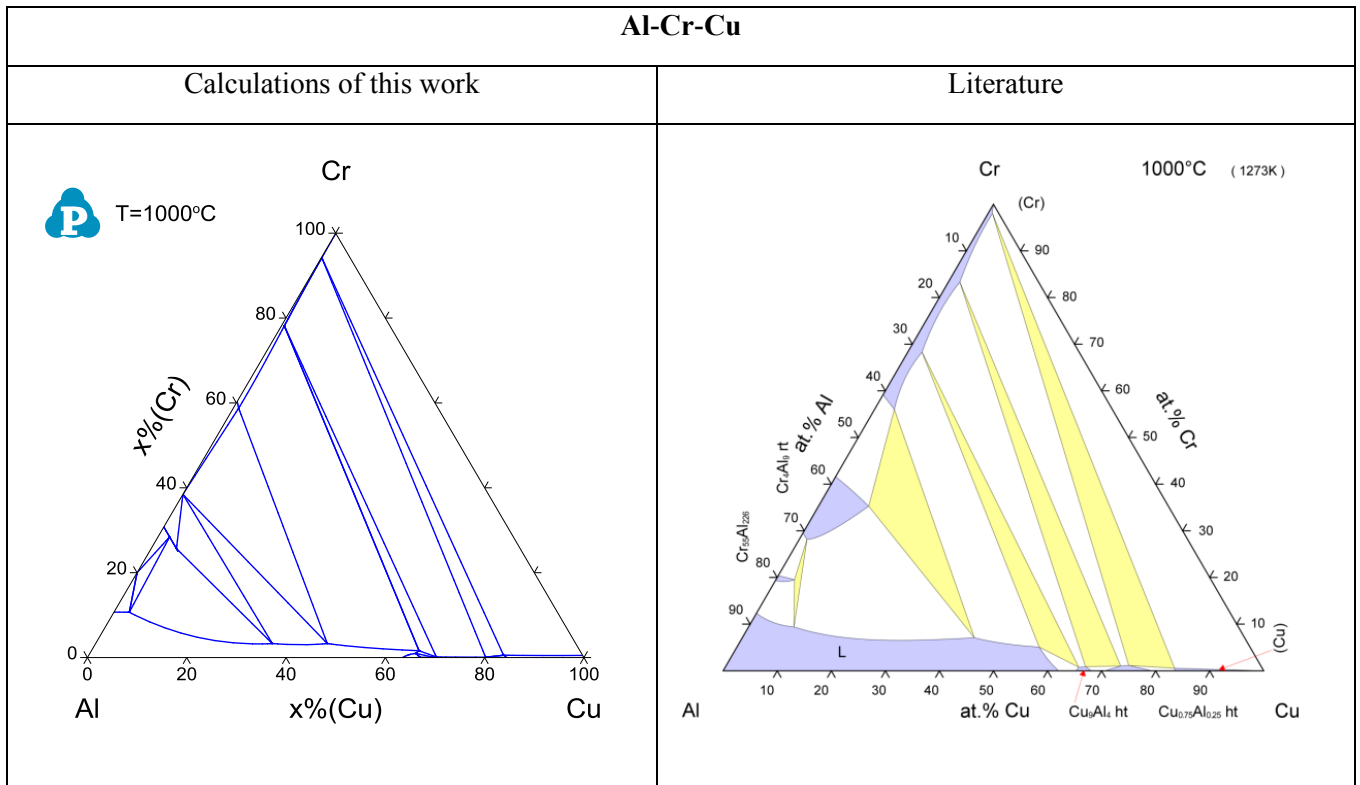
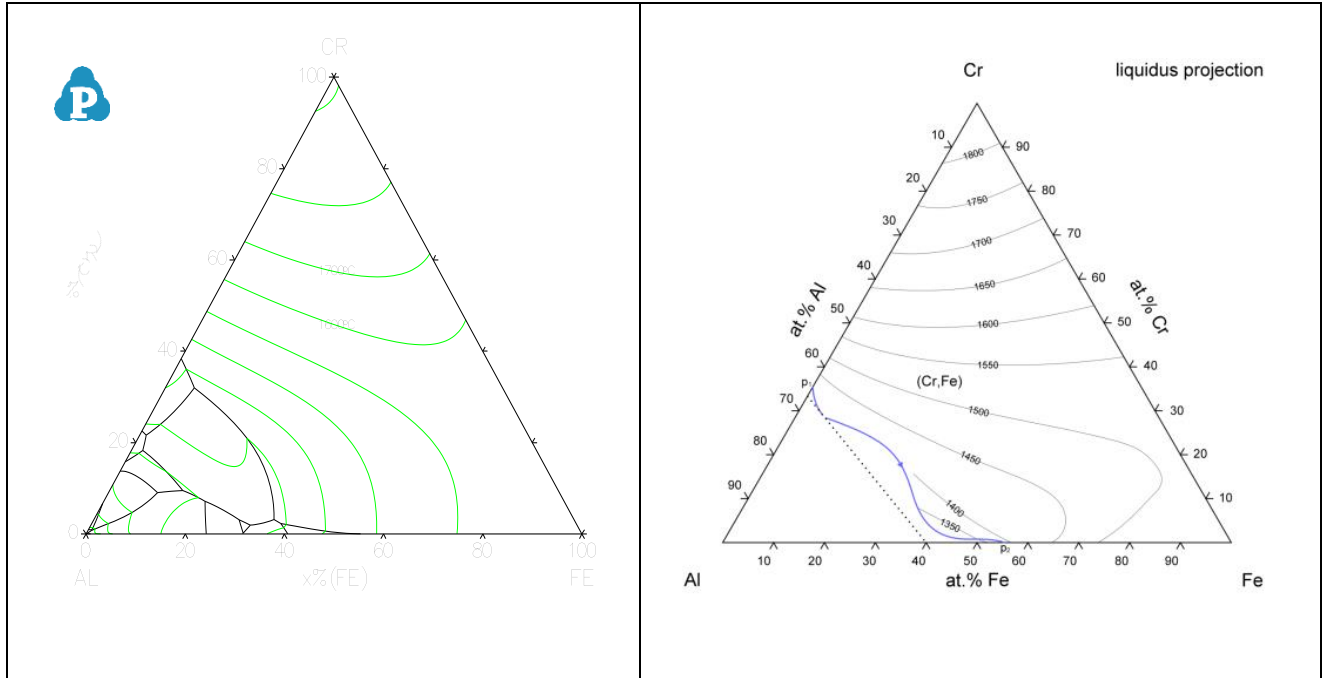
Figure 12 Calculated Mn-Ni binary phase diagram

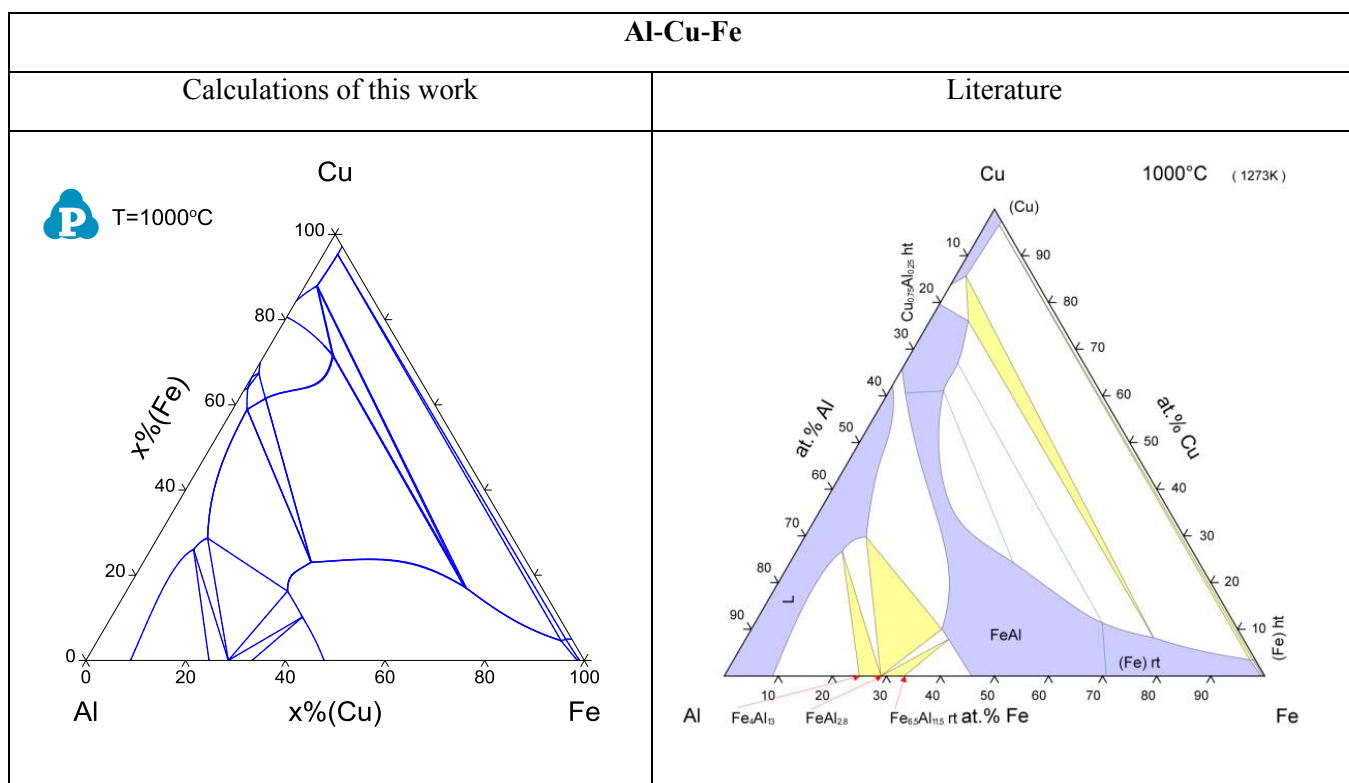
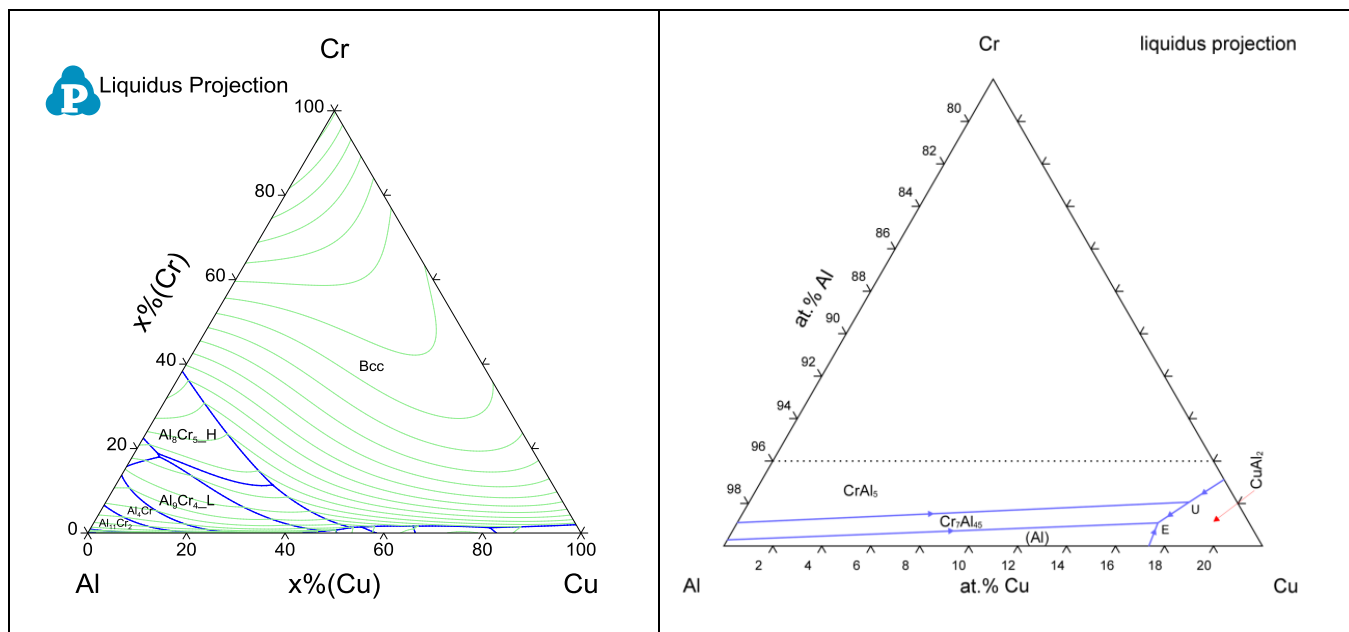
The constituent ternary systems are listed in Table 1. Thermodynamic descriptions of some ternary systems, such as Al-Cr-Fe and Al-Cr-Ni, were adopted from the literature results. In order to make our thermodynamic database consistent and reliable, validations have been done on these two ternaries of Al-Cr-Fe and Al-Cr-Ni. Followings show the comparisons between the calculated phase diagrams of the Al-Cr-Fe and Al-Cr-Ni ternary system with the literature data.

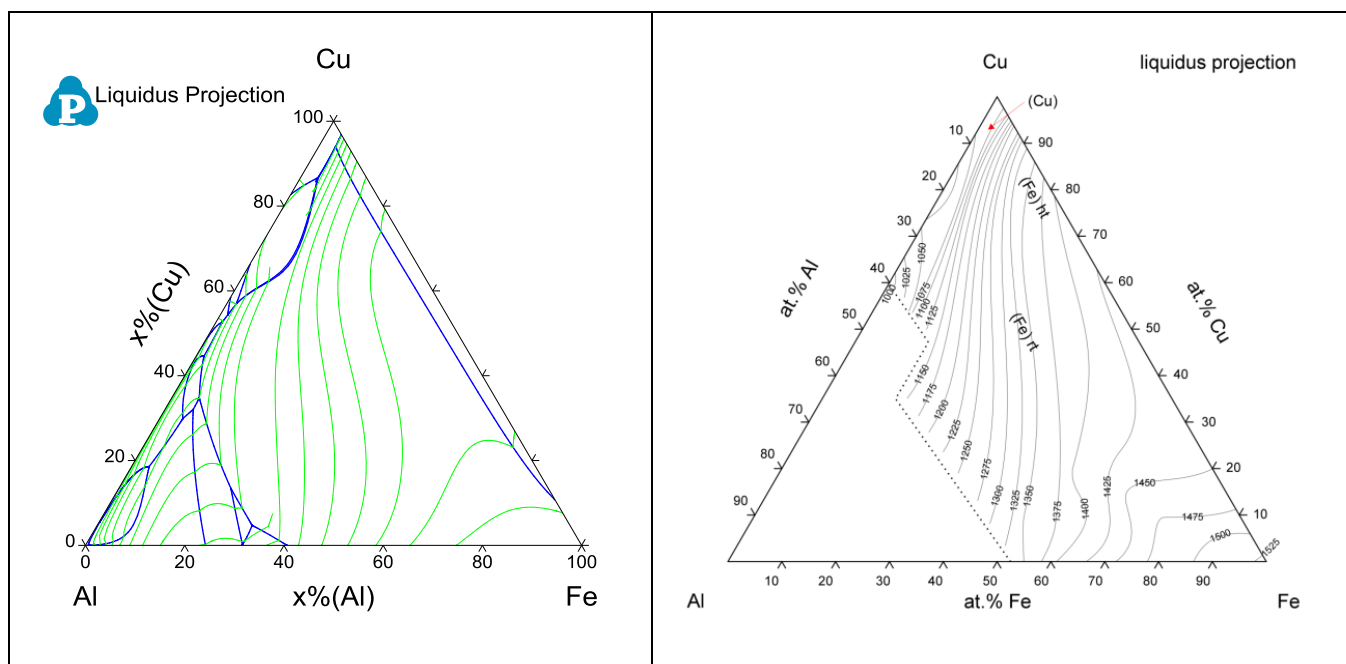
Table 2. Comparisons of calculated and experimental phase diagrams







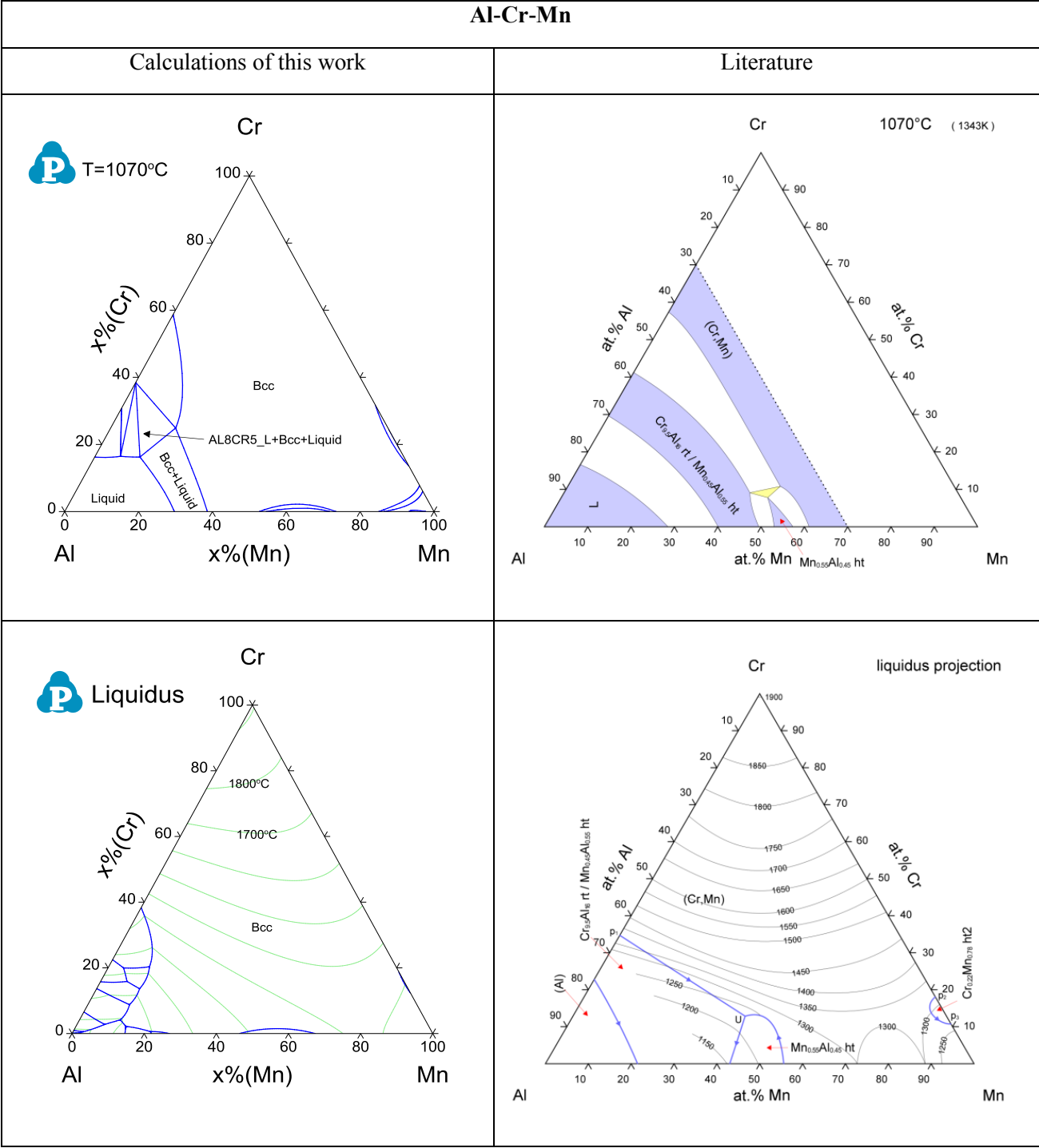


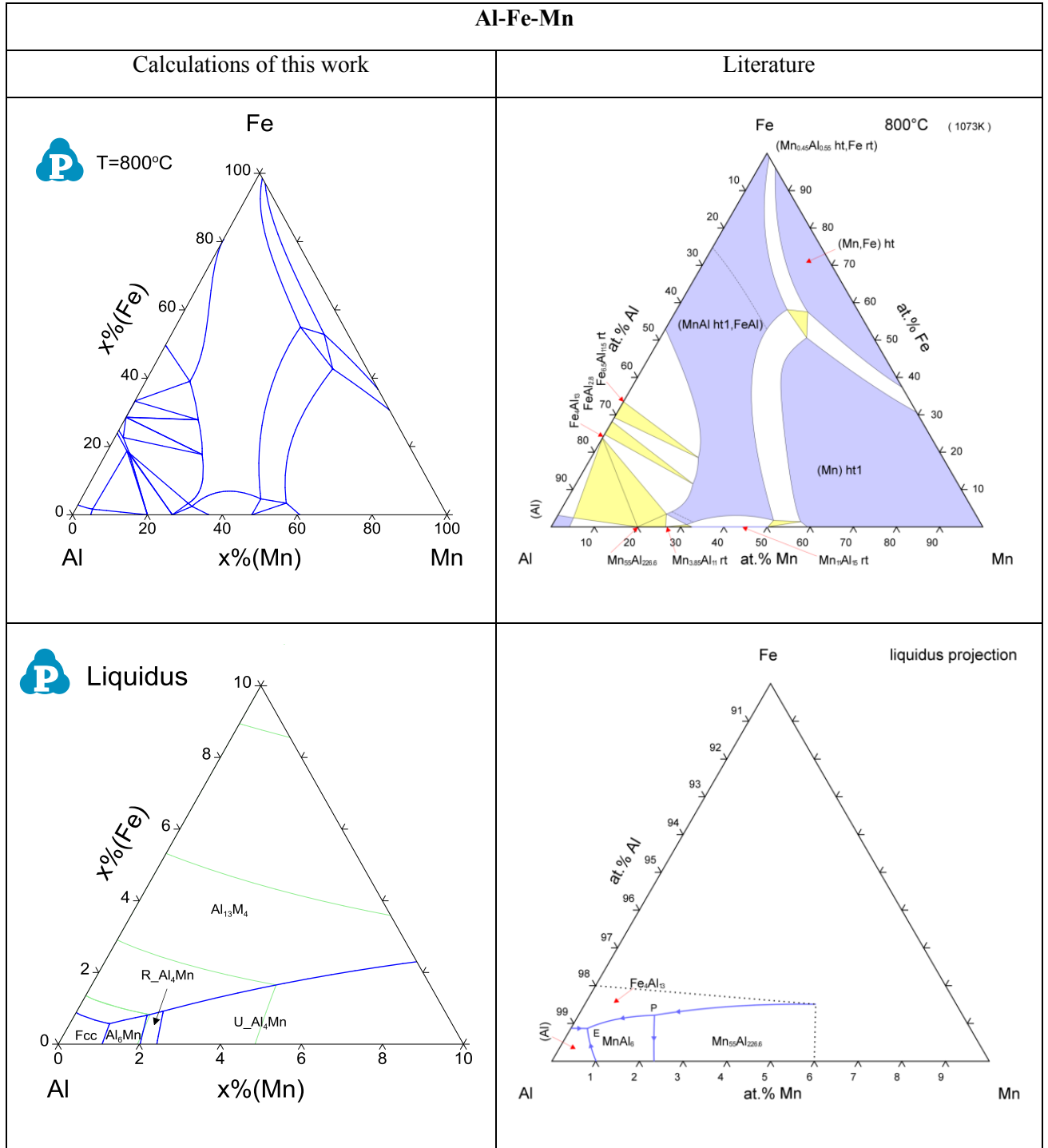


The above results show that the calculated Al-Cr-Cu isothermal section at 1,000°C is in good agreement with the literature data. However, the calculated liquidus projection has large discrepancy with the literature data. Further experimental validation is needed in order to improve our current thermodynamic description of the Al-Cr-Cu ternary system.

The calculated isothermal section of the Al-Cu-Fe system at 1,000°C agrees well with the experimental data. Note that we treat the ordered body-centered-cubic (BCC) phase as B2 in the Al-Cu system and BCC_B2 in the Al-Fe system. Thus, there is a two-phase region (B2 + BCC_B2) in our calculated phase diagram. The calculated liquidus projection of this system with isothermal lines shows reasonable agreement with the literature data

Recently, we have finished the thermodynamic modeling of the Al-Cr-Mn and Al-Fe-Mn ternary systems.

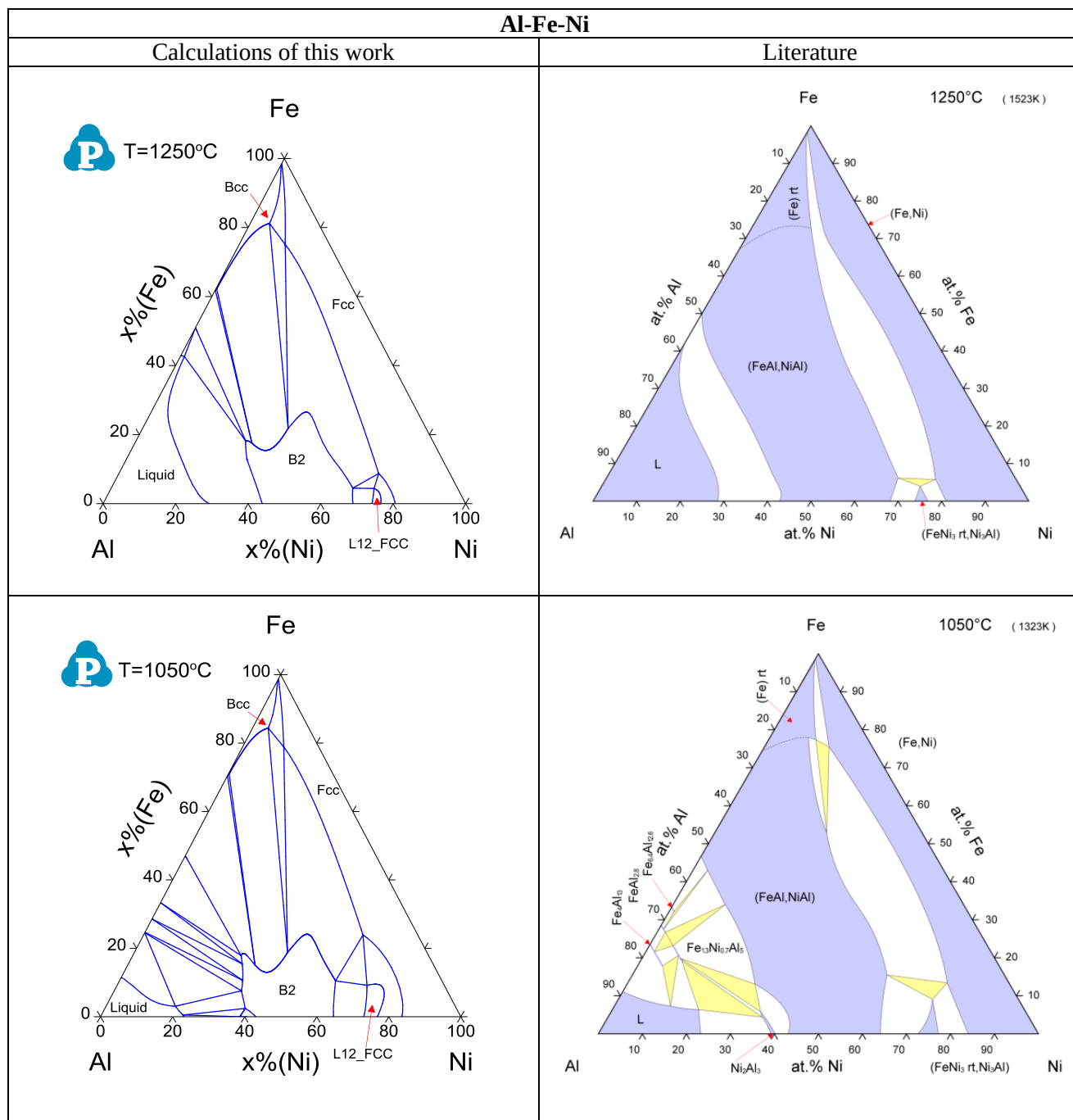


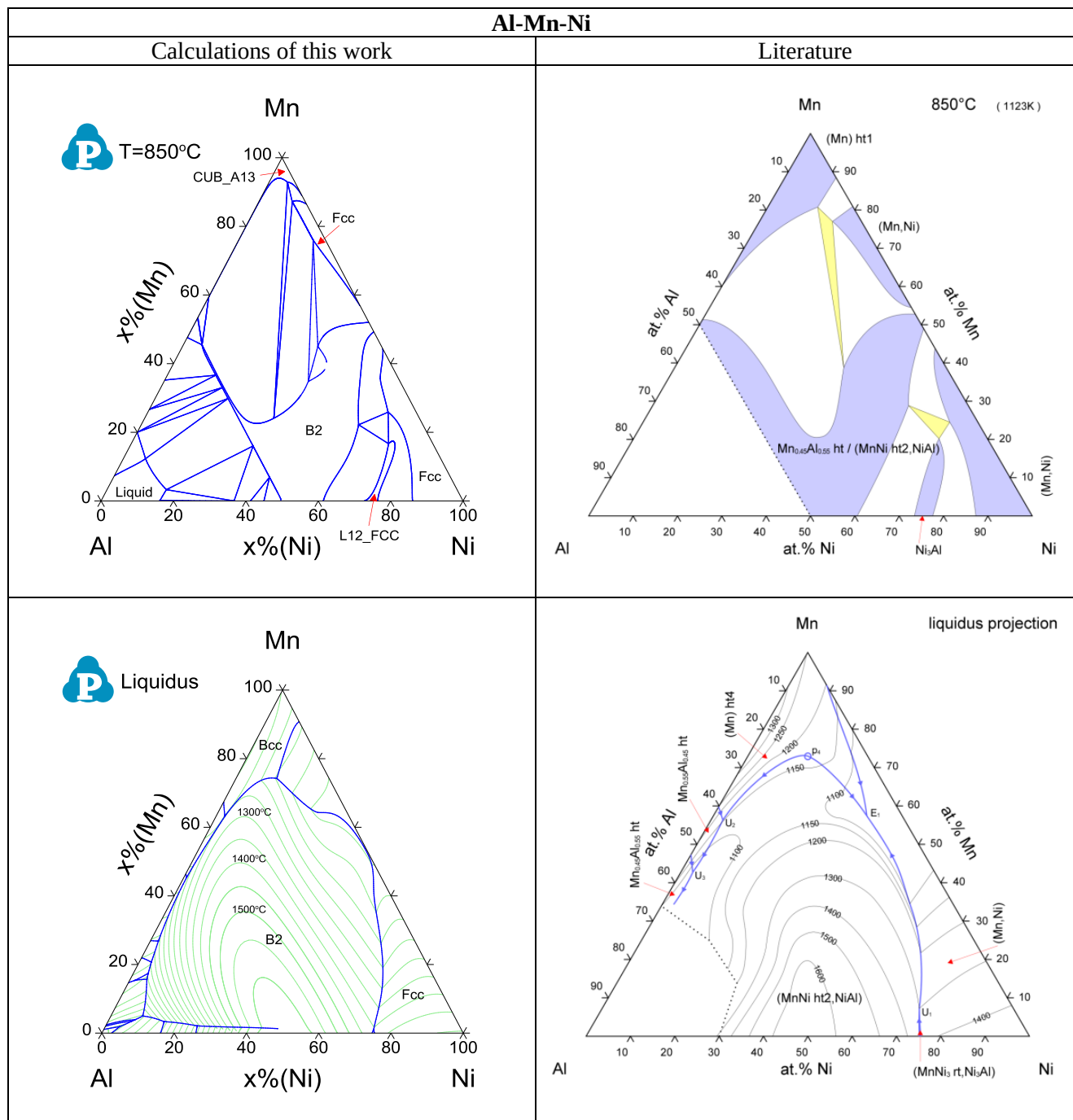


The calculated phase diagrams of the Al-Cr-Mn system show reasonable agreement with the literature data. The small discrepancies are focusing on the Al-Mn binary side, which results from the new thermodynamic description of the Al-Mn binary system. We

have validated our thermodynamic description of this Al-Cr-Mn ternary system based on the other literature results, and we believe that our calculated phase diagram could be more reliable. However, further experimental validation is needed in order to improve our current thermodynamic description of the Al-Cr-Mn ternary system. The calculated isothermal section of the Al-Fe-Mn system at 800°C agrees well with the experimental data. The calculated liquidus projection of this system with isothermal lines also shows reasonable agreement with the literature data. As mentioned above, we adopted the latest thermodynamic description of the Al-Mn binary system in our current thermodynamic database. Thus, the calculated liquidus projection at the Al-rich region has two regions of U_{Al4Mn} and R_{Al4Mn} rather than one.

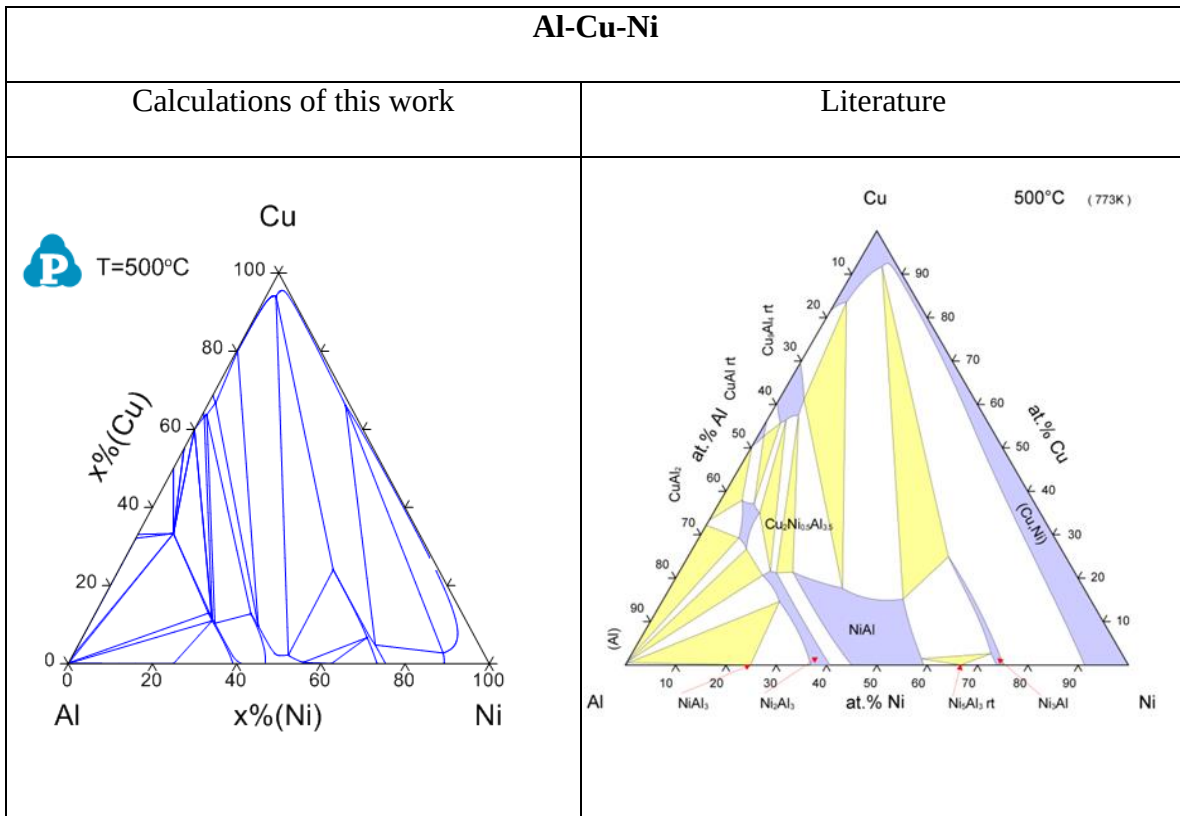
The thermodynamic modeling of the Al-Fe-Ni and Al-Mn-Ni ternary systems is shown below.

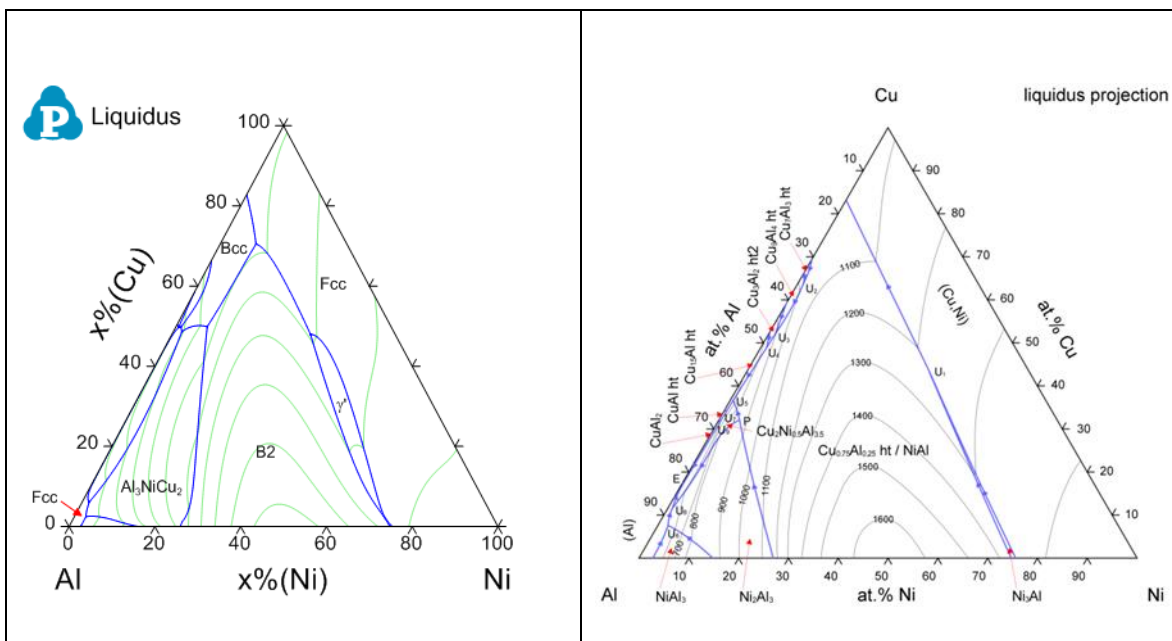




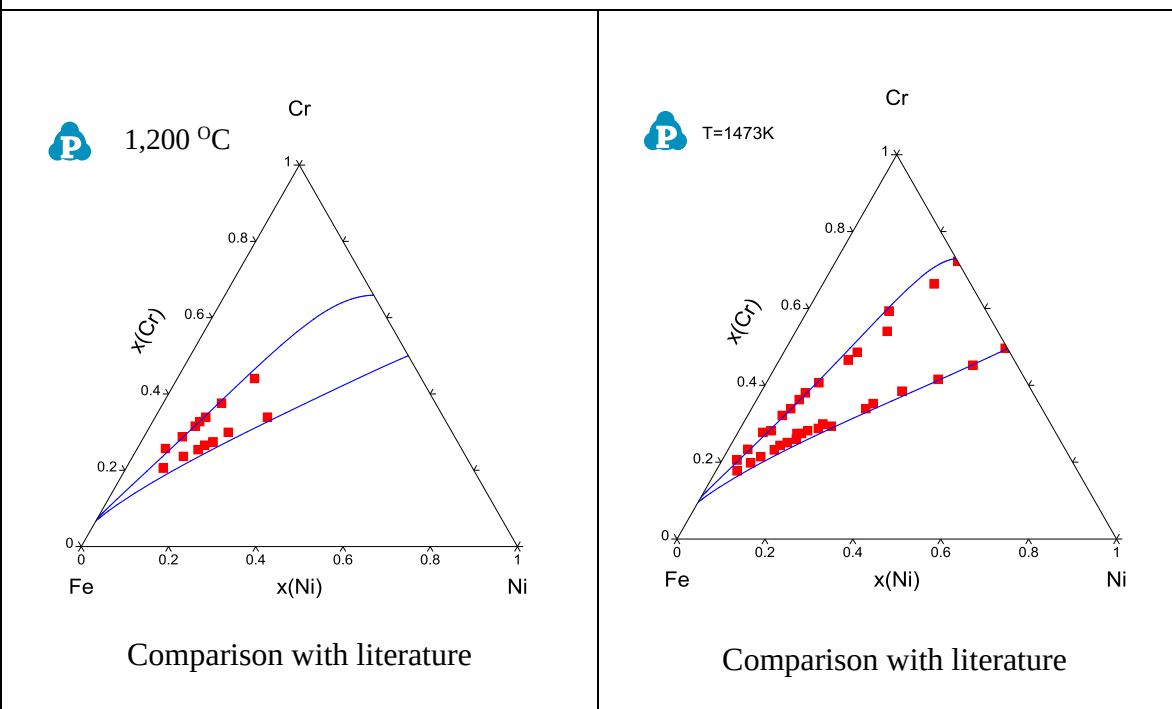
The calculated isothermal sections at 1050 and 1250 °C of the Al-Fe-Ni system show reasonable agreement with the literature data. The small discrepancies are focusing on the different treatment of B2 phases within the Al-Fe and Al-Ni binary systems. The B2 phase in

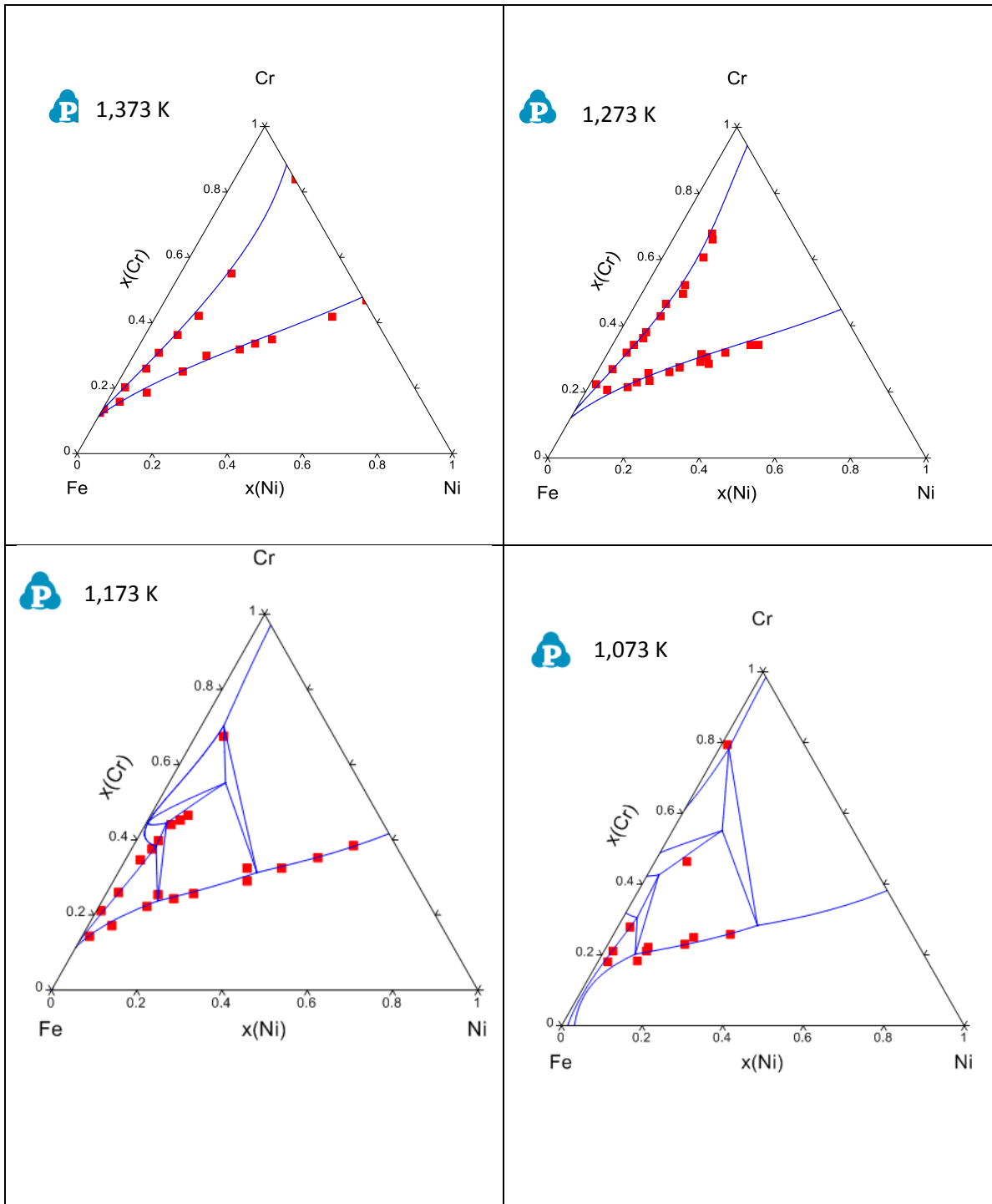
the Al-Ni binary system has crystal structure of cP2/Pm-3m (Pearson symbol/Space group), while the BCC_B2 phase from the Al-Fe binary system has crystal structure of cP8/Pm-3m. Those two phases are in the same space group, but with different Pearson symbols. In our thermodynamic modeling, we treated them as two separated phases, and described them using separate thermodynamic models. The literature outlined diagrams obviously treated these two phases as one phase. This is why the literature diagrams show continuous single B2 phase region in the ternary isothermal sections, while the calculated ones show separated B2 and BCC_B2. The calculated isothermal section of the Al-Mn-Ni system at 850°C agrees well with the experimental data. The calculated liquidus projection of this system with isothermal lines also shows reasonable agreement with the literature data.



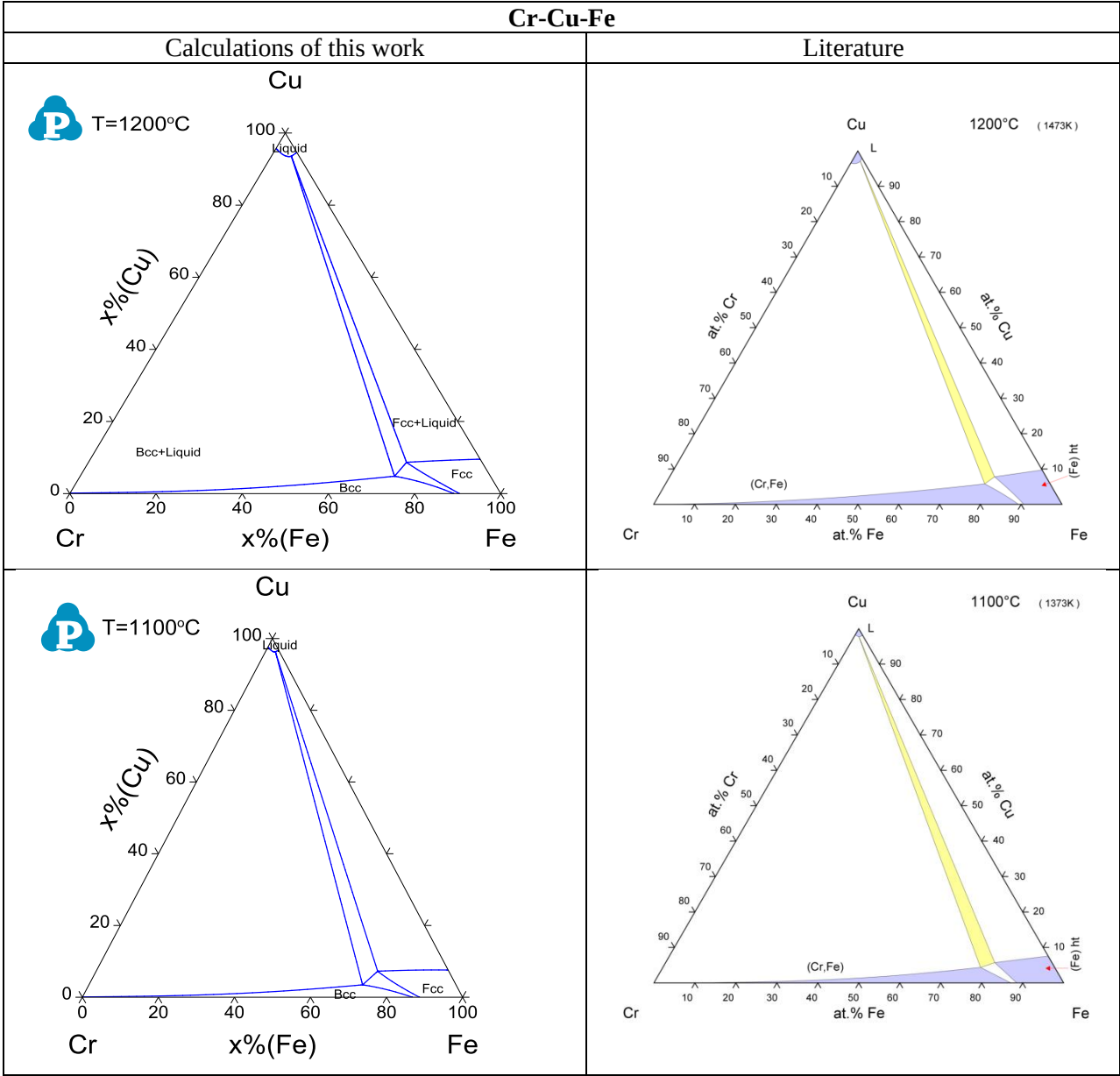


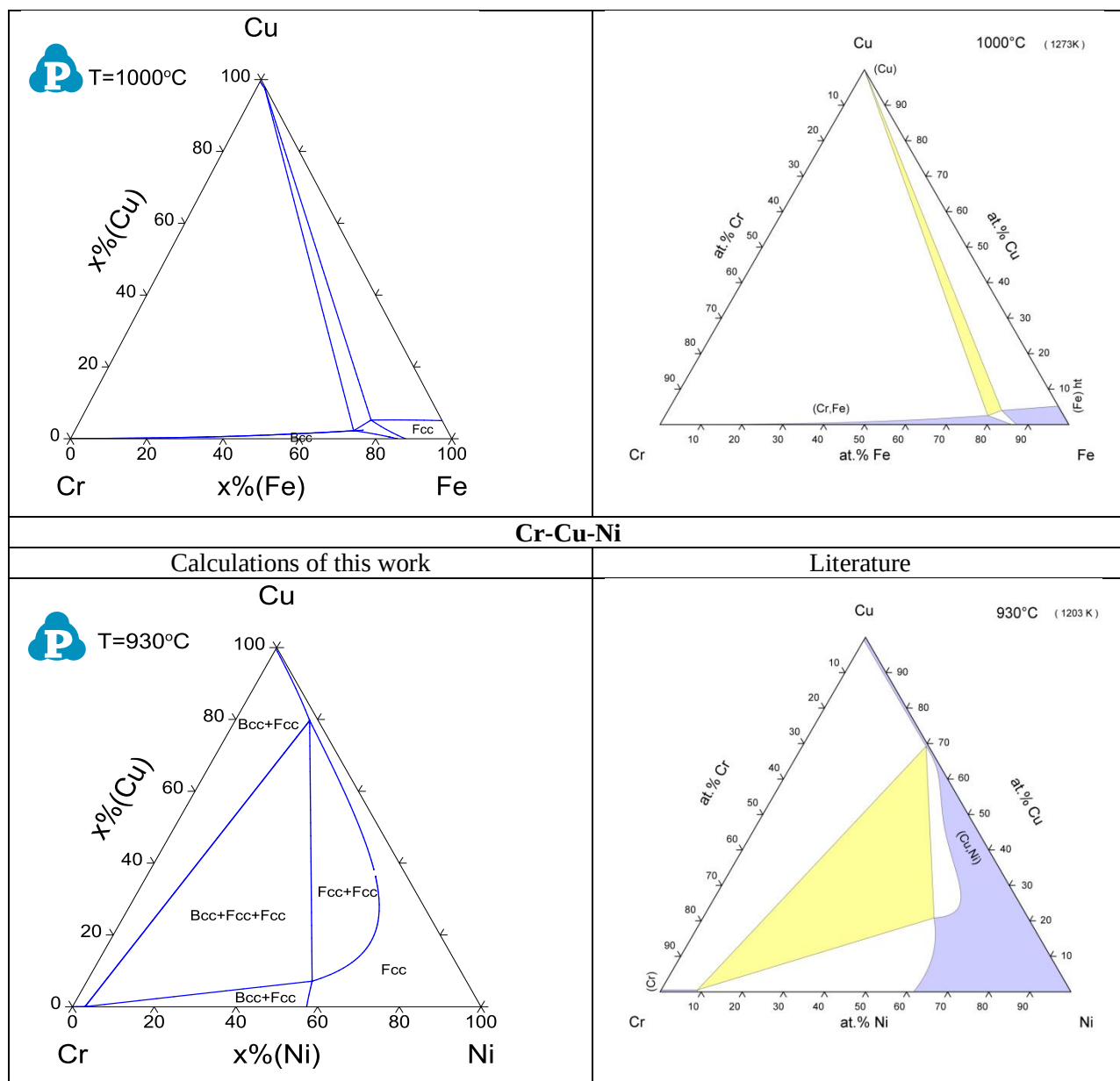
Cr-Fe-Ni



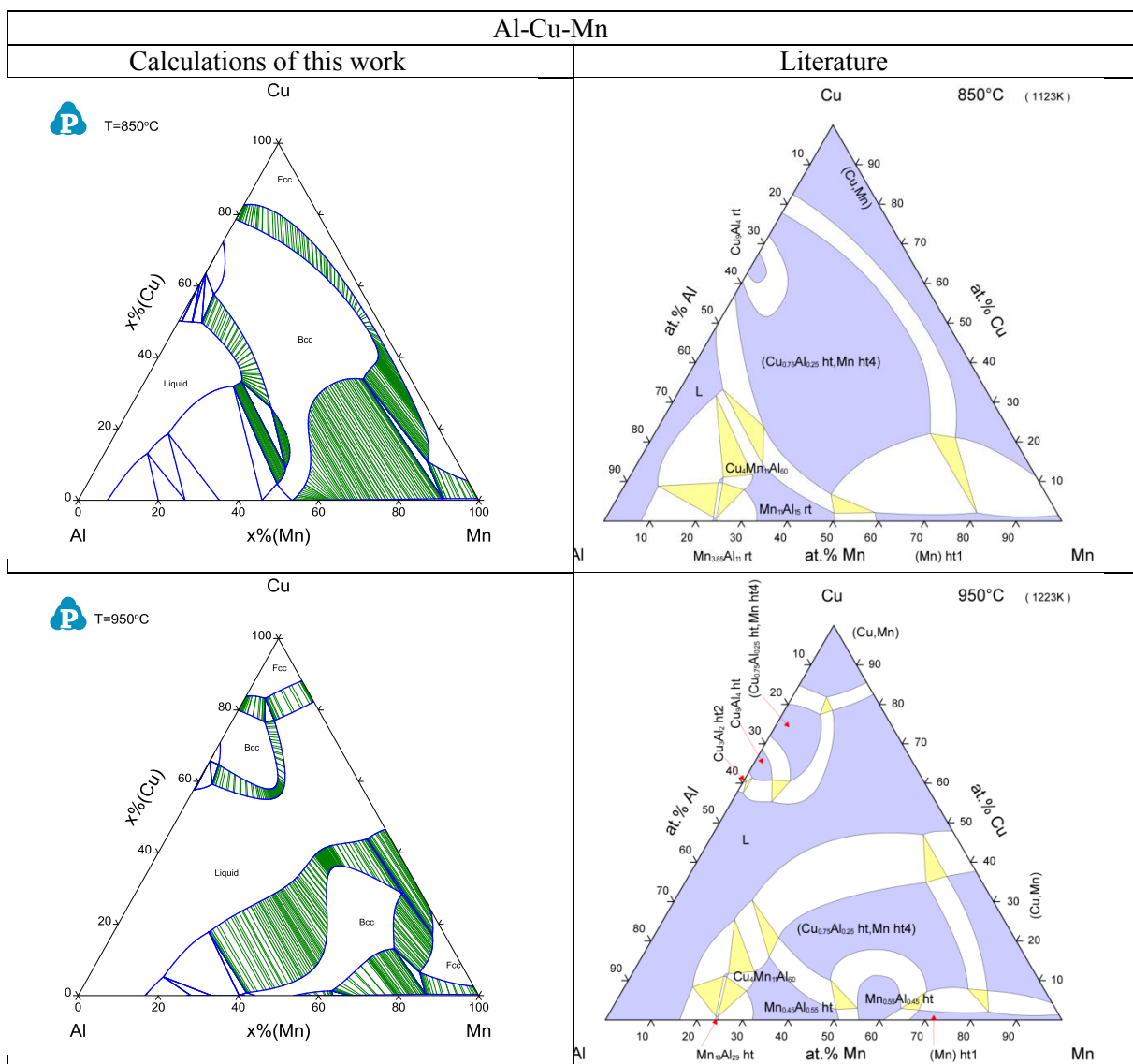


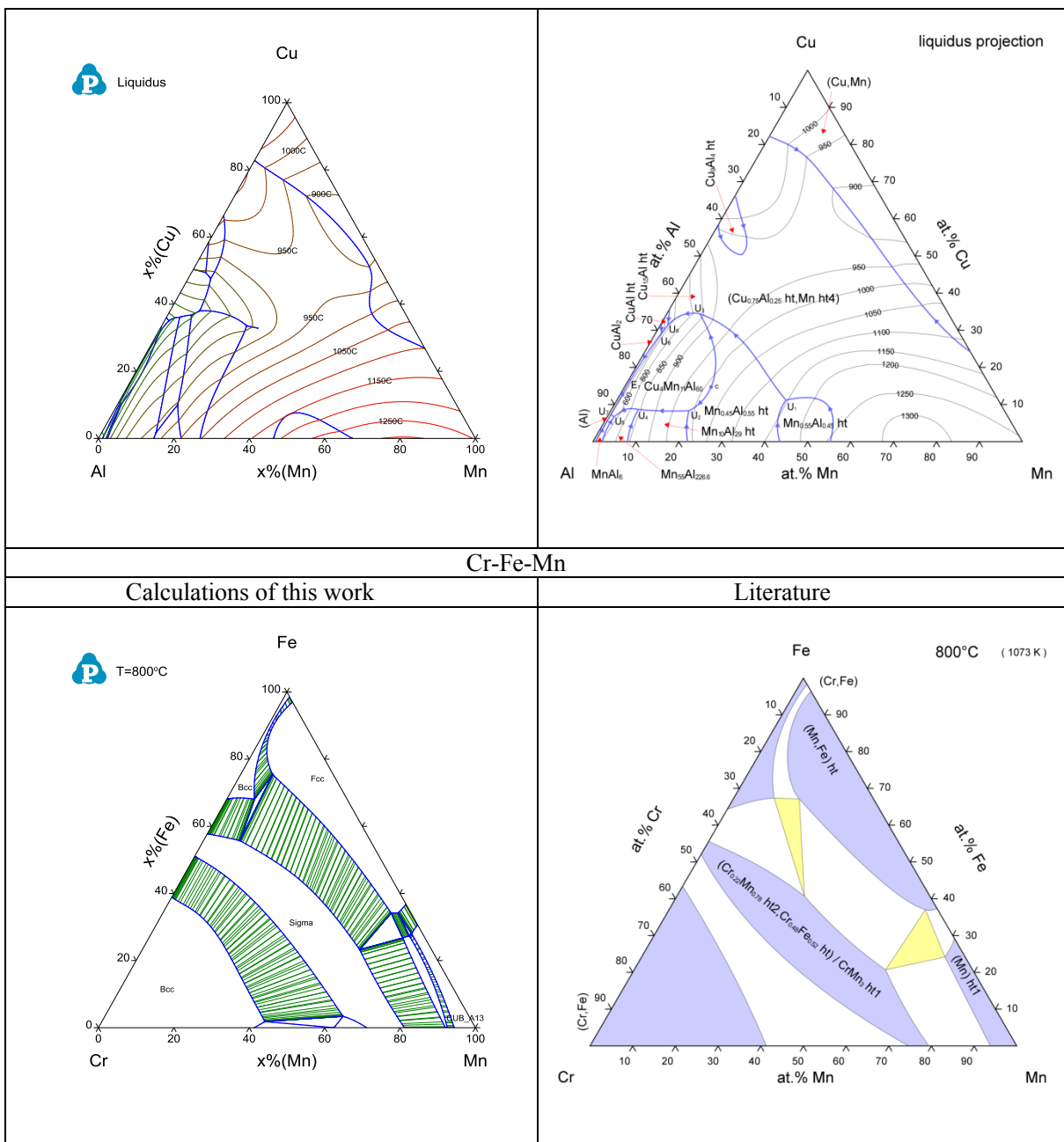
The calculated isothermal section at 773K and liquidus projection of the Al-Cu-Ni system show reasonable agreement with the literature data. Phase equilibria were extensively studied in the literature. The calculated isothermal sections of the Cr-Fe-Ni system at 800 ~ 1,000 °C agree well with the experimental data.

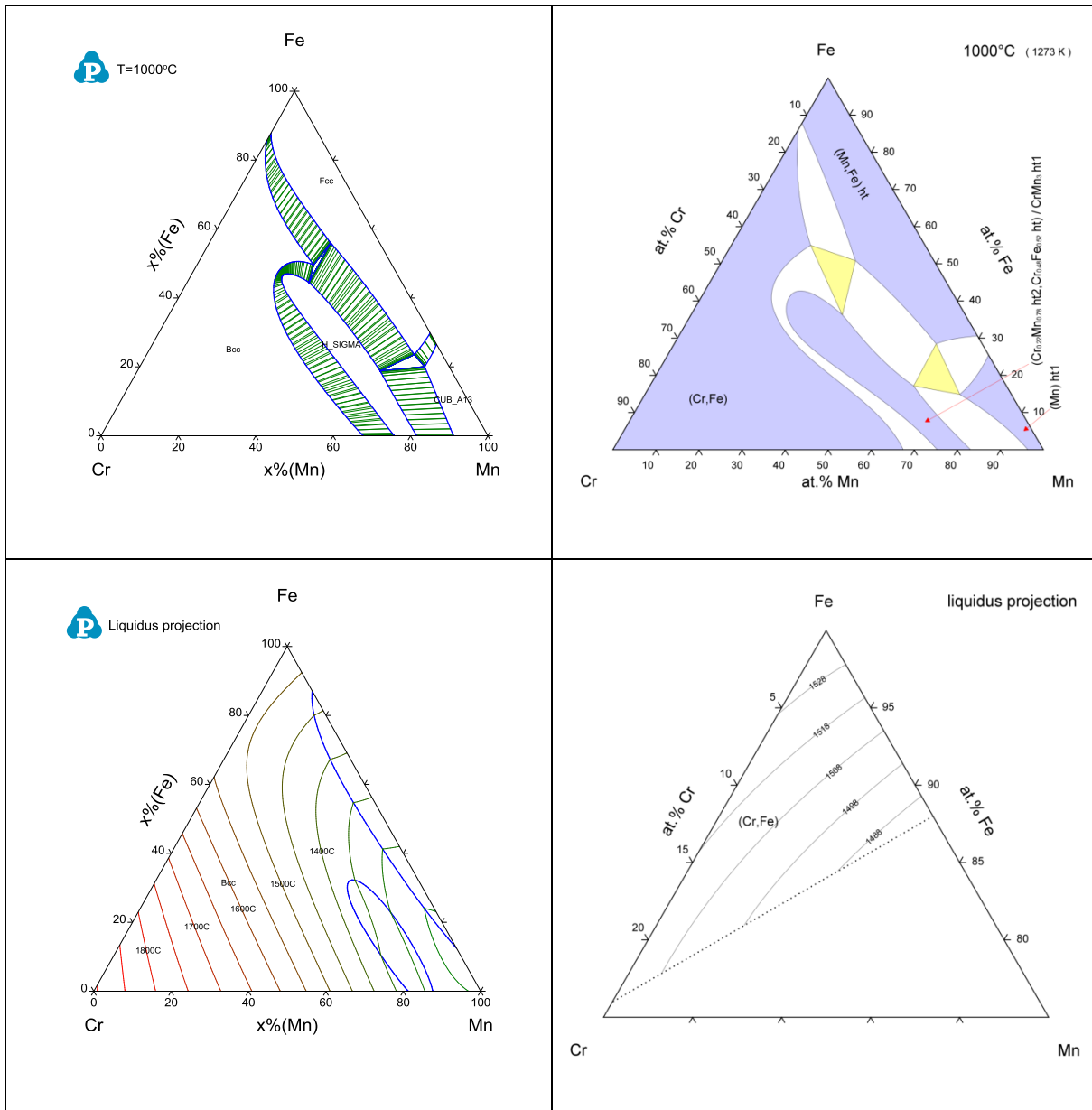




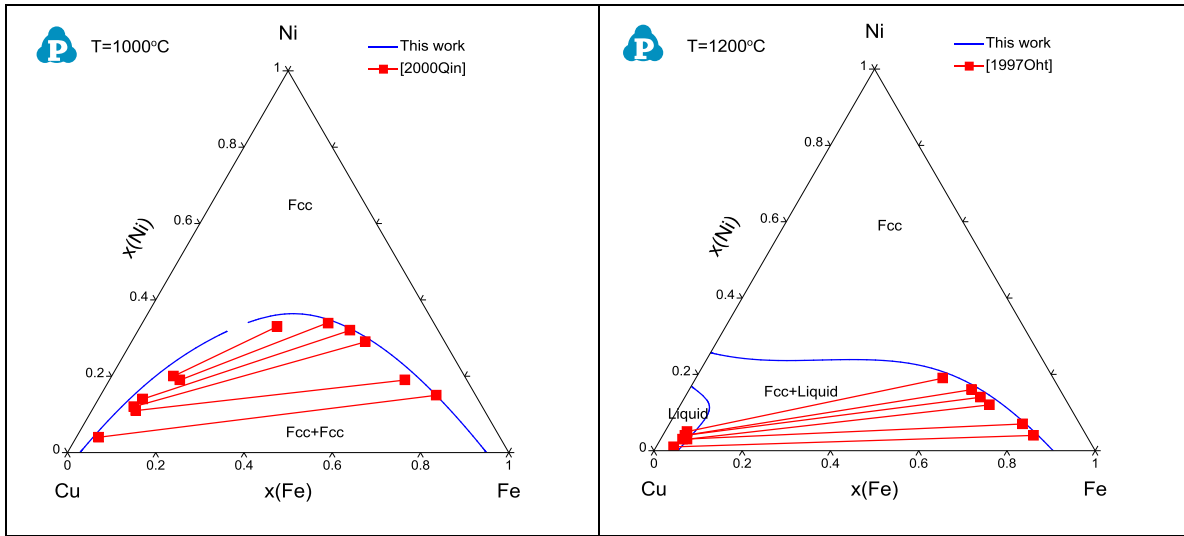
The calculated isothermal sections at 1,000, 1,100 and 1,200 °C of the Cr-Cu-Fe system show reasonable agreement with the literature data. The calculated isothermal section of the Cr-Cu-Ni system at 930 °C agrees well with the experimental data.







The calculated isothermal sections at 850 and 950°C as well as the liquidus projection of the Al-Cu-Mn system show reasonable agreement with the literature data ^[16]. The calculated isothermal section of the Cr-Fe-Mn system at 800 and 1,000°C agrees well with the experimental data ^[17]. The calculated liquidus projection of the Cr-Fe-Mn system is also in good agreement with the experimentally-investigated results.



It shows that our calculated phase equilibria of the Cu-Fe-Ni system at the 1,000 and 1,200 °C are in good agreement with the experimental measurements in the literature ^[29, 30].

3.3.2 Thermodynamic Database of the Al-Cr-Cu-Fe-Mn-Ni System

In addition to the thermodynamically-modelled subsystems (binaries and ternaries) listed in Table 2, the other constituent ternary systems were obtained via extrapolation. Thus, a preliminary thermodynamic database of the Al-Cr-Cu-Fe-Mn-Ni system was obtained at present, which enables us to perform phase-diagram calculations of the Al-Cr-Cu-Fe-Mn-Ni system. In this report, the $Al_xCrCuFeMnNi$ isopleth is calculated with the x from 0 to 2 and shown below.

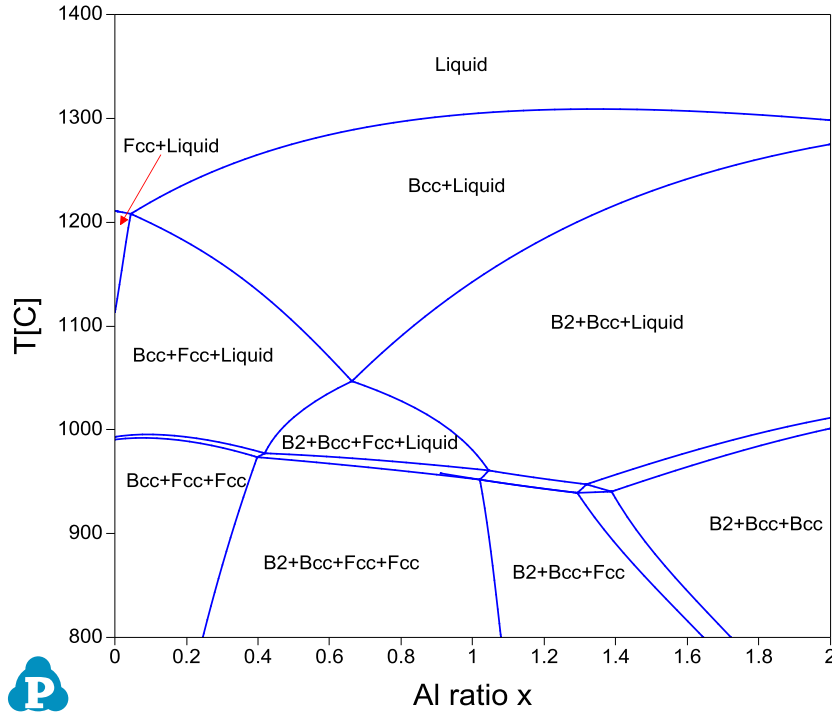


Figure 13 The calculated $\text{Al}_x\text{CrCuFeMnNi}$ isopleth using our preliminary thermodynamic database of the Al-Cr-Cu-Fe-Mn-Ni system

It shows that majority phases will be the BCC-based structure (the disordered BCC and ordered B2) for the Al-Cr-Cu-Fe-Mn-Ni HEAs with increasing the Al content. Further experimental validation will be carried out later on.

3.3.3 Thermodynamic Activities

The above results show that the calculated Al-Cr-Fe and Al-Cr-Ni phase diagrams are in good agreement with the literature data. For the Al-Cr-Fe ternary system, not only the phase-equilibrium data but also the thermochemical data, such as activity, are used to validate our current thermodynamic description. Figure 14 shows the calculated thermodynamic activities of Al, Cr, and Fe in the Fe-19.9Al-30.2Cr (at. %) alloy, comparing with the experimentally-measured data. It shows that our thermodynamic calculations agree well with the experimental data.

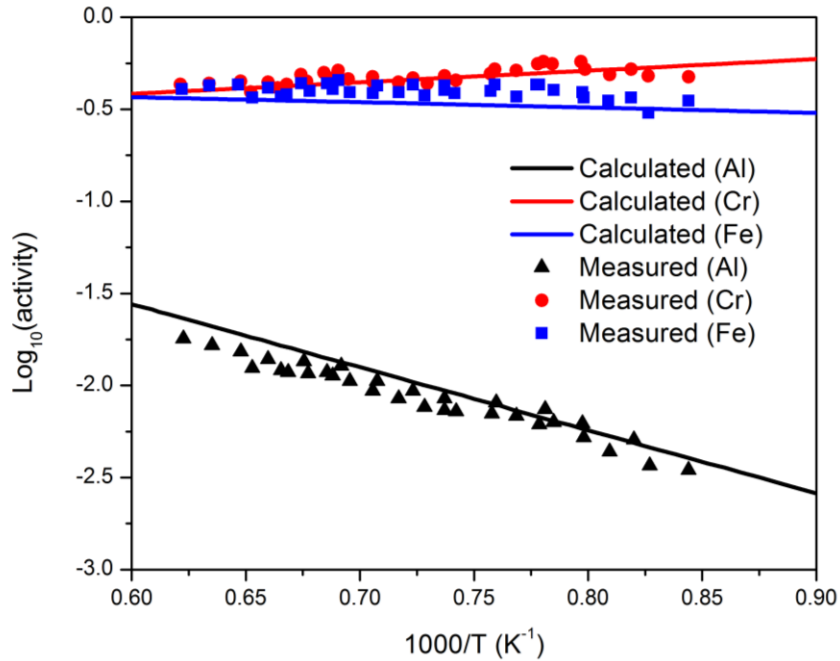


Figure 14 Comparison of the calculated and measured thermodynamic activities of Al, Cr, and Fe in the alloy with a target composition of Fe-19.9Al-30.2Cr (at.%)

Thermodynamic simulations of non-equilibrium solidification by the Scheil model and an equilibrium line calculation are shown in Figures 15 and 16, respectively.

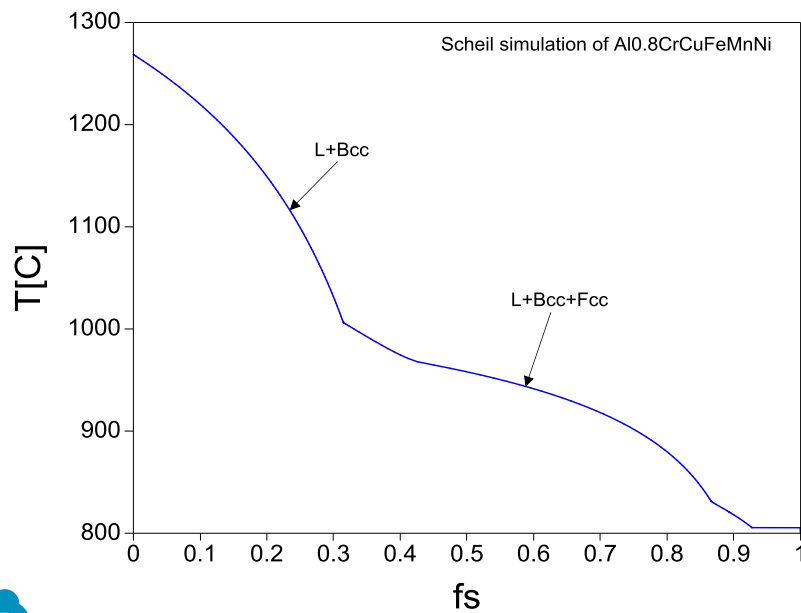


Figure 15 Thermodynamics modeling of non-equilibrium solidification by Scheil model

[81]

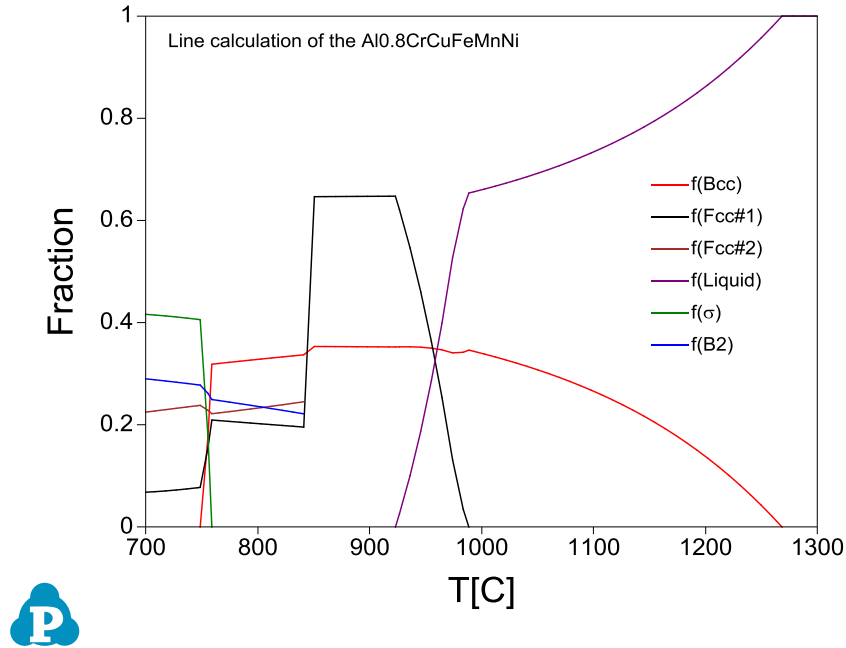


Figure 16 Thermodynamics modeling of an equilibrium phase diagram

The $\text{Al}_{0.1}\text{CrCuFeMnNi}$ solidification paths are also calculated, using the Scheil thermodynamic model. As shown in Figure 17, the primary phase of the $\text{Al}_{0.1}\text{CrCuFeMnNi}$ alloy during solidification is the BCC phase, and the FCC phase forms subsequently when the temperature slightly decreases ($\sim 3^\circ\text{C}$). Then the BCC and FCC phases are concomitant until the end of solidification. The simulated fraction of each phase within the as-cast $\text{Al}_{0.1}\text{CrCuFeMnNi}$ alloy is indicated in Figure 17b. It shows that the FCC is the majority phase ($\sim 93\%$).

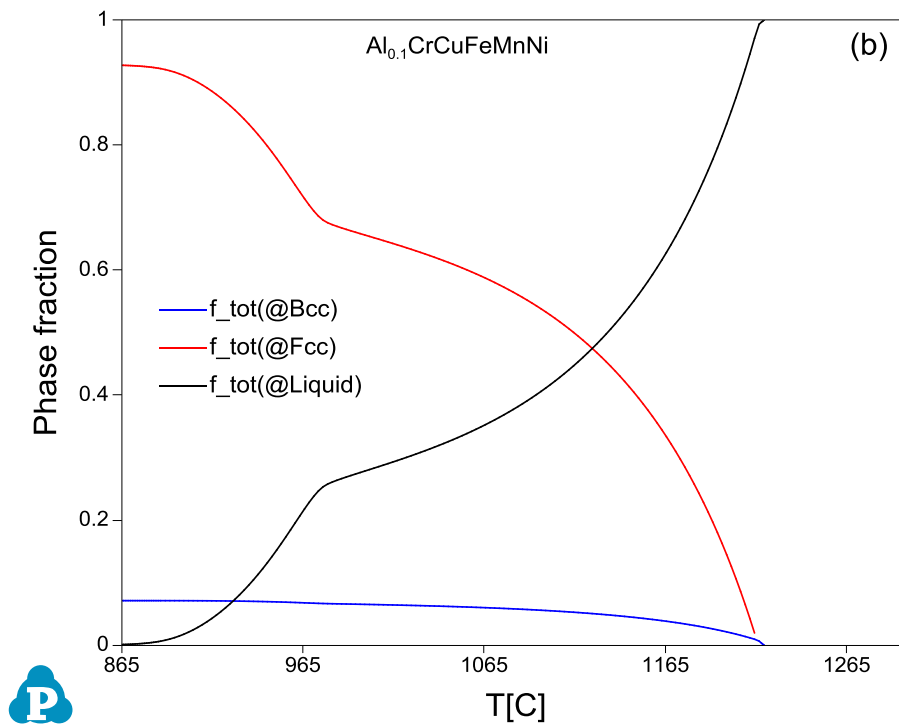
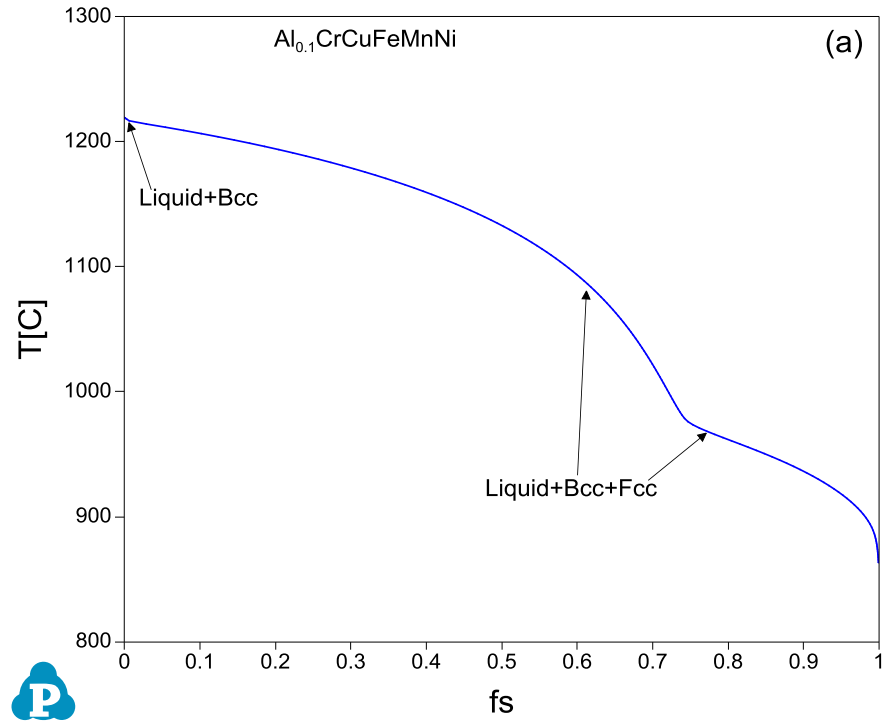


Figure 17 Calculated solidification paths of the $\text{Al}_{0.1}\text{CrCuFeMnNi}$ HEAs using the Scheil model

[81].

3.3.4 Thermodynamic Calculations of the Al_xCoCrFeNi System

On the basis of our experience, the CALPHAD approach plays a more and more important role in the design and development of HEAs [82-85]. Using the calculated multi-component phase diagrams, one can easily know the stable phases and their fractions as well as the distribution of each alloying element within different phases. For better understanding the phase stability of all three alloys (Al_{0.3}, Al_{0.5}, and Al_{0.7}) studied in the current work, equilibrium calculations are carried out on them within the temperature range from 200 to 1,500 °C (as shown in Figure 10). Six different phases (as shown in Figure 11), FCC, BCC, L12, B2, σ phase, and θ phases, are present in three alloys (Al_{0.3}, Al_{0.5}, and Al_{0.7}), and their relative fractions and phase compositions at three experiment-related temperatures can also be calculated through the CALPHAD method.

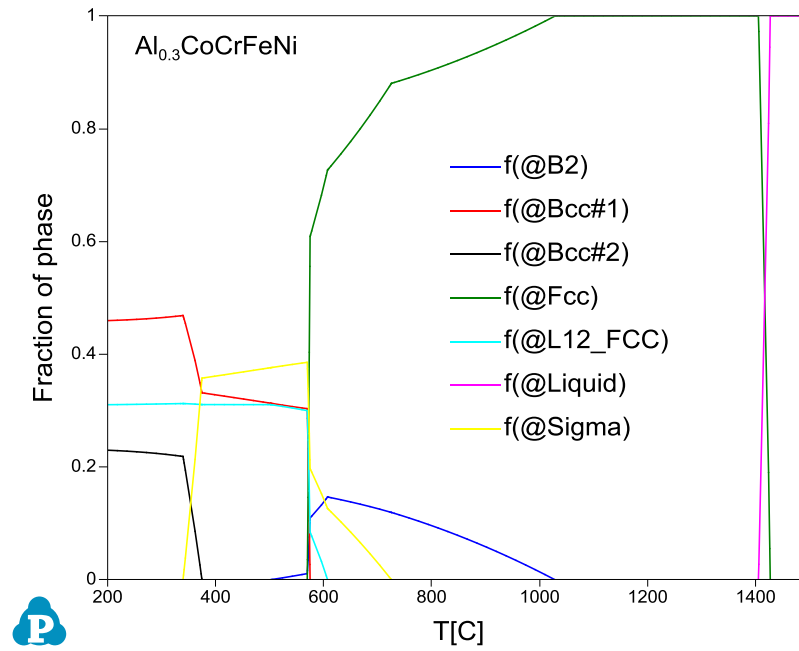
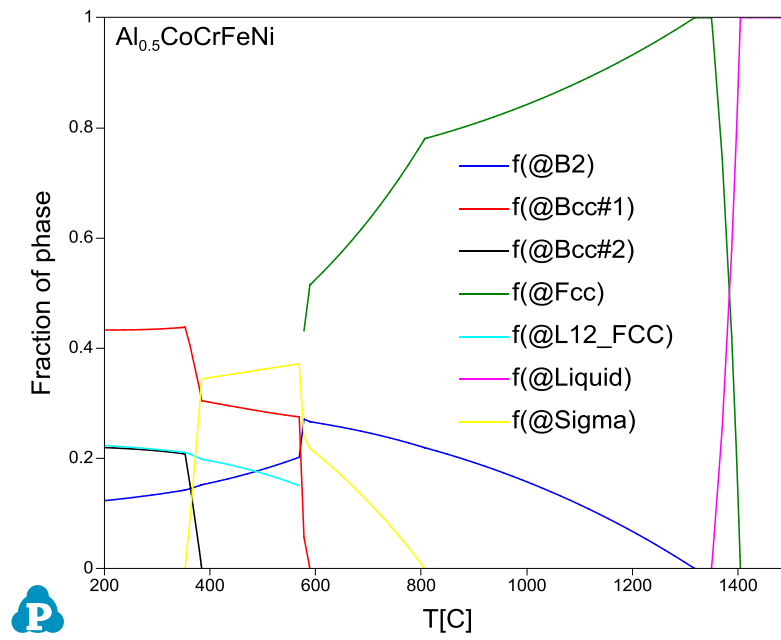
For Al_{0.3}, at about $1,026 < T < 1,402$ °C, only one fcc phase is present and stable. When temperature decreases, the ordered B2 phase will form at 1,026 °C and disappear at 550 °C. The σ phase is present at the temperature range from 350 °C to 720 °C. One may also be able to find the order L₁₂ below 600 °C. Two kinds of disordered BCC phases will present at even lower temperatures. One can also know the volume fraction of each phase at different temperatures from this figure. For example, at 500 °C, three phases, disordered bcc, L₁₂, and σ phase, are present at the volume fraction of 31.34, 31.07, and 37.59 %, respectively.

For Al_{0.5}, the ordered B2 phase will form at a larger temperature range, from 200 °C to 1,350 °C, which explains the present of B2 phase at room temperatures. The σ phase is present at the temperature range from 350 °C to 820 °C. One may also be able to find the order L₁₂, and disordered BCC phase in the temperature range of 400 to 600 °C. The disordered bcc phase will separate into two kinds of BCC phases when the temperature below 400 °C. The fraction and exiting temperatures, of each phase can also be obtained from Figure 18.

For $\text{Al}_{0.7}$, the ordered B2 phase also form at a large temperature range, from 200 °C to 1,350 °C, but owns a larger fraction volume, compared to $\text{Al}_{0.5}$. At the temperatures between 900 °C and 1,350 °C, BCC phases (around 5 at. %) are present. The start temperature of σ phase is increased to 900 °C. The σ phase will disappear at around 350 °C, which is similar to that in $\text{Al}_{0.3}$ and $\text{Al}_{0.5}$. The formation of L_{12} and two kinds of disordered BCC phase is also similar to those in $\text{Al}_{0.3}$ and $\text{Al}_{0.5}$. More detailed information, e.g., chemical compositions of each phase, from our thermodynamic calculations indicates that the ordered B2 phase is Al and Ni-rich, and the σ phase is Cr-rich.

The thermodynamically-calculated results will help us better understand the experimental observations in the present work. However, discrepancies are shown. 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 large discrepancy for the $\text{Al}_{0.7}$ alloy is due to either the unreliability of our current thermodynamic database or the error of experimental results measurements.

Discrepancies are also expected between our thermodynamic calculations and experimental observations at lower temperatures, such as 500 and 900 °C. That is because 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. Based on our previous experimental investigation on the $\text{Al}_{0.3}$ alloy at 700 °C, it will take more than 150 hours for the formation of the B2 precipitate within the FCC matrix. Thus, the experimentally-observed microstructures are not in equilibrium yet. However, these experimental results are important for readers to understand the initial stage of phase transformation.

a**b**

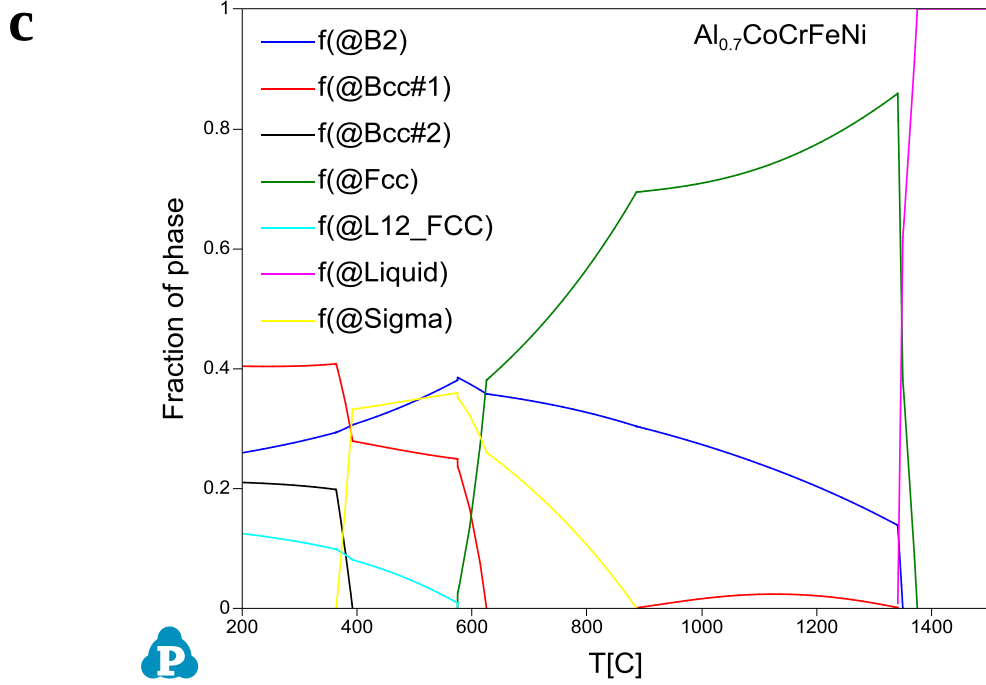


Figure 18 CALPHAD diagram showing the relationship between fractions of various phases and temperatures for (a) Al_{0.3}, (b) Al_{0.5}, and (c) Al_{0.7}, respectively.

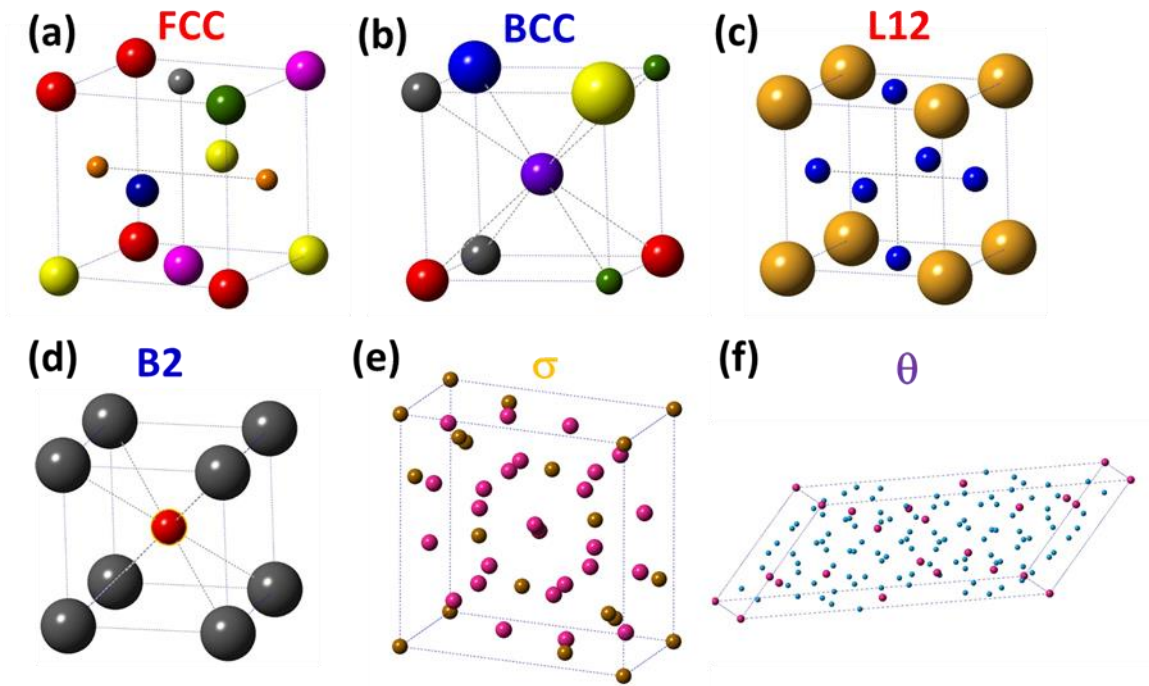
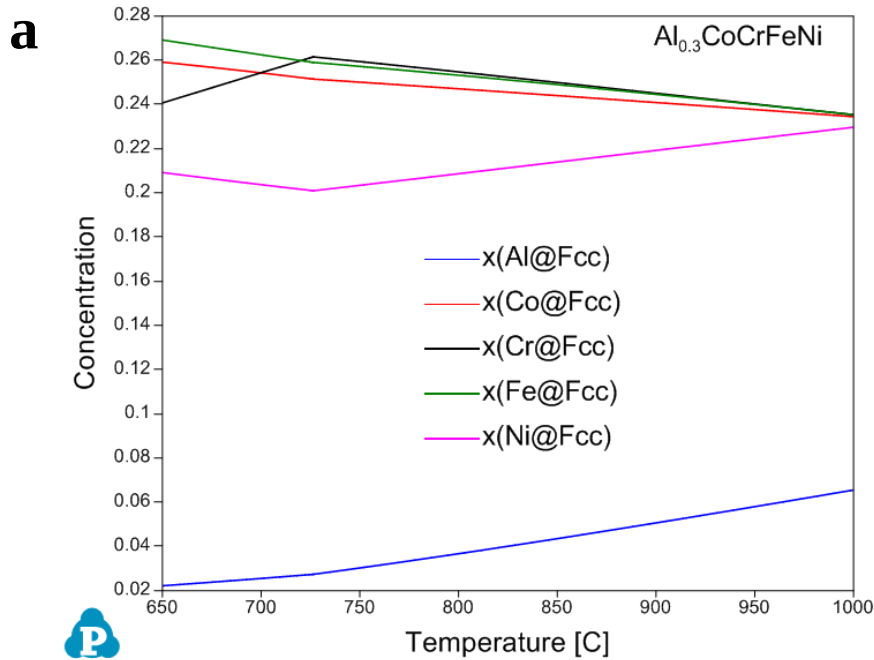


Figure 19 Six phases are present in the Al_xCoCrFeNi alloy system, verified by both experimental results and thermodynamic calculations.

3.3.5 Thermodynamic Modeling of Phase Constituents and Elemental Distributions

CALPHAD is used to predict the elemental concentration with both the FCC matrix and B2 phase of $\text{Al}_{0.3}\text{CoCrFeNi}$. Nano-sized B2 phase precipitated out from the FCC matrix within the $\text{Al}_{0.3}\text{CoCrFeNi}$ sample aged for 500 hours. In the FCC matrix, the concentration of Ni and Al decreases as the temperature decreases, while the concentration of other three elements, Co, Cr, and Fe, increases as the temperature increases. This trend is related to the phase transformation. At lower temperatures, more phases, including more Ni and Al, will separate from the FCC matrix. Thus, the Ni and Al concentration within FCC matrix decreases. For the B2 phase, the chemical composition varies a little bit in the temperature range from 650 °C to 1,000 °C. This trend is related to the stability of the B2 phase.



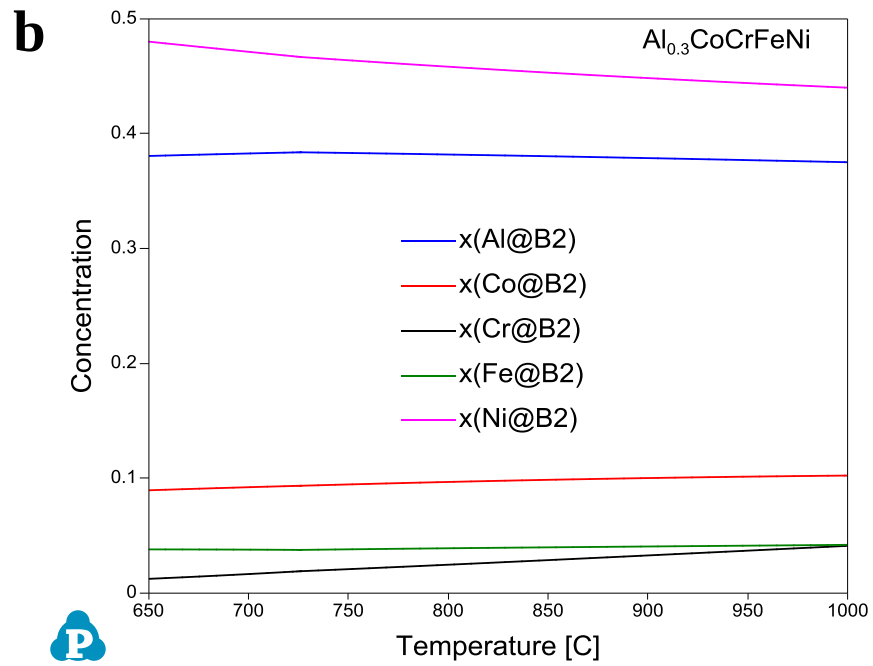


Figure 20 The elemental concentration with the FCC phase (a) and B2 phase (b) of Al_{0.3}CoCrFeNi is calculated by CALPHAD.

4. TASK 2: ALLOY FABRICATION

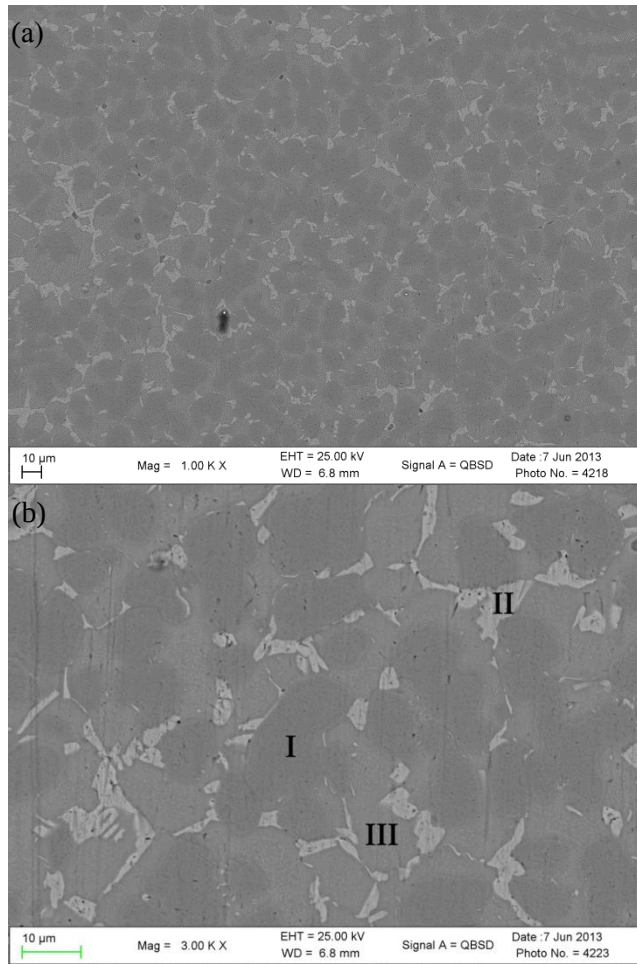
4.1 Al_{0.8}CrCuFeMnNi

An ingot of Al_{0.8}CrCuFeMnNi was cast in vacuum. The specimen has a diameter of 25.4 mm (1 inch) and a length of around 762 mm (30 inch). This bar is produced by the Sophisticated Alloys, Inc. The melting and solidification processes were repeated several times to improve the homogeneity of the sample. In an effort to reduce the effect of casting defects may have on the results of the creep and uniaxial tension and compression experiments, the cast ingot underwent hot isostatic pressing (HIP) at 899 °C. To reduce the porosity of former specimen, the shape of the material is changed to 127 mm × 254 mm × 25.4 mm, and the temperature of HIP is increased to 1,204 °C.

Table 3 The chemical composition of Al_{0.8}CrCuFeMnNi

	Al	Cr	Cu	Fe	Mn	Ni
Atomic %	13.79	17.24	17.24	17.24	17.24	17.24
Weight %	7.04	16.96	20.73	18.21	17.91	19.15

Representative SEM images of the Al_{0.8}CrCuFeMnNi alloy are presented in Figure 3. As shown on this image, one can readily observe that the HEA specimen has three phases, which are indicated as the dark-grey area (I), light-grey area (III), and white-phase layer (II), respectively. In the dark grey area, denoted by I, the chromium (Cr), and iron (Fe) concentrations are 31.88% and 29.04%, approximately two times of the average concentration. Compared with the dark grey area (I), the light grey area (III) owns a higher concentration of aluminum (Al), nickel (Ni), and copper (Cu), almost three times of the respective concentrations at the dark grey area (I). For the element copper, Cu, it is rich in the white-phase layer.



(c) Atomic %	Al	Cr	Mn	Fe	Ni	Cu
Dark-grey area (I)	8.12	31.88	15.47	29.04	9.05	6.44
White-phase layer (II)	6.97	1.65	19.12	3.11	9.90	59.25
Light-grey area (III)	20.97	4.86	19.31	6.59	28.13	20.14

Figure 21 SEM images of $\text{Al}_{0.8}\text{CrCuFeMnNi}$ (a) at low magnification; (b) at higher magnification; and (c) the nominal elemental concentrations in different regions

An X-ray diffraction pattern of the $\text{Al}_{0.8}\text{CrCuFeMnNi}$ alloy is shown in Fig. 3. The Bragg peaks are identified as belonging to three phases, which have disordered BCC + FCC crystal structures (BCC1, BCC2, and FCC).

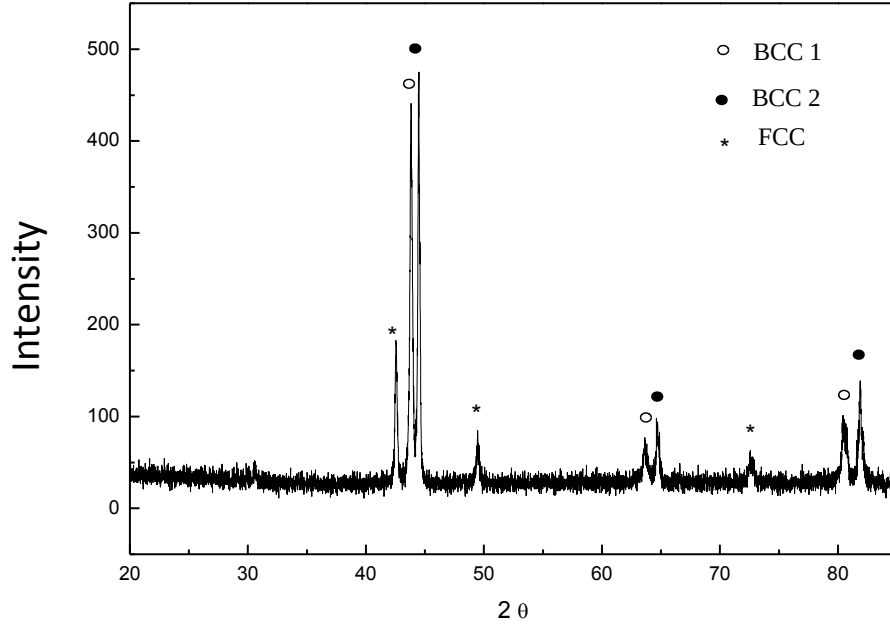


Figure 22 XRD patterns for the $\text{Al}_{0.8}\text{CrCuFeMnNi}$ alloy

4.1.1 Elemental Distributions within $\text{Al}_{0.8}\text{CrCuFeMnNi}$ HEA on Atomic Scale

The 3D APT is used to map the nano-scaled distribution of alloying elements in $\text{Al}_{0.5}\text{CoCrCuFeNi}$ [86], AlCoCrCuFeNi [87-89], $\text{Al}_{1.3}\text{CoCrCuFeNi}$ [90], AlCrCuFeNiZn [91], AlCoCrFeNi [55], and CoCrFeMnNi [34, 92, 93] HEAs. This elemental distribution on nano-scale cannot be observed by the normal Energy Dispersive Spectroscopy (EDS) on the SEM, which detects the chemical composition on μm -scale.

The CoCrFeMnNi and $\text{Co}_{0.25}\text{Co}_{0.1}\text{Fe}_2\text{Mn}_{1.35}\text{Ni}_{1.3}$ HEAs were proved to be true solid solutions down to the atomic scale by APT, since there is no segregation or enrichment observed on the atomic scale [34, 92, 93]. In $\text{Al}_{0.5}\text{CoCrCuFeNi}$, obvious chemical segregation on the atomic scale is observed by APT. The Cu-rich and FeCoCr(Ni) -rich domains are alternately distributed in

Al_{0.5}CoCrCuFeNi [86]. For AlCoCrCuFeNi and Al_{1.3}CoCrCuFeNi, there are three phases, B2 (Al-Ni-enriched), BCC (Cr-Fe-enriched), and FCC (Cu-rich) [87, 88, 90]. For AlCoCrFeNi, two phases, B2 (Al-Ni-enriched) and BCC (Cr-Fe-enriched), are present [55]. The nature of interfaces between constituent phases in the AlCoCrCuFeNi HEA is also studied by APT. The width of the transition region between B2 and disordered BCC phases is 1.5 - 7 nm [87, 88]. Even for the same phase, B2 or BCC, the APT results vary for different HEAs. Within the BCC region (Cr-Fe-enriched) of AlCoCrFeNi, the Fe- and Cr-clusters exhibit the intertwined morphology. In other words, an alternation of the Fe- and Cr- clusters is present, and the local Fe or Cr is about 2 nm in width. The fluctuation in the BCC phase of AlCoCrFeNi is larger than that of AlCoCrCuFeNi [55]. Within the B2 region, all elements show quite a homogeneous distribution in AlCoCrFeNi [55]. For Al_{1.3}CoCrCuFeNi, within the B2 phase, Cu-rich and Cr-rich nano-precipitates are found [90].

The elemental distribution within the nanocrystals and the chemical compositions across different phases and boundaries were obtained from APT. Figures 23a, 23b, 23c, 23d, 23e, and 24f display the individual atomic positions of Al, Ni, Fe, Cr, Mn and Cu, respectively. Figure 8g shows the elemental map of all ions. All elements are non-uniformly distributed and can be divided into at least three regions based on the enrichment of at least one of the alloying elements. The three regions are the Al-Ni-rich, Cr-Fe-rich, and Cu-rich areas (shown in Figure 23g). The reconstructed 3 dimensional (3D) morphology of the Al-Ni-rich region (green color) and Cr-Fe-rich region (purple color) is shown in Figure 6h. Combining the synchrotron results (Figure 24), the Al-Ni-rich region should be the B2 phase, the Cr-Fe-rich region should be the BCC phase, and the Cu-rich region should be the FCC phase. The lattice parameters of the Al-Ni-rich, Cr-Fe-rich, and Cu-rich phases, as measured from the synchrotron peak positions, correspond to $a_{\text{Al-Ni}} = 0.2888$ nm, $a_{\text{Cr-Fe}} = 0.2928$ nm, and $a_{\text{Cu}} = 0.3692$ nm. A similar Al-Ni phase ($a = 0.288$ nm) of the B2 structure with high amounts of Co, Fe, Cu, and Cr has been previously reported for an as-cast AlCoCrCuFeNi HEA [9].

In order to clearly distinguish these three regions, one dimensional concentration–depth profiles of all alloying elements of Al_{0.8}CrCuFeMnNi along the interface between Al-Ni- and Fe-Cr-

rich phases is plotted (Figure 25). The Al-Ni-rich phase also contains substantial amounts of Mn (~ 22 at. %), and Cu (~ 10 at. %). The error bars represent the 2σ standard deviation, which is used to quantify the amount of variation or dispersion of a set of data values. When a standard deviation is close to 0, it indicates that the data points tend to be very close to the mean of the data set, while a high standard deviation means that the data points are spread out over a wider range of values [94].

The formation of an Al-Ni-rich phase is due to the strong interactions of these atoms during mixing, i.e., Ni and Al have the largest negative enthalpy of mixing among all other atom pairs of the five alloying elements, namely - 22 kJ/mol. The values of the energy of formation of the corresponding intermetallic phases are even larger, namely - 60 kJ/mol for the ordered B2 phase, AlNi, and about - 40 kJ/mol for the $L1_2$ phase, Ni_3Al . The formation of a Cr-Fe-rich phase can also be explained in terms of H_{mix} . The enthalpy of mixing of the Cr-Fe binary system is 1 kJ/mol.

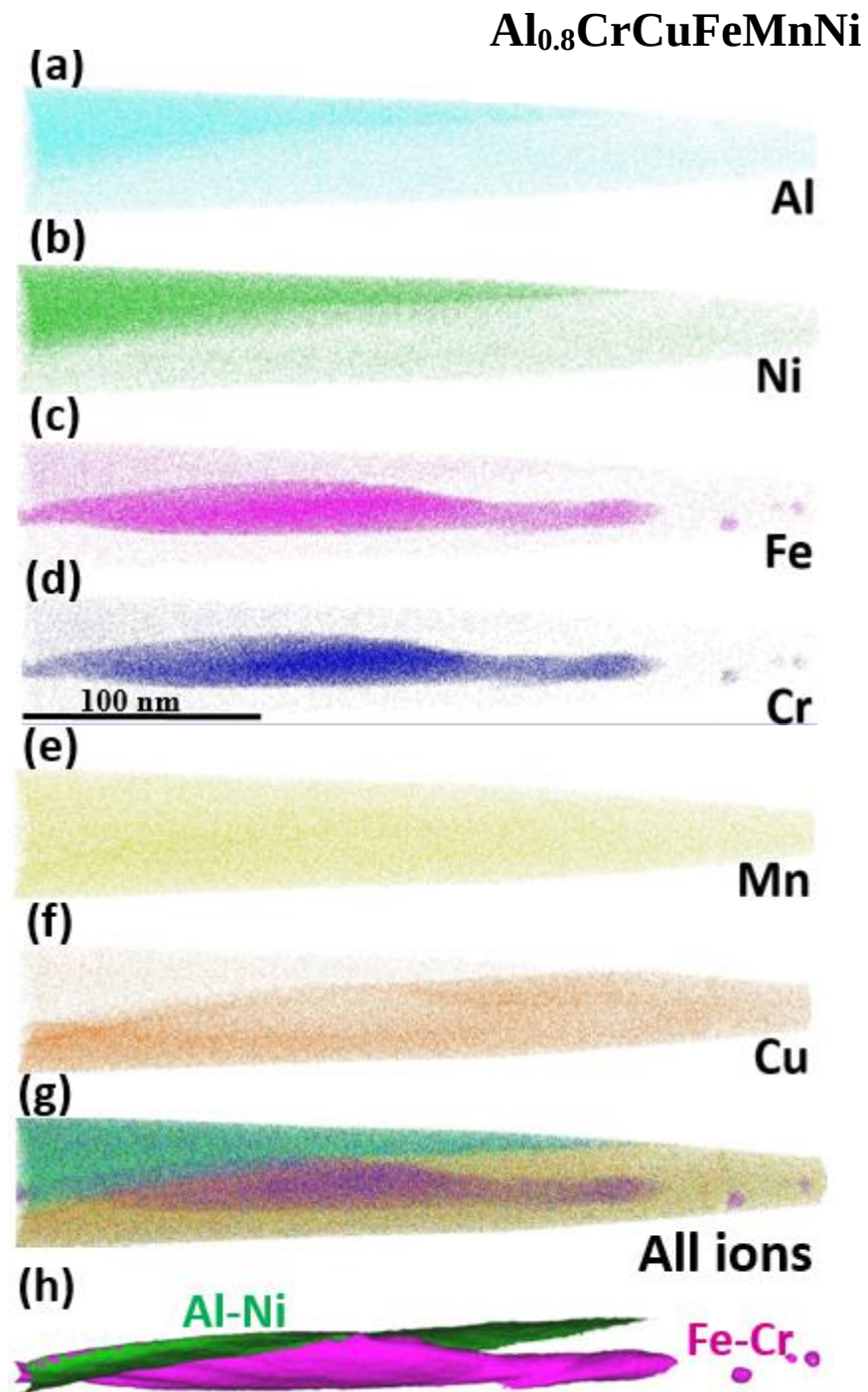


Figure 23 The APT data of $\text{Al}_{0.8}\text{CrCuFeMnNi}$. The 3D reconstruction of Al (a), Ni (b), Fe (c), Cr (d), Mn (e), Cu (f), and all atoms (g) atomic positions. Three regions are found (g, h): Al-Ni-rich phase (green, h), Fe-Cr-rich phase (purple, h), and Cu-rich phase.

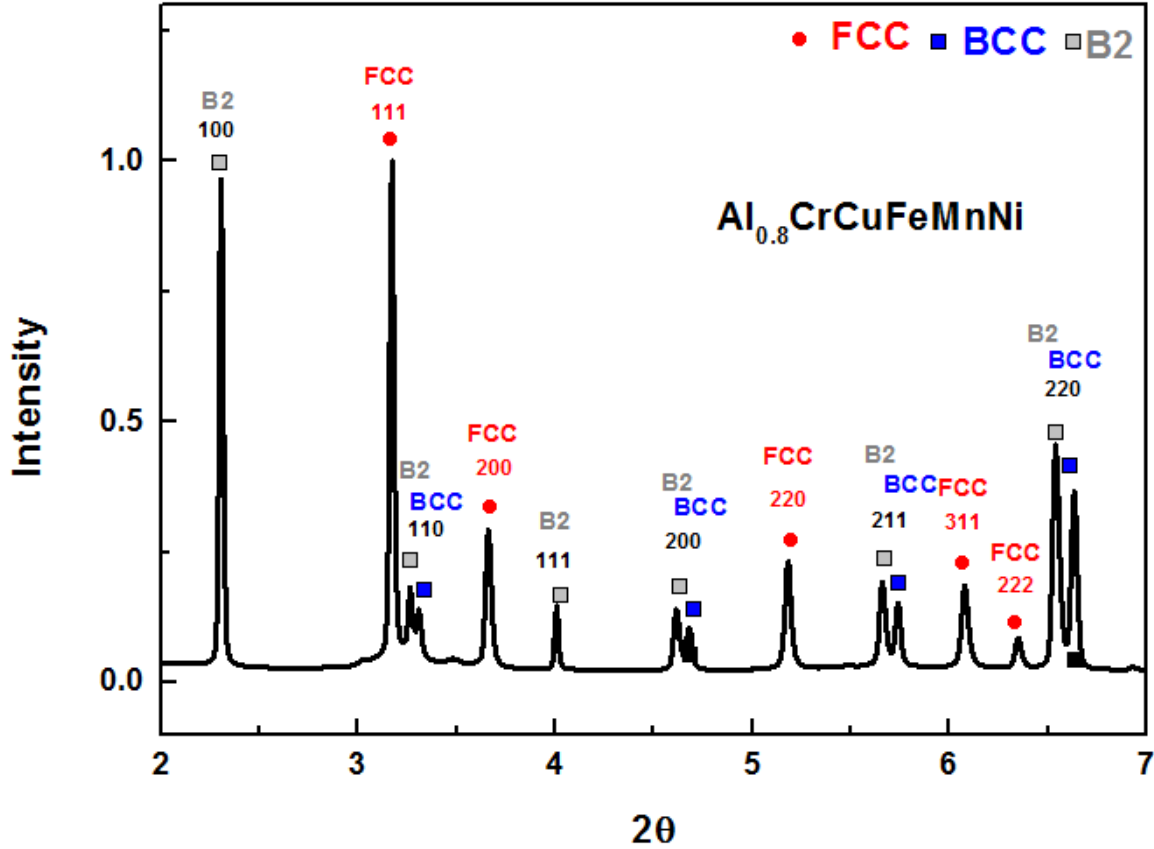


Figure 24 The synchrotron pattern of $\text{Al}_{0.8}\text{CrCuFeMnNi}$. Three phases, BCC, B2, and FCC structures, are present. The lattice parameters of BCC, B2, and FCC phases are 0.2888 nm, 0.2928 nm, and 0.3692 nm, respectively.

One dimensional concentration–depth profiles of all alloying elements of $\text{Al}_{0.8}\text{CrCuFeMnNi}$ along the interface between Cu-rich (orange) and Fe-Cr-rich (purple) phases is plotted (Figure 11). Inside the Cu-rich phase, an amount of Mn ($\sim 20\%$) is present. Inside the Fe-Cr rich phases, the Cu content is relatively low, ~ 1 at. %.

To complete the information about the interfaces between three phases, the one dimensional concentration-depth profiles of all alloying elements along the boundary between the Al-Ni and Cu rich phases is plotted (Figure 12). Inside the Al-Ni-rich phase, the content of Cu is around 10 at. %.

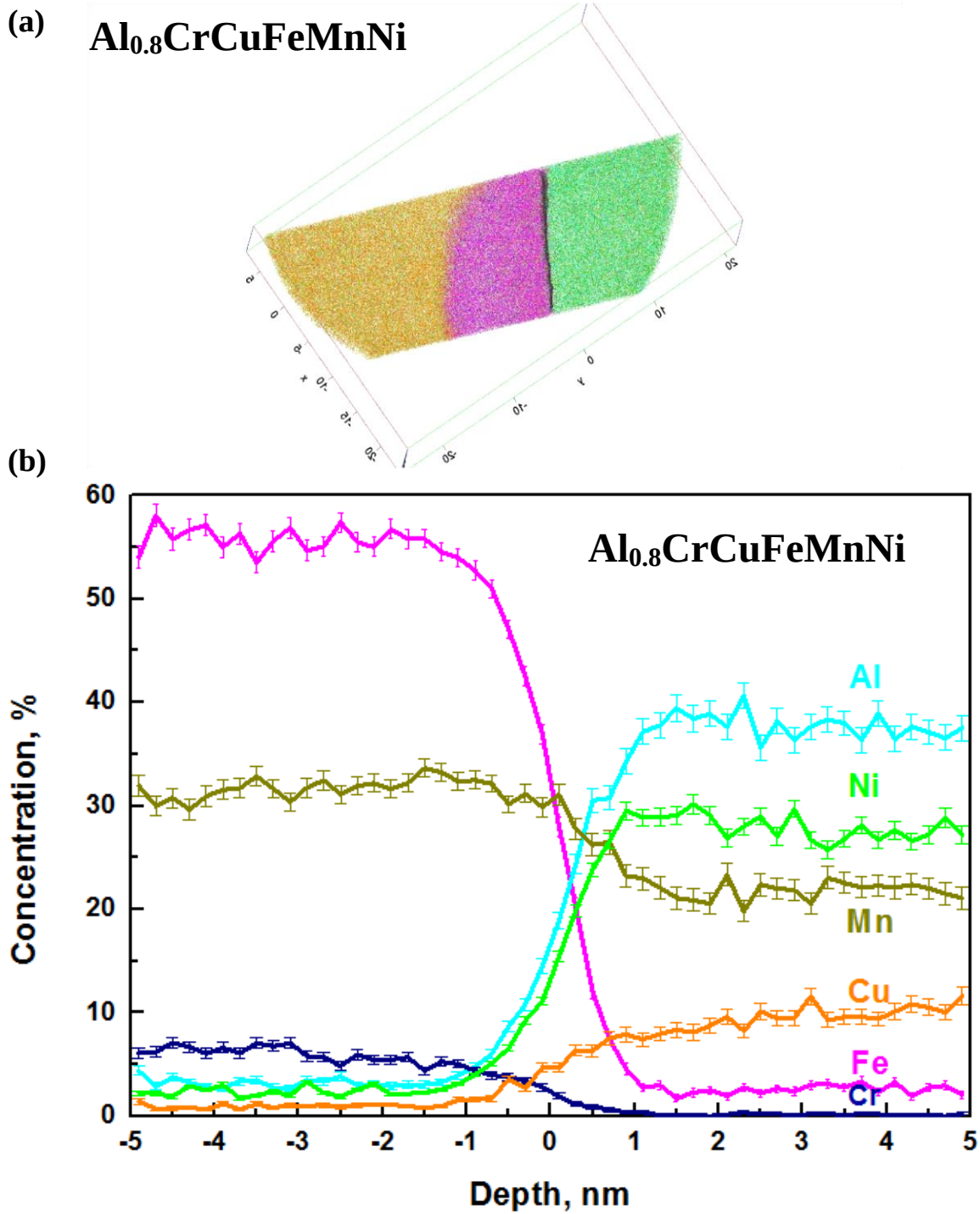


Figure 25 (a) APT illustration of $\text{Al}_{0.8}\text{CrCuFeMnNi}$. The black line indicates the interface between Al-Ni- (green) and Fe-Cr- (purple) rich phases; (b) Concentration–depth profiles of all alloying elements of $\text{Al}_{0.8}\text{CrCuFeMnNi}$ along the interface between Al-Ni- (green) and Fe-Cr- (purple) rich phases. The error bars represent the 2σ standard deviation.

(a) $\text{Al}_{0.8}\text{CrCuFeMnNi}$

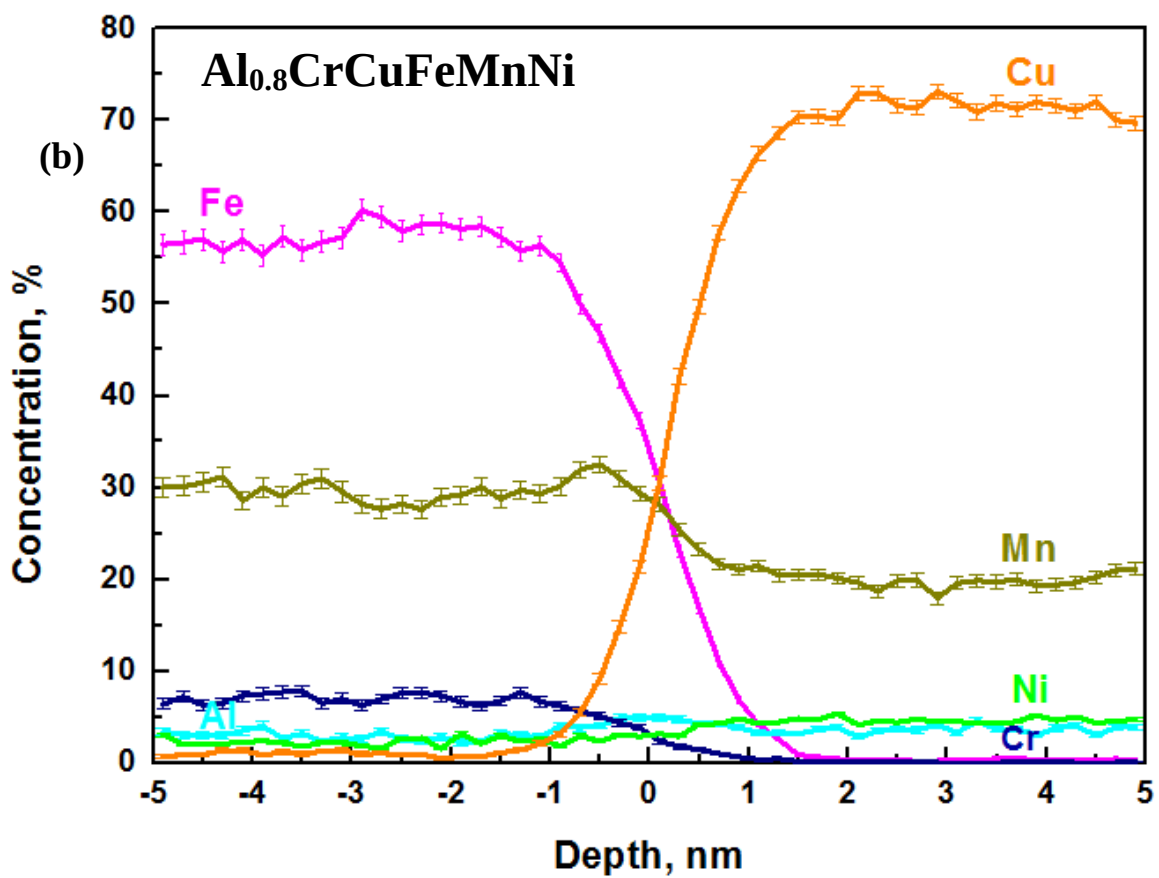
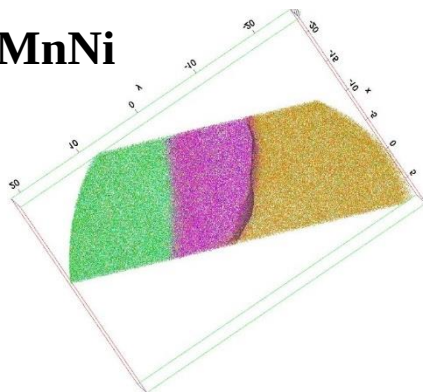
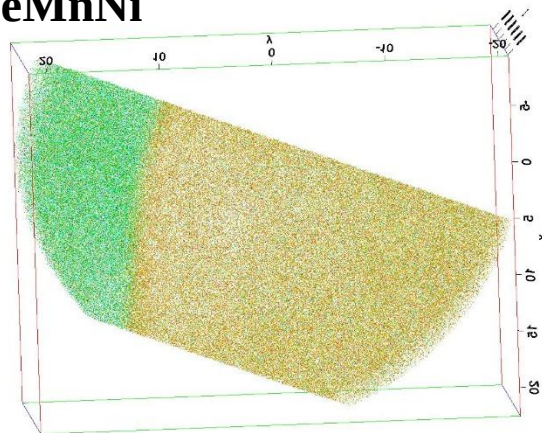


Figure 26 (a) APT illustration of $\text{Al}_{0.8}\text{CrCuFeMnNi}$. The black line indicates the interface between Fe-Cr- (purple) and Cu- (orange) rich phases; (b) Concentration–depth profiles of all alloying elements of $\text{Al}_{0.8}\text{CrCuFeMnNi}$ along the interface between Al-Ni- (green) and Fe-Cr- (purple) rich phases. The error bars represent the 2σ standard deviation.

(a) $\text{Al}_{0.8}\text{CrCuFeMnNi}$



(b)

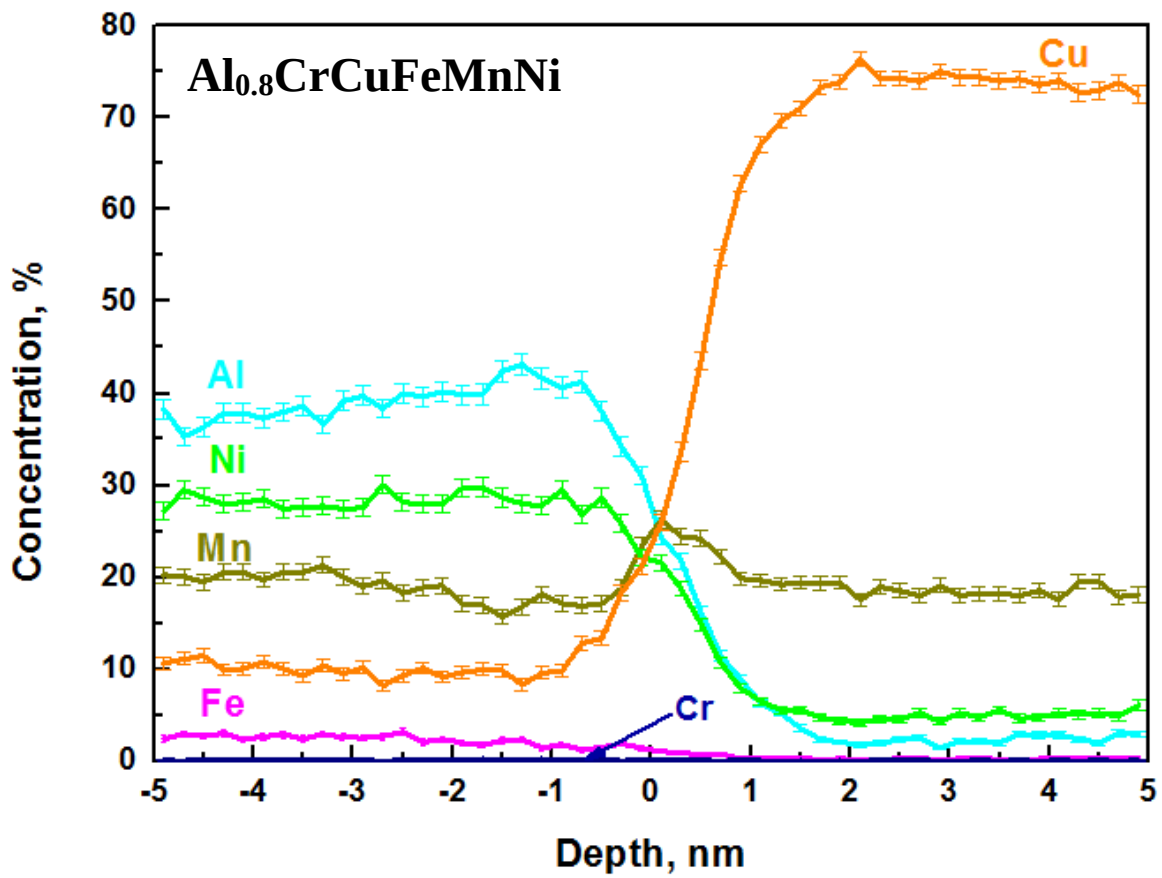


Figure 27 APT illustration of $\text{Al}_{0.8}\text{CrCuFeMnNi}$. (b) Concentration–depth profiles of all alloying elements of $\text{Al}_{0.8}\text{CrCuFeMnNi}$ along the interface between Al-Ni- (green) and Cu- (orange) rich phases. The error bars represent the 2σ standard deviation.

Since the Cu cluster is harmful to the formation of solid solutions in the field of HEAs, it is essential to study the Cu cluster distribution within Al-Ni- and Cr-Fe-rich phases. First of all, the total content of Cu within the Cr-Fe-rich phase (~ 1 at. %) is lower than that in the Al-Ni rich phase (~ 10 at. %). Secondly, there are Cu clusters starting to form inside the Al-Ni- rich phase. But there is no Cu clustering inside the Fe-Cr rich phase. The APT result of Cu clusters inside the Al-Ni-rich phase is shown in Figure 28.

The Cu-clusters-size frequency is shown in Figure 29. The results show that the probability of the cluster is the highest, 21 %, when the cluster radius is around 1.5 nm to 2 nm. The radius of more than 56 % clusters is in the range of 0.5 nm to 2 nm.

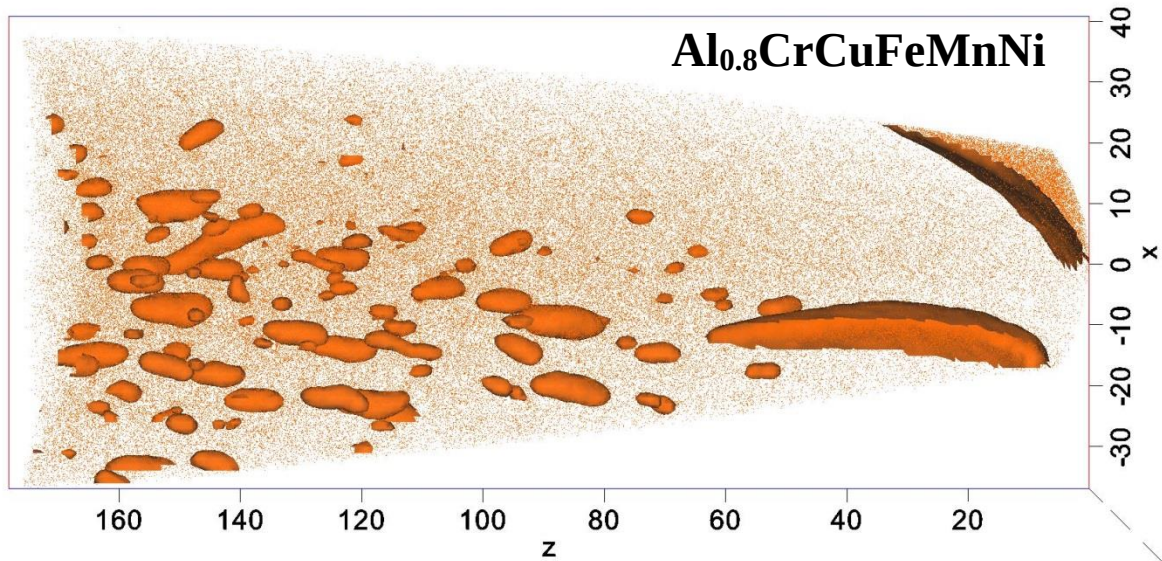


Figure 28 The APT distributions of Cu clusters inside the Al-Ni-rich phase. The scale unit is nm.

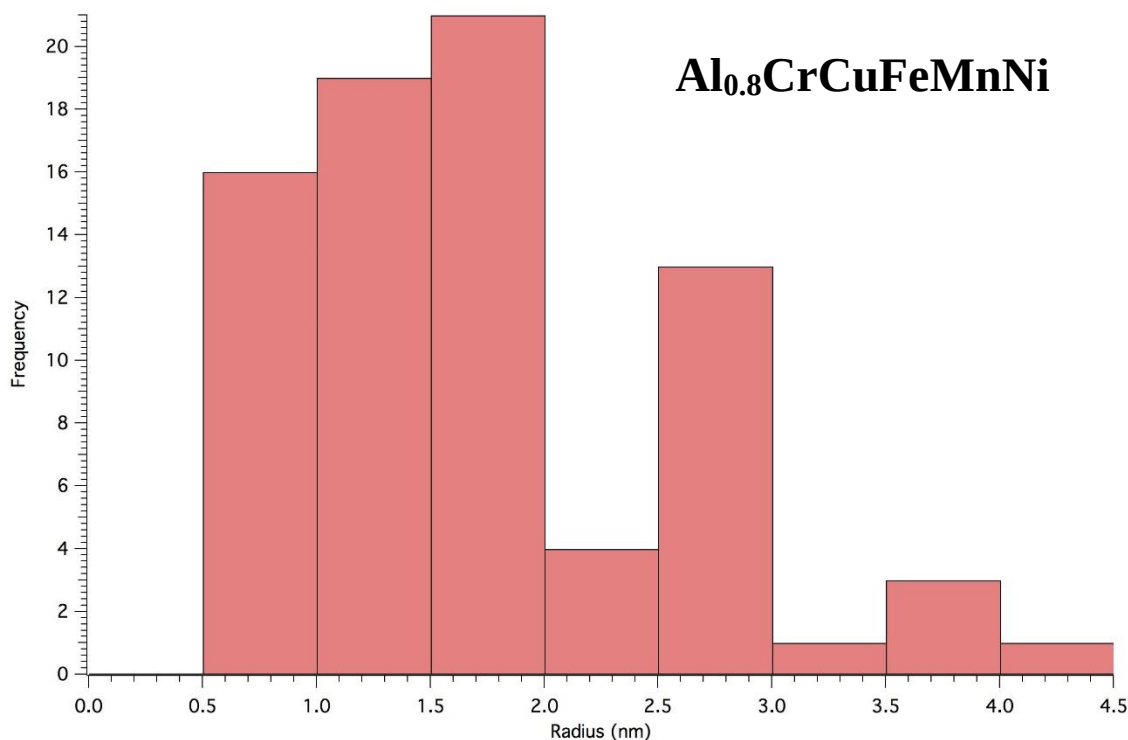


Figure 29 The radius frequency distribution of Cu clusters inside the Al-Ni-rich phase of Al_{0.8}CrCuFeMnNi. The x axis scale unit is nm and y axis scale unit is the atomic percentage (at. %)

After comparing the Mn content within three phases, the results show that the Mn distribution is very flat. In order to quantify the Mn distribution, the experimentally-measured distribution of Mn is indicated by black dots in Figure 15. Meanwhile, the experimental-frequency distribution of the nanoscale Mn atomic cluster in the 3D atom-probe data is compared with the classic binomial frequency distribution, $f(n)$ [95], shown by the red curve in Figure 15.

The results show that the Mn distribution is very flat, but the frequency distribution does not show a completely-random distribution because there is a slight Mn depletion in the Cu precipitates. The overall Mn is distributed very evenly throughout the dataset.

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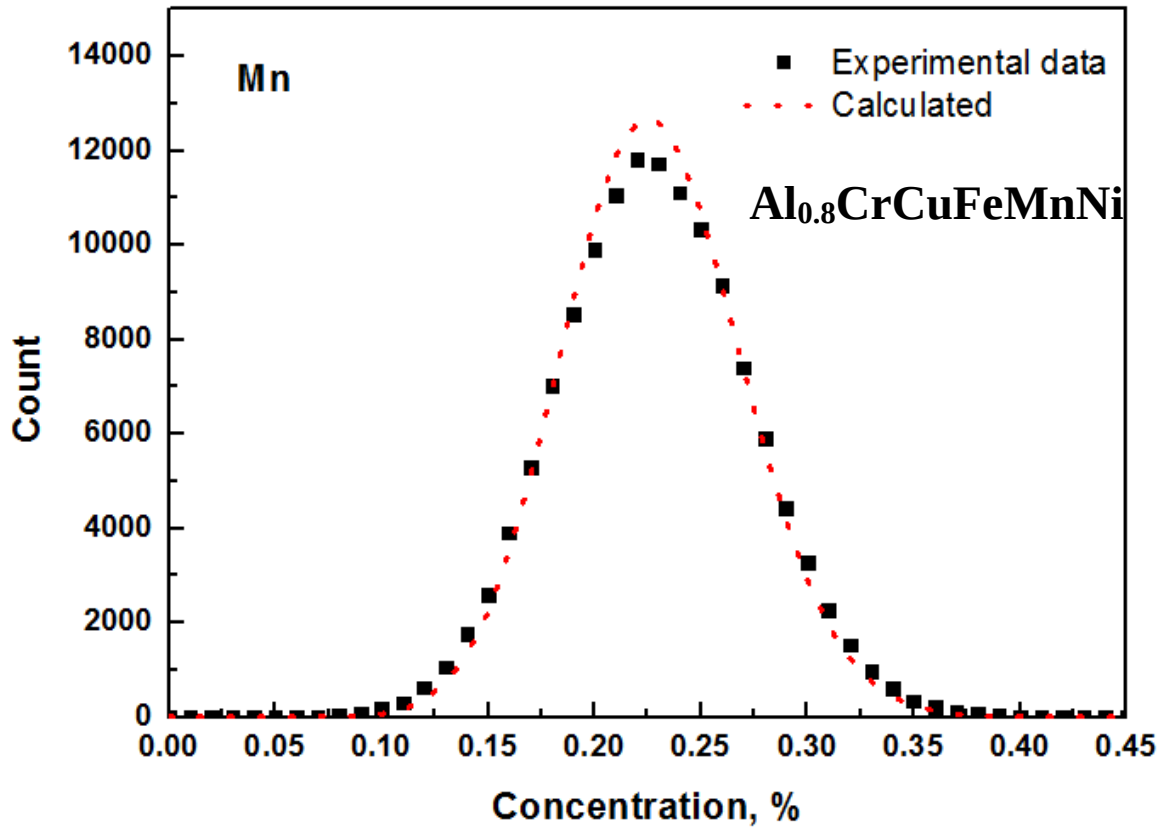


Figure 30 The frequency distribution of Mn of Al_{0.8}CrCuFeMnNi. The black dots are experimental data, while the red curve is the classic-binomial frequency distribution, $f(n)$

4.2 Al_{0.1}CrCuFeMnNi

The Al_{0.1}CrCuFeMnNi alloy was prepared by arc-melting elemental Al, Cr, Cu, Fe, Mn, and Ni raw materials in a water-cooled copper hearth. The source materials had a purity level higher than 99.0 weight percent (wt. %). Repeated melting for at least four times was done to improve the chemical homogeneity of the alloys. The ingots were approximately 80 mm in diameter and 10 mm in thickness. The actual chemical compositions of the fabricated Al_{0.1}CrCuFeMnNi alloy was obtained by the inductively-coupled plasma mass spectrometry (ICP-MS) technique. Both the target and analyzed values are shown in Table 1, respectively. From the results, we can see that the nominal chemical compositions of the received materials are within the error tolerance.

Table 4 Target versus analyzed values for Al_{0.1}CrCuFeMnNi alloys (wt. %)

Alloy Type		Al	Cr	Cu	Fe	Mn	Ni
Al _{0.1} CrCuFeMnNi	Target	0.94	18.07	22.09	19.41	19.09	20.39
	Actual	0.743	19.5	20.3	19.7	18.3	19.9

The structure of Al_{0.1}CrCuFeMnNi at room temperature is examined, using high-energy synchrotron X-ray in a transmission mode. The related results are shown in Figure 31. From Figure 31, we can learn that at room temperature, three phases (FCC-1, FCC-2, and BCC structures) exist. The lattice parameters of FCC-1, FCC-2, and BCC phases are 0.3677 nm, 0.3622 nm, and 0.2888 nm, respectively.

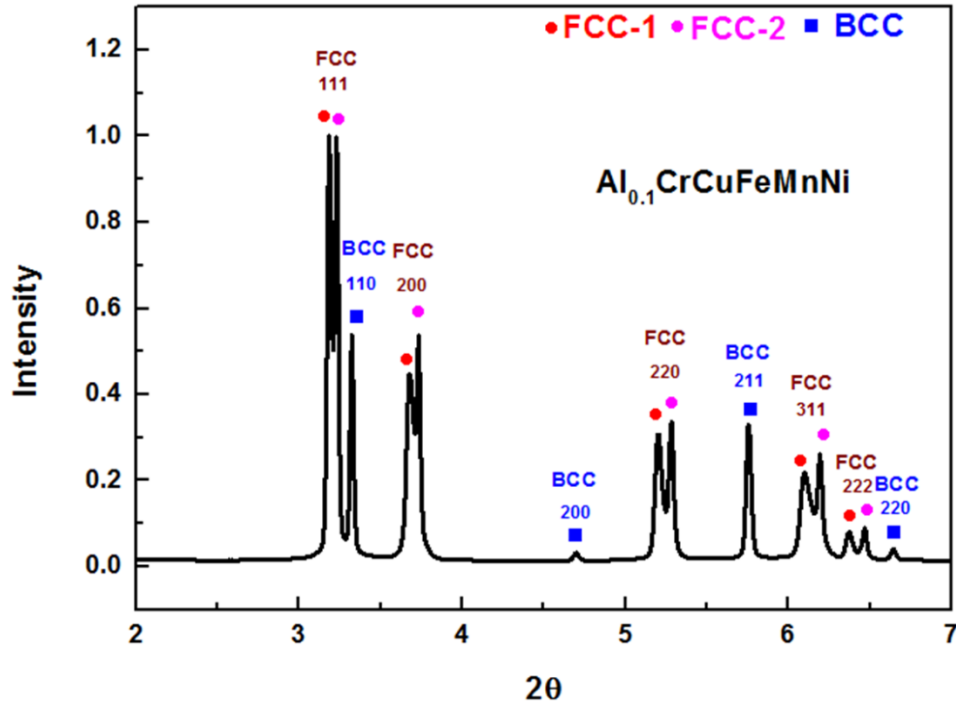


Figure 31 Synchrotron X-ray diffraction pattern of $\text{Al}_{0.1}\text{CuCrFeMnNi}$ at room temperature. Three phases (FCC-1, FCC-2, and BCC structures) exist

In order to study the morphology of three phases within the $\text{Al}_{0.1}\text{CuCrFeMnNi}$, the scanning electron microscopy (SEM) images at room temperature are studied (shown in Figure 32). Typical cast dendrite and interdendrite structures (defined as DR and ID in the figures, respectively) are observed in $\text{Al}_{0.1}\text{CrCuFeMnNi}$ alloys.

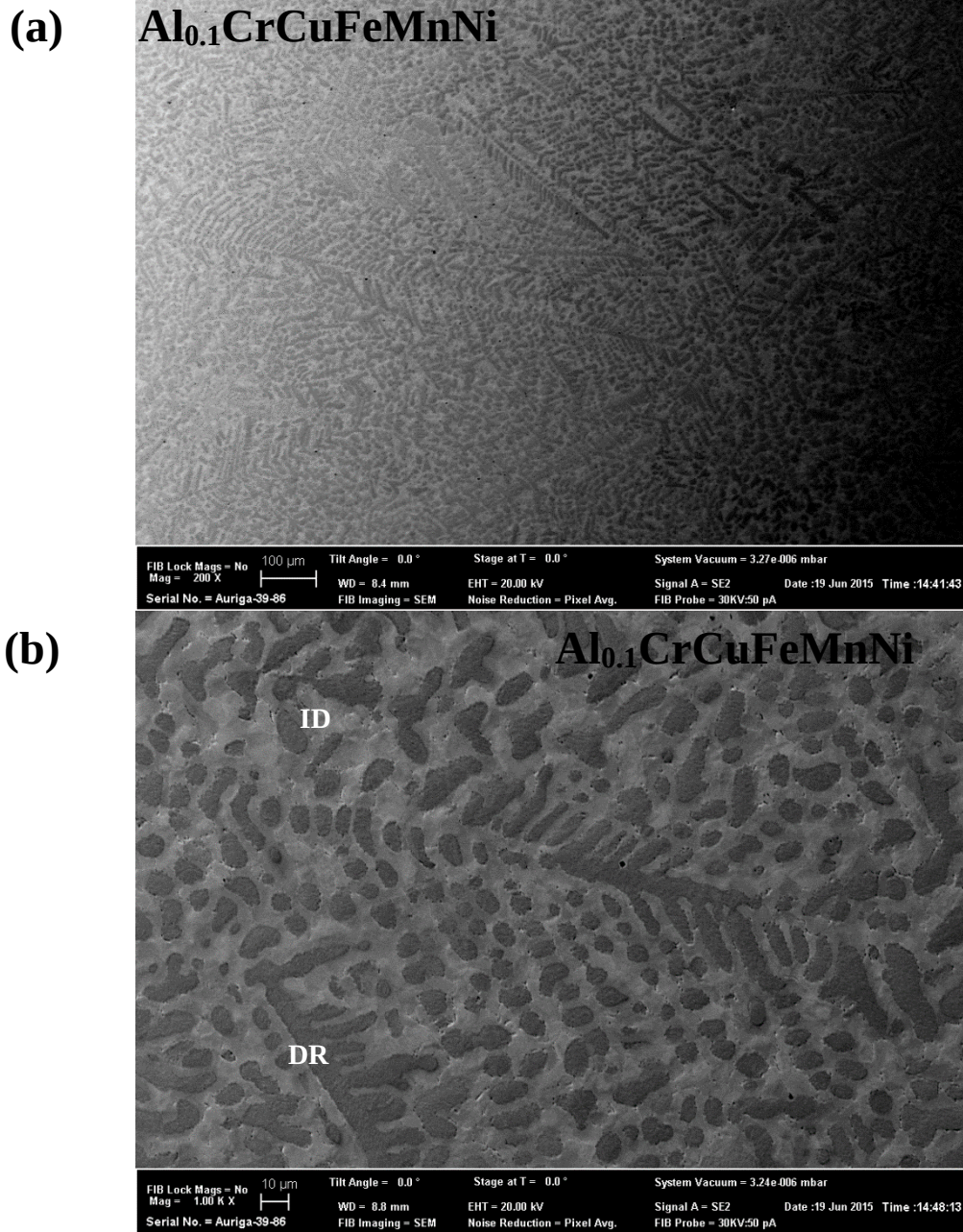


Figure 32 The SEM images of $\text{Al}_{0.1}\text{CuCrFeMnNi}$ at room temperature.

Besides room temperature (RT), phase characteristics at higher temperatures are essential to study the structural revolution during cooling (solidification path). The neutron-diffraction patterns of $\text{Al}_{0.1}\text{CuCrFeMnNi}$ from 800 °C to the molten temperature are shown in Figure 33. From Figure 33, we can learn that there are three phases [FCC-1, FCC-2, and

BCC] present from room temperature (RT) to 1,100 °C. At 1,200 °C, two phases (FCC-2 and BCC) exist. At 1,300 °C, only one BCC phase exists.

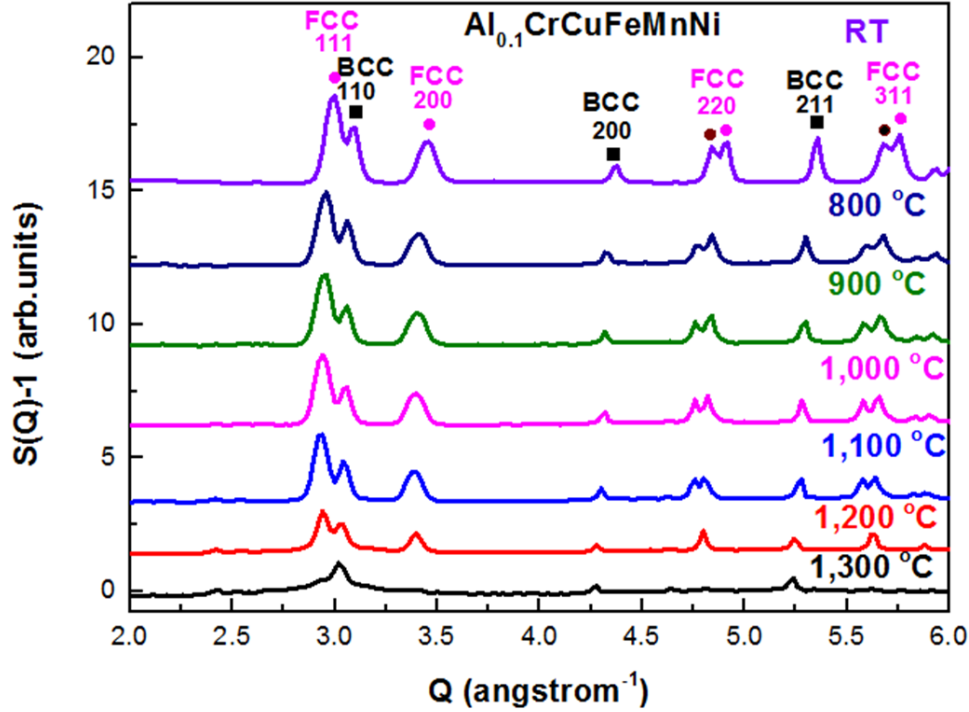


Figure 33 The neutron patterns of $\text{Al}_{0.1}\text{CuCrFeMnNi}$ from room temperature (RT) to molten temperature. Three phases (FCC-1, FCC-2, and BCC) exist from RT to 1,100 °C. At 1,200 °C, two phases (FCC-1 and BCC) exist. At 1,300 °C, only one BCC phase presents

Combing the neutron-diffraction patterns at high temperatures and the Scheil modeling [81], the solidification path of $\text{Al}_{0.1}\text{CuCrFeMnNi}$ is proposed to be,

Liquid $\rightarrow$ BCC $\rightarrow$ BCC + FCC-2 (0.3622 nm) $\rightarrow$ BCC + FCC-2 + FCC-1 (0.3677 nm)

The primary solidification phase is BCC, then FCC-2 with the lattice parameter, 0.3622 nm, and the last phase is FCC-1 with the lattice parameter, 0.3677 nm.

Furthermore, the room-temperature morphology of FCC-1 and FCC-2 is composed of dendrites and interdendrites (Figure 32). The dendrite phase should be FCC-2, while the

interdendrite phase should be FCC-1. Since the BCC content is $\sim 7\%$, we have not found any BCC phase at room temperature.

Combining the SEM results, thermodynamic modeling, and temperatures of neutron diffraction results (Figure 4), the detailed illustration of structural revolution during cooling from the molten temperature is shown below.

**Liquid $\rightarrow$ BCC ($\sim 7\%$) [at 1,300 °C] $\rightarrow$ BCC + Dendrite FCC-2 (0.3622 nm) [at 1,200 °C]
 $\rightarrow$ BCC + Dendrite FCC-2 + Interdendrite FCC-1 (0.3677 nm) [at 1,100 °C]**

4.3 Phase Formation Rules of $\text{Al}_x\text{CrCuFeMnNi}$ Systems

The XRD results of the $\text{Al}_x\text{CrCuFeMnNi}$ system are different from that of the similar $\text{Al}_x\text{CoCrCuFeNi}$ system [5]. The $\text{Al}_x\text{CoCrCuFeNi}$ with the aluminum contents from 0 to 0.5 show a simple FCC structure [5, 96]. Until now, several parameters, the atomic-size difference parameter (δ_r) [97], the parameter (Ω) [97], the electronegativity difference parameter (δ_χ) [39], the valence-electron concentration difference parameter (δ_v) [39], and valence electron concentration (VEC) [98, 99] are proposed to predict the composition range of the solid solution phase formation in HEAs. Thus, it is interesting to see if these rules also work for the $\text{Al}_x\text{CrCuFeMnNi}$ system.

The related parameters are defined and calculated as [39, 97-99]:

$$\delta_r = 100 \sqrt{\sum_{i=1}^N c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (3)$$

where N is the number of the components in an alloy system, c_i is the atomic percentage of the i th element, r_i is the atomic radius of i th element, which can be obtained from Table 2. $\bar{r} (= \sum_{i=1}^N c_i r_i)$ is the averaged atomic radius.

Table 5 Properties of the experimental elements

	Metallic atomic radius (pm)	Electro- negativity (Pauling scale)	VEC	Density (g/cm ³)	Vicker Hardness (MPa)	Young's Modulus (GPa)	Melting Temperature (°C)	Boiling Temperature (°C)
Al	143	1.61	3	2.70	167	70	660	2,470
Cr	128	1.66	6	7.19	1,060	279	1,907	2,671
Cu	128	1.90	11	8.96	369	110 - 128	1,085	2,562
Fe	126	1.83	8	7.874	608	211	1,538	2,862
Mn	127	1.55	7	7.21	-	198	1,246	2,061
Ni	124	1.91	10	8.908	638	200	1,455	2,730

The parameter, Ω , combines effects of ΔS_{mix} and ΔH_{mix} for predicting the solid-solution formation [97, 100].

$$\Omega = \frac{T_m \cdot \Delta S_{mix}}{|\Delta H_{mix}|} \quad (4)$$

$$T_m = \sum_{i=1}^N c_i (T_m)_i \quad (5)$$

$$\Delta S_{mix} = -R \sum_{i=1}^N (c_i \ln c_i) \quad (6)$$

$$\Delta H_{mix} = 4 \sum_{i=1, i \neq j}^N \Delta H_{ij}^{mix} c_i c_j \quad (7)$$

where T_m is the average melting temperature of the n-elements alloy, and $(T_m)_i$ is the melting point of the i th element. ΔH_{ij}^{mix} is the mixing enthalpy of binary alloys, which has been listed in Table 6.

Table 6 Values of ΔH_{mix} (kJ/mol) in the $Al_xCrCuFeMnNi$ system calculated using Miedema's model for atomic pairs between elements [101].

Mixing Enthalpy	Al	Cr	Cu	Fe	Mn	Ni
Al	-	-10	-1	-11	-19	-22
Cr	-	-	12	-1	2	-7
Cu	-	-	-	13	4	4
Fe	-	-	-	-	0	-2
Mn	-	-	-	-	-	-8
Ni	-	-	-	-	-	-

The valence electron concentration, VEC, has been proven useful in determining the phase stability of intermetallic compounds.

$$VEC = \sum_{i=1}^N c_i (VEC)_i \quad (8)$$

where $(VEC)_i$ is the VEC for the i th element. $(VEC)_i$ can be obtained from Table 2.

The electronegativity difference, δ_χ , out of the consideration from the classical Hume-Rothery's rule to form solid solution phases.

$$\delta_\chi = 100 \sqrt{\sum_{i=1}^N c_i \left(1 - \frac{\chi_i}{\bar{\chi}}\right)^2} \quad (9)$$

where χ_i is the Pauling electronegativity for the i th element. All χ_i values are listed in Table 2.

$\bar{\chi} (= \sum_{i=1}^N c_i \chi_i)$ is the averaged electronegativity.

The valence electron concentration difference parameter, δ_v , for the studied HEAs is defined as:

$$\delta_v = 100 \sqrt{\sum_{i=1}^N c_i \left(1 - \frac{VEC_i}{VEC}\right)^2} \quad (10)$$

ΔS_{mix} , ΔH_{mix} , Ω , δ_r , VEC, δ_χ , and δ_v for the $\text{Al}_x\text{CrCuFeMnNi}$ alloys are all listed in Table 4. Obviously, with the increase of the Al content, the mixing entropy, atomic-size difference, electronegativity difference, and VEC difference increase, while the mixing enthalpy, melting temperature, VEC decreases. Only Ω firstly increases and then decreases. According to Guo and Liu [98], VEC plays a decisive role in determining the FCC- or BCC-type solid solution in HEAs. Larger VEC (≥ 8) favors the formation of FCC-type solid solution. This trend is verified in the present work, since the percentage of FCC-type solid solution in the $\text{Al}_{0.1}\text{CrCuFeMnNi}$ is higher than that in $\text{Al}_{0.8}\text{CrCuFeMnNi}$. Although in the $\text{Al}_x\text{CrCuFeMnNi}$ system, the three parameters, ΔS_{mix} , ΔH_{mix} , and δ_χ , are all in the suitable range: $0 \leq \delta_\chi \leq 8.5$, $-22 \leq \Delta H_{\text{mix}} \leq 7$ kJ/mol, and $11 \leq \Delta S_{\text{mix}} \leq 19.5$ J/(K·mol), no single-face solid-solution phase forms. The $\text{Al}_x\text{CrCuFeMnNi}$ system doesn't satisfy Yang and Zhang's assumption [97, 100] that the high-entropy (HE) stabilized the solid-solution is located at $\Omega \geq 1.1$ and $\delta_r \leq 6.6\%$. In accordance with the Hume-Rothery rules for binary substitutional solid solutions, the solvent and solute should have the same valency and similar electronegativity. But for the $\text{Al}_x\text{CrCuFeMnNi}$ system, the electronegativity difference (8.035 % - 8.160 %) and VEC difference (23.91 % - 33.13 %) are quite high, which might be the cause of the multi-phase structure formation.

Table 7 Parameters of ΔS_{mix} , ΔH_{mix} , Ω , δ_r , VEC, δ_χ , and δ_v for the $\text{Al}_x\text{CrCuFeMnNi}$ alloys

Alloys	ΔS_{mix} (J/K·mol)	ΔH_{mix} (kJ/mol)	T_m (K)	Ω	δ_r (%)	VEC	δ_χ (%)	δ_v (%)
$\text{Al}_{0.1}\text{CrCuFeMnNi}$	13.92	1.646	1,704	14.41	2.138	8.294	8.035	23.91
$\text{Al}_{0.3}\text{CrCuFeMnNi}$	14.43	-0.271	1,675	89.19	3.183	8.094	8.105	27.07
$\text{Al}_{0.8}\text{CrCuFeMnNi}$	14.87	-3.971	1,611	6.032	4.519	7.655	8.160	33.13

4.4 $\text{Al}_{0.3}\text{CoCrFeNi}$

The $\text{Al}_{0.3}\text{CoCrFeNi}$ HEA belongs to the $\text{Al}_x\text{CoCrFeNi}$ system, which is one of the most well-developed and refined HEA systems. The microstructure of $\text{Al}_{0.3}\text{CoCrFeNi}$ is studied by transmission-electron microscopy (TEM), shown in Figure 8. It shows that $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) has a uniform microstructure. In other words, all chemical elements, including Al, Co, Cr,

Fe, and Ni, are distributed homogeneously. It suggests that no precipitation or chemical segregation forms and separates from the matrix during processing.

The selected-electron diffraction pattern shows that $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) possesses a single FCC structure. These results are consistent with the thermodynamic prediction that the main structure of $\text{Al}_{0.3}\text{CoCrFeNi}$ at room temperature is a single FCC phase.

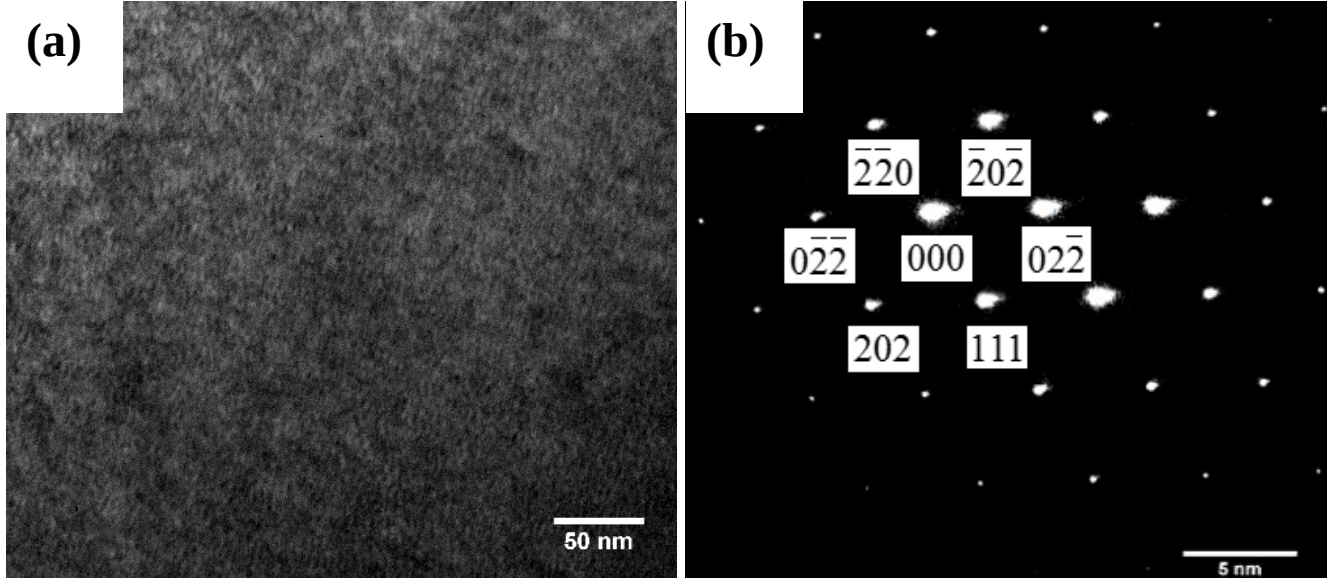


Figure 34 TEM images and selected-area electron diffraction pattern of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed)

4.4.1 Structure Stability of $\text{Al}_{0.3}\text{CoCrFeNi}$ after Hot Compression

The structures of $\text{Al}_{0.3}\text{CoCrFeNi}$ after hot compression were examined, using high-energy synchrotron X-ray in a transmission mode on beamline ID6-C, Advanced Photon Source, Argonne National Laboratory, IL. The test samples are $\text{Al}_{0.3}\text{CoCrFeNi}$ after RT compression, $\text{Al}_{0.3}\text{CoCrFeNi}$ after 550 °C compression, and $\text{Al}_{0.3}\text{CoCrFeNi}$ after 600 °C compression. The related results are shown in Figure 9. From Figure 9, we can learn that the hot compression at 550 °C and 600 °C cannot change the crystal structure of $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs. This phenomenon indicates the structure of $\text{Al}_{0.3}\text{CoCrFeNi}$ are stable under the influence of both high temperature and stress, which probably is the result of sluggish effect in HEAs.

In order to further study the microstructural stability, the structure of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-

HIPed) was investigated by neutron diffraction at high temperatures ranging from 800 °C to the melting temperature. The in-situ neutron-diffraction patterns (Figure 10) show that $\text{Al}_{0.3}\text{CoCrFeNi}$ (FCC) has a single-phase structure from RT to melting temperature. With the known d-spacing, the lattice parameter of $a = 3.57\text{\AA}$ can be calculated. After comparing the neutron-diffraction patterns at different temperatures, we can learn that the microstructure of $\text{Al}_{0.3}\text{CoCrFeNi}$ is very stable from 800 °C to the melting temperature (around 1,400 °C).

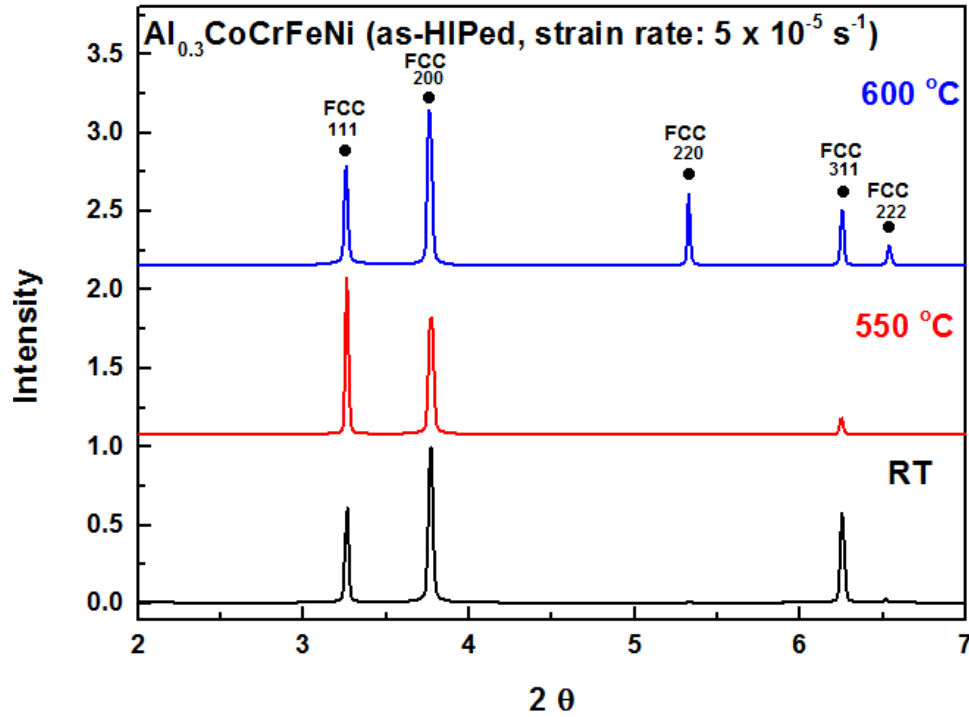


Figure 35 Synchrotron X-ray diffraction pattern of $\text{Al}_{0.3}\text{CoCrFeNi}$ after compression tests at RT, 550 °C, and 600 °C at a strain rate of $5 \times 10^{-5} \text{ s}^{-1}$

4.4.2 Local Structure Characteristics of $\text{Al}_{0.3}\text{CoCrFeNi}$

In single-phase HEAs, the lattice is locally distorted because of the occupation of the same crystallographic sites by atoms with different sizes, and this local distortion effect is an essential strengthening mechanism for the single-phase HEAs [2]. To describe the local lattice distortion on the atomic level, the atomic-level stress is introduced. The atomic-level stress was conceived by Egami [102] to describe the local structure (i.e., atomic cage surrounding atoms) by means of the

atomic pair distribution function (PDF) analysis of synchrotron and neutron diffraction data. The reduced pair distribution function, $G(r)$, is obtained through the Fourier transformation of the X-ray or neutron structure function, $S(Q)$:

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ \quad (11)$$

where r is the inter-atomic distance, and Q is the scattering vector.

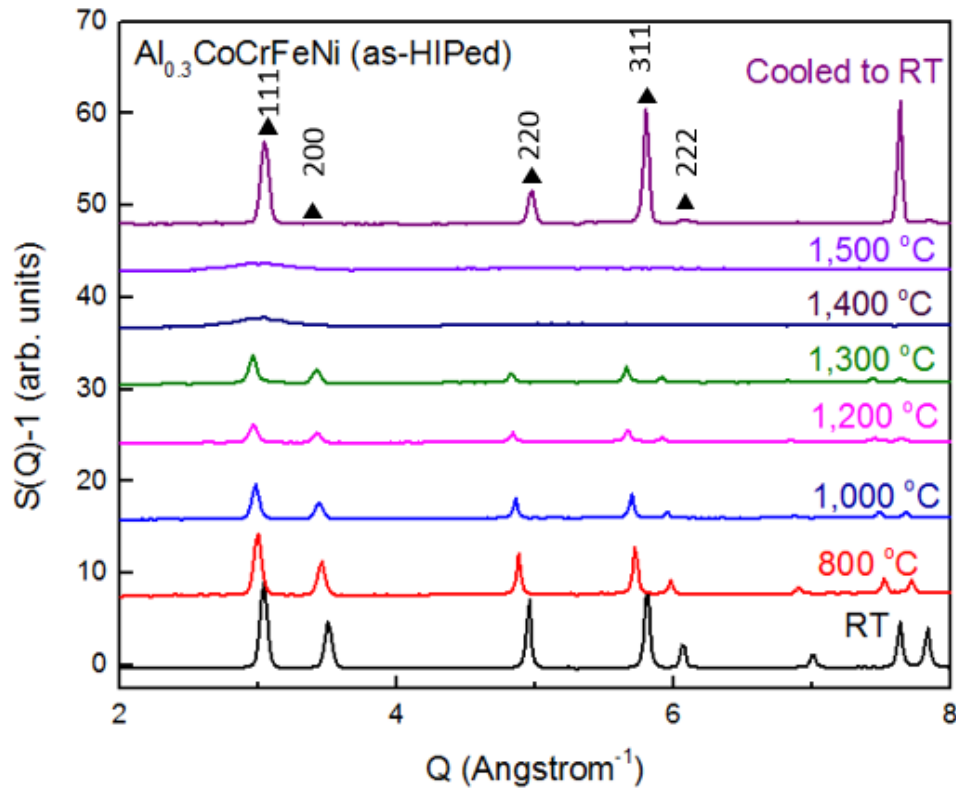


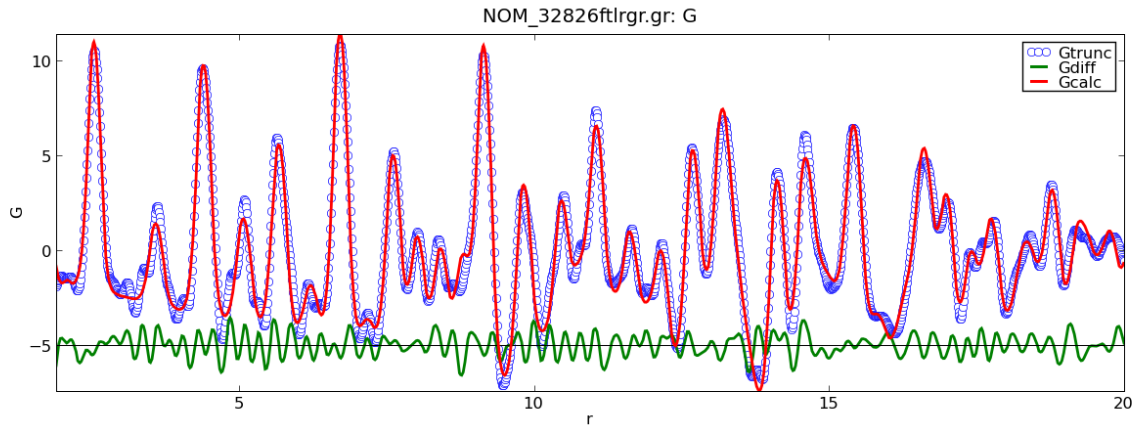
Figure 36 The neutron patterns of $\text{Al}_{0.3}\text{CoCrFeNi}$ from RT to melting temperature.

The atomic-level stresses of two kinds of HEAs, ZrNbHf and $\text{Al}_{1.3}\text{CoCrCuFeNi}$, are different and unique, compared to other conventional crystalline alloys and amorphous materials [90, 103]. For ZrNbHf HEA, the difference between the experimental and the calculated PDF is particularly significant for the second peak (shown by a black arrow) of the PDF. The strong

broadening of the second peak implies that locally, the lattice becomes distorted away from the BCC structure. For the distance, $r > 0.4$ nm, the PDFs calculated using these thermal factors agree well with the experimental PDFs [103]. However, for multi-phase $\text{Al}_{1.3}\text{CoCrCuFeNi}$ HEAs, the observed PDF matches well with the ideal model at large distances, $r > 1$ nm, as well. The greatest mismatch occurs when the distances is less than 1 nm [90]. Even though the atomic level stresses of two kinds of HEAs have different characteristics, the results for both HEAs testify local lattice distortions due to different atomic sizes in the solid solution.

To describe the local structure, on the atomic level, the experimental and calculated atomic pair distribution function (PDF) of the neutron-diffraction data of $\text{Al}_{0.3}\text{CoCrFeNi}$ at RT has been studied (Figures 37a and 37b). The results for $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-forged) testify local lattice distortions due to different atomic sizes in the solid solution.

(a)



(b)

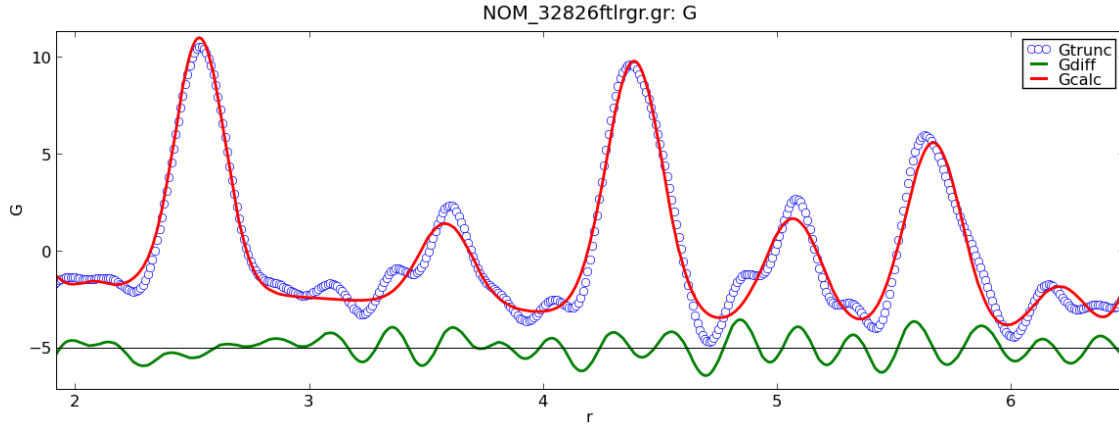


Figure 37 The pair-distribution function (PDF) of neutron patterns of $\text{Al}_{0.3}\text{CoCrFeNi}$ at RT

4.4.3 Elemental Distribution within $\text{Al}_{0.3}\text{CoCrFeNi}$ HEA on the Atomic Scale

On the atomic level, three-dimensional atomic probe tomography (3D-APT) is a good tool to map the nano-scale distribution of alloying elements. Related work has been conducted in $\text{Al}_{0.5}\text{CoCrCuFeNi}$ [86], AlCoCrCuFeNi [87-89], $\text{Al}_{1.3}\text{CoCrCuFeNi}$ [90], AlCrCuFeNiZn [91], AlCoCrFeNi [55], and CoCrFeMnNi [34, 92, 93] HEAs. The CoCrFeMnNi and $\text{Co}_{0.25}\text{Co}_{0.1}\text{Fe}_{2}\text{Mn}_{1.35}\text{Ni}_{1.3}$ HEAs were proved to be true solid solutions down to the atomic scale by APT, since there is no segregation or enrichment observed on the atomic scale [34, 92, 93]. In $\text{Al}_{0.5}\text{CoCrCuFeNi}$, obvious chemical segregation on the atomic scale is observed by APT. The Cu-rich and $\text{FeCoCr}(\text{Ni})$ -rich domains are alternately distributed in $\text{Al}_{0.5}\text{CoCrCuFeNi}$ [86]. For AlCoCrCuFeNi and $\text{Al}_{1.3}\text{CoCrCuFeNi}$, there are three phases, B2 (Al-Ni-enriched), BCC (Cr-Fe-enriched), and FCC (Cu-rich) [87, 88, 90]. The nature of interfaces between constituent phases in the AlCoCrCuFeNi HEA is studied by APT. The width transition region between the B2 and disordered BCC phases is 1.5 - 7 nm [87, 88]. For AlCoCrFeNi , two phases, B2 (Al-Ni-enriched) and BCC (Cr-Fe-enriched), are present [55]. Within the B2 region, all elements show quite a homogeneous distribution. But within the BCC region, the Fe- and Cr-clusters exhibit the intertwined morphology. The fluctuation is larger than that of AlCoCrCuFeNi [55].

In the present work, shown in Figure 38, the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) HEA was proved to

be true solid solutions down to the atomic scale by APT, since there is no segregation or enrichment observed on the atomic scale.

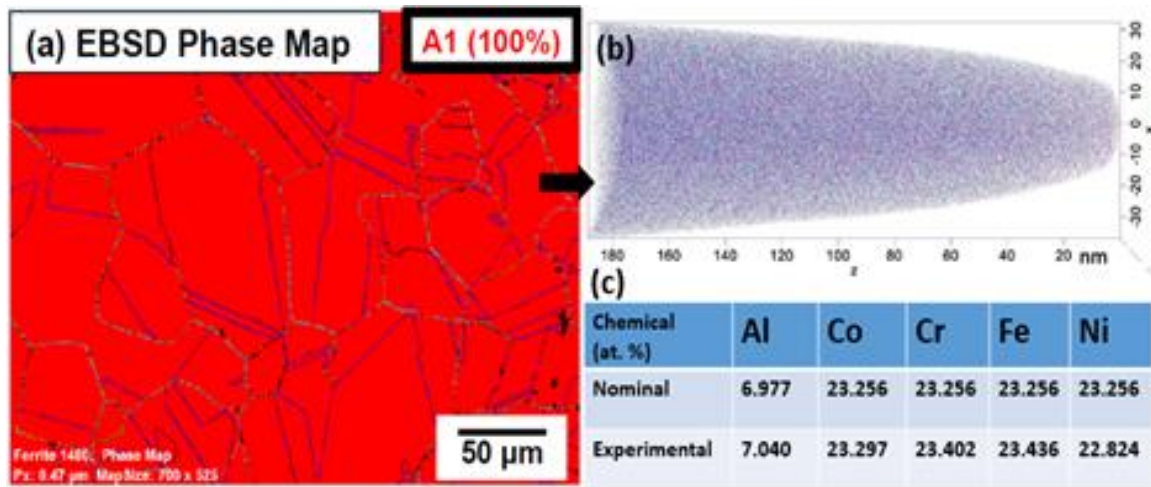


Figure 38 The atomic probe tomography (APT) and related chemical compositions of $\text{Al}_{0.3}\text{CoCrFeNi}$

The 3D APT is used to map the nano-scaled distribution of alloying elements in $\text{Al}_{0.3}\text{CoCrFeNi}$ after the heat treatment at 1,250 $^{\circ}\text{C}$ for 72 h, shown in Figure 39. All elements distribute evenly. There is no segregation or enrichment observed on the atomic scale.

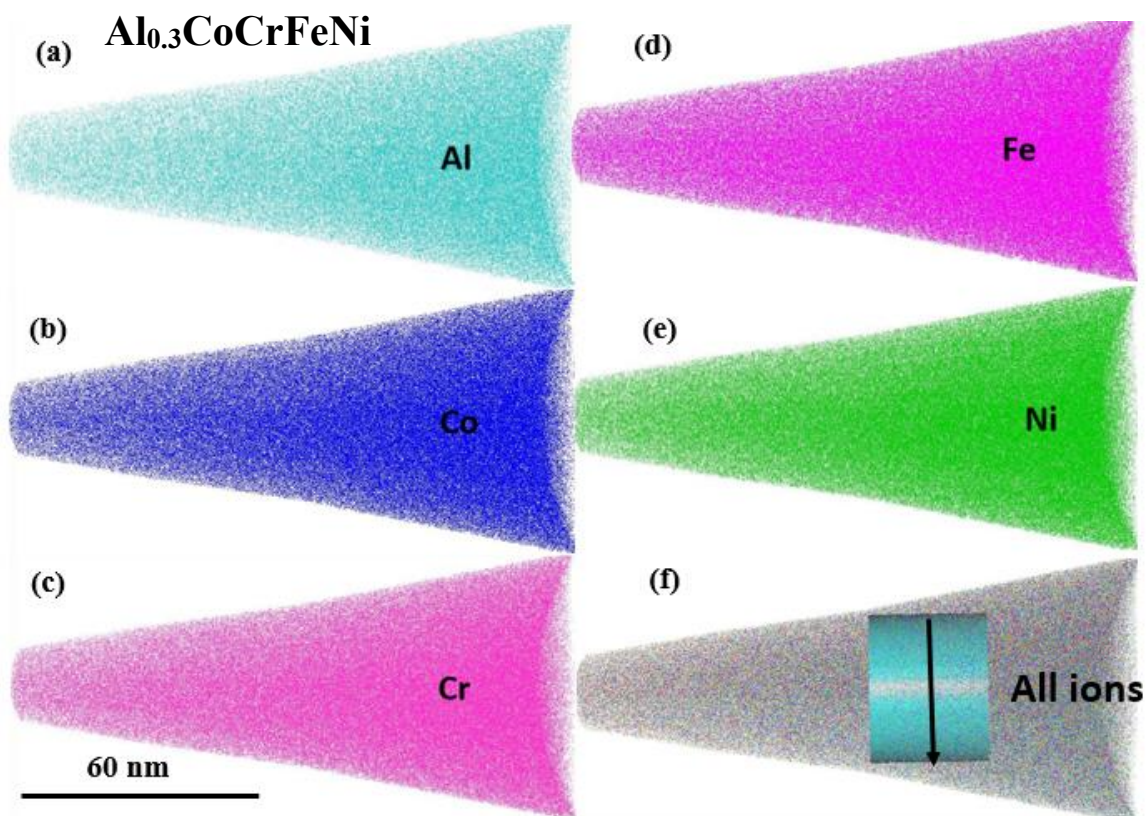


Figure 39 The APT data of $\text{Al}_{0.3}\text{CoCrFeNi}$ after heat-treatment at 1,250 °C for 72 h. The 3D reconstruction of Al (a), Co (b), Cr (c), Fe (d), Ni (e), and all ions (g) atomic positions.

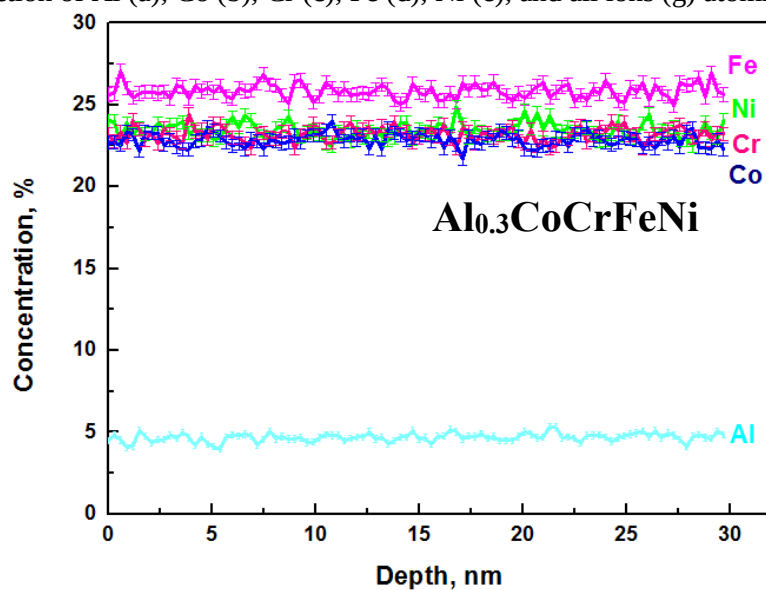


Figure 40 Concentration–depth profiles of all alloying elements within $\text{Al}_{0.3}\text{CoCrFeNi}$ along the arrow shown in Figure 39f. The error bars represent the 2σ standard deviation

Strictly, the experimental frequency distribution of nanoscaled atomic clusters in the 3D-atom-probe data is quantified and compared with the classic binomial-frequency distribution, $f(n)$ [95]. The deviation of the experimentally-measured distribution from the binomial can be quantified by means of the normalized χ^2 statistics, μ [95]. μ can track the changes in the degree of solute segregation. When μ is equal to 0, it means a random distribution. But when μ is 1, it means a complete association in the occurrence of the solute atoms.

$$f(n) = \binom{n}{k} p^k (1-p)^{n-k} \quad (12)$$

where n is the number of solute atoms.

$$\chi^2 = \sum_{n=0}^N \frac{(e(n) - f(n))^2}{f(n)} \quad (13)$$

where $e(n)$ is the number of blocks containing n solute atoms in the experimental data.

$$0 \leq \mu = \sqrt{\frac{\chi^2}{N + \chi^2}} \leq 1 \quad (14)$$

The experimentally-measured frequency distributions of the Al, Co, Cr, Fe, and Ni, are indicated by black dots in Figure 41. Meanwhile, the experimental frequency distribution is compared with the classic binomial-frequency distribution, $f(n)$ [95], shown by red curves in Figure 42.

The μ values, calculated by Equation (7), of Al, Co, Cr, Fe, and Ni are 0.0889, 0.0424, 0.0667, 0.0561, and 0.1303, respectively. Since the μ values are relatively small, it means the distribution of elements within $\text{Al}_{0.3}\text{CoCrFeNi}$ after the heat treatment at 1,250 °C for 72 h is random.

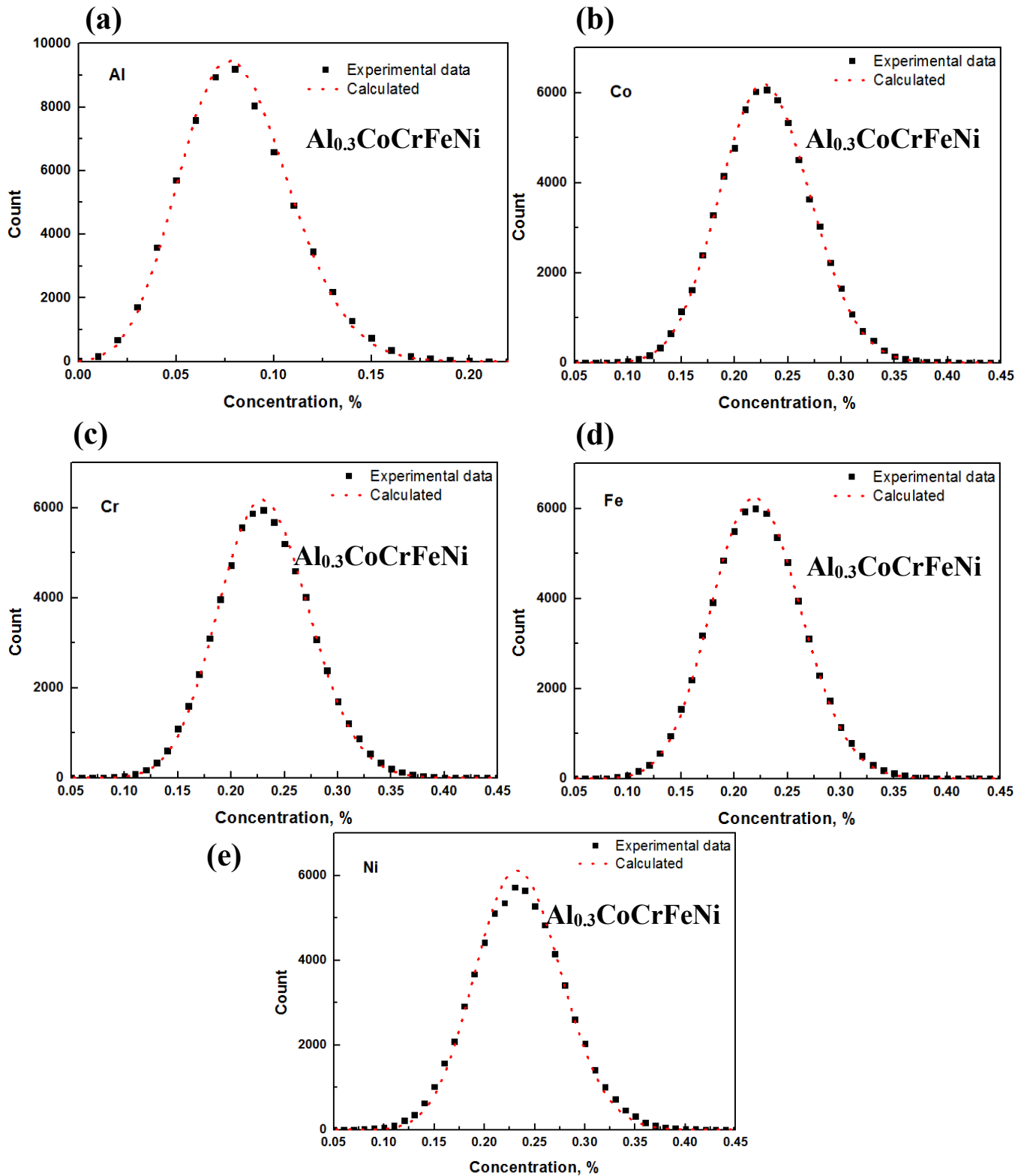


Figure 41 The frequency distributions of Al (a), Co (b), Cr (c), Fe (d), and Ni (e) within the $\text{Al}_{0.3}\text{CoCrFeNi}$ after the heat treatment at 1,250 °C for 72 h. The black dots are experimental data, while the red curve is the classic binomial frequency distribution, $f(n)$

4.4.4 Heat-treatment (700 °C for 500 h) Effects on the Structures of Al_{0.3}CoCrFeNi.

As we reported in former quarterly reports, the Al_{0.3}CoCrFeNi alloy is FCC single-phase HEA and exhibits low yielding strength (around 170 MPa). In order to increase the yielding stress of the Al_{0.3}CoCrFeNi HEA, we tried different heat-treatments, with the assistance of thermodynamic modeling. The microstructure after ageing at 700 °C for 500 h is shown in Figure 42. A second phase appears in the FCC matrix. Since the width of the second phase is around 100 - 200 nm, it is hard to get the chemical distribution by the normal EDS on the SEM, which can detect the chemical composition on μm -scale.

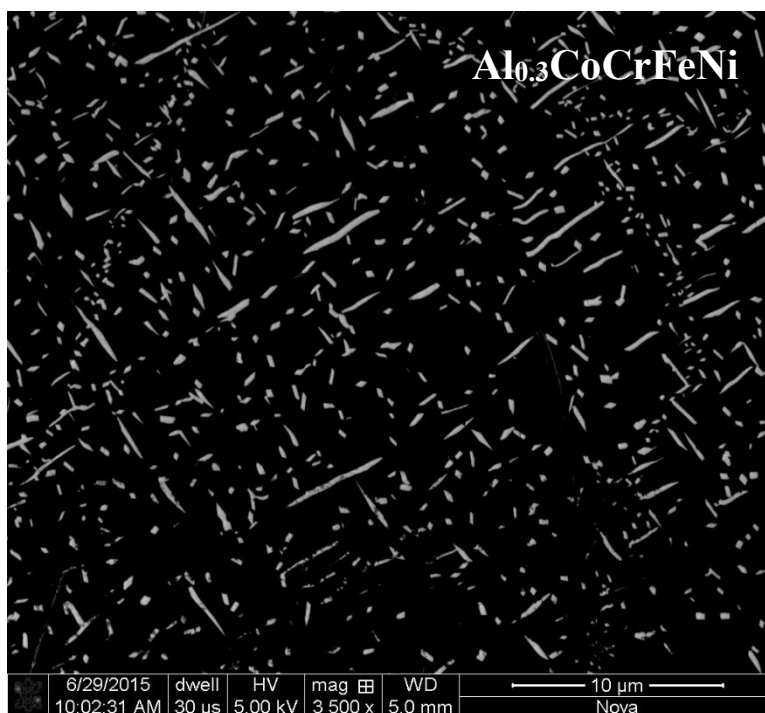
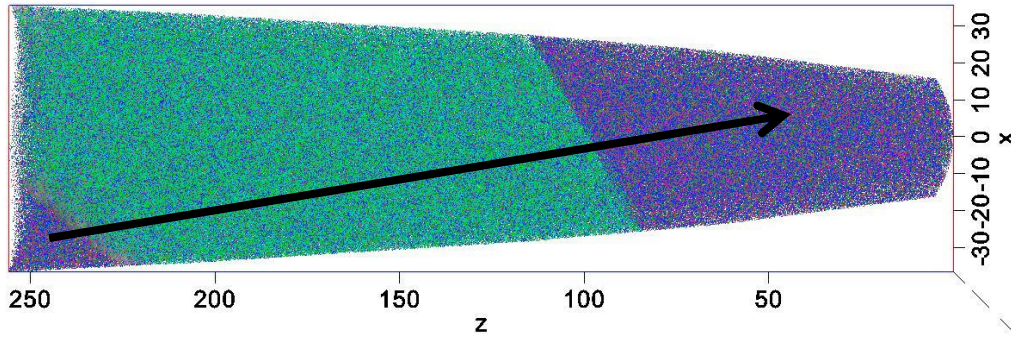


Figure 42 SEM image of Al_{0.3}CoCrFeNi after heat-treatment at 700 °C for 500 h. Second phase appears in the FCC matrix.

Then the APT technique is chosen to study the elemental distribution on the nanometer level. The APT of the Al_{0.3}CoCrFeNi HEA after ageing at 700 °C for 500 h is shown in Figure 43a. The dimension of the second phase, ~ 140 nm, is consistent with the SEM results. The concentration profile of all alloying elements within both the second phase and the matrix is shown in Figure 43b. The results show that the second phase is the Al-Ni-rich B2 phase.

(a)

$\text{Al}_{0.3}\text{CoCrFeNi}$



(b)

$\text{Al}_{0.3}\text{CoCrFeNi}$

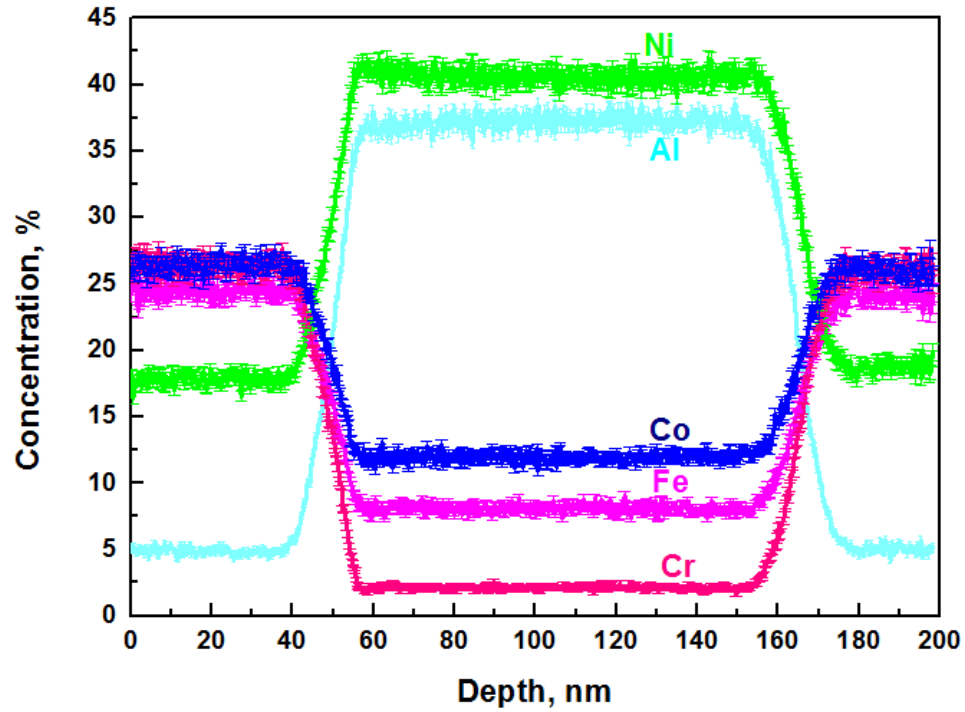


Figure 43 (a) The APT of $\text{Al}_{0.3}\text{CoCrFeNi}$ after heat-treatment at 700 °C for 500 h and (b) Concentration–depth profiles of all alloying elements within $\text{Al}_{0.3}\text{CoCrFeNi}$ along the arrow shown in a. The error bars represent the 2σ standard deviation

4.5 Cold-rolling and Following Annealing Effect on the Microstructure of $\text{Al}_{0.1}\text{CoCrFeNi}$

Cold rolling is a process, by which the sheet metal or strip stock is introduced between rollers and then compressed and squeezed. The amount of strain introduced determines the hardness and other material properties of the finished product. The cold rolling and following annealing processes are successful to reduce the grain size of $\text{Al}_{0.1}\text{CoCrFeNi}$, shown in Figure 21. Before cold rolling, the grain size is more than 5 mm. However, after cold rolling, the grain size is reduced to around 10 μm . The effect of cold rolling on reducing the grain size is remarkable for $\text{Al}_{0.1}\text{CoCrFeNi}$ HEAs.

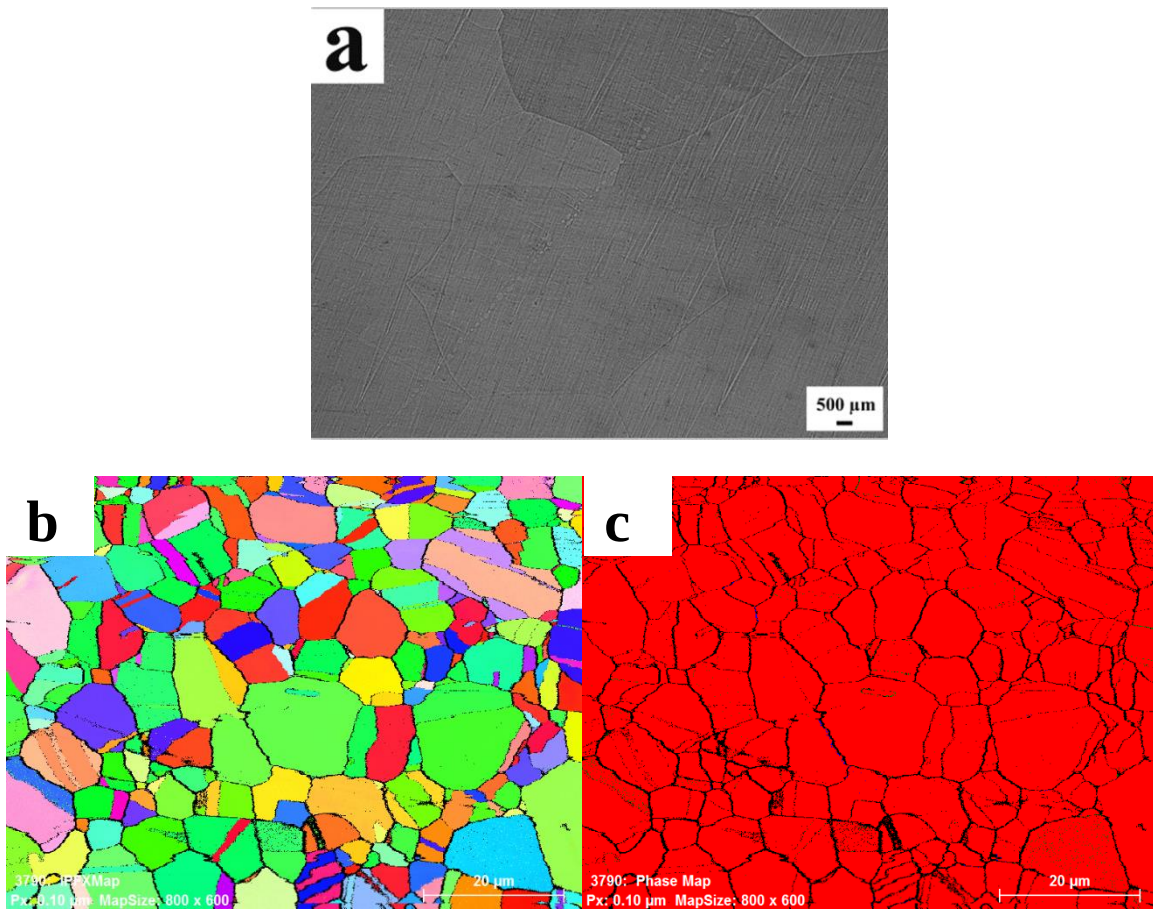


Figure 44 Microstructure of $\text{Al}_{0.1}\text{CoCrFeNi}$. (a) OM image before cold-rolling, (b) EBSD image after cold-rolling, and (c) Phase map after cold-rolling.

Furthermore, in order to check whether the cold-rolling could affect the microstructure of $\text{Al}_{0.1}\text{CoCrFeNi}$ or not, we conducted high-energy synchrotron experiments at Advanced Photon Source, Argonne National Laboratory. Sample heated in the flowing Ar to 1,000 °C using the Linkham TS1500 furnace. The heating and cooling rates are around 50°C/min. Exposure time is 0.25 s, while hold time is around 2 min. The experimental setup and typical diffraction pattern are shown in Figure 45.

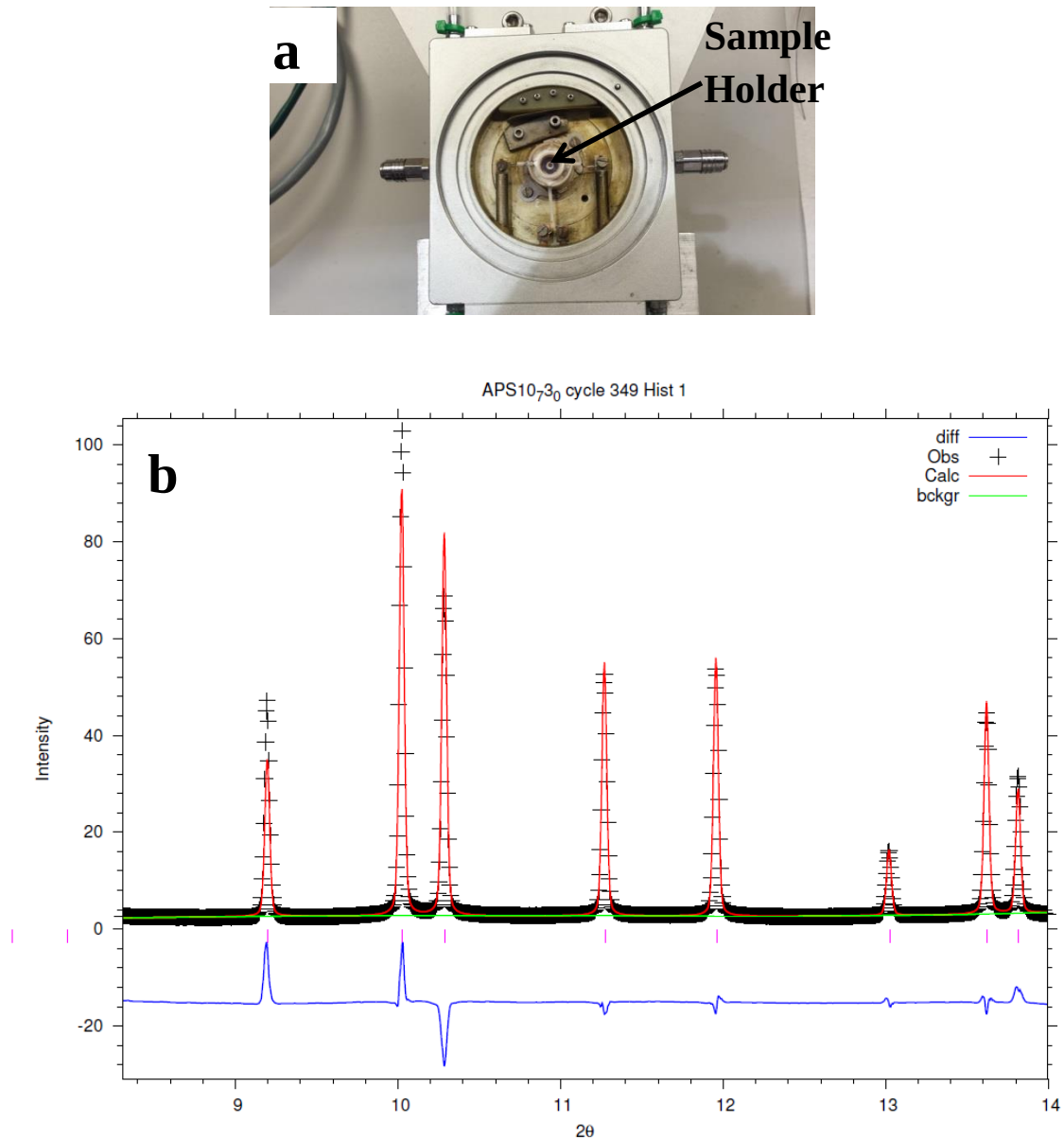


Figure 45 Diffraction pattern of $\text{Al}_{0.1}\text{CoCrFeNi}$ (cold-rolled + annealed). (a) Experimental setup and (b) typical diffraction pattern. The symbols are the experimental results, while the red curve is calculated based on the perfect FCC polycrystalline structure. The blue curve shows the difference between experimental results and calculations.

The data converted to XY data files using the FIT2D software, shown in Figure 23. Only FCC peaks seen. At high structural factor, Q , the shift in peak position can be observed.

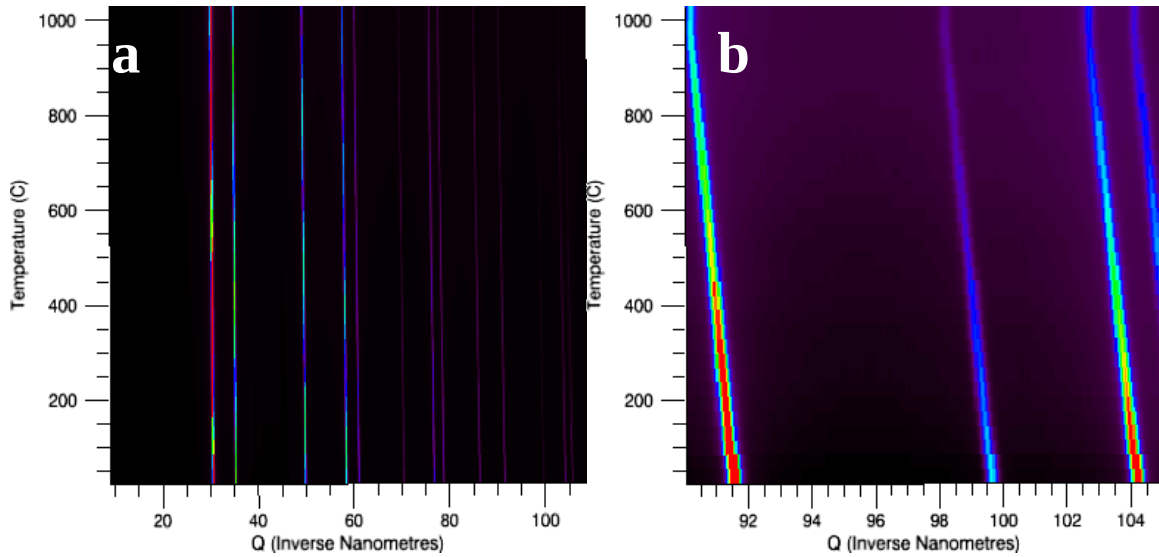


Figure 46 2D diffraction pattern of $\text{Al}_{0.1}\text{CoCrFeNi}$ at temperatures from room temperature to 1,000 °C. (a) at the full structural vector, Q , range and (b) at high Q range.

With the known d -spacing, the lattice parameter can be calculated. The evolution of lattice parameters for $\text{Al}_{0.1}\text{CoCrFeNi}$ as a function of temperature is shown in Figure 47. It indicates that nearly identical thermal expansions are observed for both the heating and cooling processes. The small shift during cooling appears to be a fitting uncertainty.

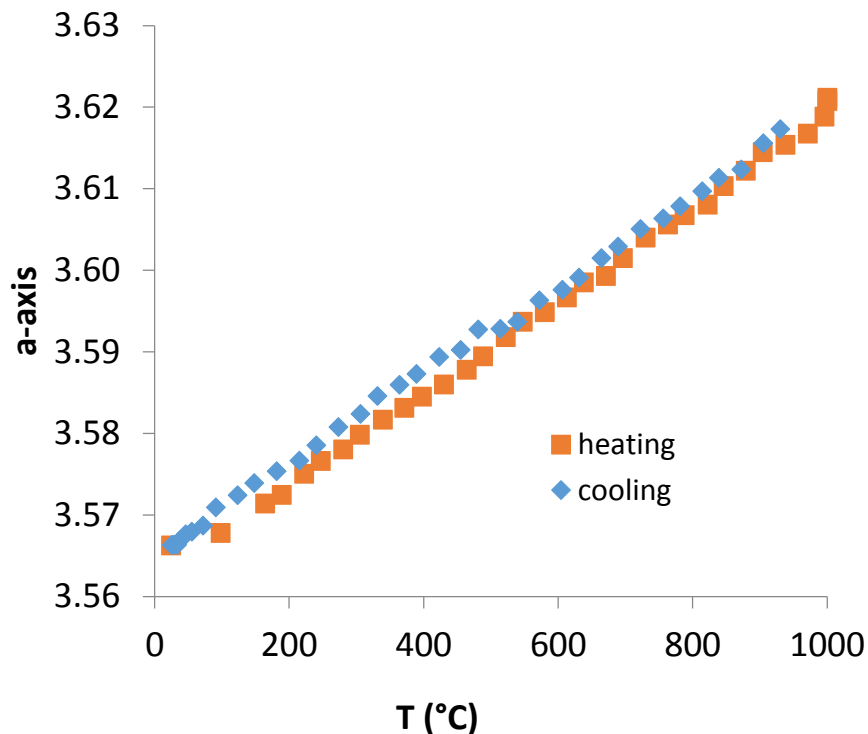


Figure 47 The lattice parameter evolution as a function of temperature for $\text{Al}_{0.1}\text{CoCrFeNi}$ at temperatures from room temperature to 1,000 °C in both heating and cooling processes.

In order to further study the microstructural stability on a large scale, the structure of $\text{Al}_{0.1}\text{CoCrFeNi}$ was investigated by neutron diffraction [90] at high temperatures ranging from 800 °C to the melting temperature. The in-situ neutron-diffraction patterns (Figure 48) show that $\text{Al}_{0.1}\text{CoCrFeNi}$ has a single-phase structure from room temperature to melting temperature. After comparing the neutron-diffraction patterns at different temperatures, we can learn that the microstructure of $\text{Al}_{0.1}\text{CoCrFeNi}$ is very stable from 800 °C to the melting temperature (around 1,400 °C).

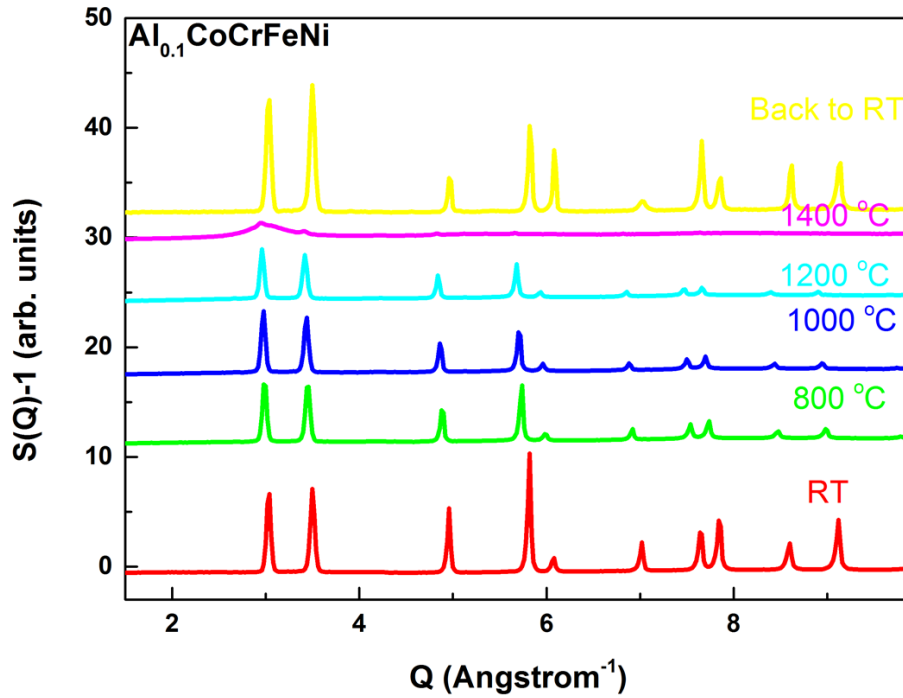


Figure 48 The neutron patterns of $\text{Al}_{0.1}\text{CoCrFeNi}$ from RT to melting temperature.

As reported in last quarterly report, the cold rolling and following annealing processes are successful to reduce the grain size of $\text{Al}_{0.1}\text{CoCrFeNi}$ from 5 mm to around 10 μm , while the structure of the cold-rolled $\text{Al}_{0.1}\text{CoCrFeNi}$ is still pure FCC. However, the cold-rolling and following annealing introduce twins into the matrix. APT is used to test the elemental distribution within twin (Figure 49) and without twin (Figure 50).

Figure 49 shows microstructures on the atomic level of $\text{Al}_{0.1}\text{CoCrFeNi}$ outside annealing twin. The inverse polar figure (a) and phase map (b) of $\text{Al}_{0.1}\text{CoCrFeNi}$ obtained by the EBSD measurements. The selected sample area includes a pure FCC phase. An atom map outside the twin region presents that the atomic distribution outside the twin is homogenous. The proximity histogram (Figure 49e), establishing atomic concentrations within the blue column along the back line in (d). Only small fluctuation is found.

Figure 50 shows microstructures on the atomic level of $\text{Al}_{0.1}\text{CoCrFeNi}$ within annealing

twin. The inverse polar figure (a) of $\text{Al}_{0.1}\text{CoCrFeNi}$ is obtained by the EBSD measurements. An atom map from twin region shows the atomic distribution within the twin is homogenous, and the proximity histogram (b), presenting atomic concentrations along the back line in (d). Compared with Figure 18e, the concentration of Cr is higher.

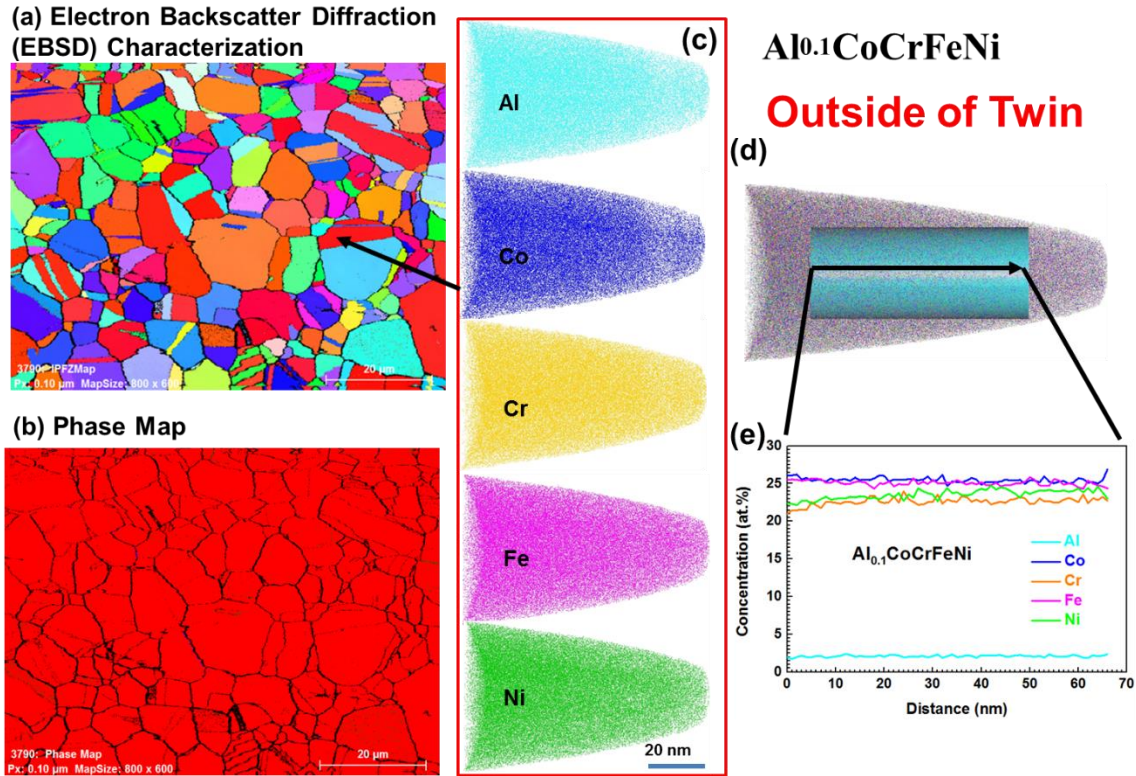


Figure 49 Room-temperature microstructures on the atomic level of $\text{Al}_{0.1}\text{CoCrFeNi}$ outside of annealing twin. The inverse polar figure (a) and phase map (b) of $\text{Al}_{0.1}\text{CoCrFeNi}$ obtained by the EBSD measurements. The selected sample area includes a pure FCC phase. Black lines represent grain boundaries. (c) An atom map from the FCC region shows the atomic distribution within the FCC phase homogenously, and the proximity histogram (e), presenting atomic concentrations along the back line in (d).

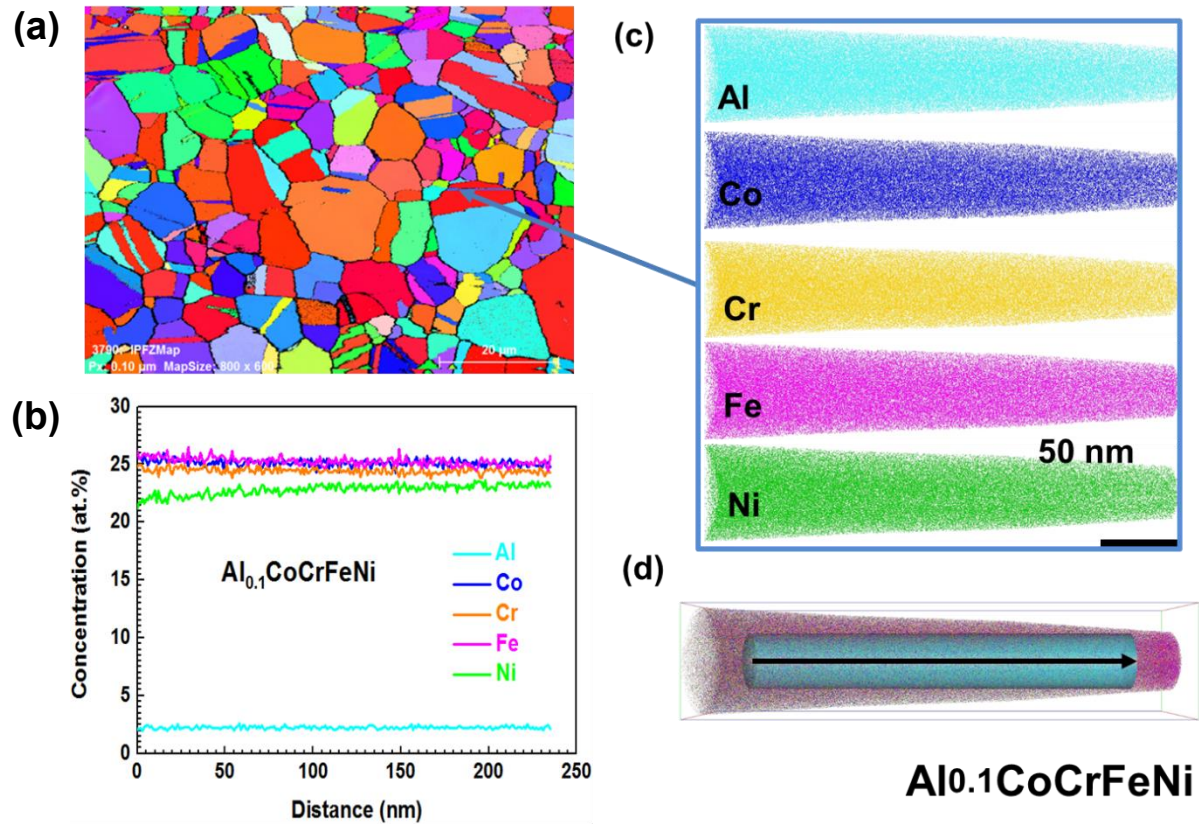


Figure 50 Room-temperature microstructures on the atomic level of $\text{Al}_{0.1}\text{CoCrFeNi}$ within annealing twin. Inverse polar figure (a) of $\text{Al}_{0.1}\text{CoCrFeNi}$ is obtained by the EBSD measurements. The selected sample area includes still the pure FCC phase. Black lines represent grain boundaries. (c) An atom map from the twin region shows that the atomic distribution within the twin is homogenous, and the proximity histogram (b), presenting atomic concentrations along the back line in (d).

5. TASK 3: MICROSTRUCTURAL CHARACTERIZATIONS

5.1 Al Effect on the Microstructures of $\text{Al}_x\text{CoCrFeNi}$

5.1.1 Room-temperature X-ray and Neutron Diffraction Studies

To obtain the phase types and fractions, both XRD and neutron profiles of $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$ samples are performed (Figure 51). In Figure 51a, the FCC (face-centered cubic, A1 structure) and BCC (a body-centered cubic structure, A2 structure) phases are shown clearly. Here A1 and A2 are the Strukturbericht designation as well as B2 in the following text. The lattice parameters can be derived from them as $a_{\text{fcc}} = 0.36009 \text{ nm}$ and $a_{\text{bcc}} = 0.28786 \text{ nm}$, for example, of the $\text{Al}_{0.5}$ sample.

Neutron scattering on $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$ was conducted at the ambient temperature, using aerodynamic levitation [104, 105]. The data were fit to the solid-solution FCC and BCC structures, too, denoted by circles and squares in Figure 51b, respectively. For all three alloys, $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$, the primary phase is identified as FCC solid solution. For $\text{Al}_{0.3}$, there is only the FCC phase, while both FCC and BCC phases are present at room temperature in $\text{Al}_{0.5}$ and $\text{Al}_{0.7}$ alloys. Compared to XRD results (Figure 51a), neutron diffraction patterns (Figure 51b) provide more information of super lattice, i.e., $\{100\}$, in the $\text{Al}_{0.7}$, which indicates that the main phases in $\text{Al}_{0.7}$ are the FCC and B2 (ordered BCC) phase, not the BCC phase.

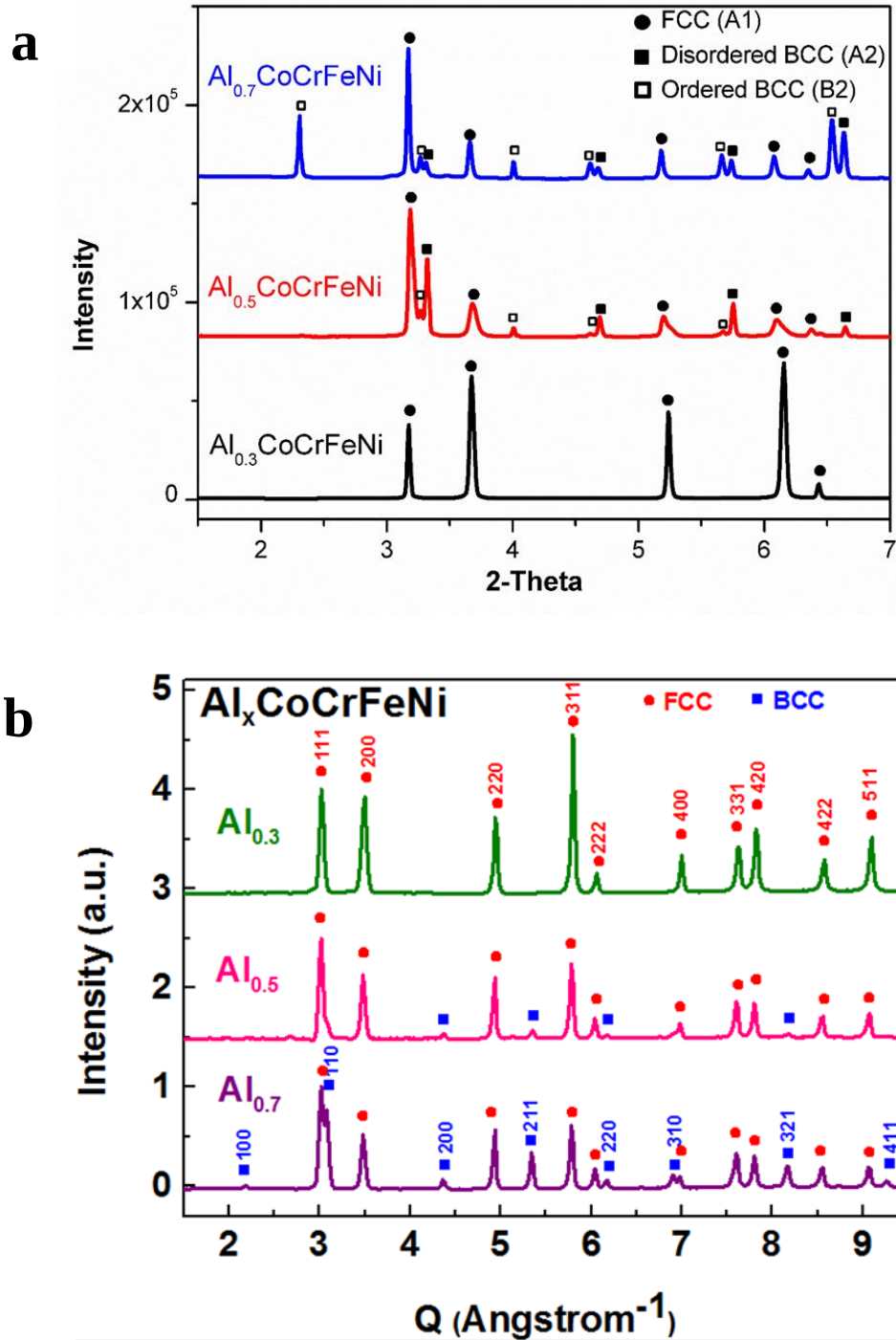


Figure 51 XRD (a) and neutron-diffraction (b) profiles of $\text{Al}_{0.3}\text{CoCrFeNi}$, $\text{Al}_{0.5}\text{CoCrFeNi}$, and $\text{Al}_{0.7}\text{CoCrFeNi}$ samples at room temperature (RT). Data were fit to the FCC and BCC/B2 structures, and the corresponding peaks are denoted by circles and squares, respectively. The primary phase is, therefore, identified as a FCC solid solution in all three alloys. However, except $\text{Al}_{0.3}$, both $\text{Al}_{0.5}$ and $\text{Al}_{0.7}$ have BCC phase.

5.1.2 Room-temperature SEM/EBSD/APT Microstructural Characterization

The morphologies, phase compositions, and phase fractions of both fcc and bcc phases in $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$ are obtained through electron backscattered diffraction images (EBSD), equipped with EDS, and APT techniques.

The EBSD phase map results (Figure 52) of The $\text{Al}_{0.3}$ sample show that $\text{Al}_{0.3}$ is almost a single solid-solution FCC phase. The mean grain size is larger than 600 μm . The $\text{Al}_{0.5}$ sample consists of around 98 volume-percent (vol. %) FCC phase and about a 2 vol. % BCC phase. The mean grain size of FCC grains decreased to around 40 μm . The bcc phase exists in both grains and along grain boundaries. The $\text{Al}_{0.7}$ sample consists of 64 vol. % dendritic FCC (red color in Figure 52c) and 36 vol. % interdendritic bcc phases (blue color in Figure 52c), 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 grains exists. Please note the EBSD cannot differentiate BCC and B2. There are annealing twins in the FCC phase, detected by EBSD in $\text{Al}_{0.3}$ (Figure 52d).

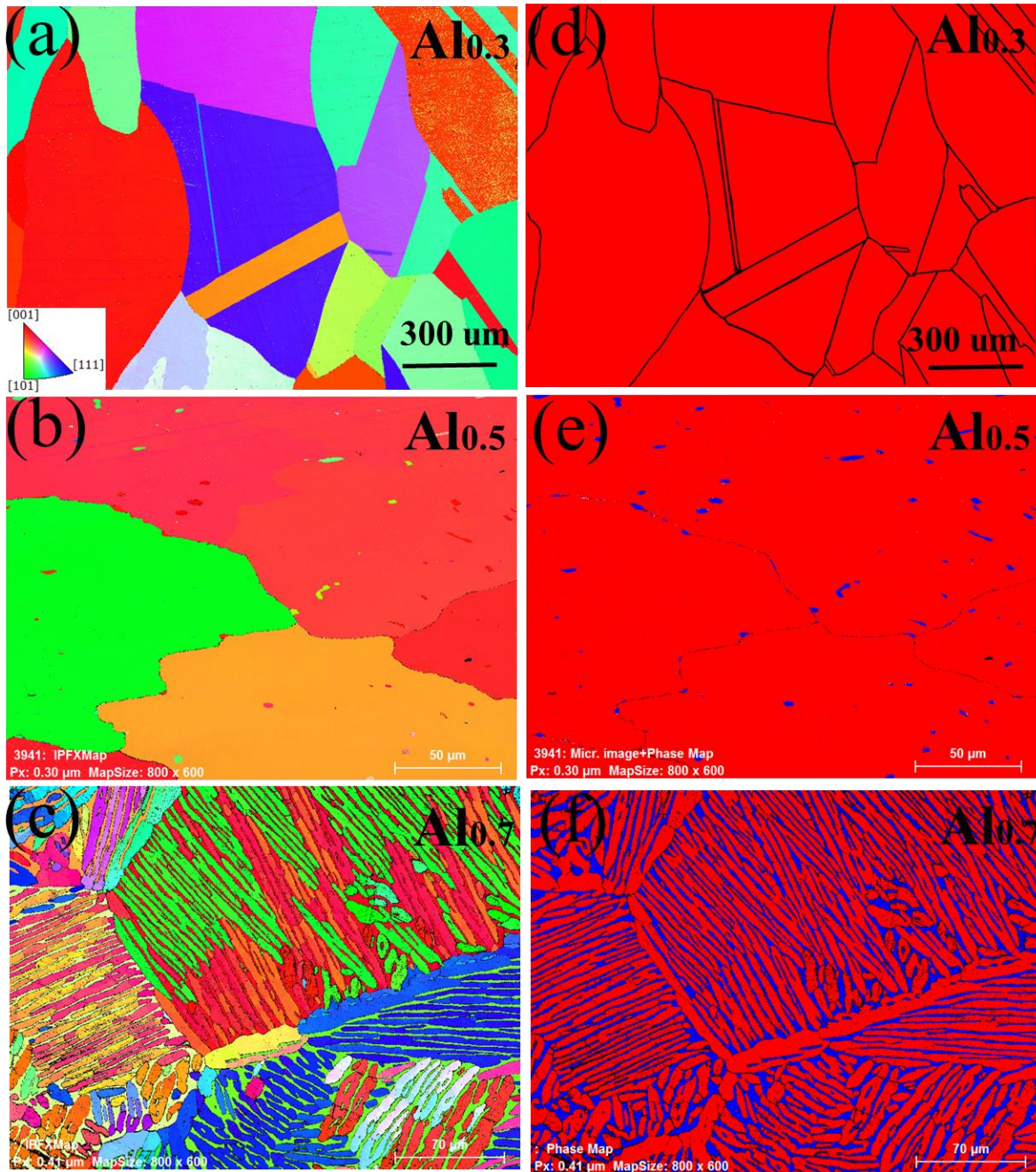


Figure 52 Phase-constitution maps obtained by EBSD measurements. The FCC phases (red) are almost 100%, 98%, 64% and the BCC phases (blue) 0%, 2%, and 36% in Al_{0.3} (a), Al_{0.5}, (b) and Al_{0.7} (c) samples, respectively. Black lines represent grain boundaries.

Figure 53 shows the room-temperature microstructures of both FCC phase and BCC phase at the atomic level of $\text{Al}_{0.5}$ alloy. An atom map (Figure 53b) lifted from the FCC region (a red region in Figure 53a) shows the atomic distribution within the fcc phase, which contains NiAl-rich nanoprecipitates (which will refer to the B2 phase). The below proximity histogram presents atomic concentrations across the fcc–nanoprecipitate interface. An atom map (Figure 53c) from the bcc / B2 region (a blue region in Figure 53a) shows the atomic distribution within the bcc / B2 phase, which contains Cr-rich nanoprecipitates (which will refer to bcc phase, combined both APT and TEM results). The below proximity histogram shows atomic concentrations across the B2–Cr-rich nanoprecipitate interface. The chemical composition of the bcc phase is $\text{Al}_{33}\text{Ni}_{35}\text{Co}_{18}\text{Fe}_{10}\text{Cr}_4$, which means the BCC phase is actually B2 phase (ordered BCC phase). Thus, APT is efficient to reveal the nanostructures within FCC and B2 phases in $\text{Al}_{0.5}$.

Alloy composition : $\text{Al}_{0.5}\text{CoCrFeNi}$

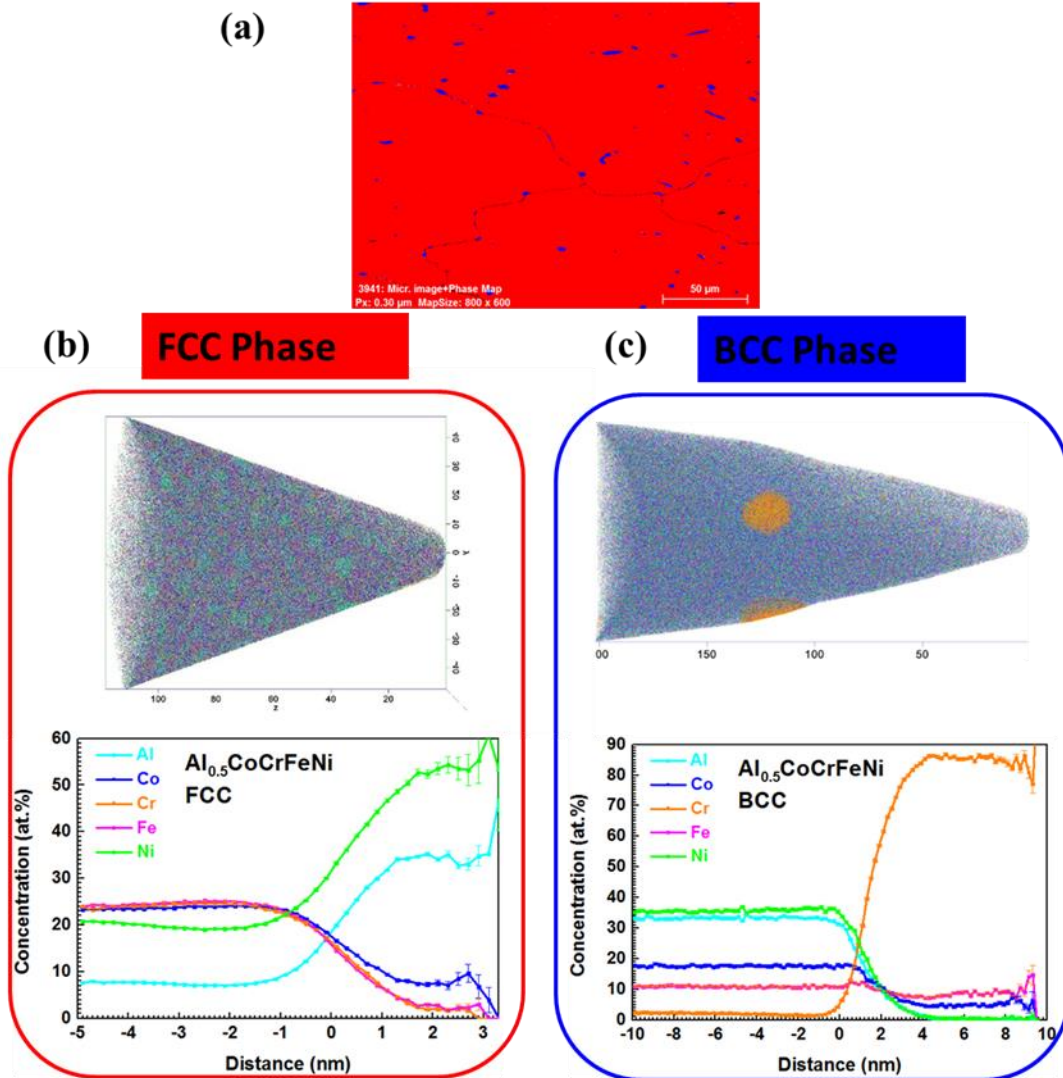


Figure 53 Room temperature microstructures on the atomic level of $\text{Al}_{0.5}\text{CoCrFeNi}$. (a) Phase map of $\text{Al}_{0.5}\text{CoCrFeNi}$ obtained by EBSD measurements. The selected sample area includes the FCC region (red) and the BCC region (blue). Black lines represent grain boundaries. (b) An atom map from the FCC region shows the atomic distribution within the FCC phase, which contains NiAl-rich nanoprecipitates, and the below proximity histogram, presenting atomic concentrations across the FCC–nanoprecipitate interface. (c) An atom map from the BCC region shows the atomic distribution within the bcc phase, which contains Cr-rich nanoprecipitates, and the below proximity histogram, presenting atomic concentrations across the BCC–nanoprecipitate interface.

5.2 Microstructure Evolution during Creep

The stress vs. strain rate of $\text{Al}_{0.3}\text{CoCrFeNi}$, compared with conventional alloys, on a double logarithmic scale at 700 °C is shown in Figure 54. The creep behavior of $\text{Al}_{0.3}\text{CoCrFeNi}$ is superior to conventional alloys. For the case at 100 MPa for example, the creep rate of $\text{Al}_{0.3}\text{CoCrFeNi}$ is two orders of magnitude slower than P92 and P122 alloys.

In order to study the microstructural evolution during creep test, the creep tests at 700 °C and 35 MPa are interrupted at 50 hours, 100 hours, 150 hours, and 250 hours. The related curves of strain as a function of crept time are shown in Figure 55. Even though the sample (c) has a larger strain fluctuation, the slope of samples a, b, and c is almost the same, $4.35 \times 10^{-9} \text{ s}^{-1}$.

APT is conducted to study the elemental distribution and segregation during the creep tests. Figure 56 shows the microstructures on the atomic level of $\text{Al}_{0.3}\text{CoCrFeNi}$ after creep test at 700 °C and 75 MPa for 50 hours. The upper right figure of $\text{Al}_{0.3}\text{CoCrFeNi}$ is obtained by SEM measurements. We can found granular precipitates around the grain boundary. An atom map from the grain boundary region shows the atomic distribution, which contains Cr-rich precipitates, and down left proximity histogram, presenting atomic concentrations across the interface between matrix and Cr-rich precipitates.

Figure 57 presents the microstructures on the atomic level of $\text{Al}_{0.3}\text{CoCrFeNi}$ after the creep test at 700 °C and 75 MPa for 100 hours. The upper right figure of $\text{Al}_{0.3}\text{CoCrFeNi}$ is obtained by SEM measurements. Even though we cannot find precipitates within grains using SEM within grain, an atom map shows the atomic distribution of Al, Co, Cr, Fe, and Ni, which contains NiAl-rich precipitates. The proximity histograms present the Al concentration of small precipitate is lower than that of larger precipitates.

The microstructures on the atomic level of $\text{Al}_{0.3}\text{CoCrFeNi}$ after creep test at 700 °C and 75 MPa for 150 hours are shown in Figure 58. The upper right figure of $\text{Al}_{0.3}\text{CoCrFeNi}$ is obtained by SEM measurements. SEM image shows large granular precipitates along the grain boundary and

needle-shape precipitates within the grain. The atom map shows the atomic distributions of Al, Co, Cr, Fe, and Ni, which contains also NiAl-rich precipitates. The proximity histograms present the Al concentration of precipitate is similar to that of large precipitates in Figure 59.

The microstructures on the atomic level of $\text{Al}_{0.3}\text{CoCrFeNi}$ after the creep test at 700 °C and 75 MPa for 250 hours are presented in Figure 60. The SEM images show the needle-shape precipitates within grain. An atom map shows the atomic distribution of Al, Co, Cr, Fe, and Ni, which contains large NiAl-rich precipitates. The proximity histograms present the ratio of Ni and Al is close to 1, which indicates that the NiAl-rich precipitates is the B2 phase.

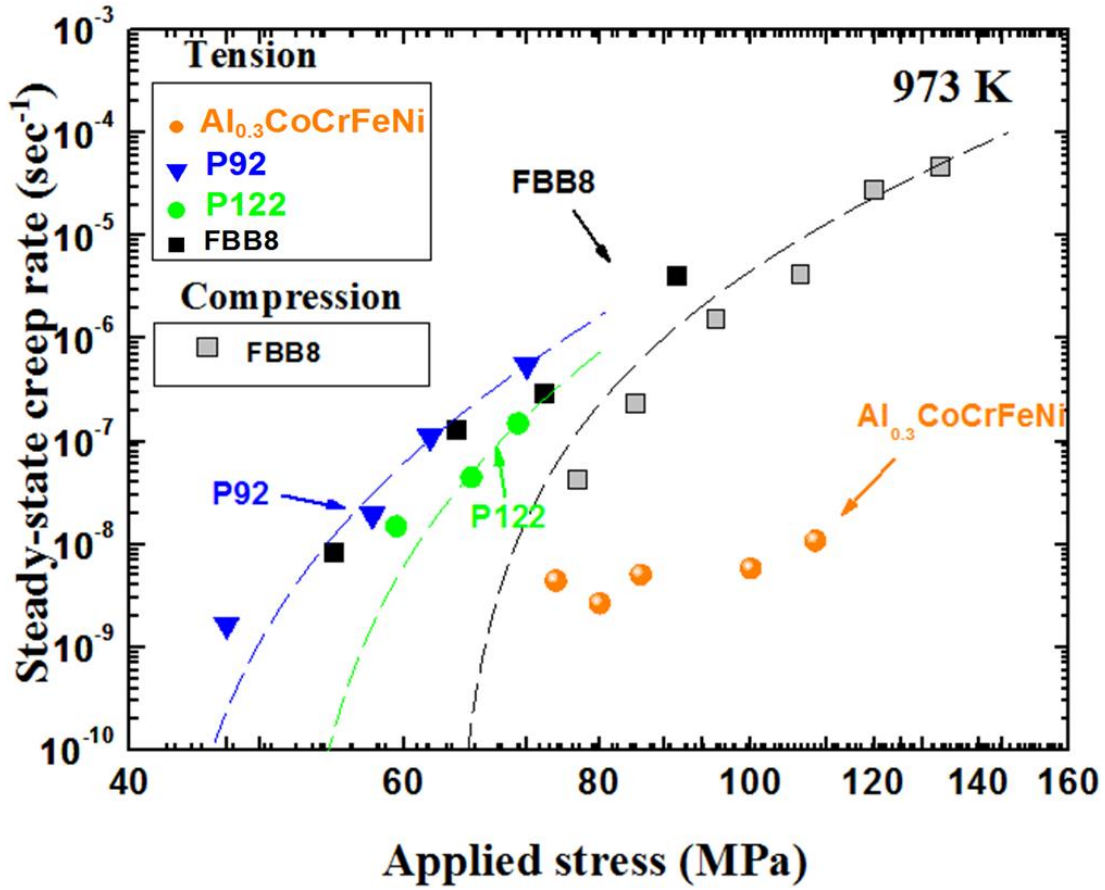


Figure 54 Minimum strain rate as a function of applied stress for the $\text{Al}_{0.3}\text{CoCrFeNi}$ at 700 °C, compared with conventional alloys.

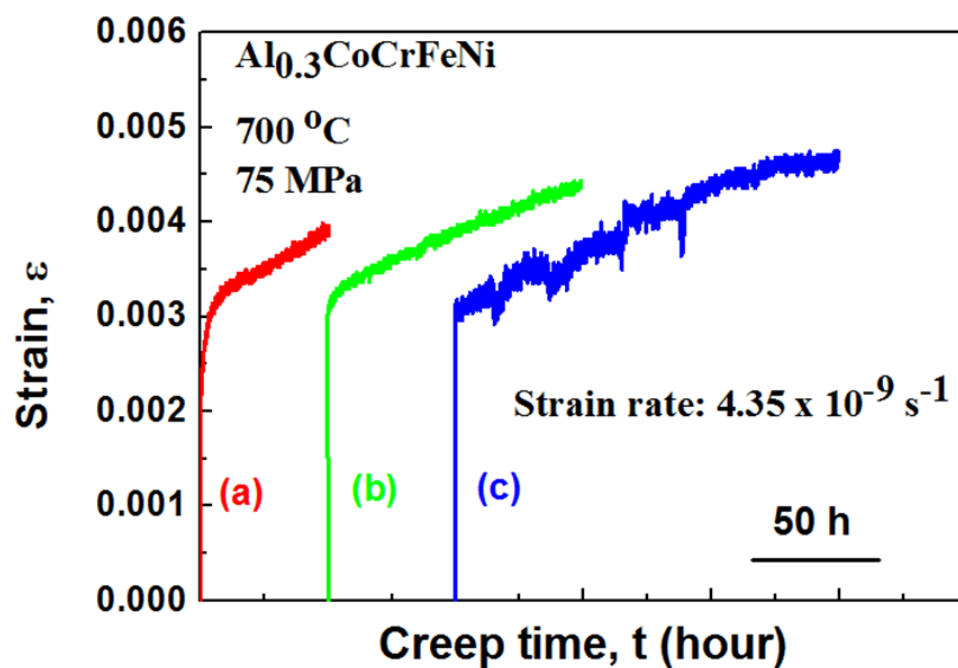


Figure 55 Strain as a function of creep time for the Al_{0.3}CoCrFeNi at 700 °C and 35 MPa. The creep tests are interrupted at 50 hours (a), 100 hours (b), and 150 hours (c).

Creep @ 700 °C, 75 Mpa for 50 hours

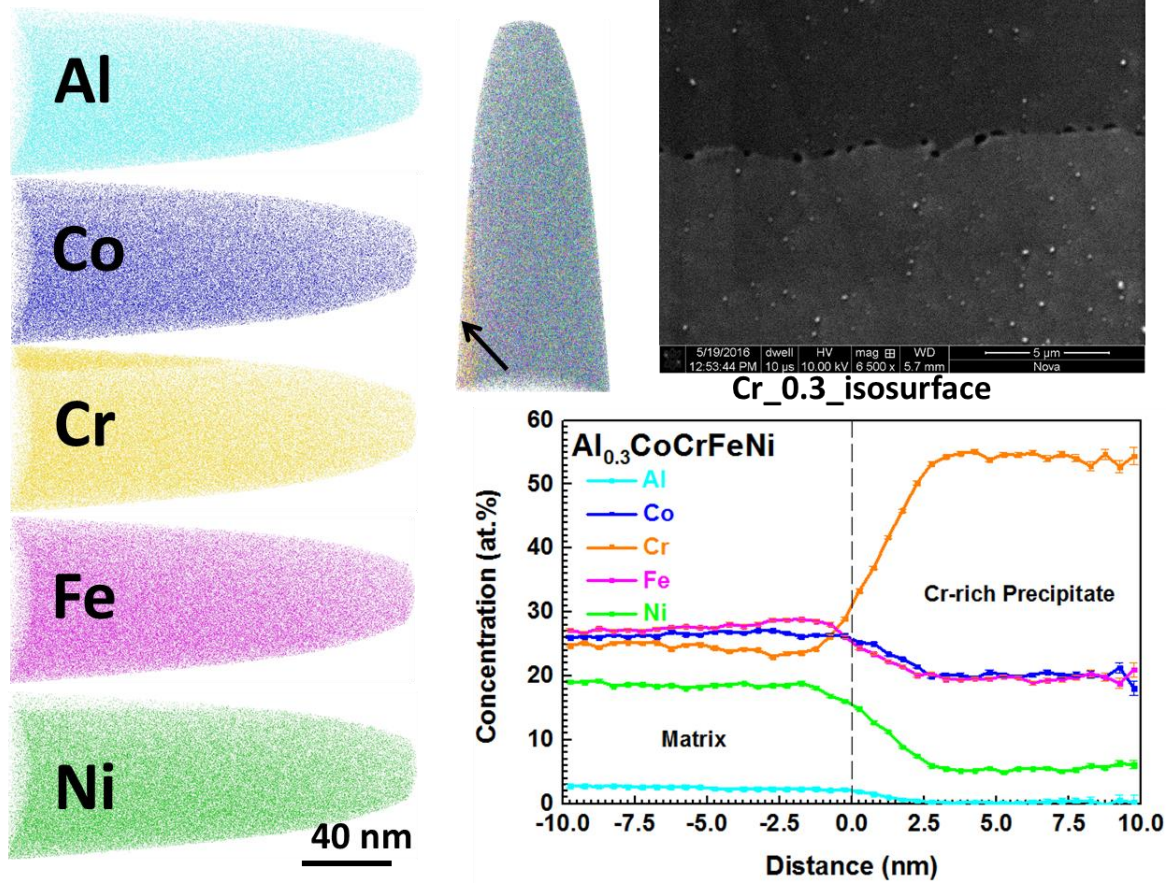


Figure 56 Microstructure after the creep test at 700 °C and 75 MPa for the $\text{Al}_{0.3}\text{CoCrFeNi}$. The APT results show that Cr-rich precipitates are present along the grain boundary.

Creep @ 700 °C, 75 Mpa for 100 hours

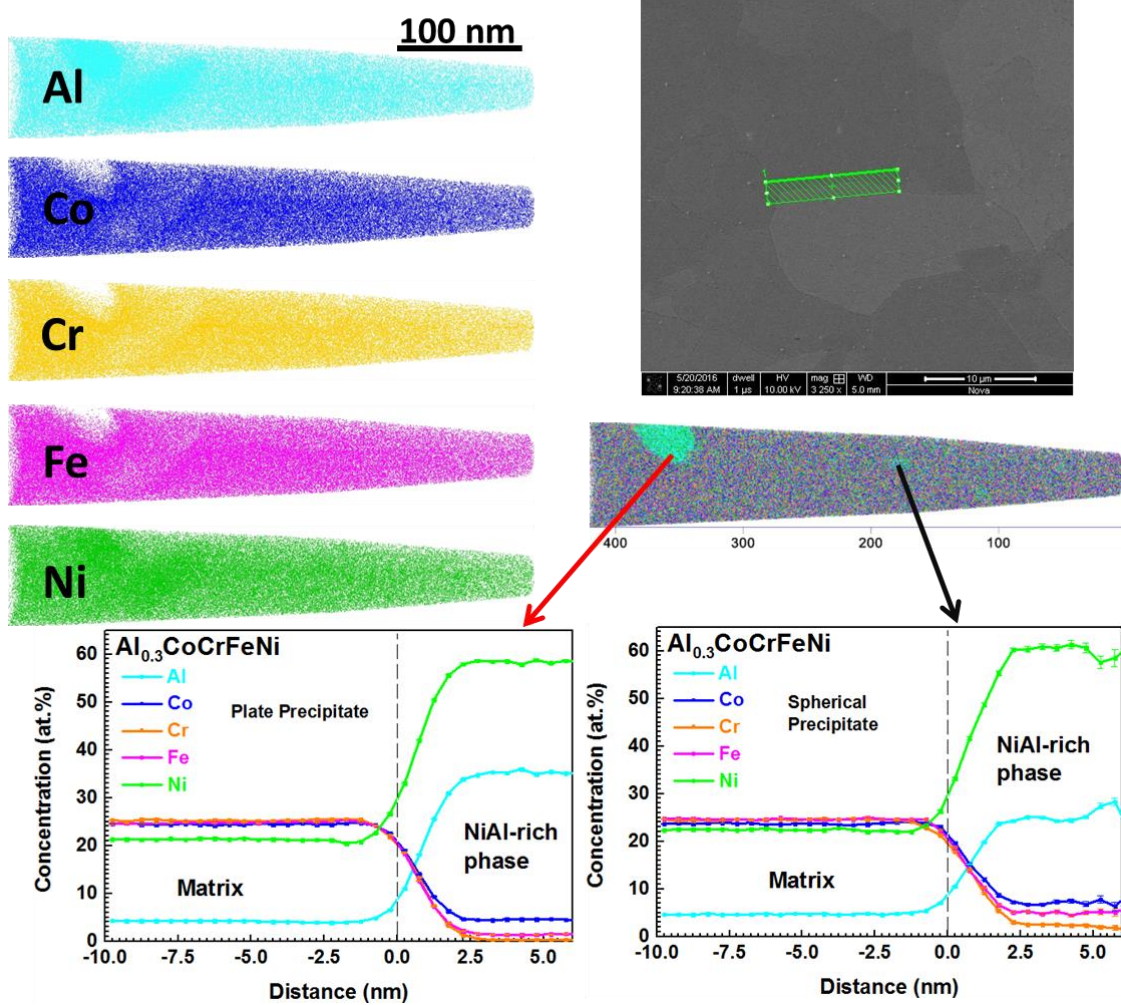


Figure 57 Microstructure after the creep test at 700 °C and 75 MPa for 100 hours for the $\text{Al}_{0.3}\text{CoCrFeNi}$. The APT results show that nanoscale NiAl-rich precipitates are present within grains. For large precipitates, the Al concentration is higher than their counterpart, small precipitates.

Creep @ 700 °C, 75 Mpa for 150 hours

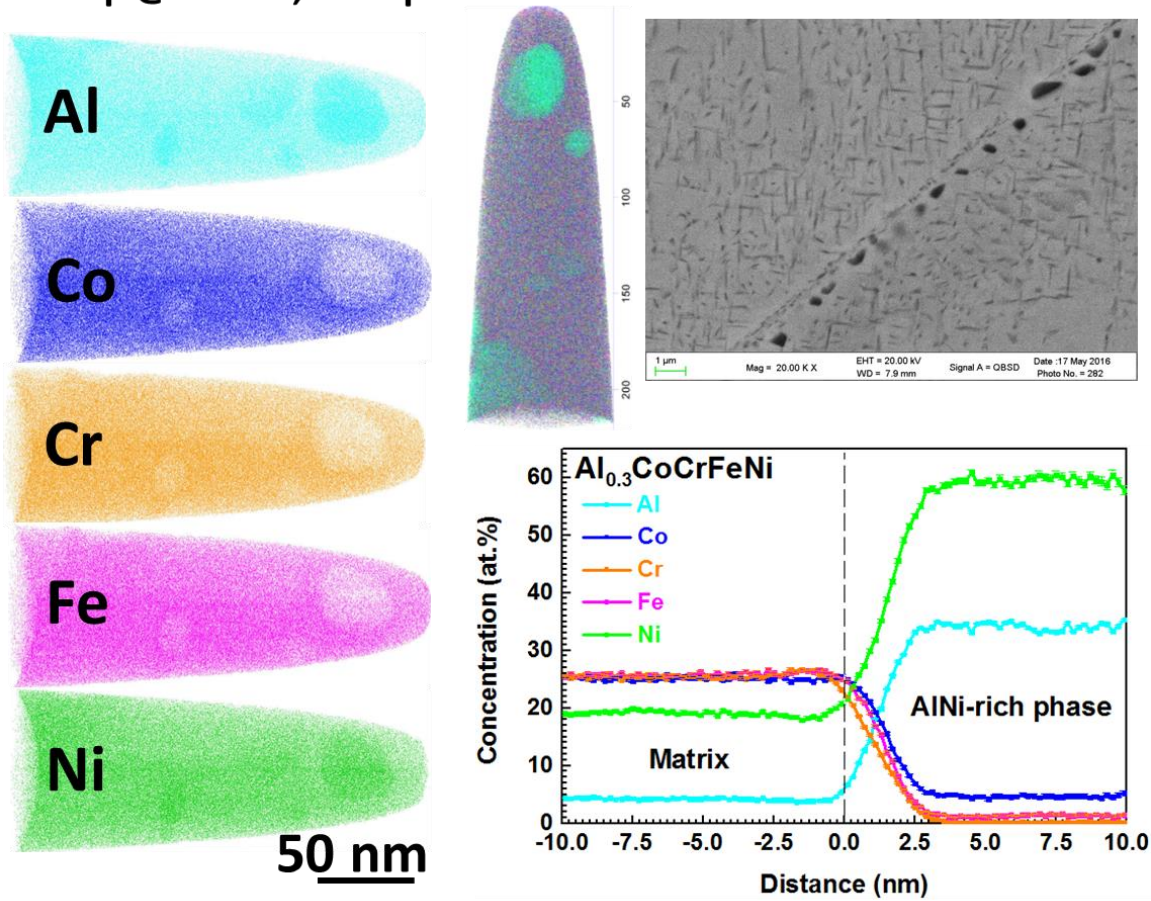


Figure 58 Microstructure after the creep test at 700 °C and 75 MPa for 150 hours for the $\text{Al}_{0.3}\text{CoCrFeNi}$. The APT results show that needle-shape NiAl-rich precipitates are present within grains. The Al concentration is half of the Ni concentration.

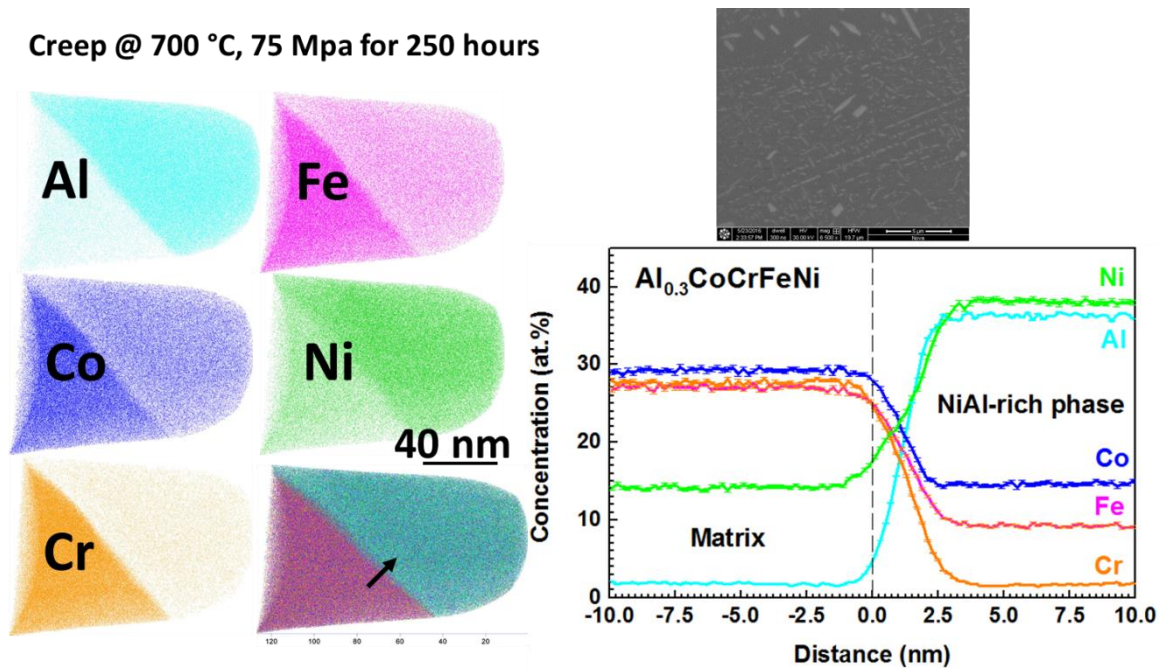


Figure 59 Microstructure after the creep test at 700 °C and 75 MPa for 250 hours for the $\text{Al}_{0.3}\text{CoCrFeNi}$. The APT results show that needle shape NiAl-rich precipitates are present within grains. The ratio of Al and Ni is around 1, which indicated the precipitates are B2 phase.

5.3 The Fracture Morphology of Crept Samples

A characteristic fractography provides an efficient way to study the fracture mechanism of $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs. Based on the understanding of conventional alloys, the fracture surfaces of HEAs can be categorized to be ductile and brittle fracture as well. After creep tests at 700 °C and stress level of 55, 75, and 100 MPa, respectively, fracture surfaces of the crept samples were investigated using scanning electron microscope (SEM), shown in Figures 60, 61, and 62. By comparing Figures 60a, 61a, and 62a, the striation spacing increases as the stress level increases, which agrees very well with the corresponding strain vs. time curves. Under high magnification, as shown in Figures 60b, 61b, and 62c, a high density of dimple-like structures can be observed on the fracture surfaces at all three stress levels. A dimple-like structure is related to the microvoid coalescence or aggregation [106], which is a typical feature of ductile fracture. As the stress level increases, the percentage of dimple-like structures gradually decrease, and instead, tear edges and cleavage steps begin to appear, as denoted in Figure 62b, which is caused by the coordinated operation of dislocations and microvoids. The combination of both features (tear edges and cleavage steps) can be classified as the quasi-cleavage fracture, which lies in-between brittle and ductile fracture modes. Planer facets and river-like patterns can also be identified in Figure 63, which is the typical cleavage fracture morphology, and cleavage fracture usually leads to brittle behavior. Thus, as the stress level increases, the striation spacing increases, and the fracture mode changes from the ductile to brittle fracture.

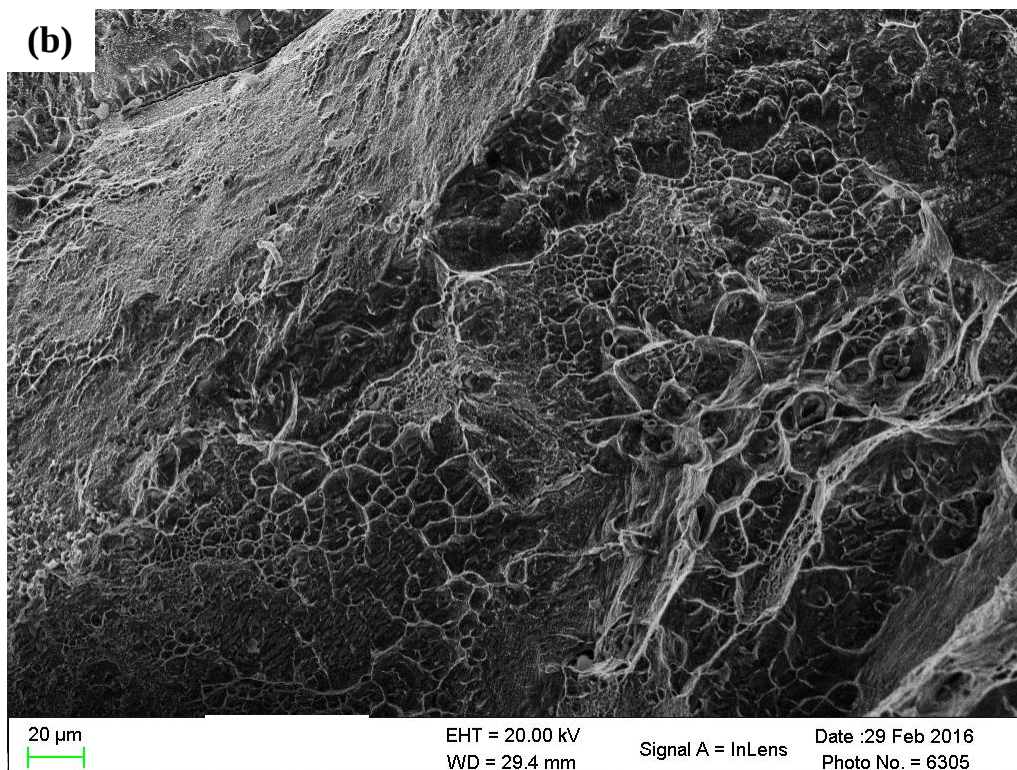
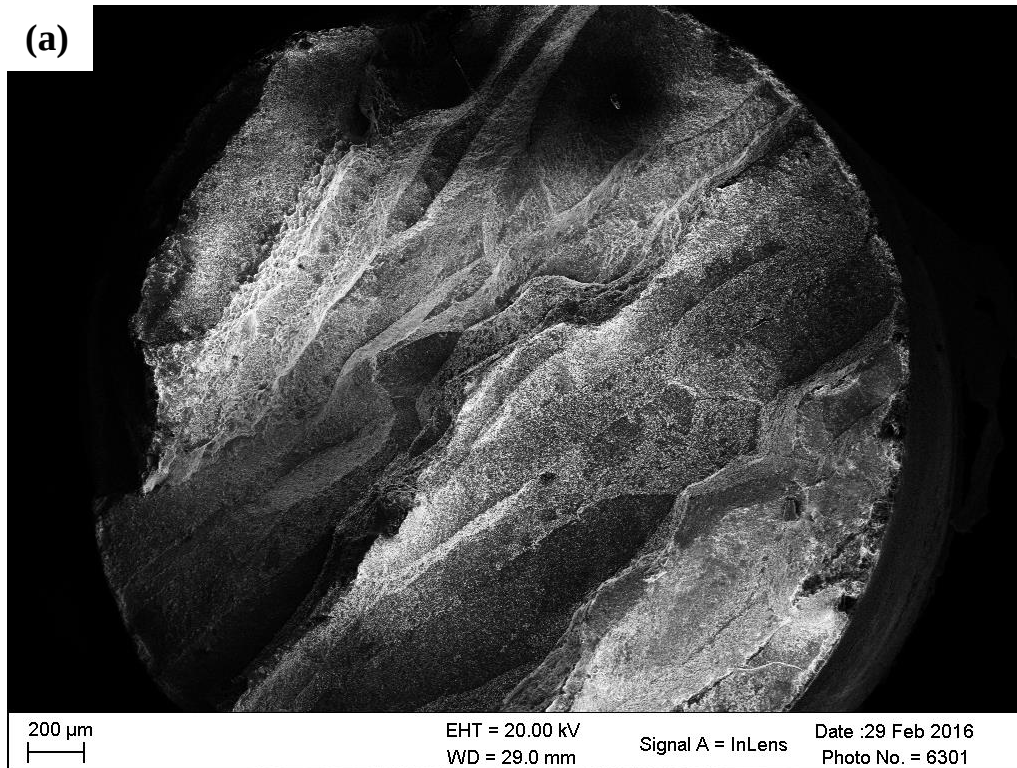


Figure 60 SEM image of the fracture surface after the creep test conducted at 700 °C and 55 MPa

(a)



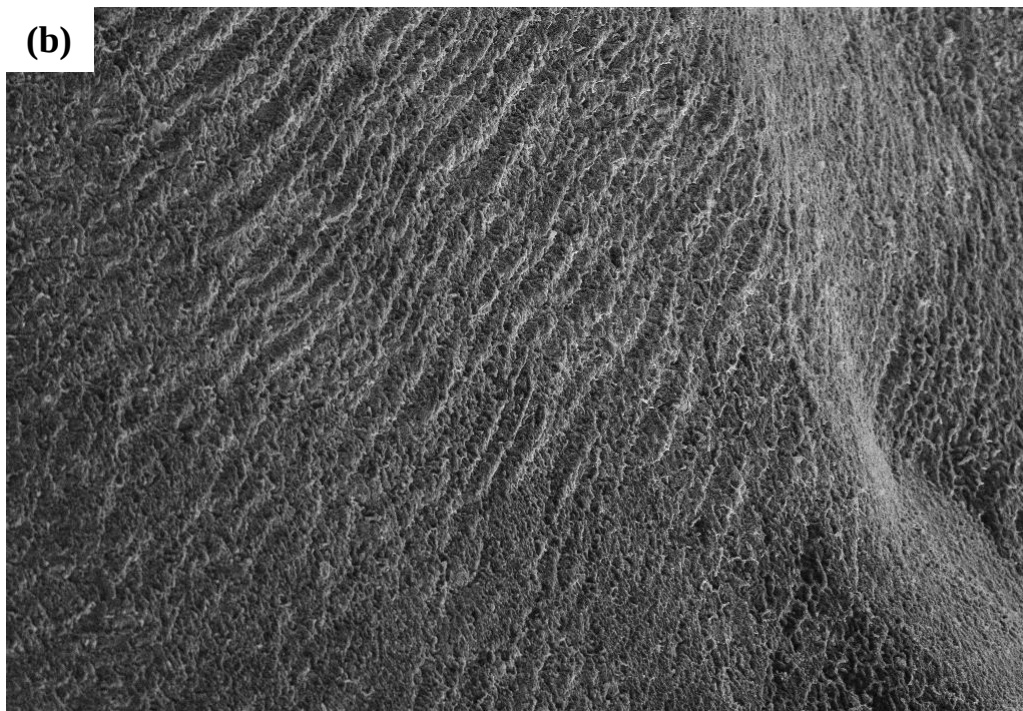
100 μ m
H

EHT = 20.00 kV
WD = 29.4 mm

Signal A = InLens

Date :29 Feb 2016
Photo No. = 6307

(b)



10 μ m
H

EHT = 20.00 kV
WD = 30.0 mm

Signal A = InLens

Date :29 Feb 2016
Photo No. = 6310

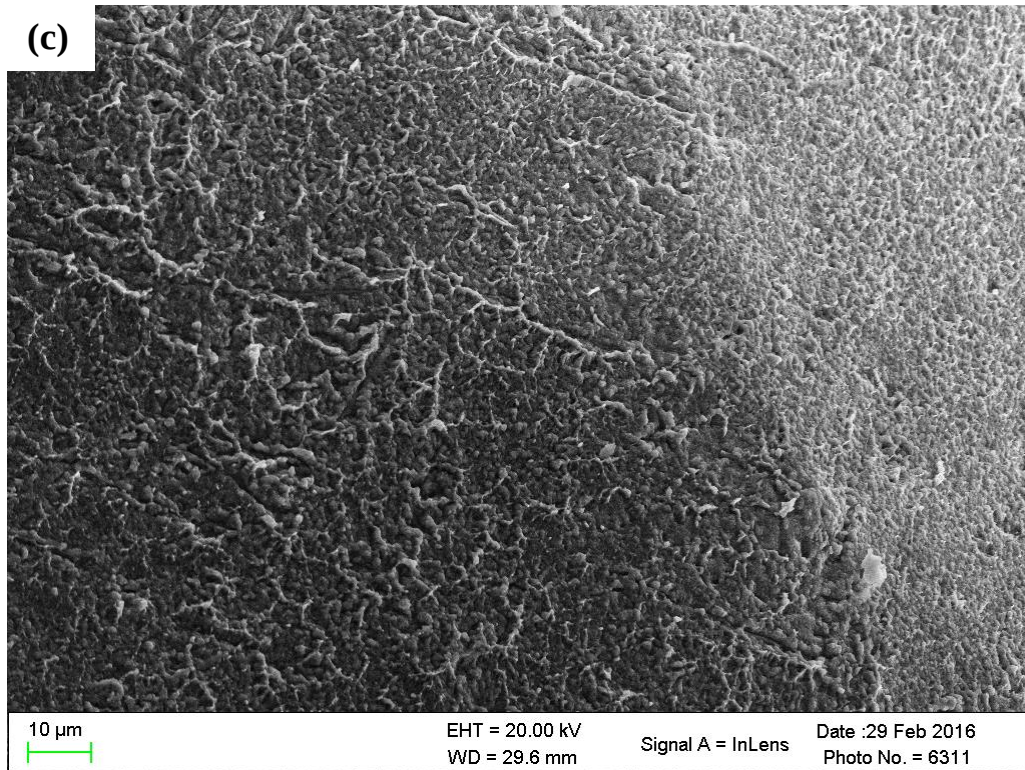
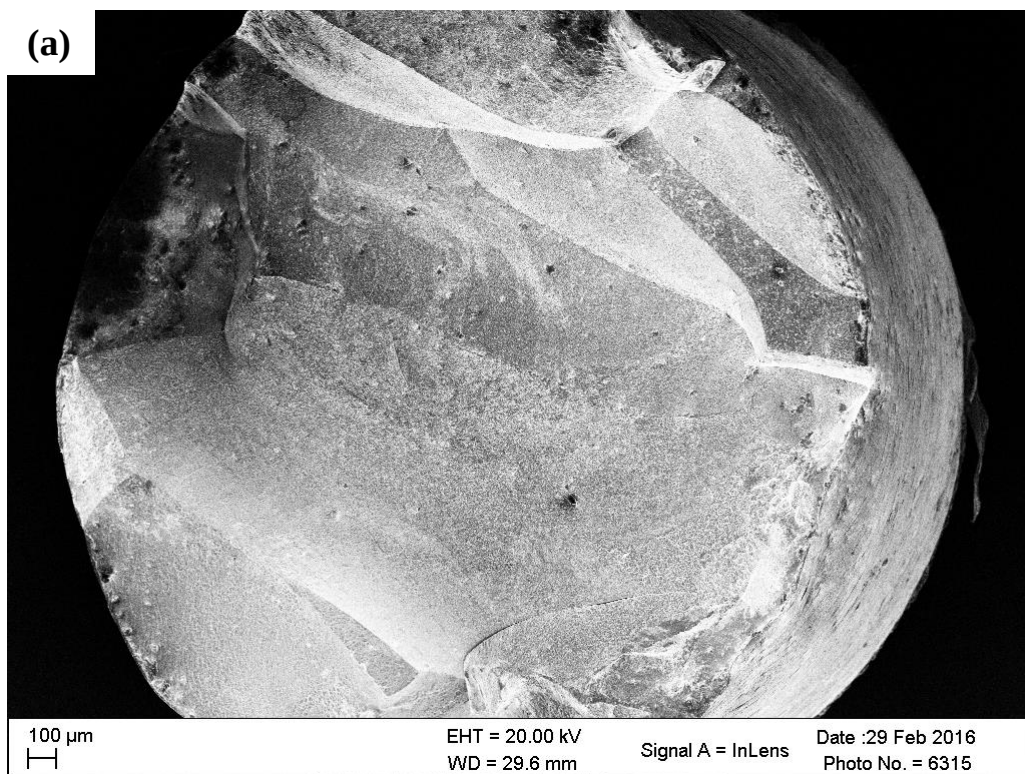


Figure 61 SEM image of the fracture surface after the creep test conducted at 700 °C and 75 MPa



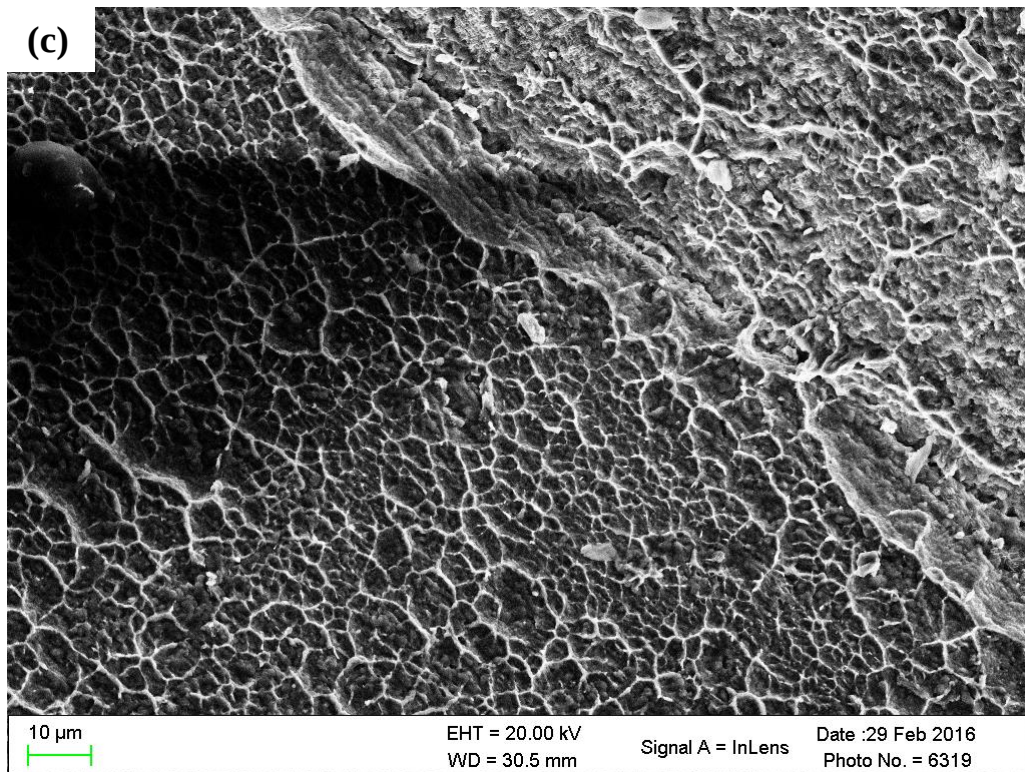
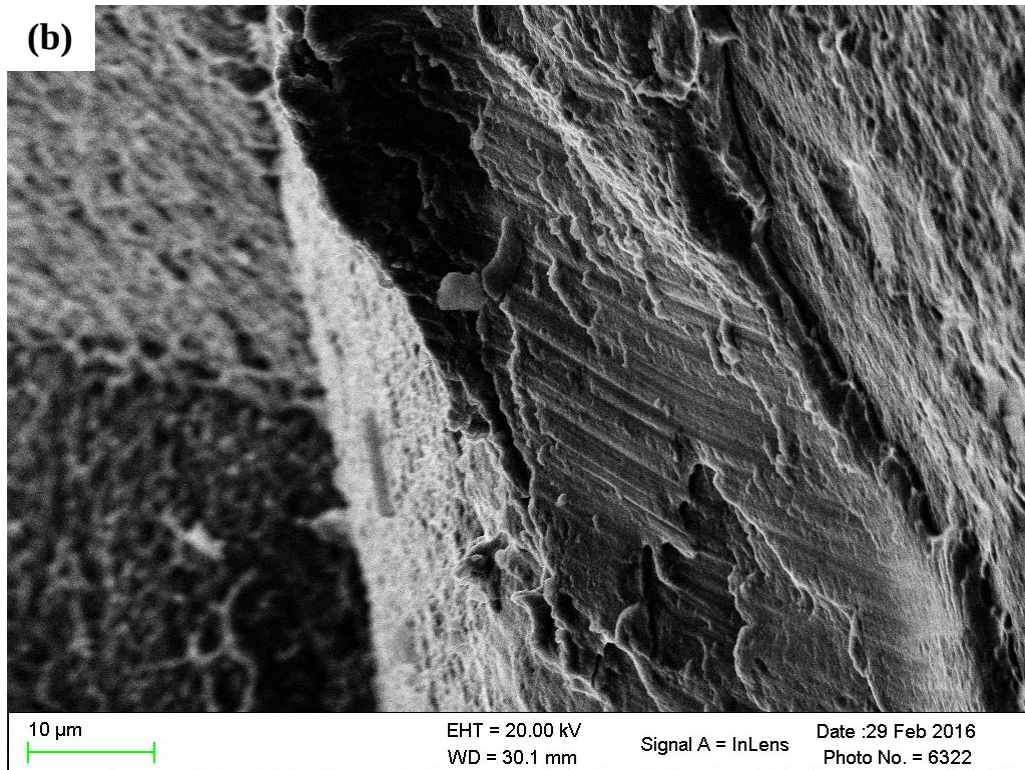


Figure 62 SEM image of the fracture surface after the creep test conducted at 700 °C and 100 MPa

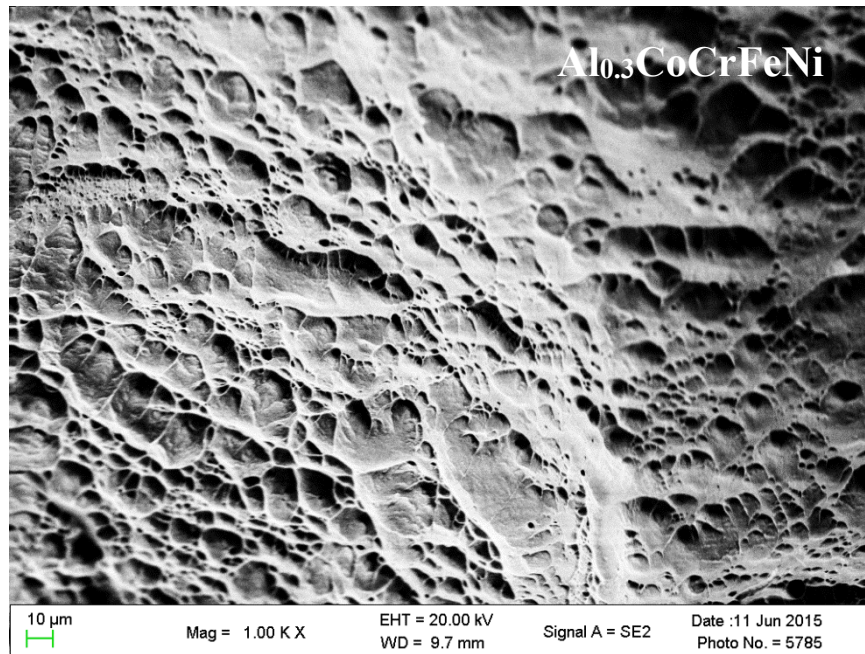


Figure 63 The fracture surface of heat-treated (700 °C for 500 h) Al_{0.3}CoCrFeNi HEA after tension test at room temperature at a strain rate of $5 \times 10^{-5} \text{ s}^{-1}$. Only dimples are found.

6. TASK 4: MECHANICAL PROPERTIES

6.1 Tension Properties of $\text{Al}_x\text{CoCrFeNi}$

Compared to hardness and compression tests, tensile tests are sensitive to detect the embrittlement. For the $\text{Al}_{0.3}$, $\text{Al}_{0.5}$, and $\text{Al}_{0.7}$ HEA samples, tensile tests are more suitable to reveal the mechanical properties in the stressed state, which is frequently encountered in practical applications. Shown in Figure 64, for $\text{Al}_{0.3}$, the values of the yielding stress, ultimate tension stress, and ductility are 210 MPa, 500 MPa, and 97 %, respectively. For $\text{Al}_{0.5}$, the values of the yielding stress, ultimate tension stress, and ductility are 550 MPa, 725 MPa, and 56 %, respectively. For $\text{Al}_{0.7}$, the values of the yielding stress, ultimate tension stress, and ductility are 600 MPa, 740 MPa, and 8 %, respectively.

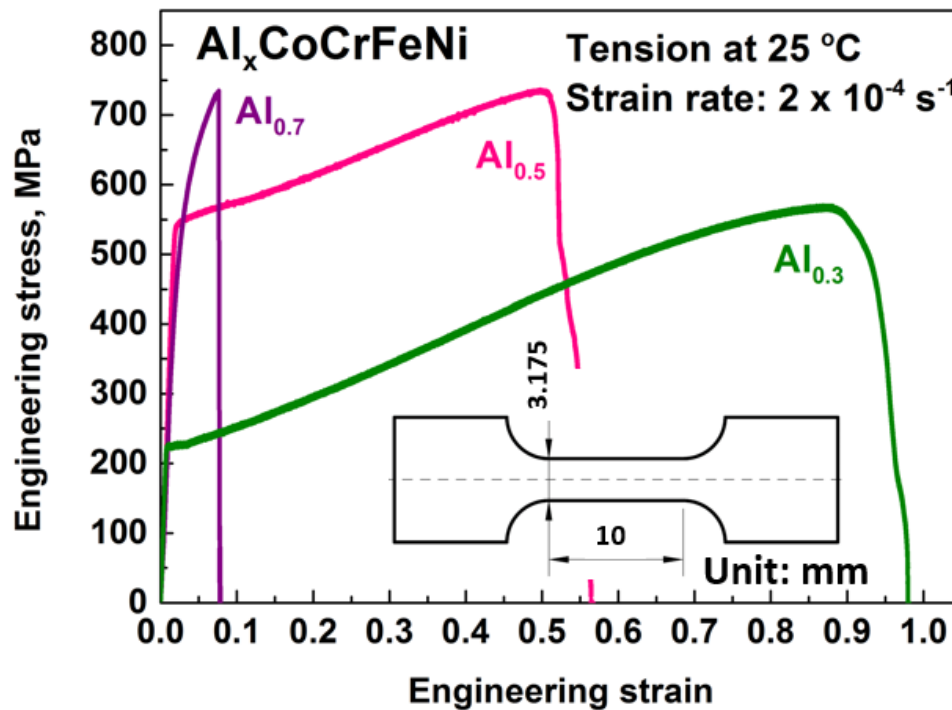
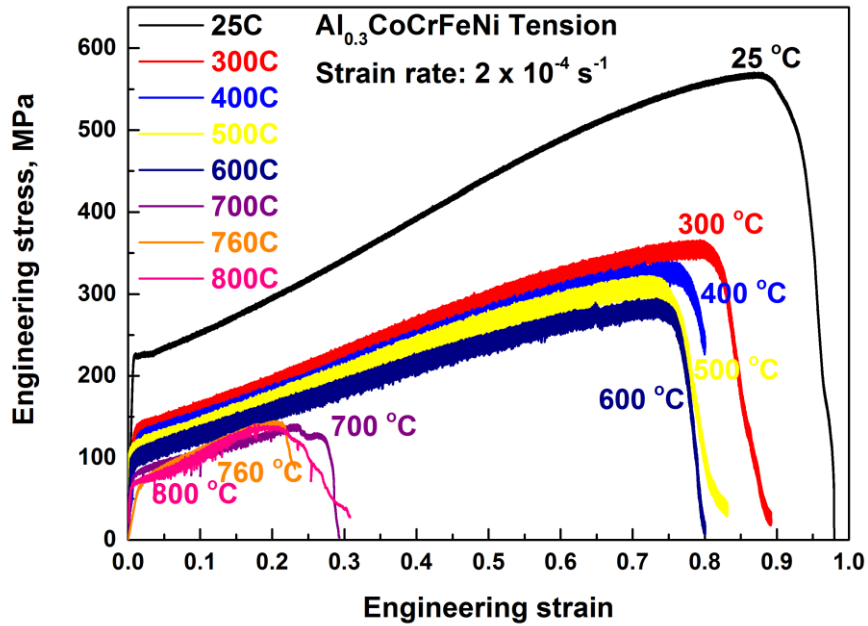


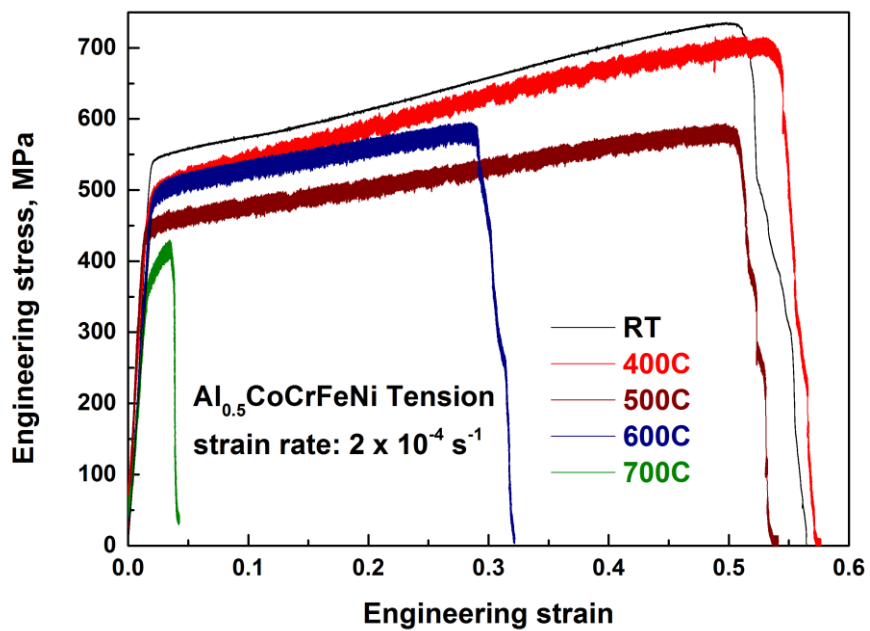
Figure 64 Tensile engineering stress-strain curves of $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.3, 0.5, \text{ and } 0.7$).

In order to study the mechanical properties at elevated temperatures, tension tests are conducted. The tension behavior of $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.3, 0.5, \text{ and } 0.7$) at elevated temperatures is described in Figure 65. For $\text{Al}_{0.3}\text{CoCrFeNi}$, all curves below 700°C exhibit low yield strength but remarkable plasticity. When a small amount of Al is introduced, $\text{Al}_{0.5}\text{CoCrFeNi}$ and $\text{Al}_{0.7}\text{CoCrFeNi}$ have higher yield strength than $\text{Al}_{0.3}\text{CoCrFeNi}$, which is the result of hard BCC phase and solid-solution-strengthening mechanisms. Microstructural examinations will be conducted to study why the yielding strength at 600°C is higher than that of 500°C . The yielding strength of $\text{Al}_{0.3}\text{CoCrFeNi}$, $\text{Al}_{0.5}\text{CoCrFeNi}$, and $\text{Al}_{0.7}\text{CoCrFeNi}$ as a function of temperature is summarized in Figure 65. This results show that $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.3, 0.5, \text{ and } 0.7$) have great potential for high-temperature nuclear reactor applications.

a



b



c

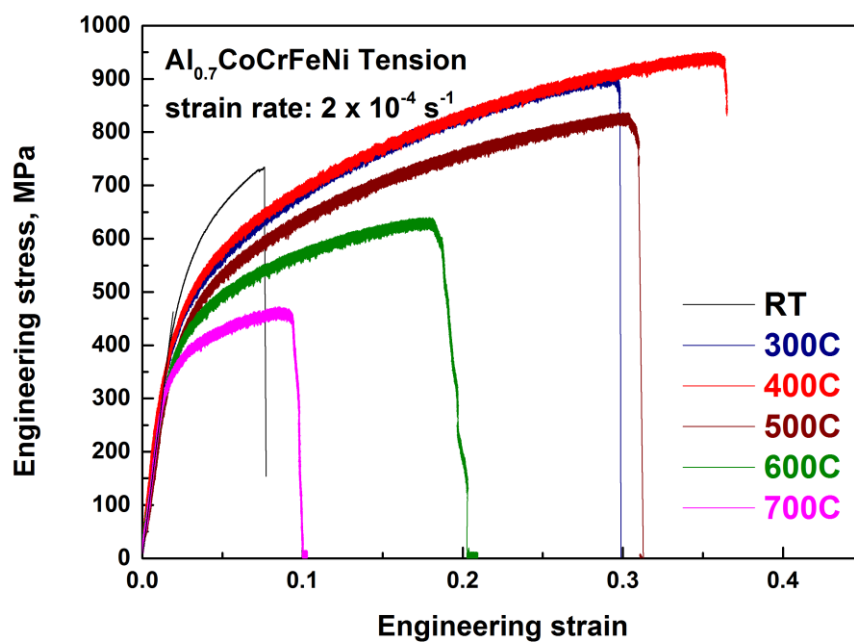


Figure 65 Tensile engineering stress-strain curves of $\text{Al}_x\text{CoCrFeNi}$ at high temperatures. (a) $x = 0.3$, (b) $x = 0.5$, and (c) $x = 0.7$.

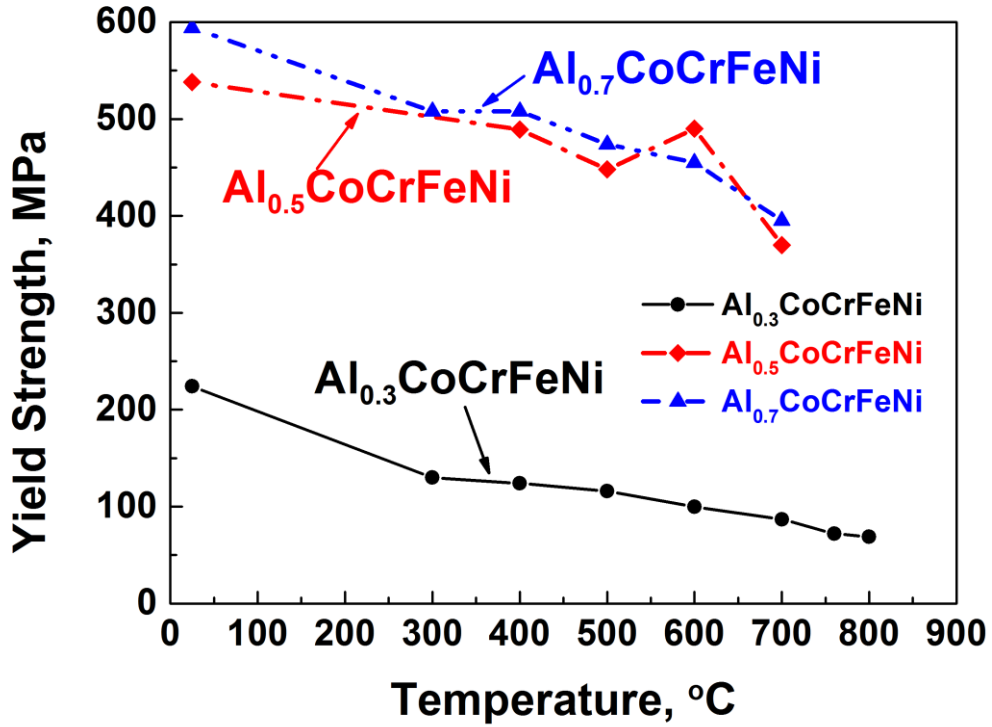


Figure 66 The yielding stress as a function of temperature for (a) Al_{0.3}CoCrFeNi, (b) Al_{0.5}CoCrFeNi, and (c) Al_{0.7}CoCrFeNi.

6.2 Tension Properties of Single-phase Al_{0.3}CoCrFeNi

Compared to hardness and compression tests, tensile tests are sensitive to detect the embrittlement. For the HEA samples with a dendritic structure and some shrinkage pores, tensile tests are more suitable to reveal the mechanical properties in the stressed state, which is frequently encountered in practical applications.

The study of tensile properties of HEAs are limited in few alloy systems [34, 37, 64, 73, 74, 77, 107-111]. Tsai *et al.* are the first to study the tensile properties of HEAs [77]. The temperature effects on the yielding stress is discussed in this part.

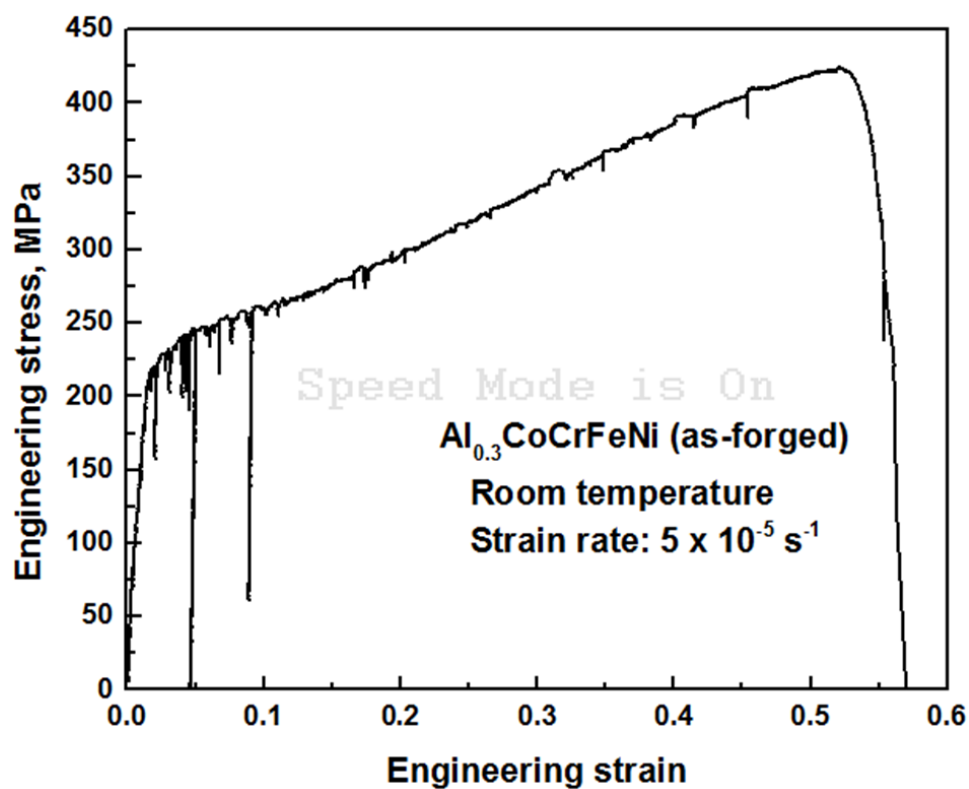
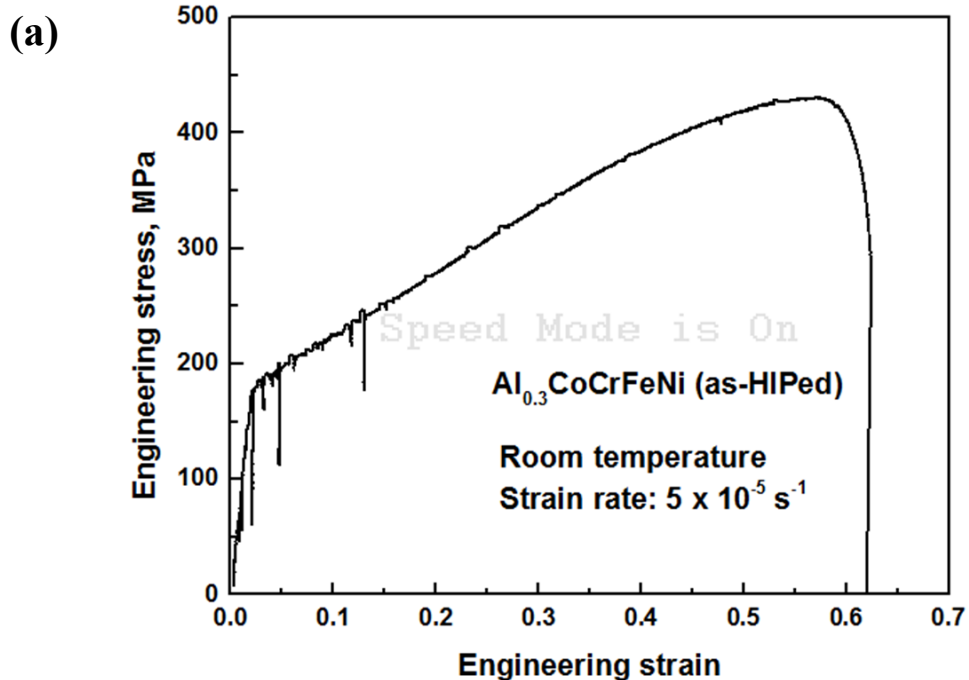


Figure 67 Tensile stress-strain curves of the $\text{Al}_{0.3}\text{CoCrFeNi}$ HEA at room temperature at a strain rate of $5 \times 10^{-5} \text{ s}^{-1}$ in the state of as-HIPed (a) and as-forged (b) conditions.

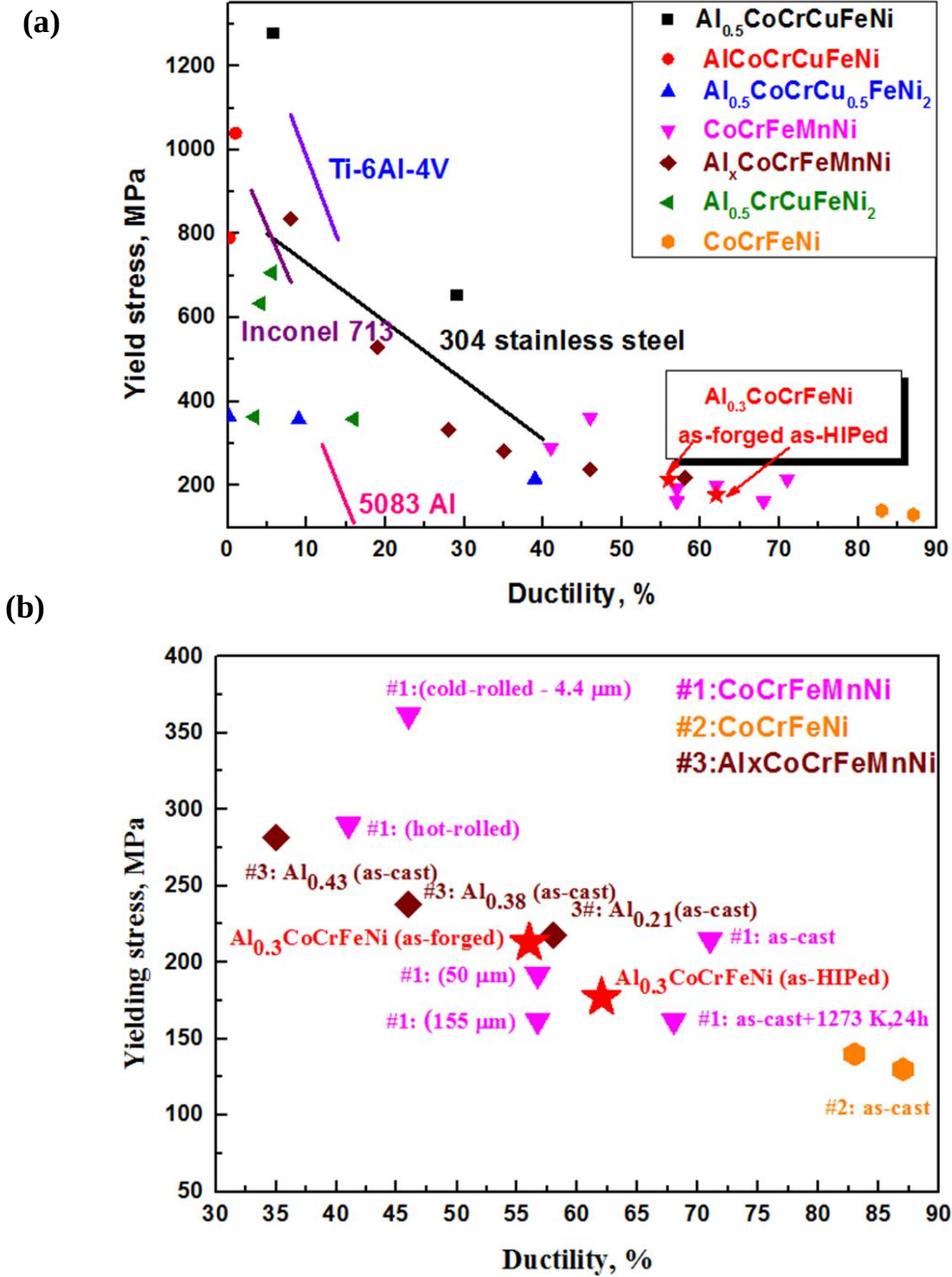
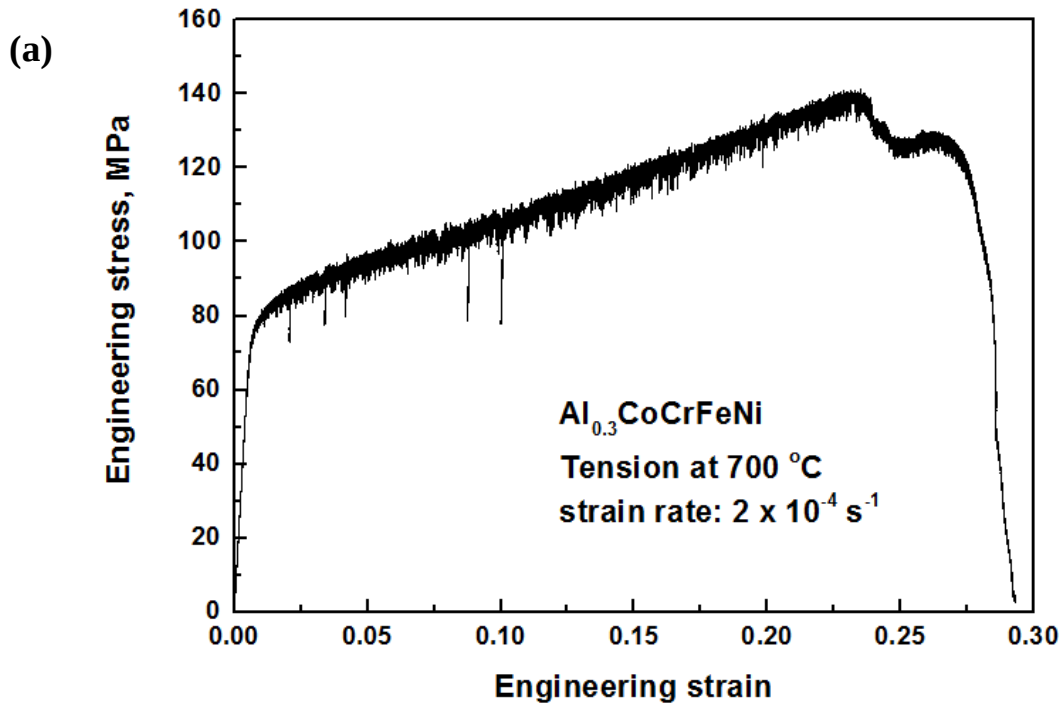


Figure 68 (a) Summarization of all published tensile yielding stresses and ductility of HEAs, compared with conventional alloys. (b) Summarization of all published tensile yielding stresses and ductilities of single-phase HEAs.

The tensile stress-strain curves of $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs at the temperature of 700 °C, 760 °C, and 800 °C at the strain rate of $2 \times 10^{-4} \text{ s}^{-1}$ are shown in Figure 69. Compared with other HEAs[37], the single-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ behaved like a solid solution with relatively-low strengths but extended ductility. The values of yielding stress and ultimate tensile strength (UTS) as a function of temperature is listed in the below table.

Table 8 The tensile yielding stress and ultimate tensile strength (UTS) at high temperatures of the single-phase $\text{Al}_{0.3}\text{CoCrFeNi}$

Temperature \ Strength	700 °C	760 °C	800 °C
Yielding Stress	77	64	62
UTS	137	135	135



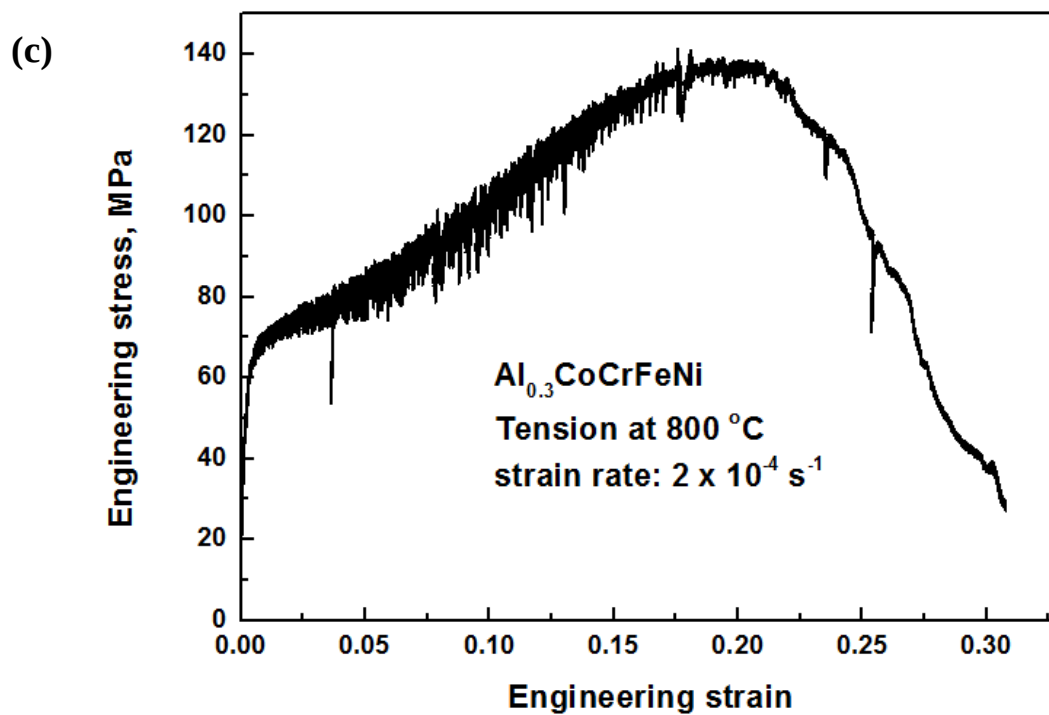
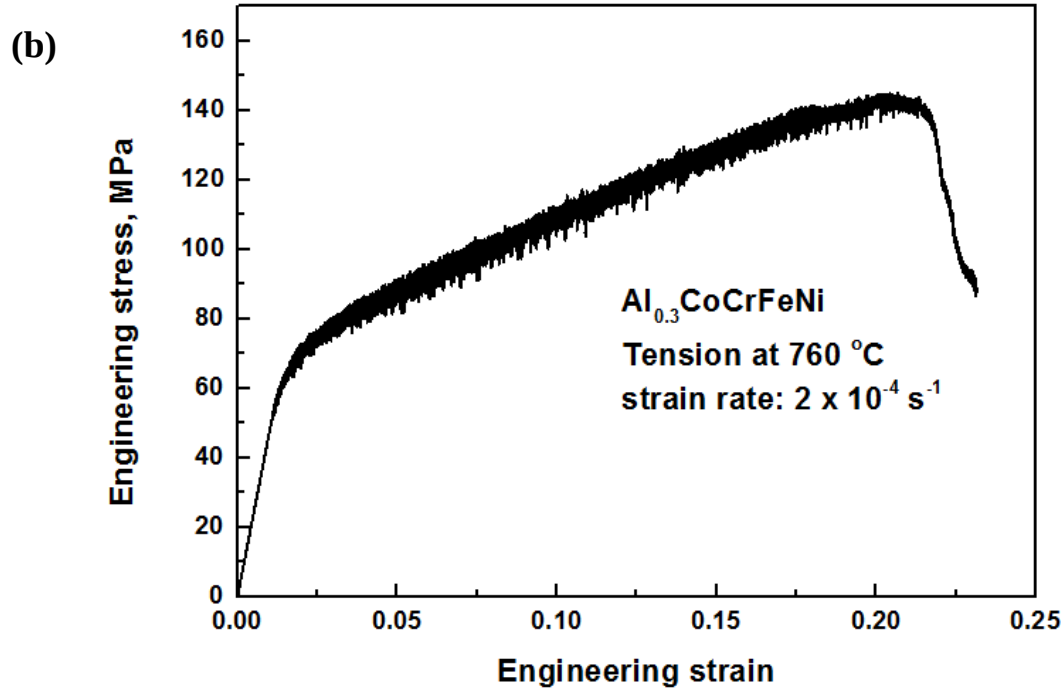


Figure 69 The tensile engineering stress vs. strain curves of Al_{0.3}CoCrFeNi at the temperature of 700 °C (a), 760 °C (b), and 800 °C (c) at the strain rate of $2 \times 10^{-4} \text{ s}^{-1}$

6.2.1 Heat Treatment on Tensile Behavior

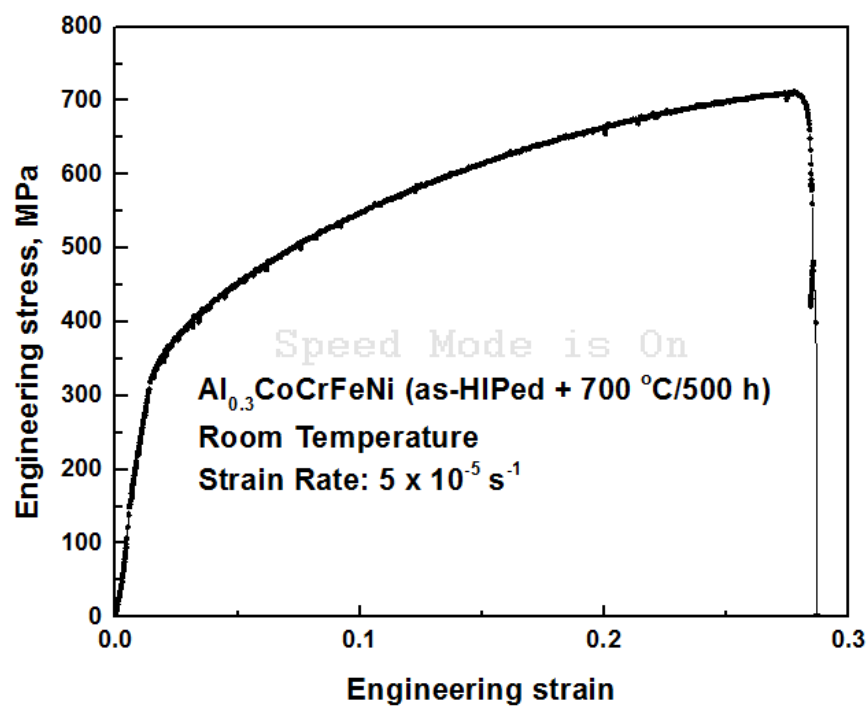
After the heat treatment, the $\text{Al}_{0.3}\text{CoCrFeNi}$ HEA behaved like a composite with a sharp increase in strength but reduced ductility. The yielding stress at high temperatures are listed in the below Table 9.

Table 9 The tensile yielding stress and ultimate tensile strength (UTS) of $\text{Al}_{0.3}\text{CoCrFeNi}$ (annealed at 700 °C for 500h) at high temperatures

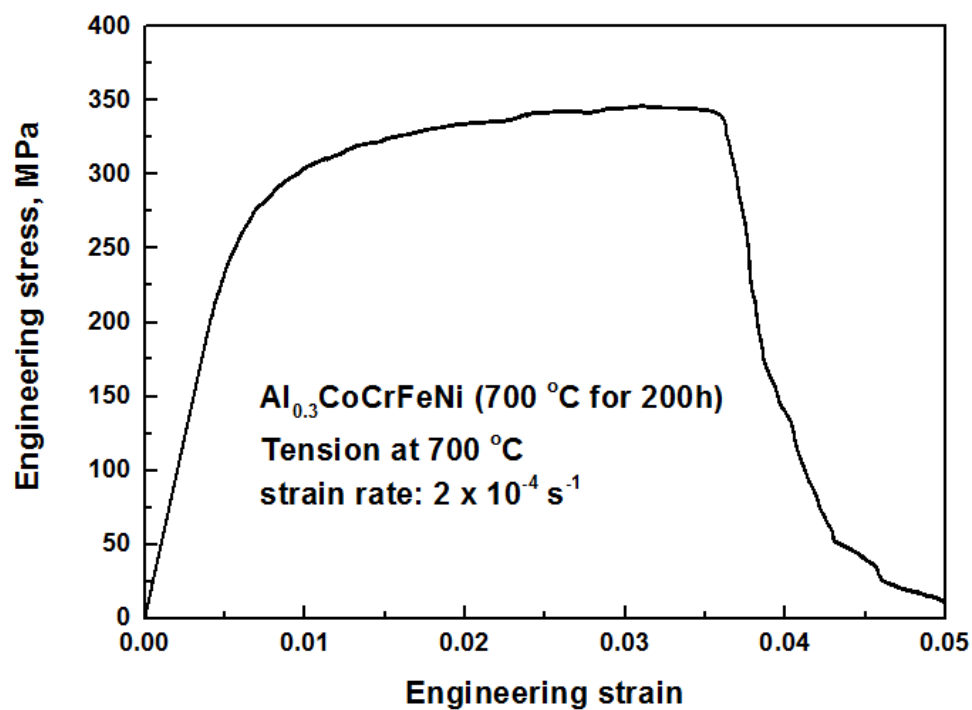
Temperature Strength	700 °C	760 °C	800 °C
Yielding Stress	251	260	190
UTS	340	280	200

Compared with Tables 8 and 9, the results show that the strengthening effect of B2 phases is obvious even at high temperatures around 760 °C. The tensile yielding stresses of $\text{Al}_{0.3}\text{CoCrFeNi}$ (annealed at 700 °C for 200h) are three times higher than those of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed). The detailed stress-strain curves of $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs (annealed at 700 °C for 200h) at the temperatures of 700 °C, 760 °C, and 800 °C at the strain rate of $2 \times 10^{-4} \text{ s}^{-1}$ are shown in Figure 15. The B2 effect on the creep behavior will be discussed further.

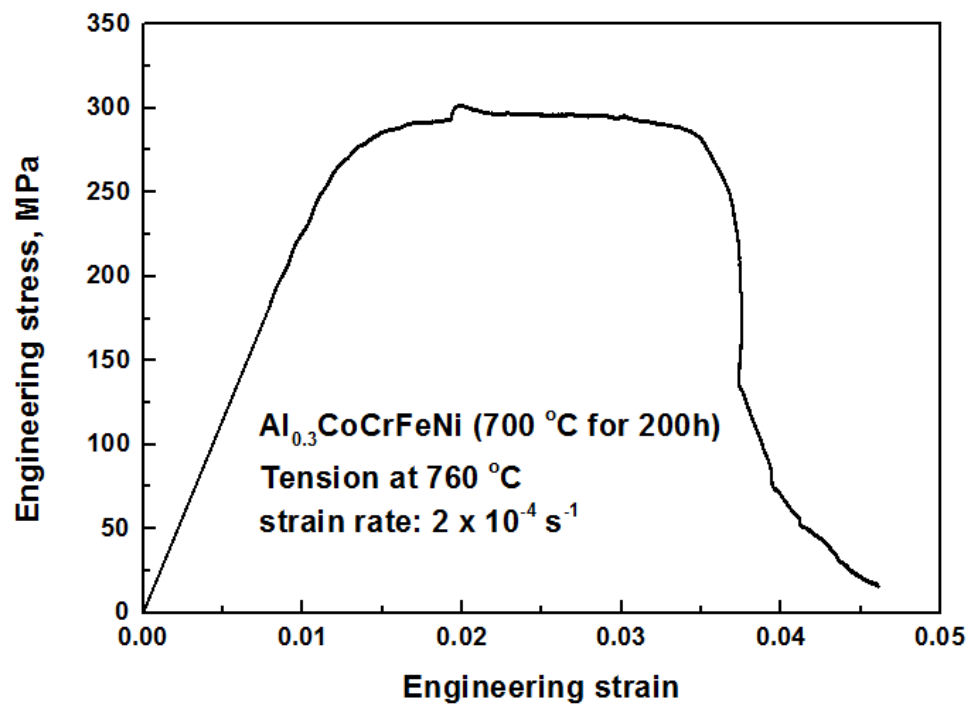
(a)



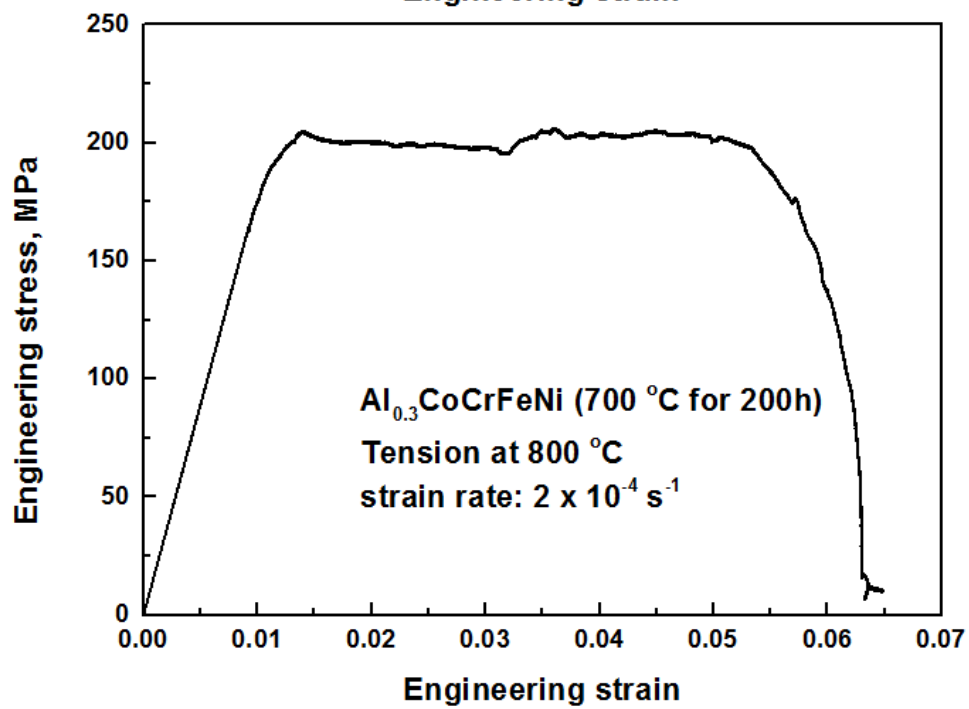
(b)



(c)



(d)



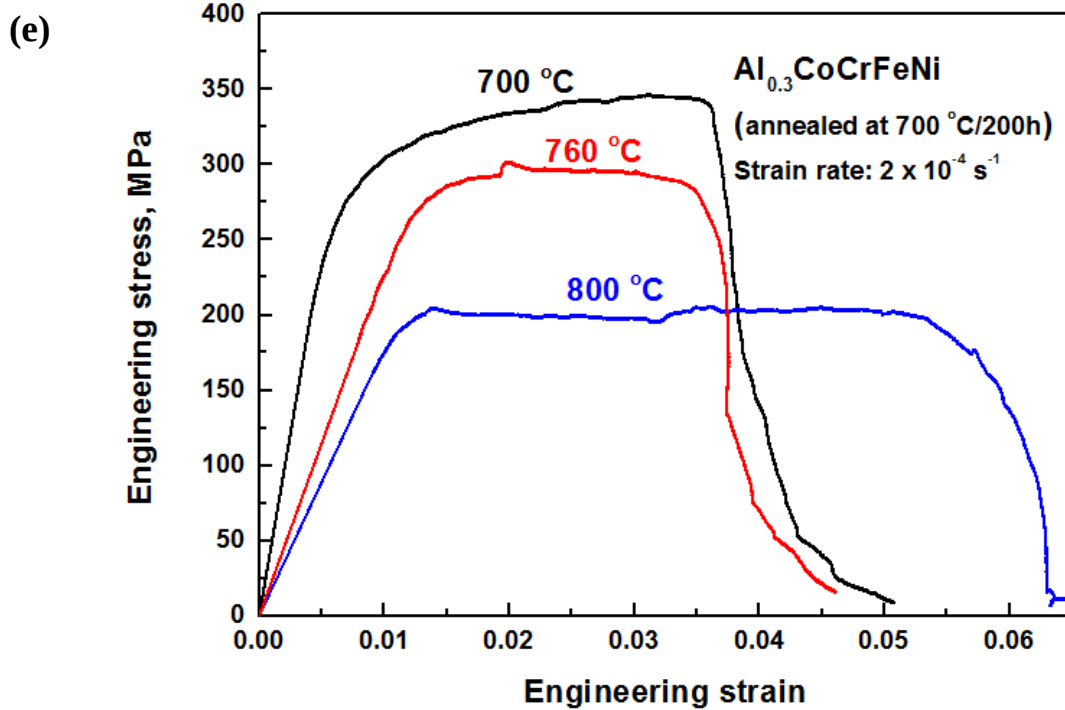


Figure 70 The tensile engineering stress vs. strain curves of $\text{Al}_{0.3}\text{CoCrFeNi}$ (annealed at 700 °C for 200h) at the temperatures of 25 °C (a), 700 °C (b), 760 °C (c), and 800 °C (d) at the strain rate of $2 \times 10^{-4} \text{ s}^{-1}$

6.3 Serration Behavior of Al_{0.3}CoCrFeNi HEAs

6.3.1 Experimental and Data Analysis

The Al_{0.3}CoCrFeNi (as-HIPed) and Al_{0.3}CoCrFeNi (after heat treatment) HEAs, with a geometry of 4 mm in length and 2 mm in diameter, were uniaxially compressed at the constant strain rate, $2 \times 10^{-4} \text{ s}^{-1}$ at the temperatures from room temperature (RT) to 600 °C. Loading of the specimens was terminated when deformation was ~ 20 - 30 % in the whole temperature range.

In order to characterize the serrated flow, the compression data is analyzed by the LOESS (Local regrESS) method [112], which is a strongly related non-parametric regression methods that combine multiple regression models in a k-nearest-neighbor-based meta-model. "LOESS" is a later generalization of LOWESS (locally weighted scatterplot smoothing). LOESS build on "classical" methods, such as the linear and nonlinear least- squares regressions. They address situations in which the classical procedures do not perform well or cannot be effectively applied without undue labor. LOESS combines much of the simplicity of the linear least-squares regression with the flexibility of nonlinear regression. It does this by fitting simple models to localized subsets of the data to build up a function that describes the deterministic part of the variation in the data, point by point. In fact, one of the chief attractions of this method is that the data analyst is not required to specify a global function of any form to fit a model to the data, only to fit segments of the data. A smooth curve through a set of data points obtained with this statistical technique is called a LOESS Curve, particularly when each smoothed value is given by a weighted quadratic least-squares regression over the span of values of the y-axis scattergram criterion variable. The snapshot of the data analysis of compressive stress-time curves for Al_{0.3}CoCrFeNi (as-HIPed) is shown in Figure 71.

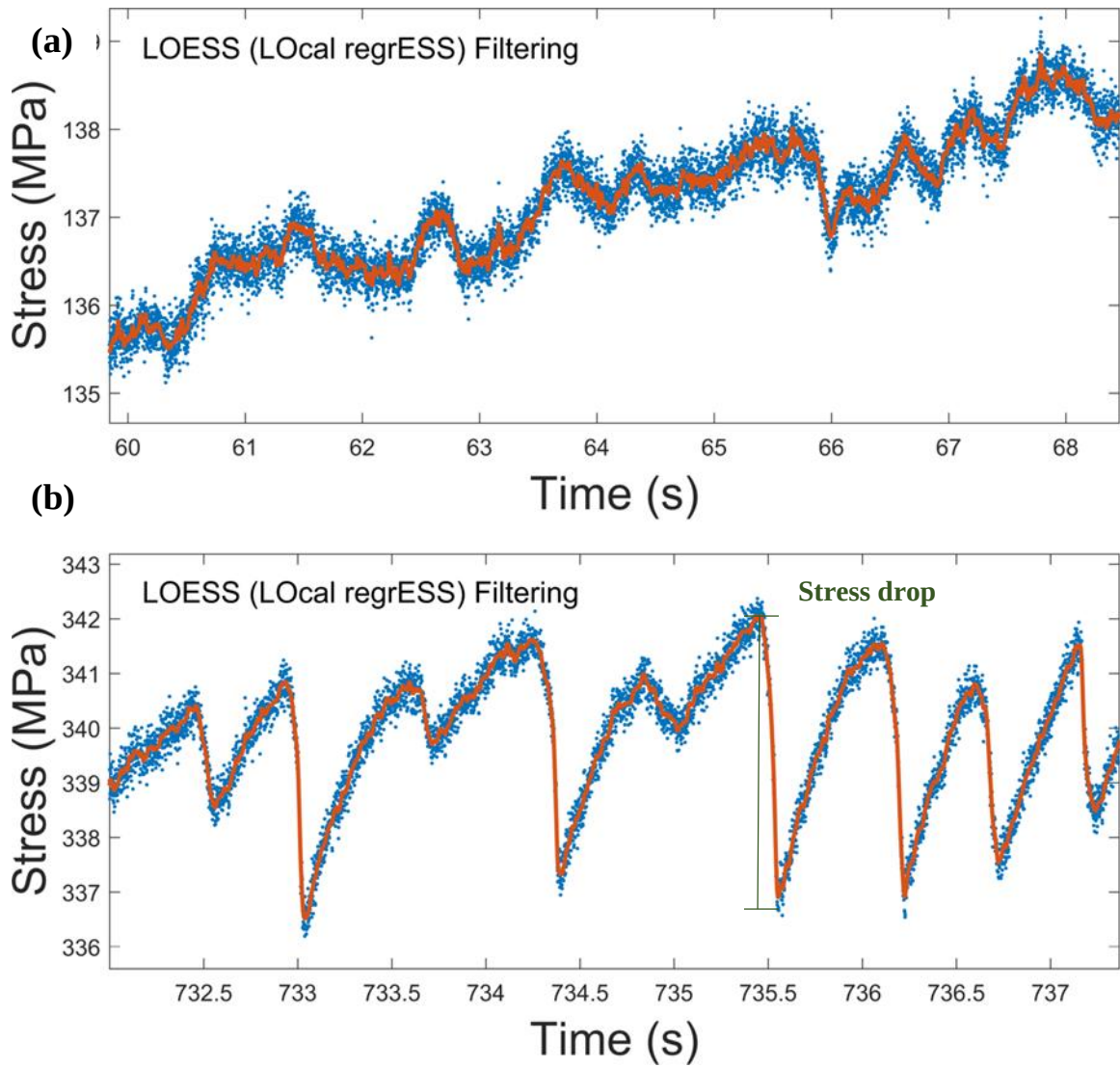
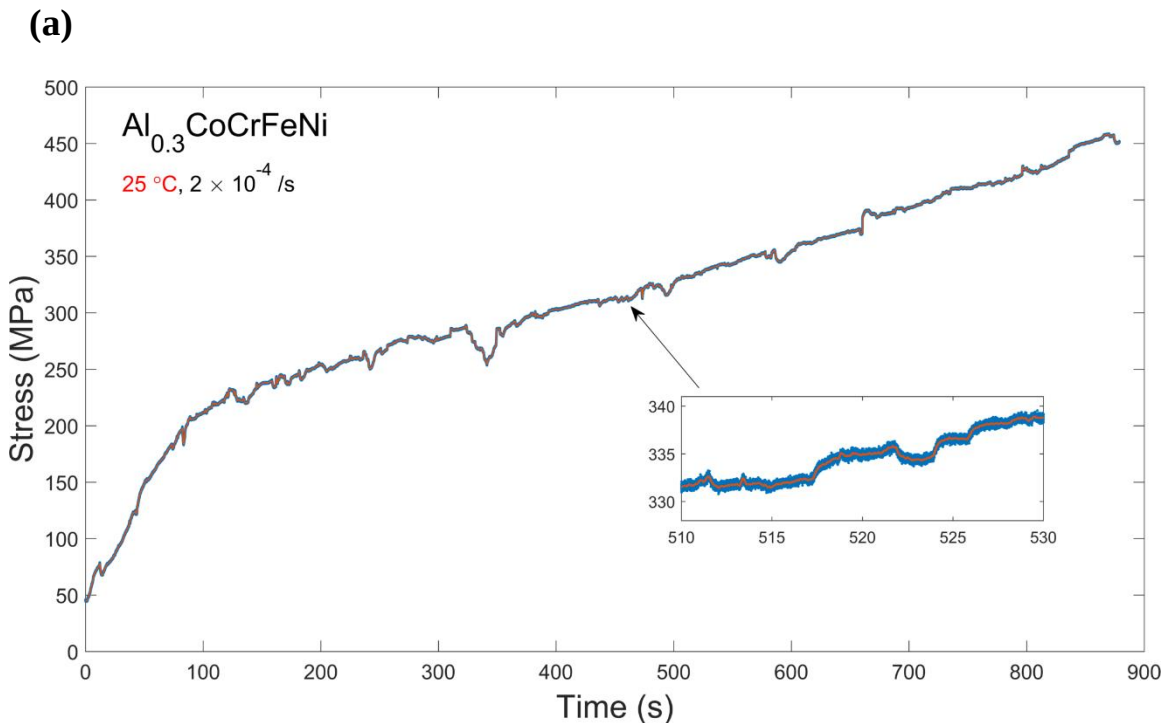


Figure 71 The snapshot of the compressive data analysis of a single-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ HEA using the LOESS method. The blue dots are the experimental data and the red curves are the related LOESS curves. The green line shows the definition of the stress-drop magnitude.

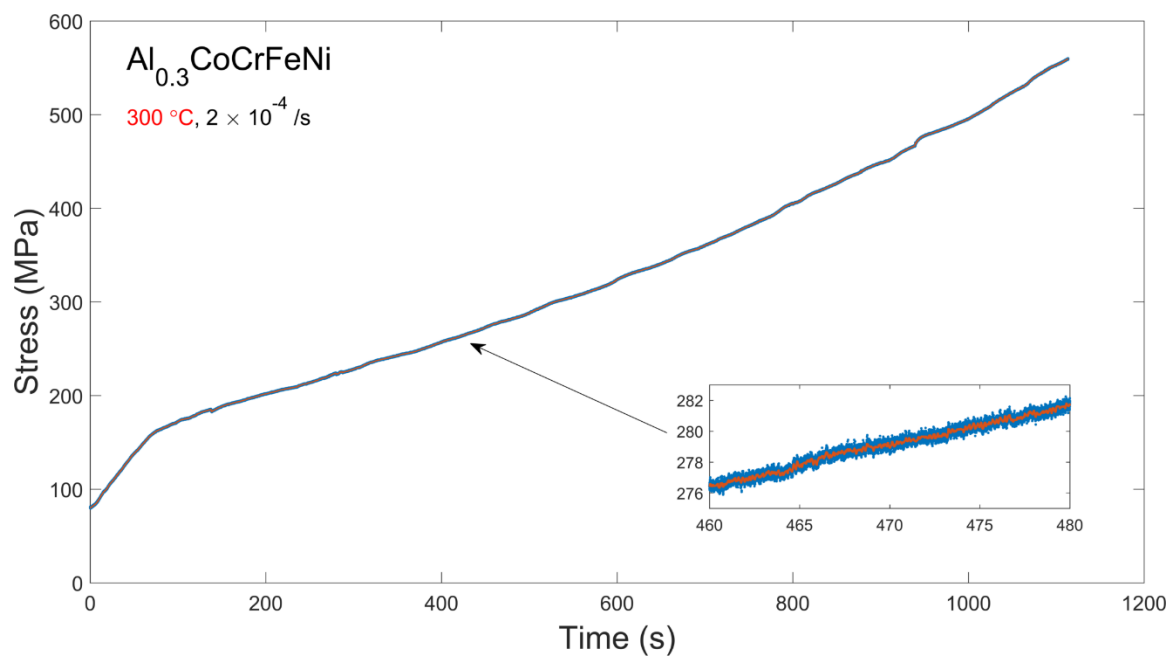
6.3.2 Results and Discussion

1) Compressive properties at high temperatures and related serration behaviors of single-phase HEAs

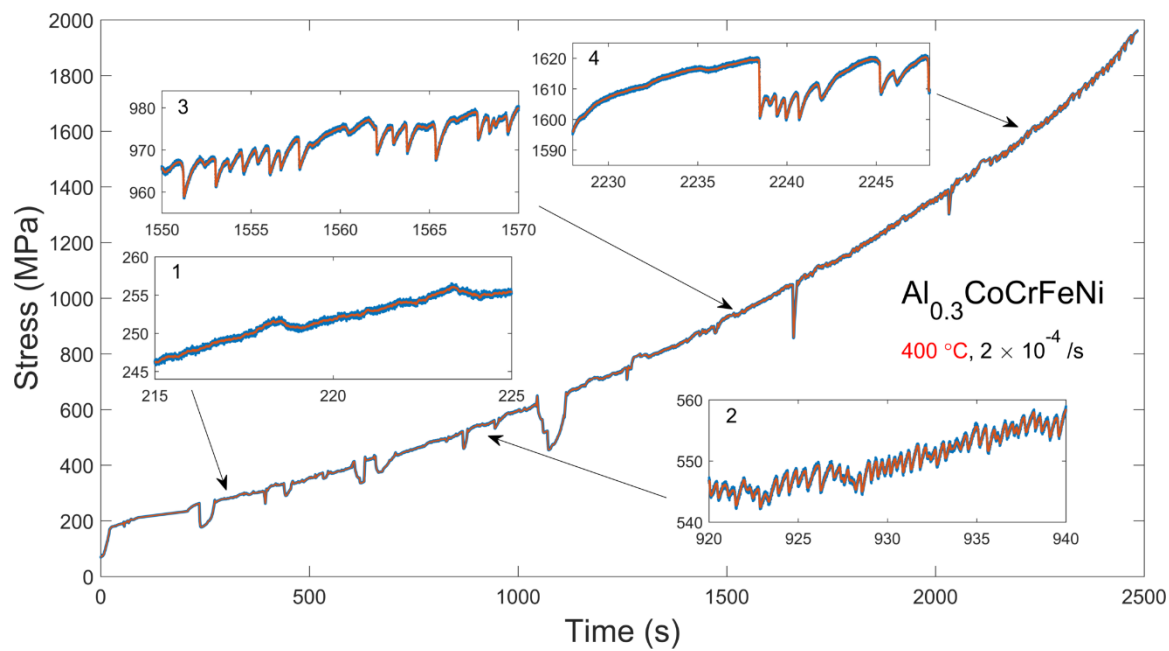
Figure 72 shows the stress-time curves of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) HEA at 25 °C, 300 °C, 400 °C, 500 °C, 550 °C, and 600 °C, respectively. Two parameters, serration type and stress drop magnitude, are discussed in this part to characterize the serration behavior of HEAs. The saw-like plastic flow confirms the presence of the Type-C serration behavior at 400 °C, 500 °C, 550 °C, and 600 °C. A closer look at the curves at 400 °C, 500 °C, 550 °C, and 600 °C reveals the magnitude of serrations to dramatically changes with an increase in the compression strain. Interestingly, a similar trend has been reported for amorphous materials [113-115].



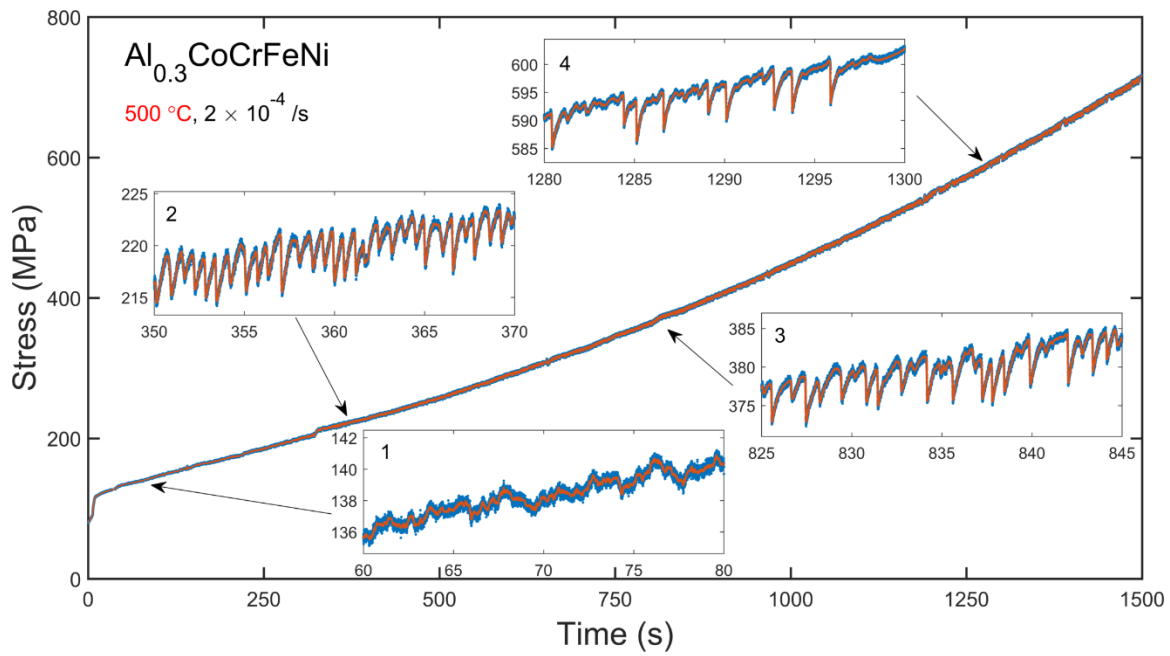
(b)



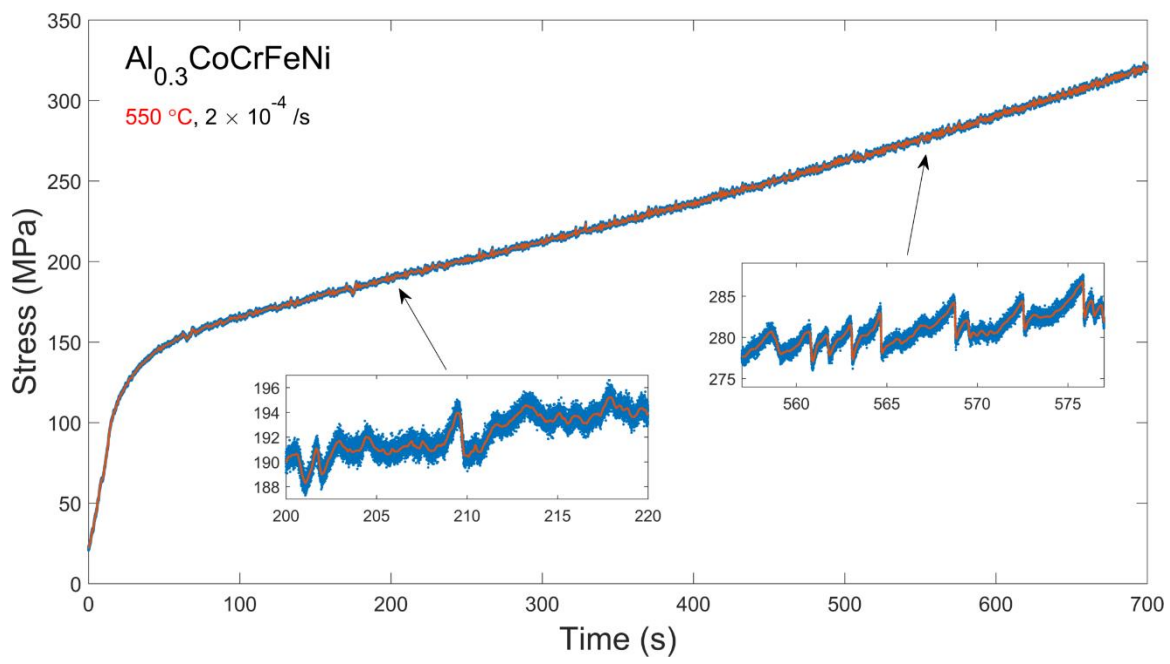
(c)



(d)



(e)



(f)

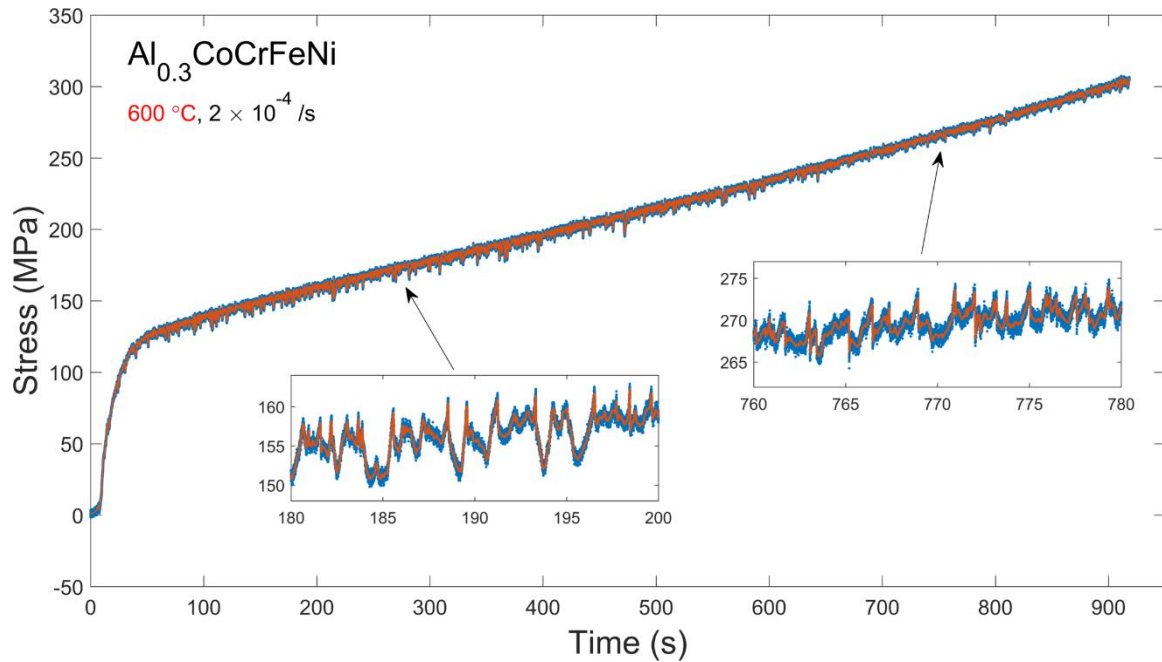
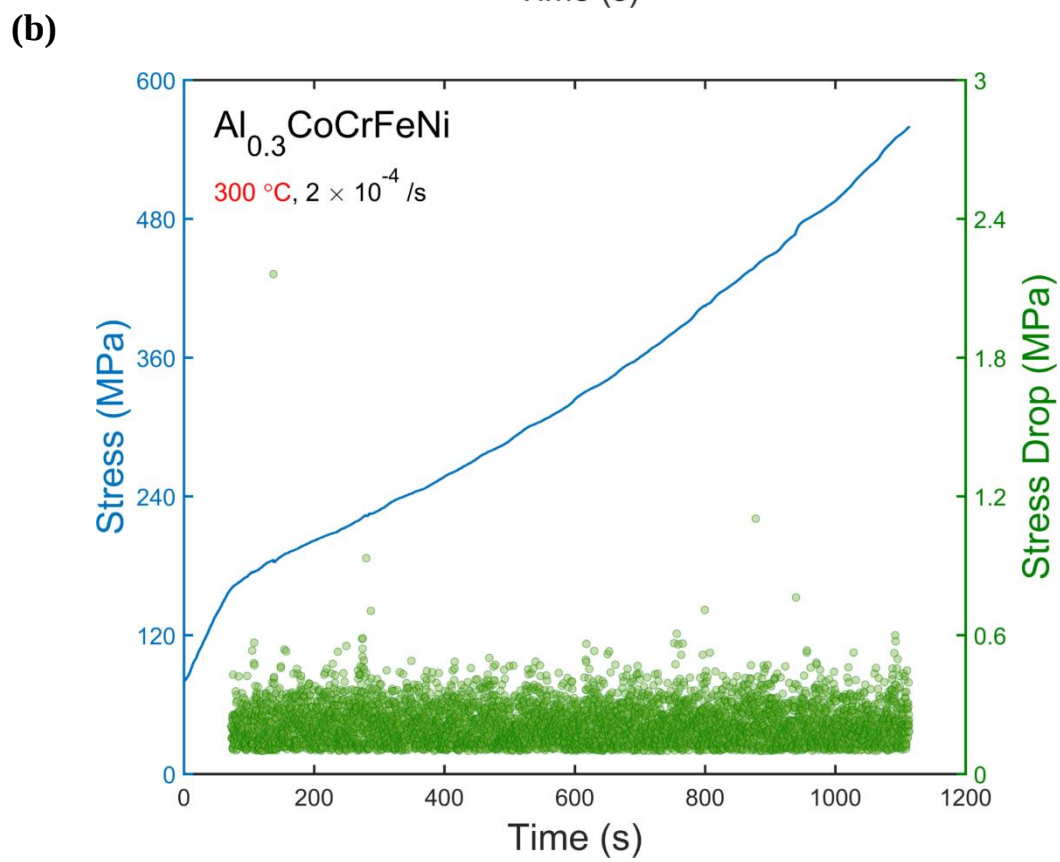
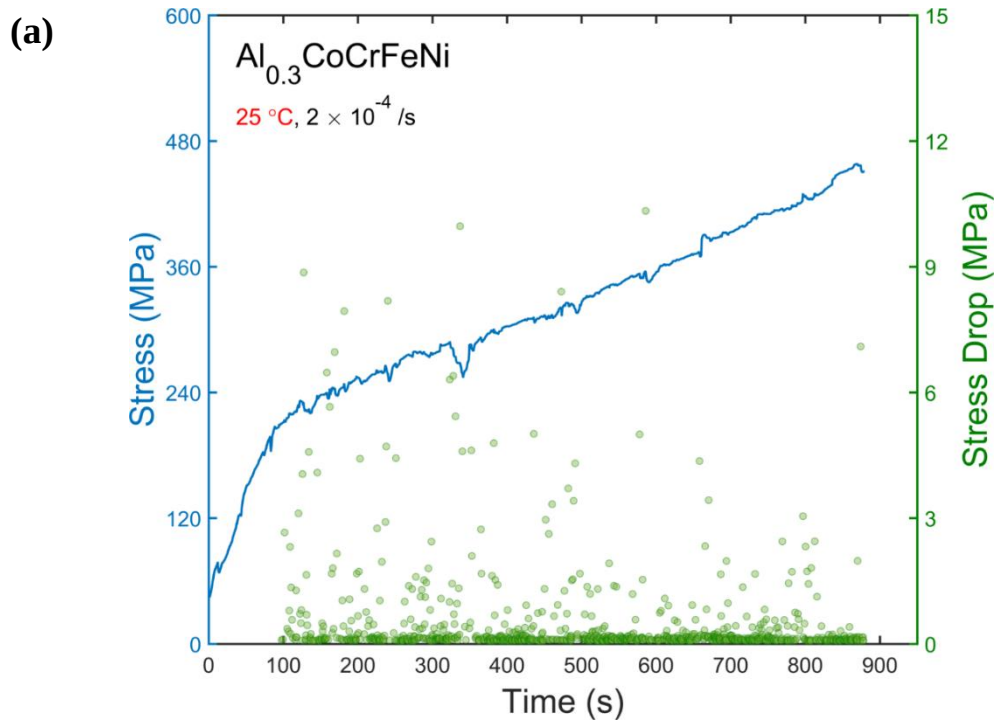
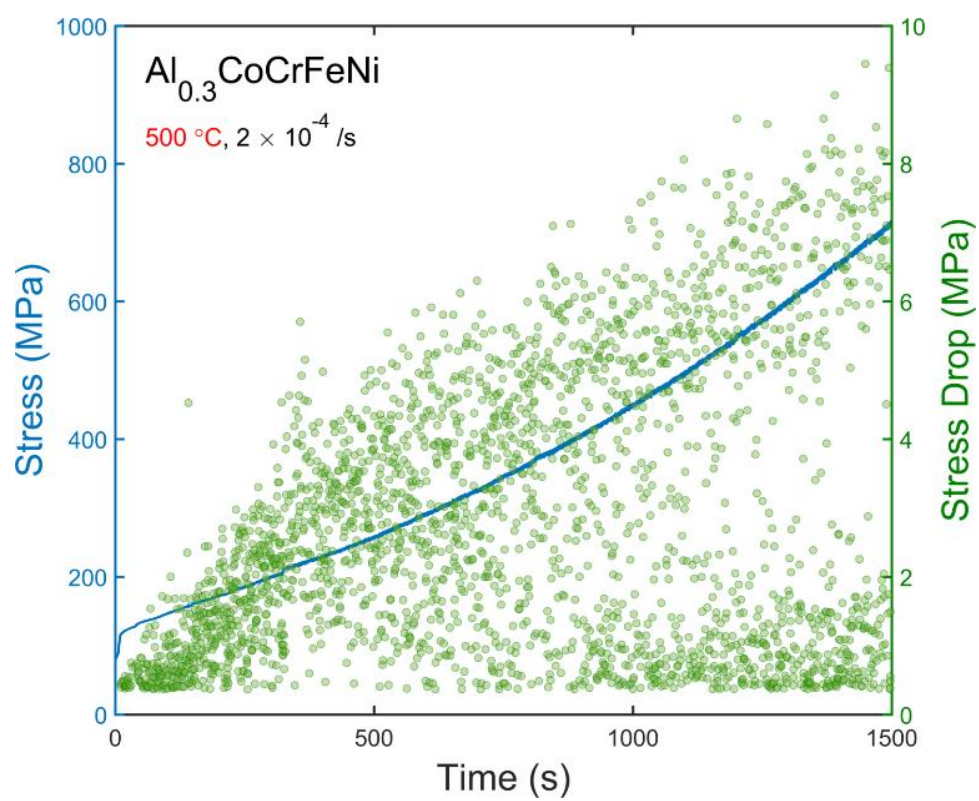
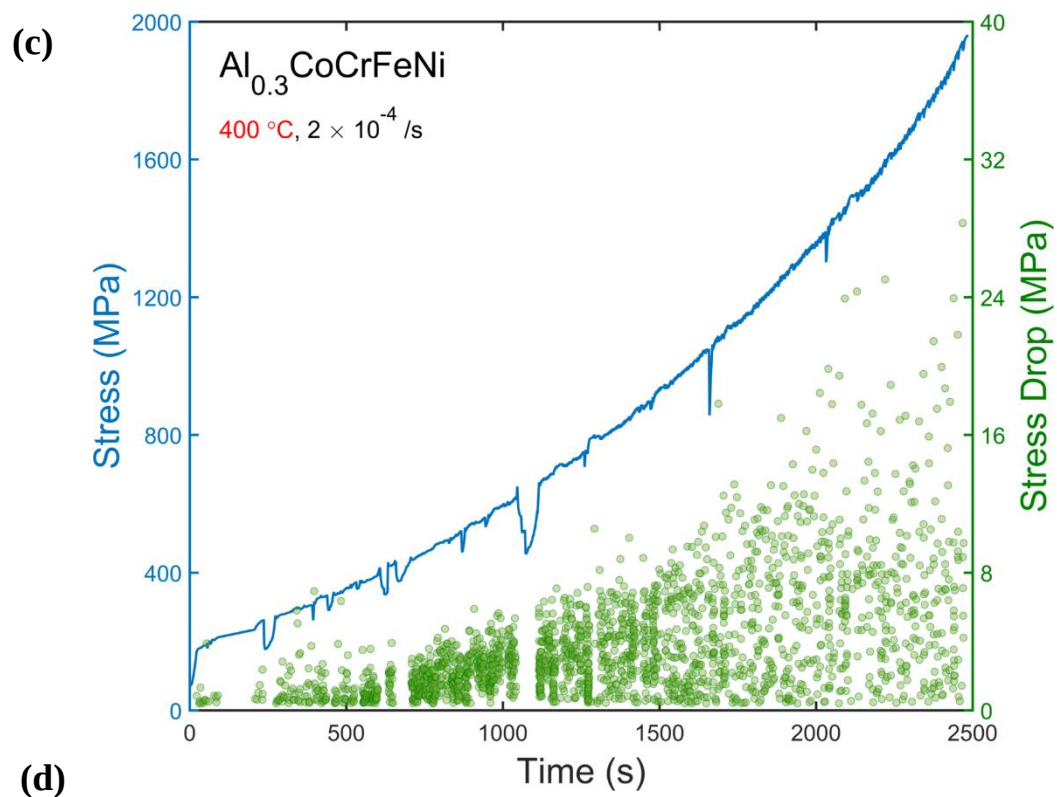


Figure 72 The stress vs. time as a function of compressive temperatures for $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed). The blue dots are the experimental data, and the red curves are the related LOESS curves. (a) $25\text{ }^{\circ}\text{C}$, (b) $300\text{ }^{\circ}\text{C}$, (c) $400\text{ }^{\circ}\text{C}$, (d) $500\text{ }^{\circ}\text{C}$, (e) $550\text{ }^{\circ}\text{C}$, and (f) $600\text{ }^{\circ}\text{C}$

Besides serration types, the magnitude of serration drops is another important parameter to characterize the serration behavior. The magnitude of serration drops is defined, as shown in Figure 71. Then the magnitude of serration drops is quantified by the statistical software. The results are shown in Figure 73.





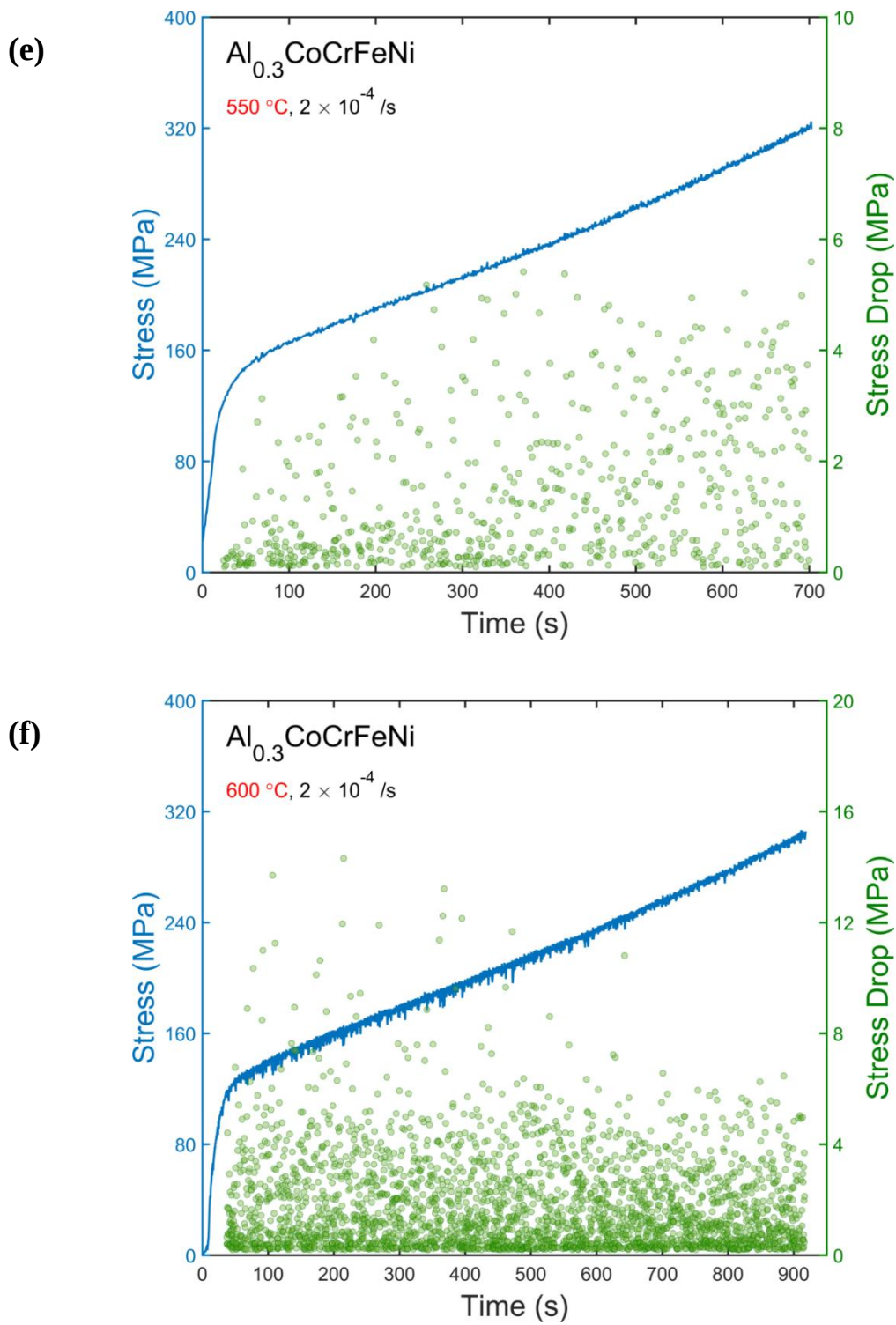
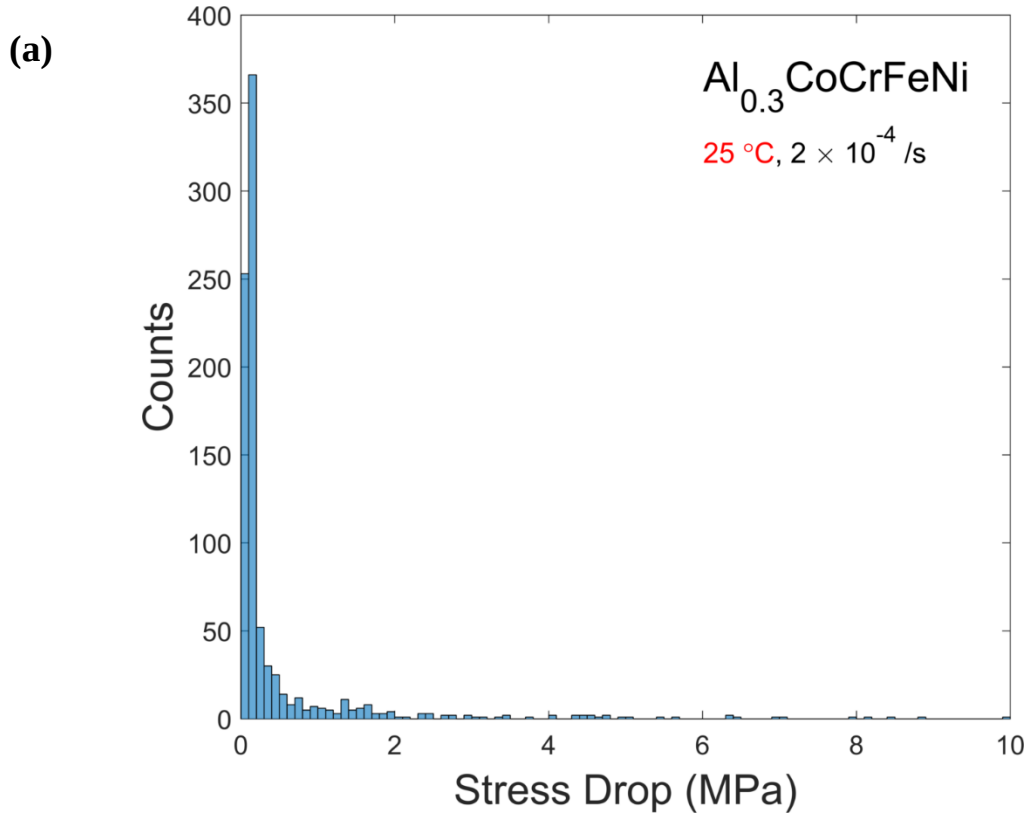
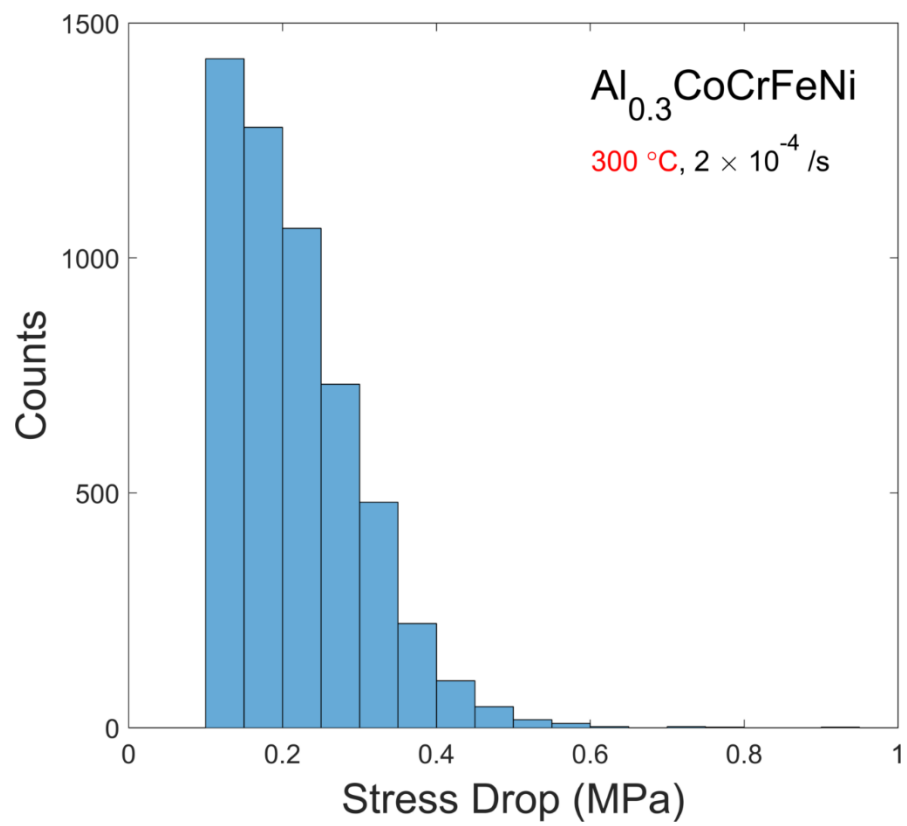


Figure 73 The statistics of the stress-drop magnitude as a function of compressive time at the temperatures of (a) 25 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 550 °C, and (f) 600 °C

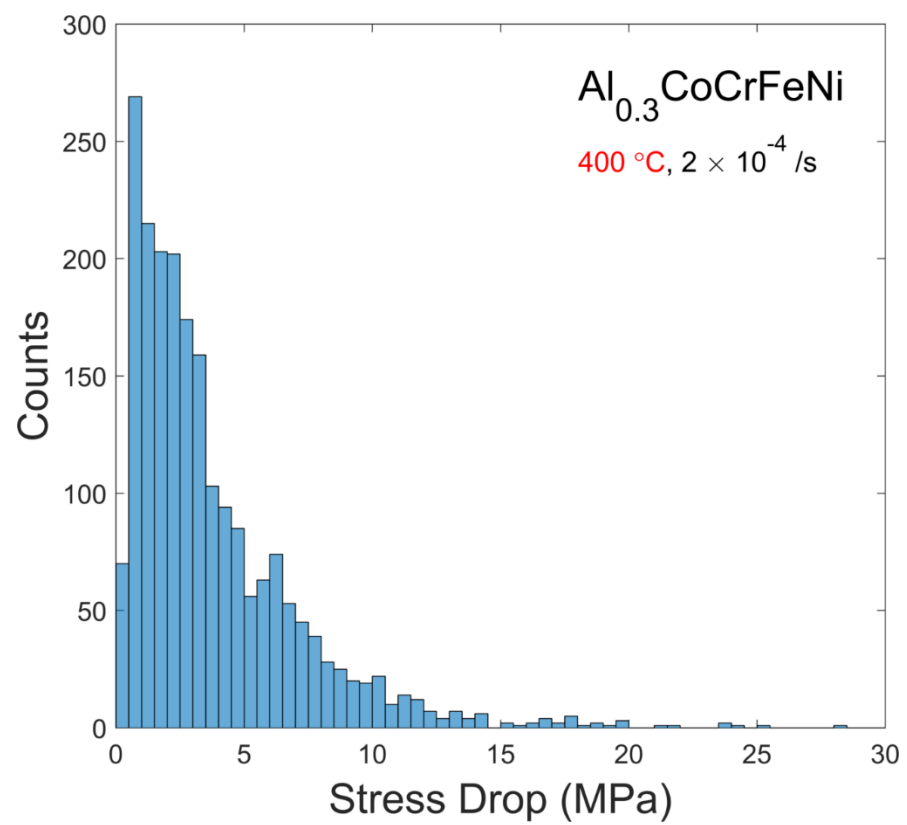
In order to obtain the information of the distribution of stress drops, further statistical work have been done. Figure 5 is the histogram of stress drops at different compressive tests at 25 °C, 300 °C, 400 °C, 500 °C, 550 °C, and 600 °C, respectively.



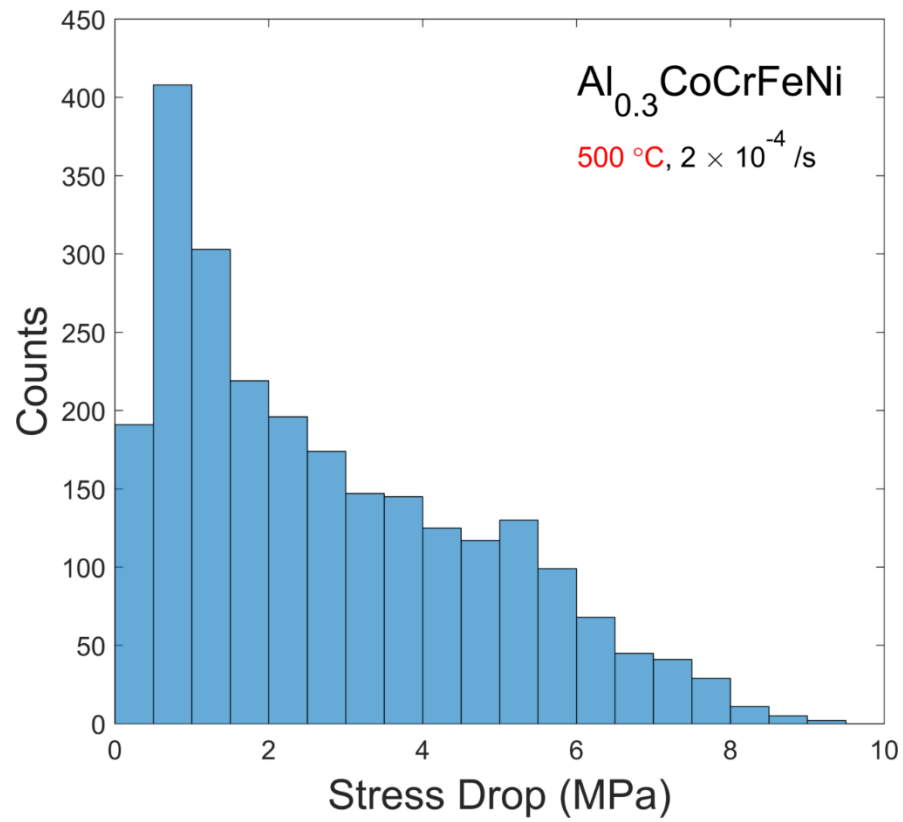
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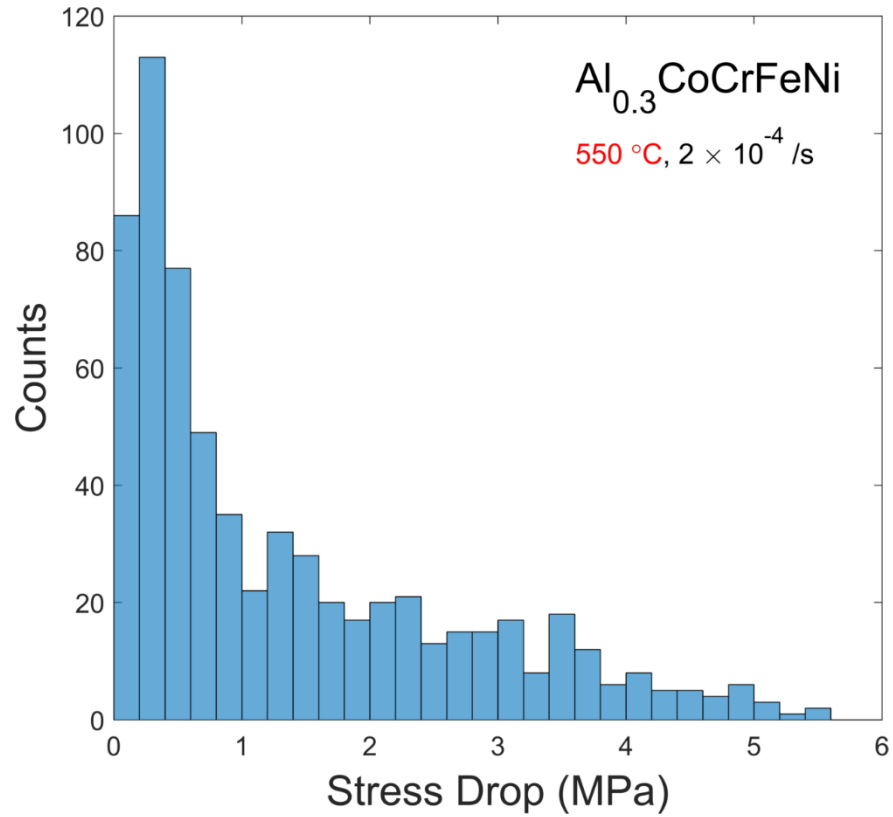
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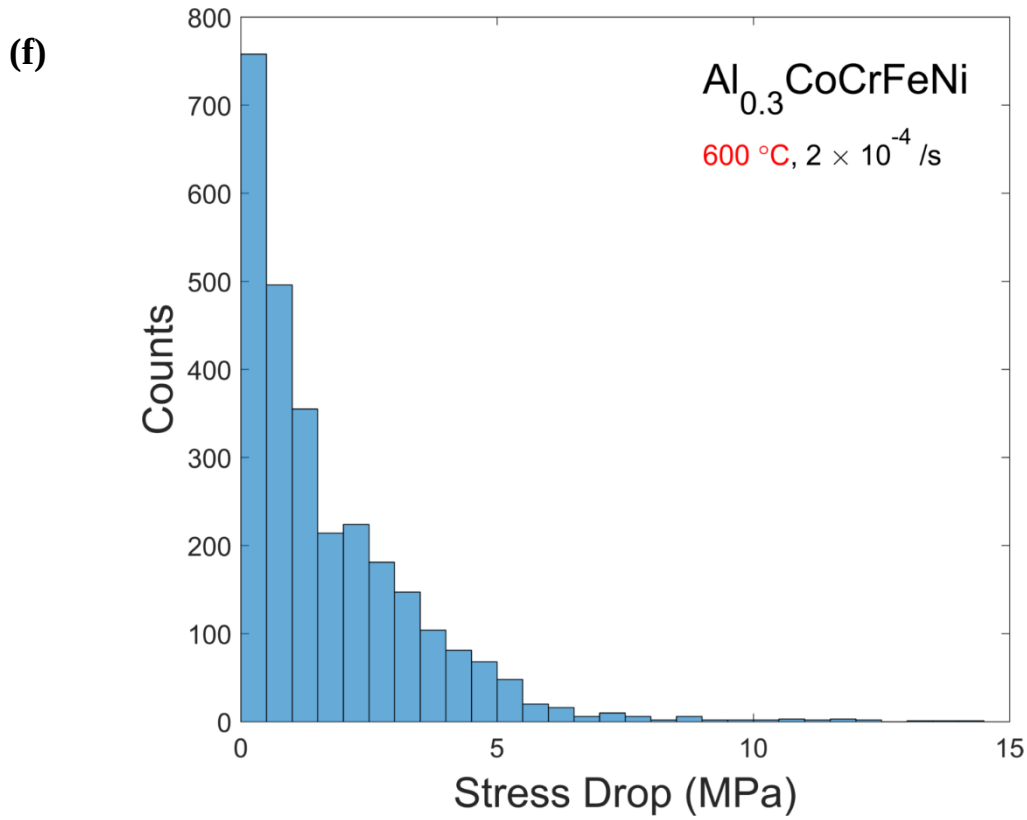


Figure 74 The histogram of stress drops at the temperatures of (a) 25 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 550 °C, and (f) 600 °C

6.3.3 Modeling of Serration Behavior of Single-phase Al_{0.3}CoCrFeNi (as-HIPed)

Recent studies of serration statistics in slowly-compressed single crystals [116, 117], and bulk metallic glasses [115] have shown that the serration statistics can display the detail-independent (universal) scaling behavior predicted by a mean-field model (MFT). A simple mean-field theory (MFT) model successfully predicts the slip-avalanche statistics [118] observed in many recent simulations of plastic deformation [119-128]. This analytic model has the advantage that as simple as it is and as few ingredients as it has, the model is able to give exact quantitative predictions of avalanche dynamics [118]. According to the MFT model [118]:

- (1) A slowly-sheared material undergoes a local slip, when the local stress at a weak spot exceeds the local threshold stress, or failure stress. A local slip stops and the weak spot re-sticks, when the local stress is reduced to a lower arrest stress, or sticking stress.
- (2) The stress released by a microscopic slip at one weak spot may trigger other weak spots to slip as well, and the process may go on and result in a macroscopically-large slip avalanche.
- (3) The material is sheared-slowly enough to prevent the slip avalanches from overlapping in time, so that each avalanche has enough time to finish before the next avalanche initiates.
- (4) Each weak spot in the slowly-sheared material interacts with every other weak spot equally strongly. In other words, the interactions between the weak spots do not decay with distance.

The MFT model predicts the avalanche statistics for two boundary conditions, a slowly-increasing stress applied to the boundaries, or a small strain rate imposed at the boundaries [118]. Here we present a brief review of the discrete version of the MFT model for the slowly-increasing stress-boundary condition. This discrete version treats the slowly-sheared material as a system with N lattice points. Under the applied stress, F , that is below but close to the failure stress, F_c , the local stress at a lattice point, l , is [115, 118, 129]

$$\tau_l = J / N \sum_m (u_m - u_l) + F \quad (15)$$

When the local stress, τ_l , exceeds the local threshold stress at the weak spot, l , the spot slips by Δu_l , and releases a stress of the amount, $2G\Delta u_l$, where $G \sim J$ is the elastic shear modulus. The stress released by this microscopic slip at one weak spot is equally redistributed to other weak spots of the material, which may trigger new slips. These new slips further increase the stress at other weak spots and may cause more slips. The process may continue and lead to a macroscopically-large slip avalanche. A slip avalanche stops, when the local stress is lower than the current local threshold stress at each weak spot of the material. The current local threshold stress may be different from the

initial local threshold stress at the beginning of the slip avalanche due to weakening or strengthening [118].

Next we present some of the main MFT model predictions [118] in the absence of weakening effects:

- (1) For a small stress-bin around the failure stress, F_c , the probability distribution, $D(s, F_c)$, of avalanche sizes, s , obeys a universal power law, $D(s, F_c) \sim 1/s^\tau$, and the model predicts that the universal exponent of $\tau = 1.5$.
- (2) For small stress-bins around the stress, F , the maximum avalanche size is related to the stress by $s_{max} \sim (F_c - F)^{1/\sigma}$, and the model predicts that the universal cutoff exponent is $\sigma = 0.5$.
- (3) For the distribution, $D(s, F)$, of avalanche sizes, s , observed in a small stress bin around F , the model predicts that

$$D(s, F) \sim 1/s^\tau D[s \cdot (F_c - F)^{1/\sigma}] \quad (16)$$

where $\tau = 1.5$ and $\sigma = 0.5$, and $D(x) \sim A \exp(-Bx)$ is a universal scaling function. The values of A and B depend on the material details. When the number of avalanches is small, the stress-integrated form, $D_{int}(s) \sim \int_0^{F_c} D(s, F) dF \sim 1/s^{\tau+\sigma}$, can be more useful. In addition, using the complementary cumulative distribution, $C(s)$, instead of the probability density distribution, $D(s)$, may also improve the statistics for a small number of avalanches. Here $C(s)$ is defined as $\int_s^\infty D(s) ds$, i.e., $C(s)$ gives the probability of finding an avalanche larger than s .

- (4) The model predicts that the local slope, G_e of the stress-strain curve, scales as

$$G_e \sim 1/\langle s \rangle \sim (F_c - F)^{(2-\tau)/\sigma} \sim (F_c - F) \quad (17)$$

where $\langle s \rangle$ is the mean avalanche size for a small stress bin around the stress, F .

(5) For the loading condition of a small imposed strain rate, $\dot{\epsilon}$, the model predicts that

$$S_{\max} \sim \dot{\epsilon}^{-\lambda} \quad (18)$$

$$D(s, \dot{\epsilon}) \sim 1/s^\tau K(s \cdot \dot{\epsilon}^\lambda) \quad (19)$$

where $\tau = 1.5$ and $\lambda = 2$ according the analytical predictions, and the universal scaling function, K , is quickly decaying.

Widom-scaling collapses can be used to test these predictions [130]. For example, in order to test $D(s, F) \sim 1/s^\tau D[s \cdot (F_c - F)^{1/\sigma}]$, or equivalently $D(s, F)s^\tau \sim D[s \cdot (F_c - F)^{1/\sigma}]$, one plots $D(s, F)s^\tau$ on the y axis and $s \cdot (F_c - F)^{1/\sigma}$ as the x axis. Next the values for F_c , τ , and σ are tuned until the distributions, $D(s, F)$, for different, F , lay on top of each other.

A recent study indicates that the above MFT model could be applied on HEAs [131]. Figure 5 shows the complementary cumulative distribution functions of the stress-drop sizes for single-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs at different temperatures and strain rates. It's clear that the temperature could dramatically affect the stress-drop size. Generally in a specific temperature range, the stress-drop size will increase as the temperature increases, which is true for the $\text{Al}_{0.3}\text{CoCrFeNi}$ HEA from RT to 600 Celsius (Figures 72 and 73). This experimental results agree well with the MFT model prediction that the slip avalanches are expected to become smaller for larger temperatures.

This study gives a glimpse of the usefulness of studying the serration statistics to understand the creep-deformation mechanics of new materials, which can be used to compare with the Portevin–Le Chatelier (PLC) effect in conventional alloys [132-136]. To further test the theory, experimental studies of the slip statistics for a broader range of temperatures should be performed, and the characterization of microstructures during and

after deformation, e.g., using transmission-electron microscopy (TEM) to investigate the dislocation and nanotwinning [137], is essential to corroborate with our analysis results.

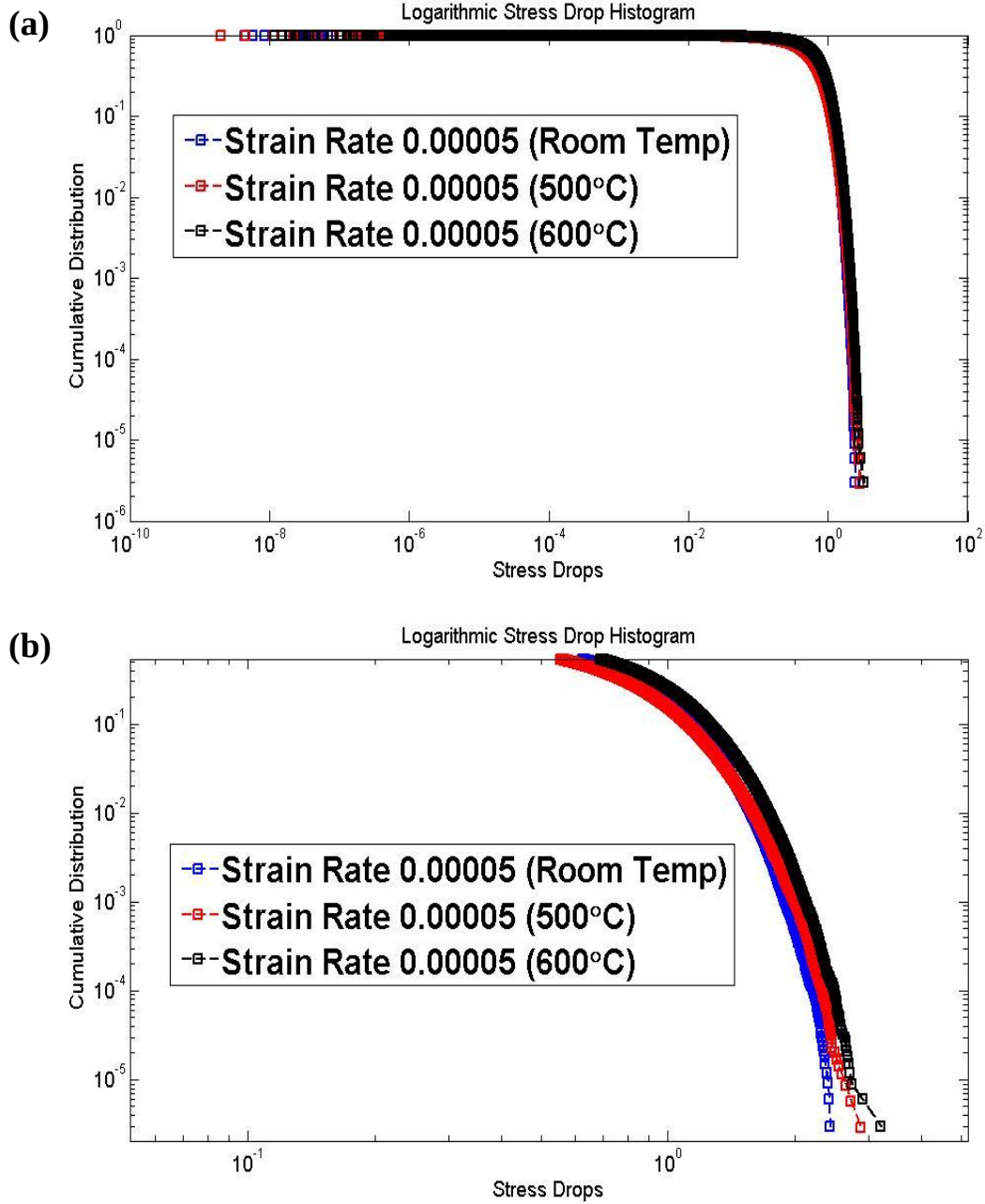


Figure 5. CCDF curve at room temperature, 500 and 600 °C of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) at the strain rate of $5 \times 10^{-5} \text{ s}^{-1}$.

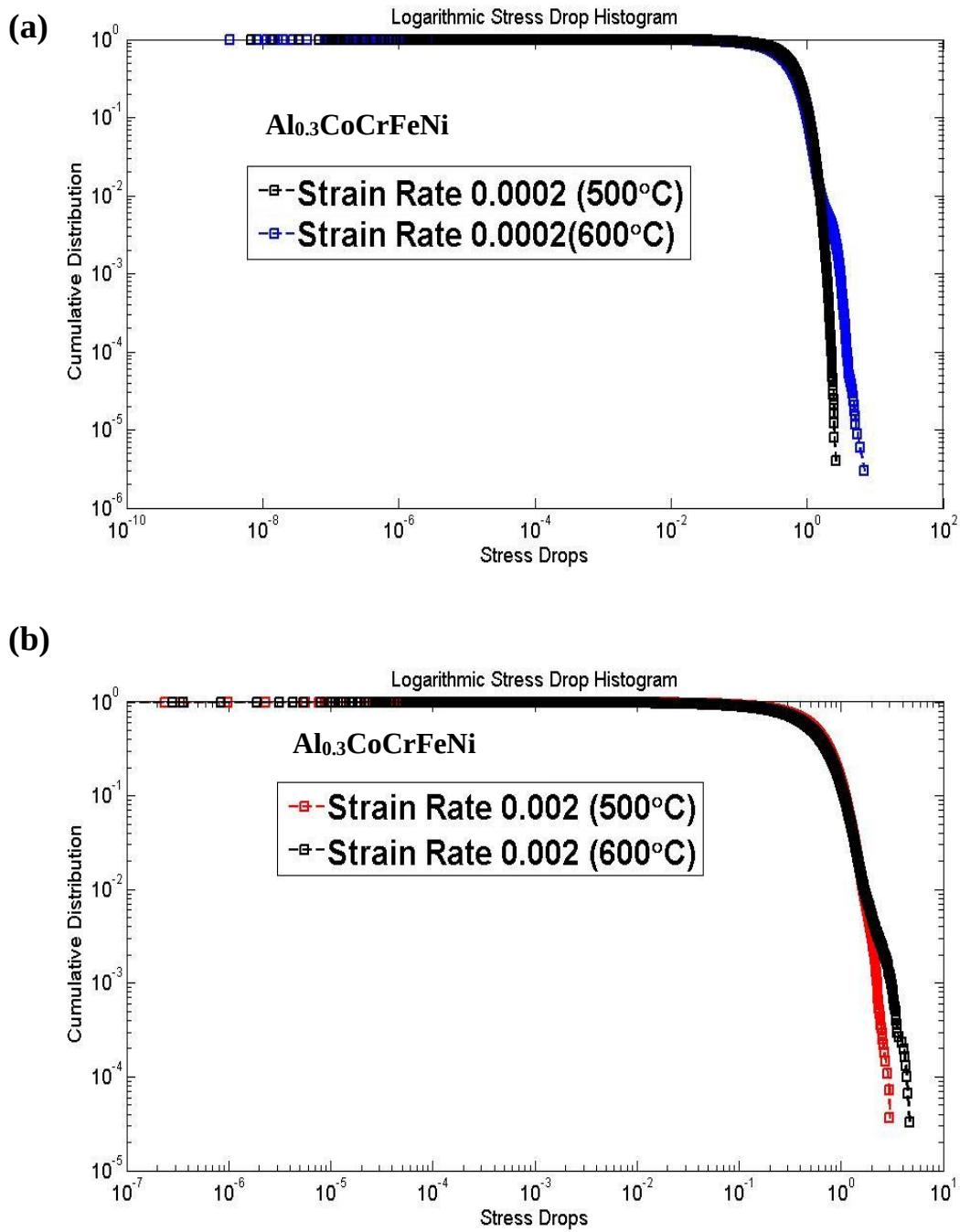


Figure 75 CCDF curve at room temperature, 500 and 600 °C of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) at the strain rates of (a) $2 \times 10^{-4} \text{ s}^{-1}$ and (b) $2 \times 10^{-3} \text{ s}^{-1}$.

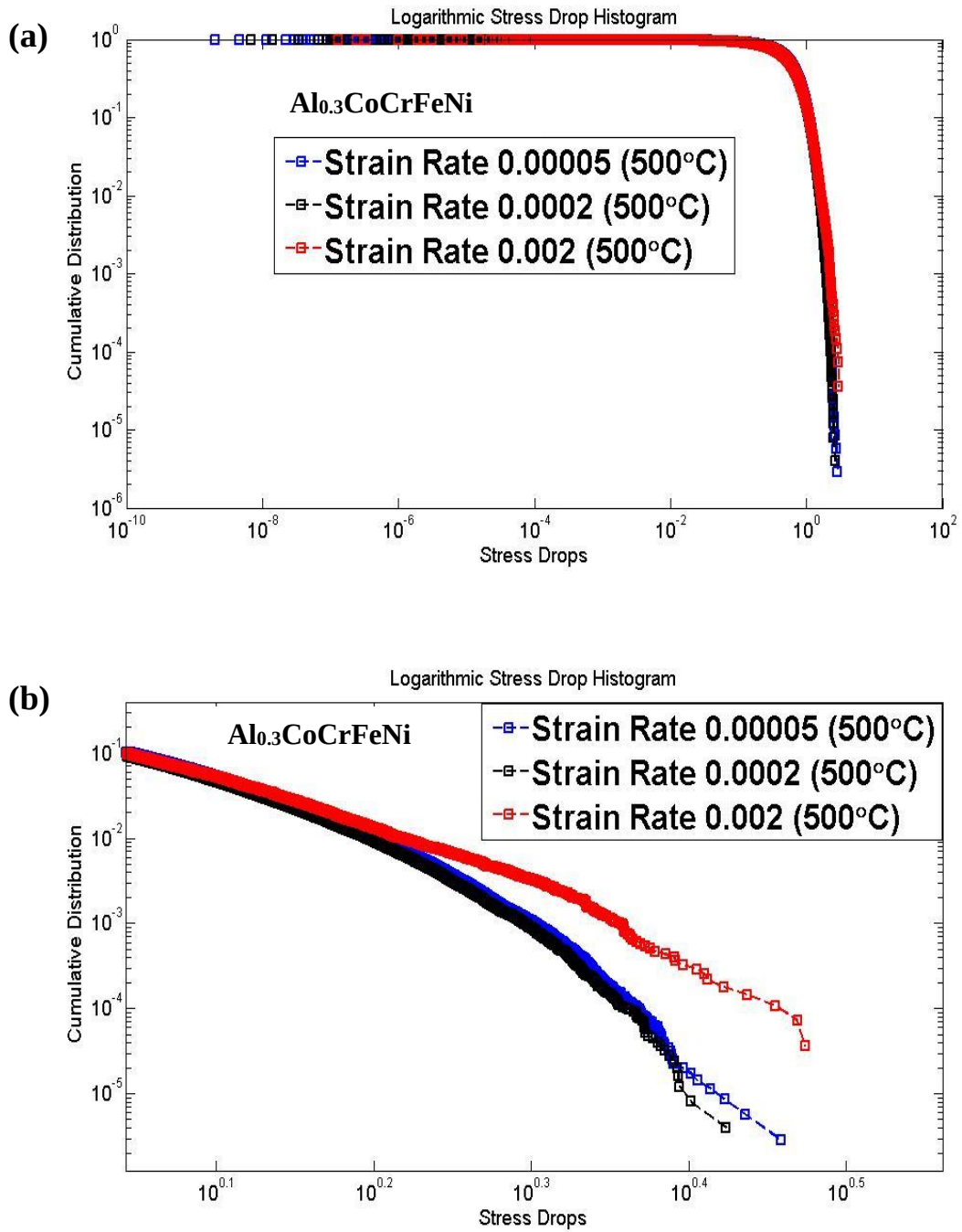


Figure 76 CCDF curve at the strain rates of $2 \times 10^{-3} \text{ s}^{-1}$, $2 \times 10^{-4} \text{ s}^{-1}$ and $5 \times 10^{-5} \text{ s}^{-1}$ at the compressive deformation temperature of 500 °C of Al_{0.3}CoCrFeNi (as-HIPed).

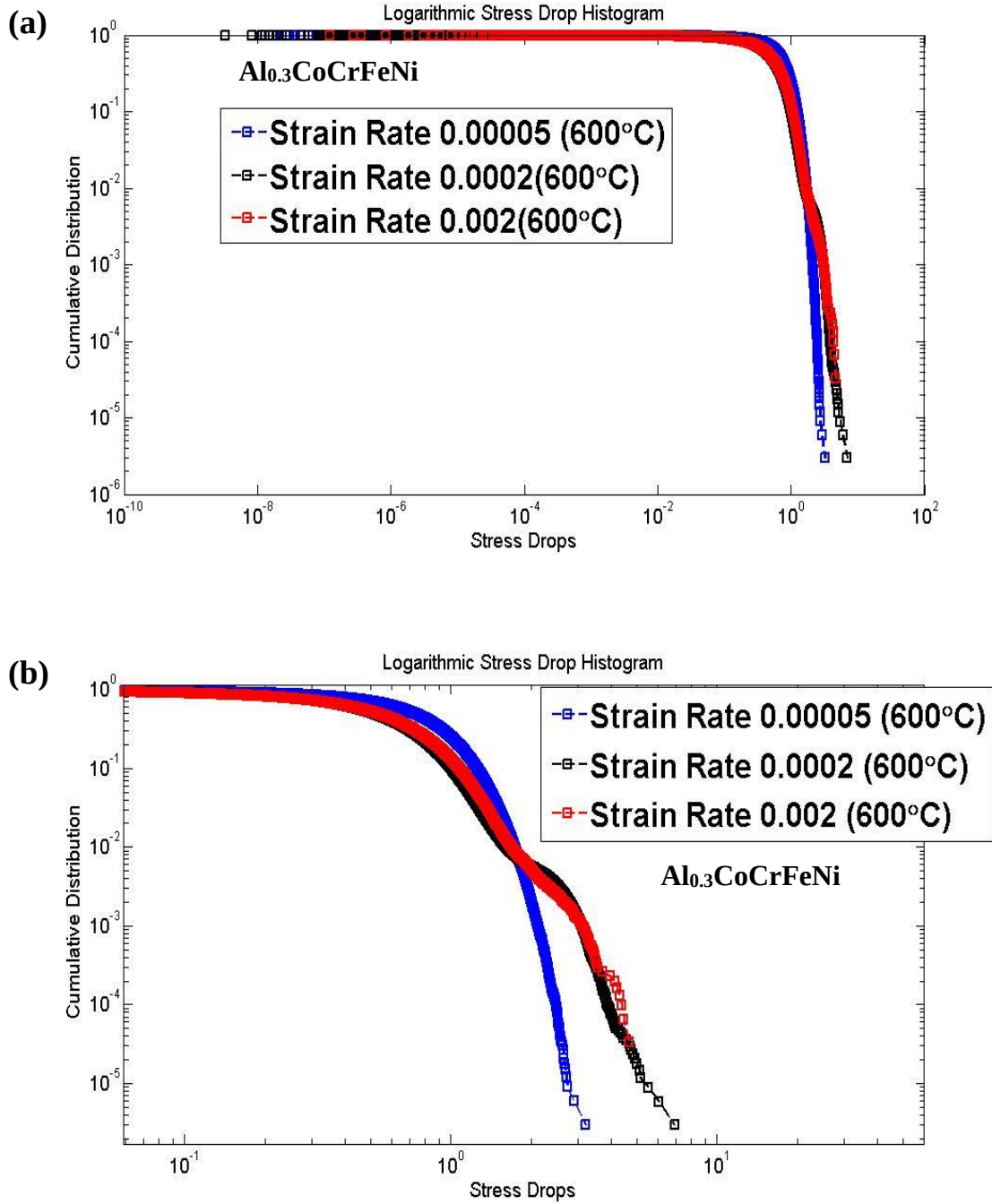


Figure 77 CCDF at the strain rates of $2 \times 10^{-3} \text{ s}^{-1}$, $2 \times 10^{-4} \text{ s}^{-1}$ and $5 \times 10^{-5} \text{ s}^{-1}$ at the compressive deformation temperature of 600 °C of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed).

6.3.4 Heat Treatment Effect on Serration Behavior

Besides the microstructures of $\text{Al}_{0.3}\text{CoCrFeNi}$ after the heat treatment at 700 °C for 500 h, the mechanical-property studies show that the strengthening effect of B2 phase is obvious. Because of the B2 phase, the yielding strength at room temperature increases from 177 MPa to 349 MPa. The B2 effect on the serration behavior is also studied by the compression tests at the strain rate of $2 \times 10^{-4} \text{ s}^{-1}$ and different temperatures from RT to 600 °C. The stress-time curves are analyzed by LOESS method [112] (shown in Figure 71), and related the magnitude (Figure 78) and distribution of stress drops (Figure 79) are also conducted. The results show that there are no obvious Type-C serrations in the temperature range from RT to 600 °C.

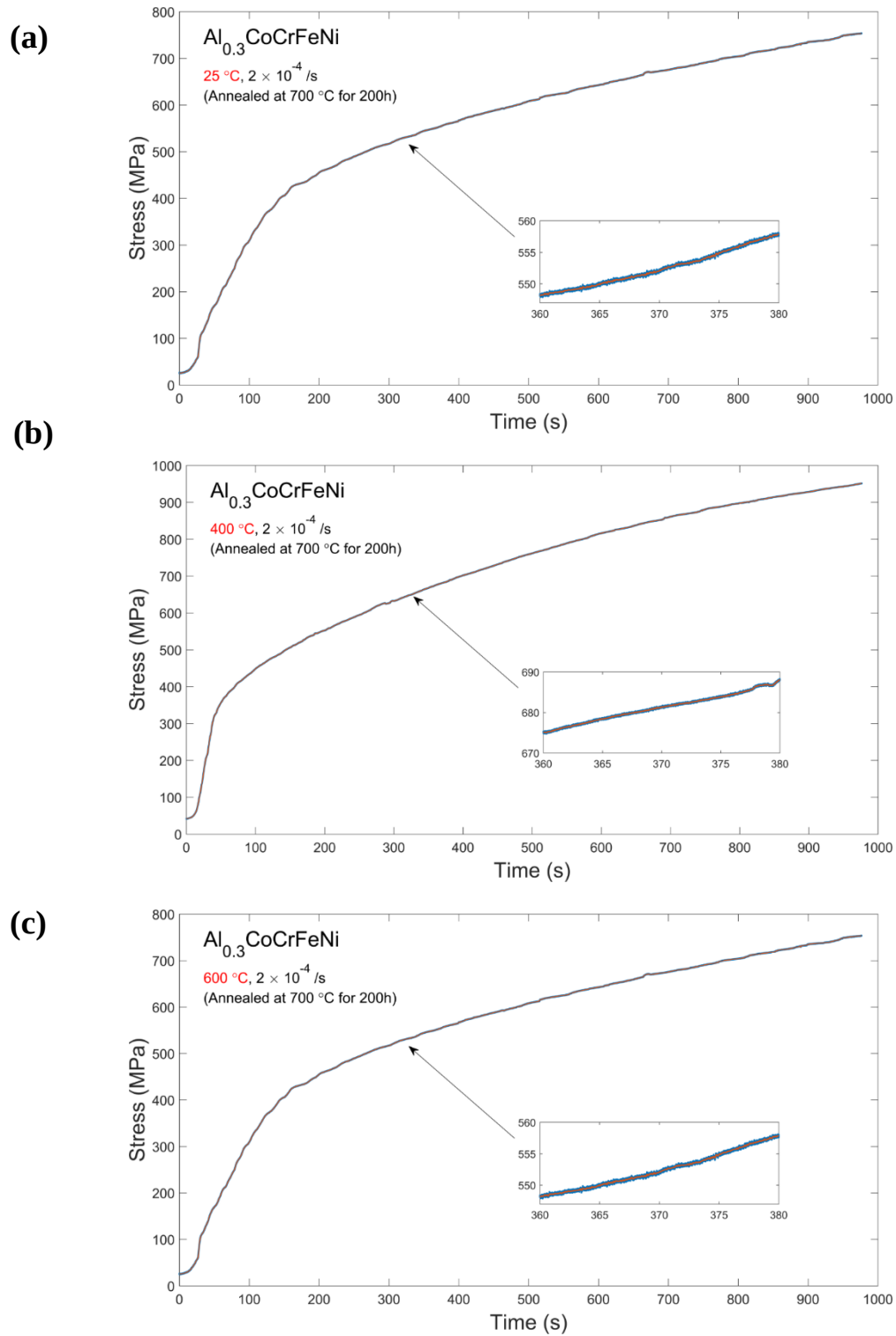


Figure 78 The stress vs. time as a function of compressive temperatures for Al_{0.3}CoCrFeNi (annealed 700 °C for 200 h). The blue dots are the experimental data, and the red curves are related to LOESS curves. (a) 25 °C, (b) 400 °C, and (c) 600 °C

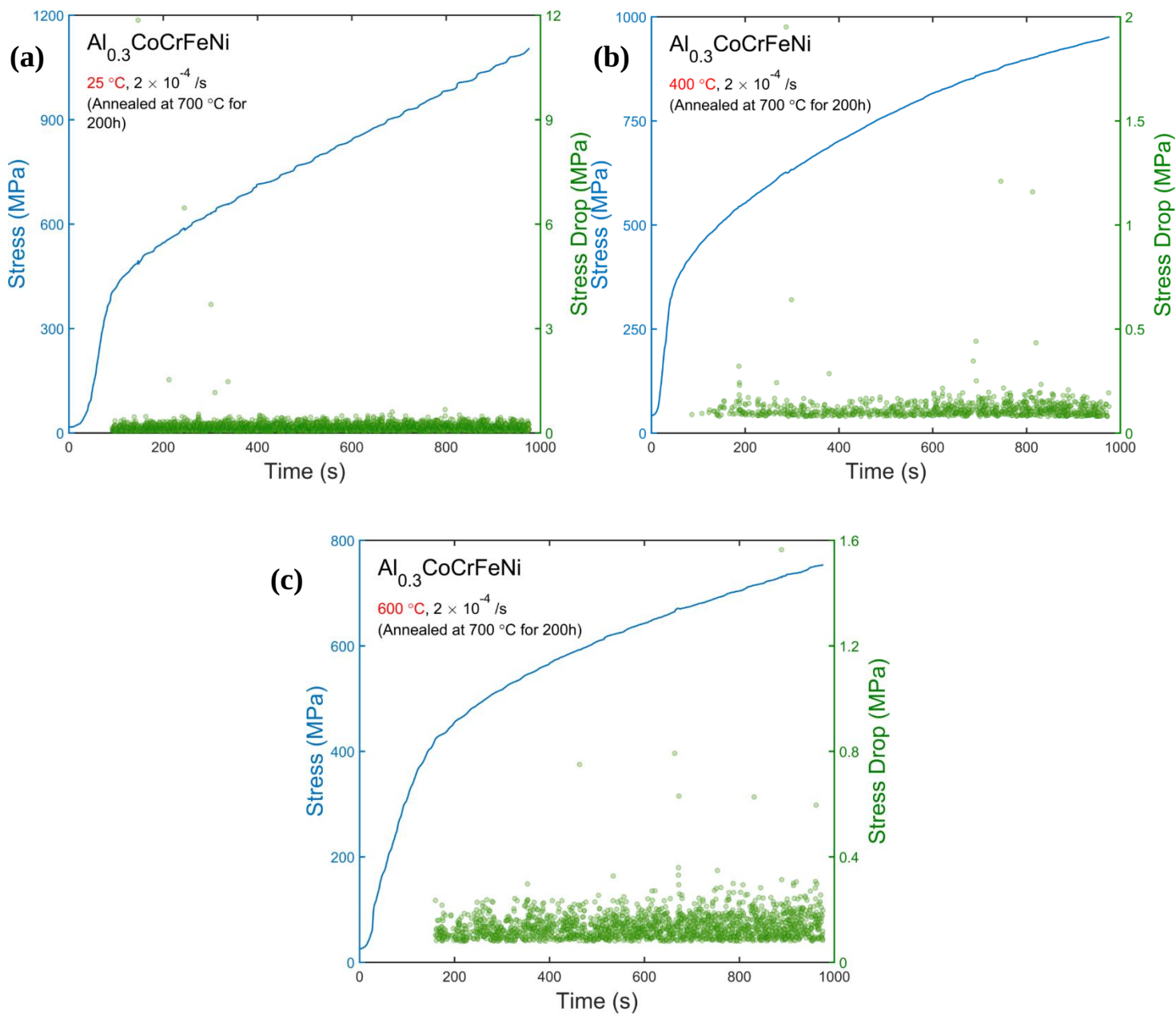


Figure 79 The statistics of the stress-drop magnitude for $\text{Al}_{0.3}\text{CoCrFeNi}$ (annealed 700°C for 200 h) as a function of compressive time at the temperature of (a) 25°C , (b) 400°C , and (c) 600°C

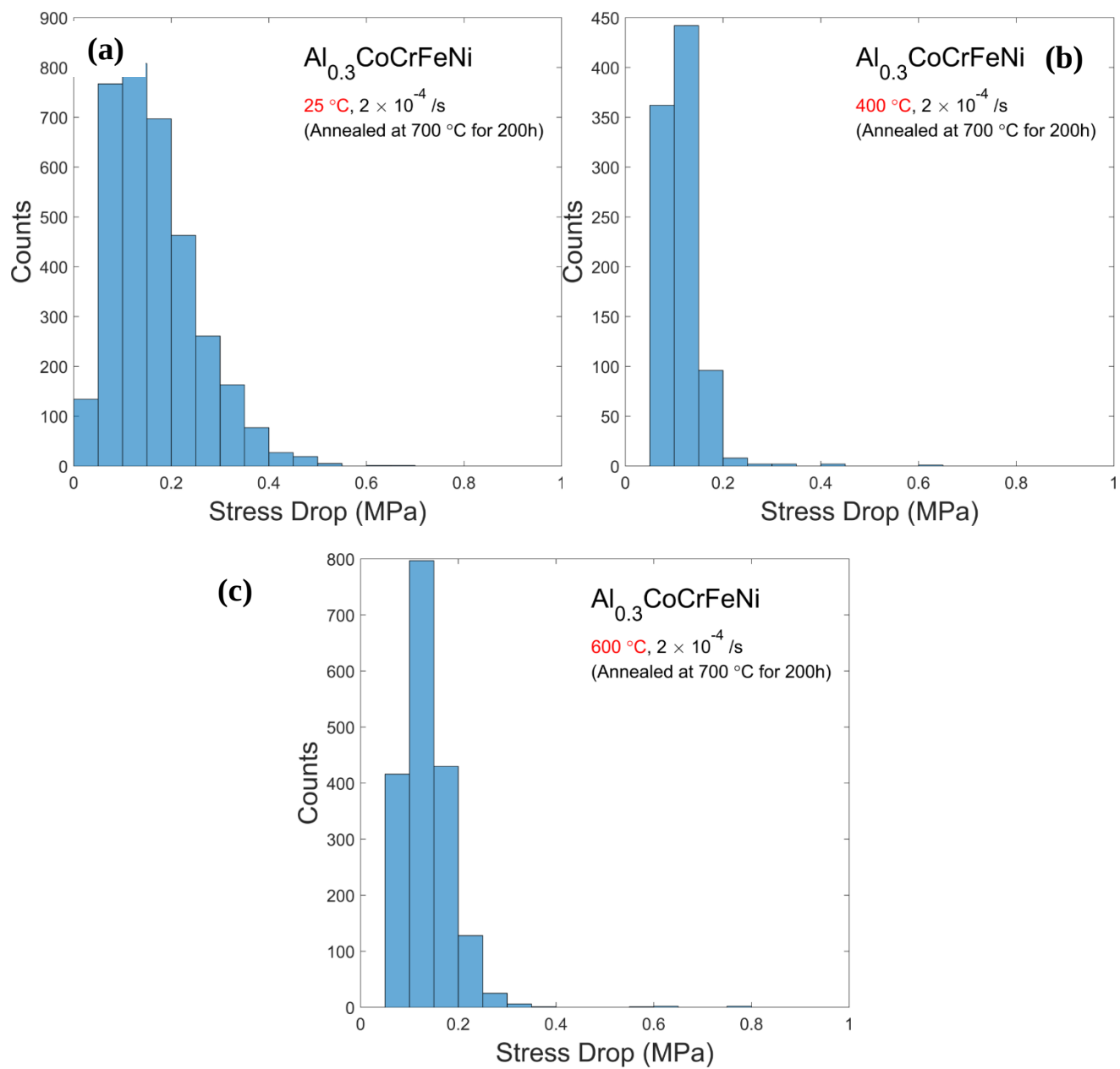


Figure 80 The histogram of stress drops for $\text{Al}_{0.3}\text{CoCrFeNi}$ (annealed $700\text{ }^{\circ}\text{C}$ for 200 h) at the temperature of (a) $25\text{ }^{\circ}\text{C}$, (b) $400\text{ }^{\circ}\text{C}$, and (c) $600\text{ }^{\circ}\text{C}$

6.3.5 Discussion of Serration Deformation Mechanism for Single-phase HEAs

It is essential to explain why the serration behavior happens in the single-phase HEAs and why not in the HEAs after heat treatment.

Former studies show that the MFT model [118, 128, 138] could also be related to the deformation mechanism for HEAs, including the dislocation motion and deformation twinning. In high-temperature ranges, the thermal vibration energy of pinning solute atoms should be considered at high temperatures. Since single-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs are regarded as solid solutions, each constituent element can be a solute atom. However, the Al atom has a larger radius (143 picometers) than other constituents, Co, Cr, Fe, Ni (125 picometers). At certain temperatures (*e.g.*, from 400 °C to 600 °C), the pinning effect of Al solutes around dislocations becomes obvious, since Al solute atoms tend to shake away from their low energy sites for pinning as the thermal vibration energy increases [139], which will lead to serrated flows. However, after annealing at 700 °C for 200 h, the Al solute atom is repelled from the FCC matrix to form a new B2 phase. When dislocation moves in the FCC matrix, there is the less Al atom-pinning effect, which results in no obvious Type-C serrations. The pinning effect of Al atoms to dislocation is illustrated in Figure 81.

For different solid-solution systems, for instance, the twinning process may overwhelm the dislocation process and dominate in the high-temperature range, or the combination of both mechanisms may exist at the same time. Other possible reasons may also exist, like phase-transformation-induced changes in the deformation mechanism. Thus, more detailed studies for the temperature effects are needed.

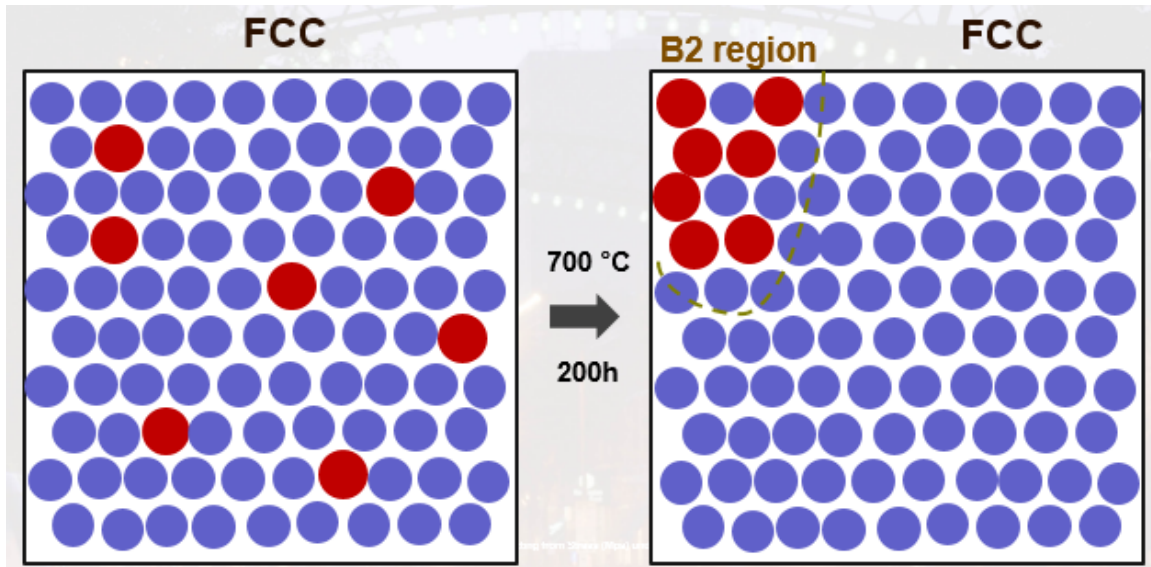


Figure 81 The schematic of solute atoms pinning effect to dislocation. The red ball represents for Al atom (which has a large atomic radius of 143 picometers), while blue ball does for the Co, Cr, Fe, Ni atoms (which has similar atomic radii, 125 picometers)

6.4 Creep Behavior of Al_{0.3}CoCrFeNi HEAs

The Al_{0.3}CoCrFeNi HEA belongs to the Al_xCoCrFeNi system, which is one of the most well-developed and refined HEA systems. Our former results show that Al_{0.3}CoCrFeNi is a single-phase HEA. The former compression results indicate that the yielding stresses do not decrease, when the temperature increases from room temperature to 550 °C. Thus, it is essential to study the conventional creep behavior of the Al_{0.3}CoCrFeNi HEA.

Creep is used in describing the continuous plastic strain over long periods of time at loads below the yielding point. A computer-controlled Material Test System (MTS) servohydraulic-testing machine was employed for tension experiments on samples of Al_{0.3}CoCrFeNi (as-HIPed) and Al_{0.3}CoCrFeNi (after heat treatment) HEAs to characterize the mechanical behavior of the alloys. The tension-sample geometry is shown below in Figure 1. The creep-sample geometry is the same as the tension sample.

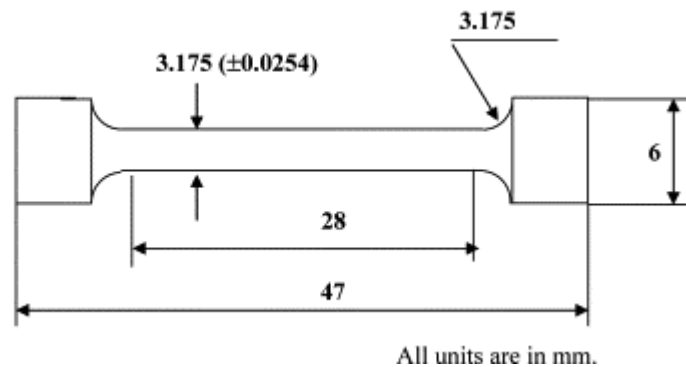


Figure 82 The tensile and creep sample geometry

A typical creep curve includes three stages, shown in Figure 13a. The first stage is also called as the primary creep, which denotes that portion where the creep rate is changing with time. Under secondary creep (constant strain-rate conditions), the metal hardens, resulting in increasing flow stresses. Eventually, at the third stage (tertiary creep), cavitation and/or cracking increase the apparent strain rate or decrease the flow stress. The conventional creep tests mainly concern about

the steady-state empirical scaling law between the creep rate and the stress, where the exponent parameter suggests the creep mechanism: diffusion-controlled or dislocation-movement-controlled.

Conventional creep tests have not been reported in the area of HEAs. Only two papers using indentation tests to study the creep behavior of HEAs have been reported [22, 23]. The indentation creep has been defined as a time-dependent motion of a hard indenter into a solid under a constant load for a long time. The indentation-creep experiments were conducted for the multi-phase $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.3, 0.5, 0.7, 0.9, \text{ and } 1.5$) in the temperature range of 500 - 900 °C using a load 1 kgf for dwell times of 5, 10, and 30s [22]. The indentation creep behavior is strongly dependent on the crystal structure of HEAs. For the FCC single-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ alloy, hot hardness resist without large changes for all experimental temperatures in the time range of 30s. The situation is different for the multi-phase $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.5, 0.7, 0.9, \text{ and } 1.5$) HEAs. The variations of hot hardness as a function of dwell time are negligible below 600 °C, while the hot hardness decreases with increasing the dwell time above 873 K. It confirms that creep happens for the multi-phase HEAs above a certain temperature (e.g., 873 K for $\text{Al}_x\text{CoCrFeNi}$, $x = 0.5, 0.7, 0.9, \text{ and } 1.5$).

Nanoindentation is also used in characterizing the initial transient creep stage in FeCoNi by Wang *et al.* [23] by the visco-elastic fitting theory. The FeCoNi is a single-phase FCC HEA [30]. The displacement curve for the initial creep stage can be described by an empirical law [140]:

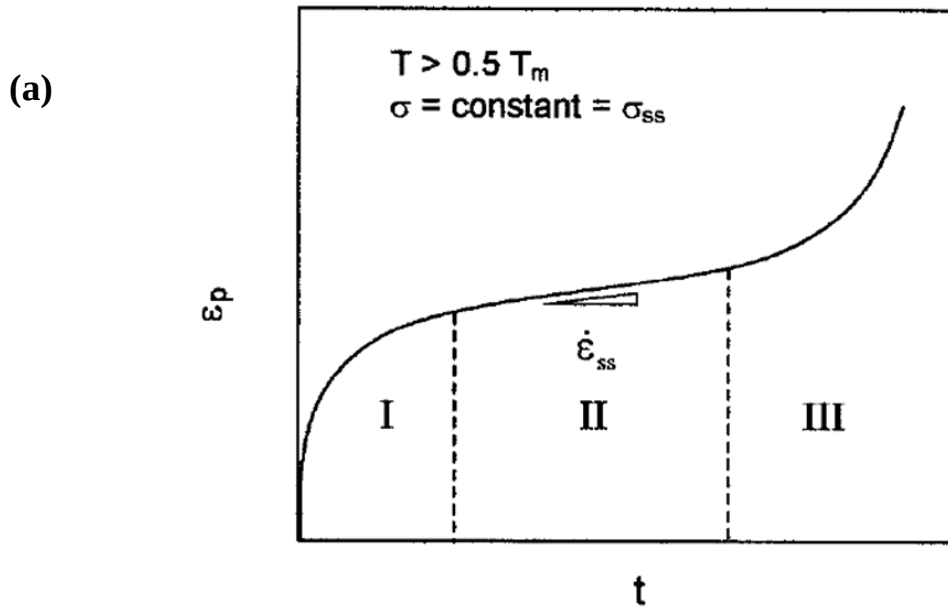
$$h(t) = h_i + \beta(t - t_i)^m + kt \quad (20)$$

where β , m , and k are fitting parameters. The fitting protocol in Equation (20) is found to produce very good fits for the FeCoNi HEA at a constant load of 4,000 μN . Unlike conventional alloys, a crossover point where the slope changes in the initial creep stage are found in the FeCoNi HEA. A further study shows that the value of the crossover point increases with increasing holding time at the same constant load and with the increase in the holding stress at a constant holding time.

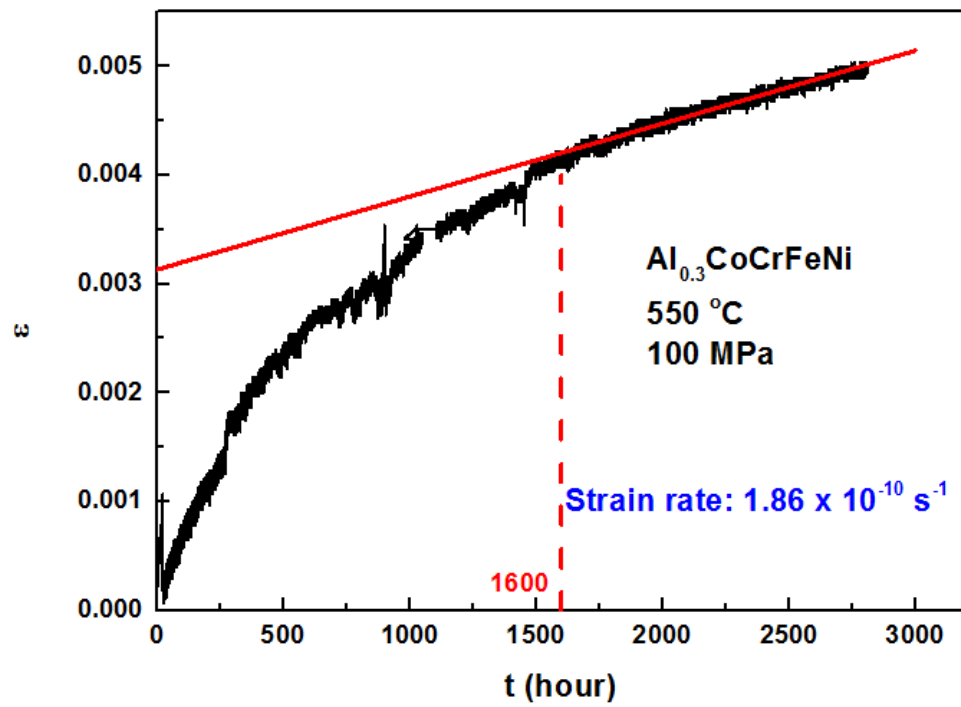
A hypothesis is proposed for the crossover point in the initial creep stage from the viewpoint of the dislocation migration beneath the indenter [23]. The formation of the dislocation cells

corresponds to the crossover behavior. Before the crossover point, the separated dislocation entanglement leads to the work-hardening effect. After the crossover point, the work-hardening effect is saturated, and the residual dislocations migrate into the domain boundary of the dislocation cell, which determines the viscous behavior [23].

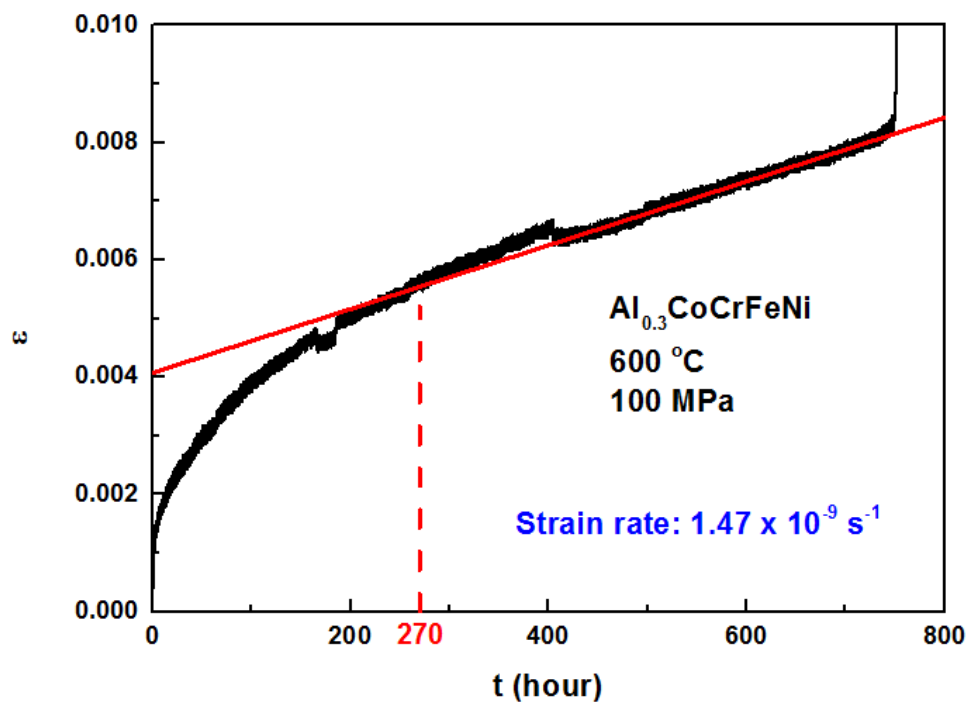
The macroscopic tensile-creep curves at (a) 550 °C under 100 MPa, (b) at 600 °C under 100 MPa, (c) at 700 °C under 100 MPa, (d) at 700 °C under 85 MPa, (e) 700 °C under 80 MPa, (f) 700 °C under 75 MPa, (g) 700 °C under 70 MPa, (h) 700 °C under 65 MPa, (i) 700 °C under 60 MPa, (j) 700 °C under 55 MPa, (k) at 700 °C under 50 MPa, (l) at 730 °C under 70 MPa, (m) at 730 °C under 65 MPa, (n) at 730 °C under 60 MPa, (o) 730 °C under 50 MPa, (p) 760 °C under 65 MPa, (q) 760 °C under 60 MPa, (r) 760 °C under 55 MPa, (s) 760 °C under 50 MPa, and (t) 760 °C under 40 MPa of the Al_{0.3}CoCrFeNi (as-HIPed) are shown in Figure 83. At all conditions temperatures, the creep curves exhibit typical primary-creep and secondary-creep stages.

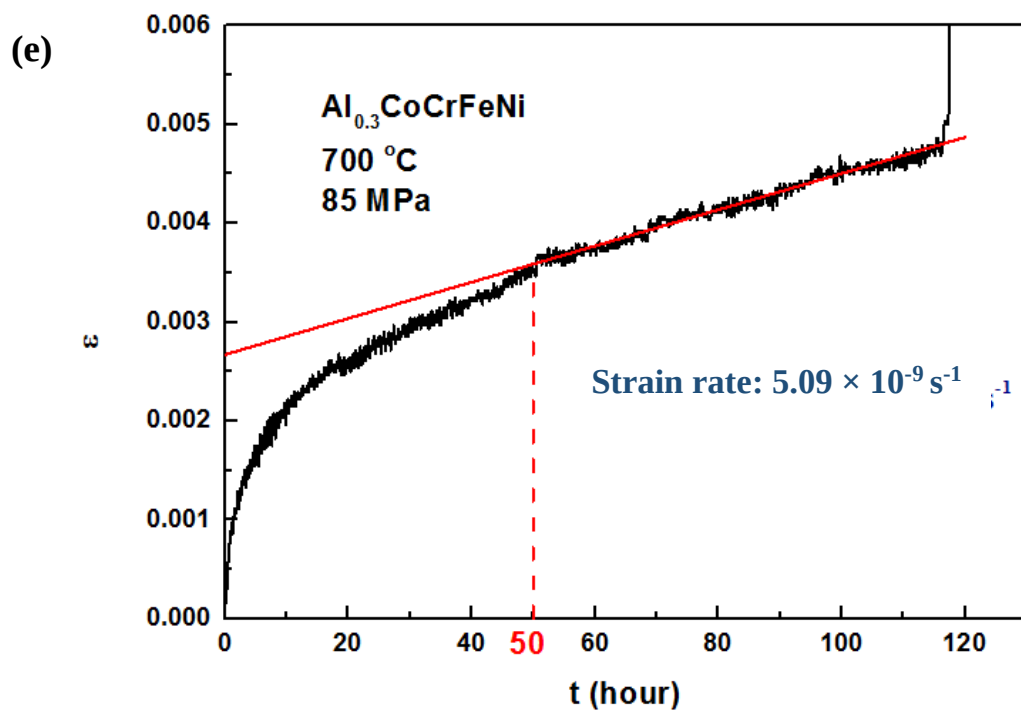
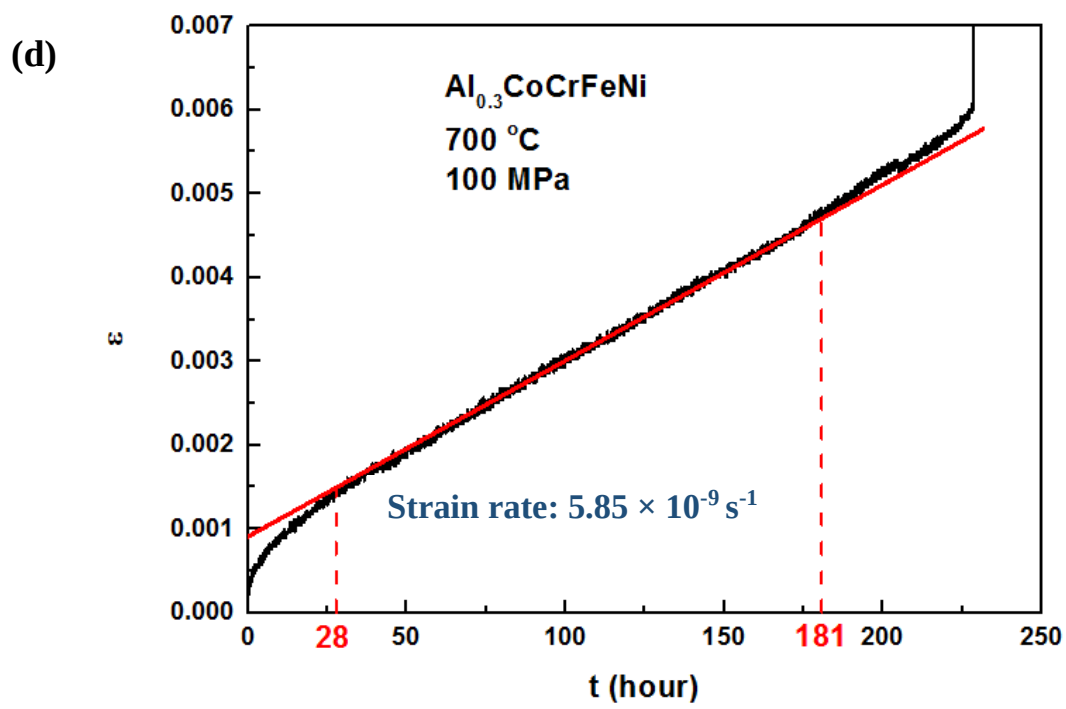


(b)

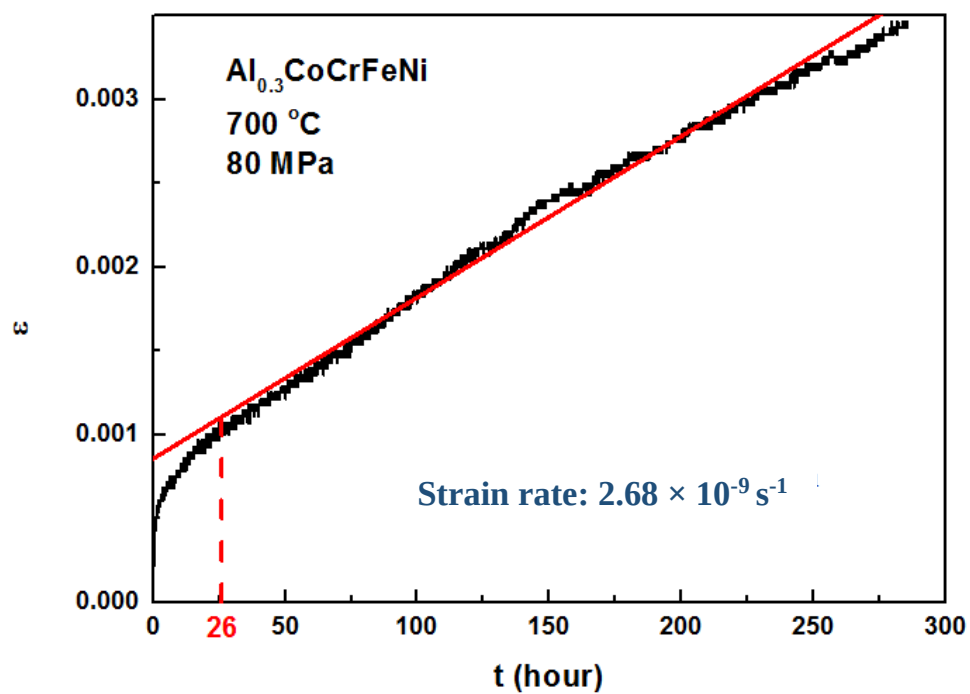


(c)

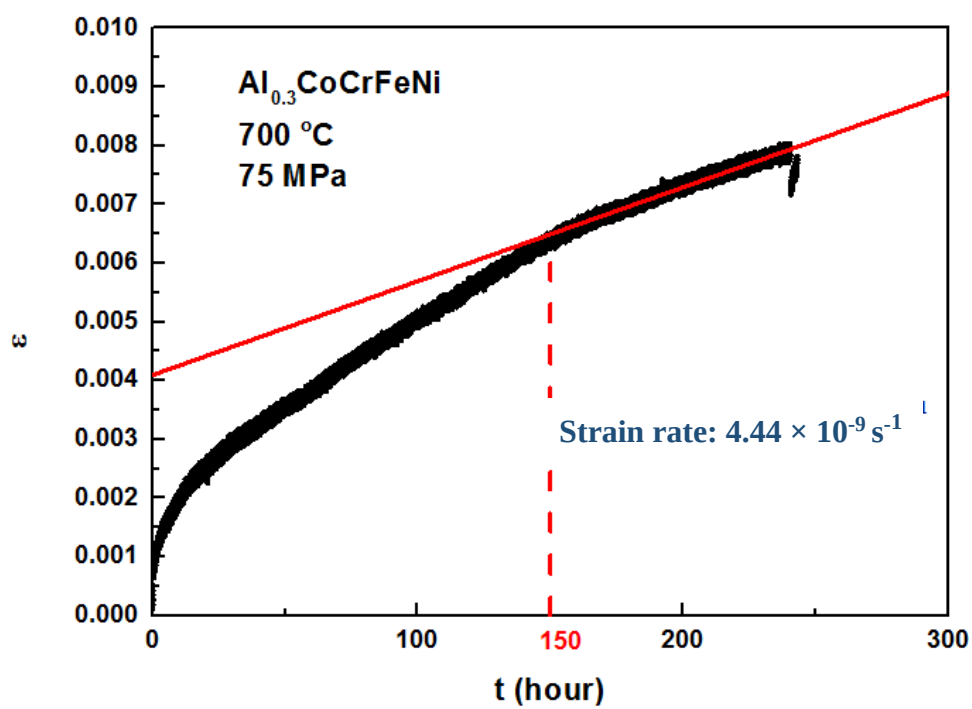




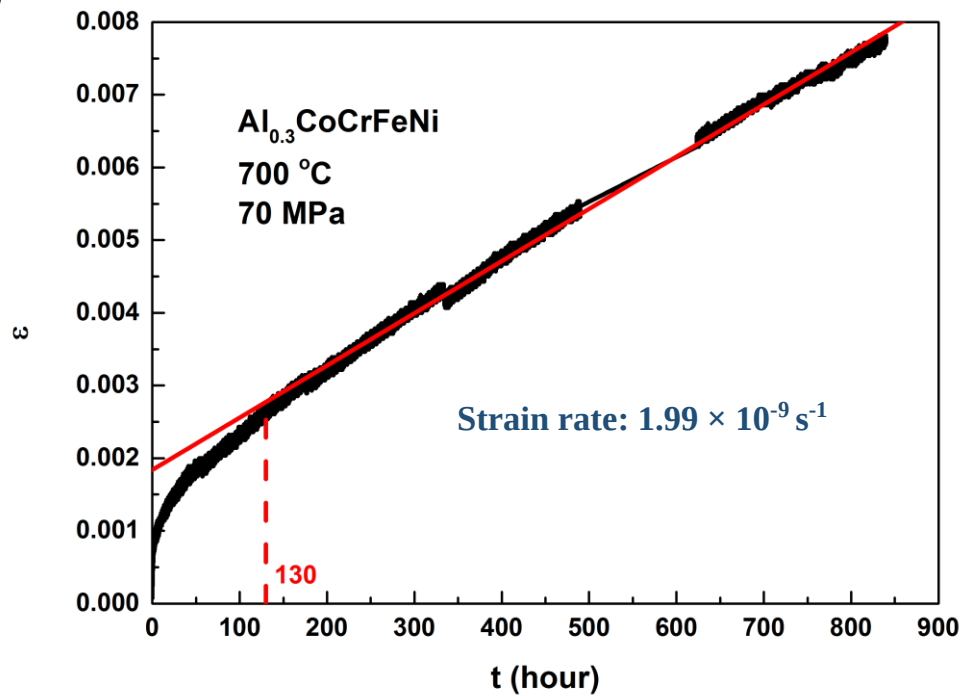
(f)



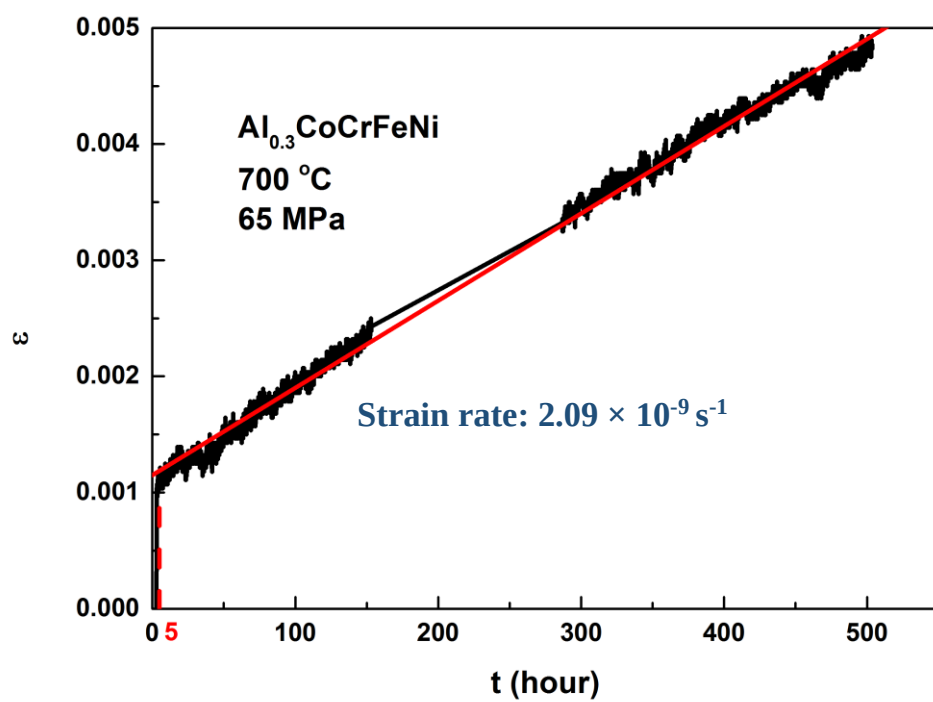
(g)



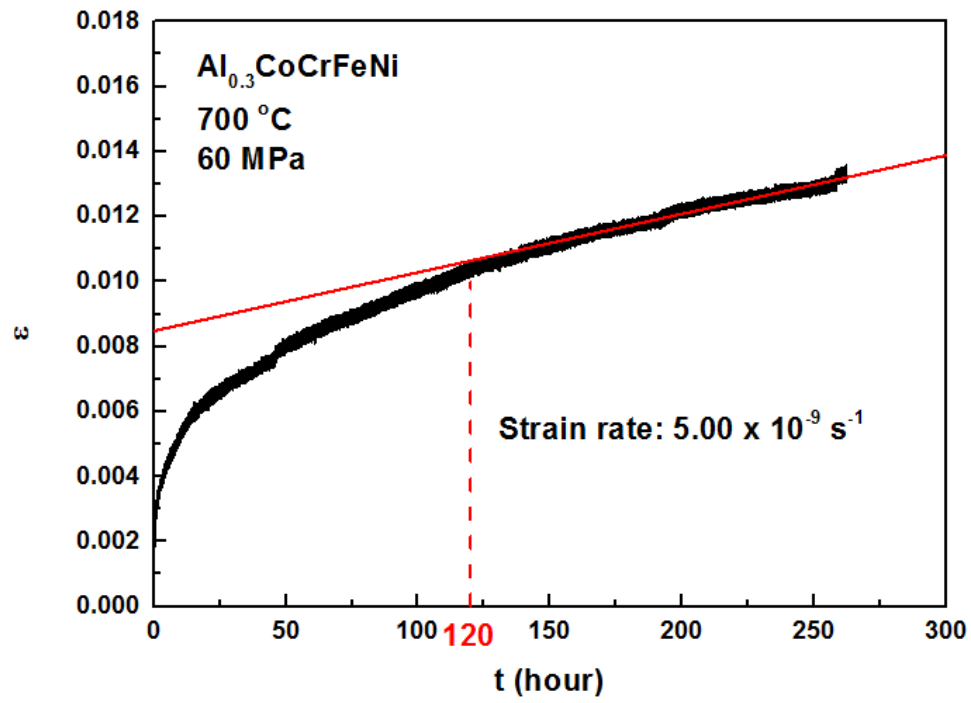
(h)



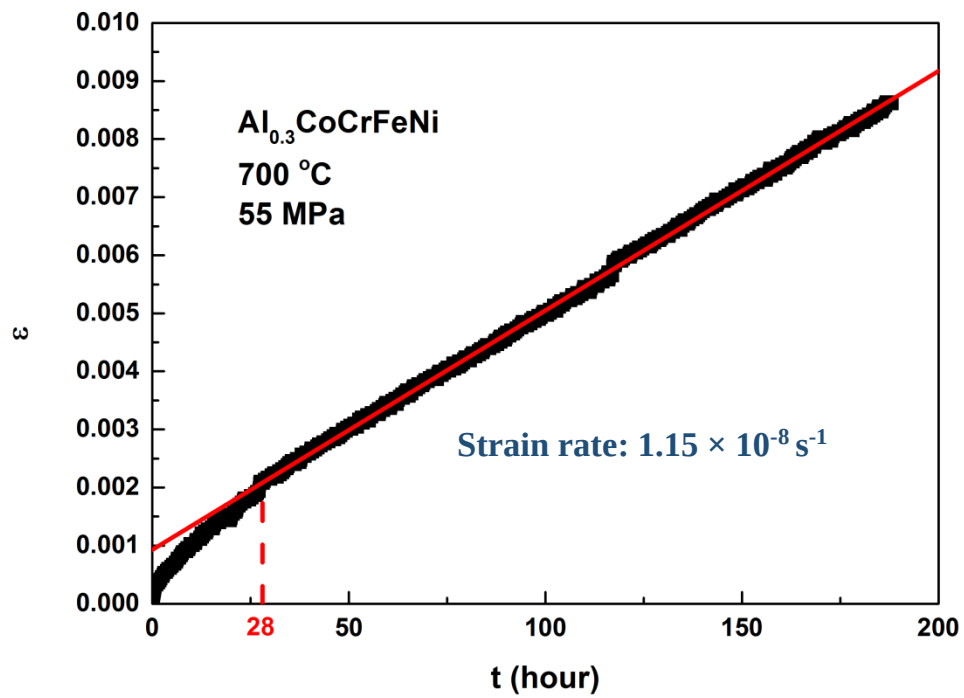
(i)



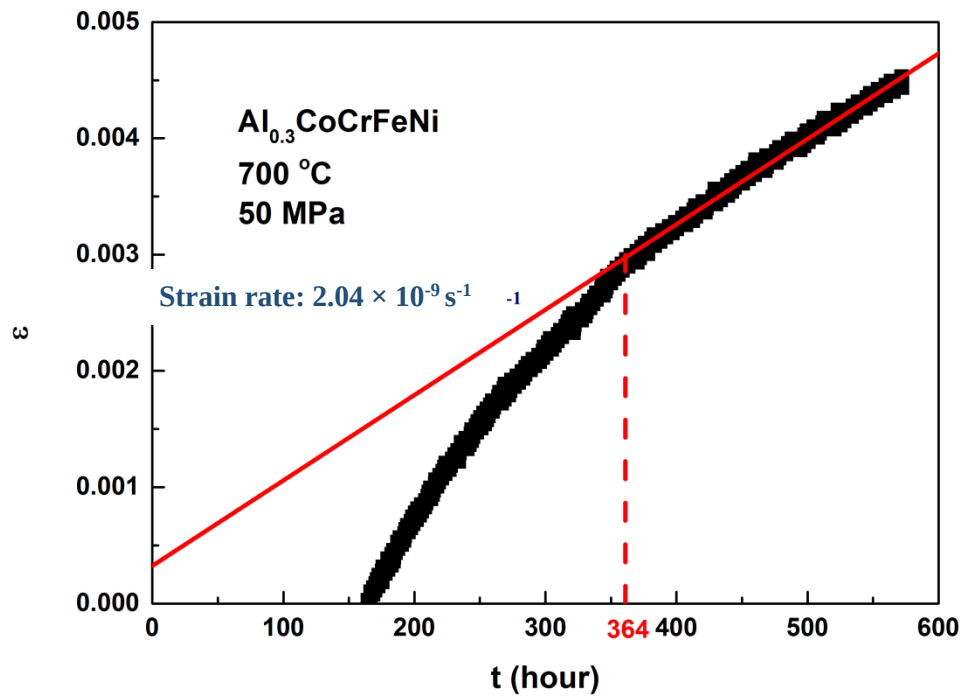
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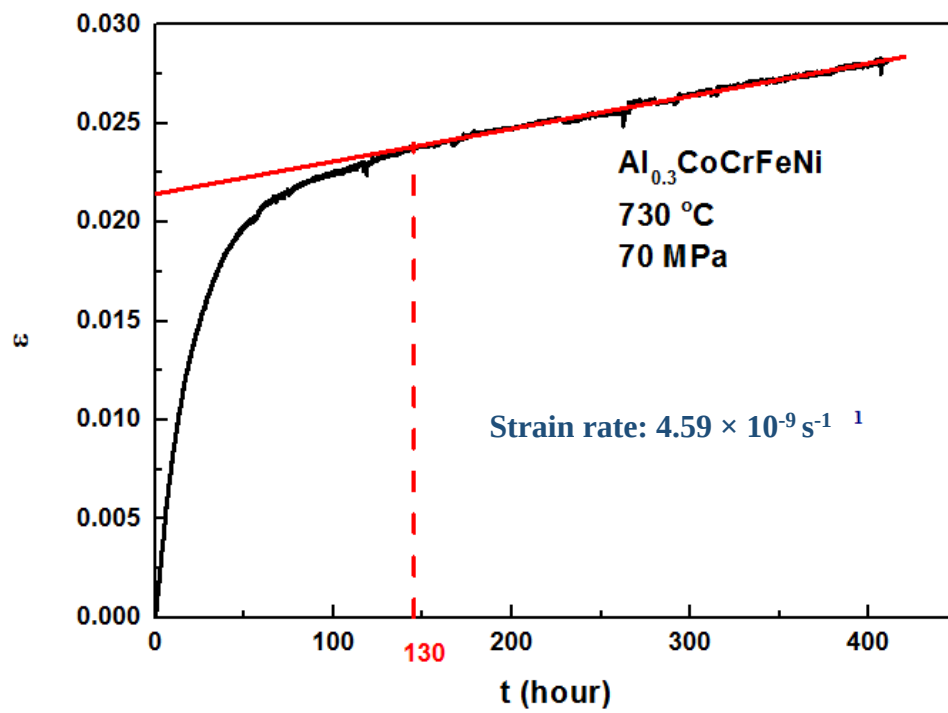
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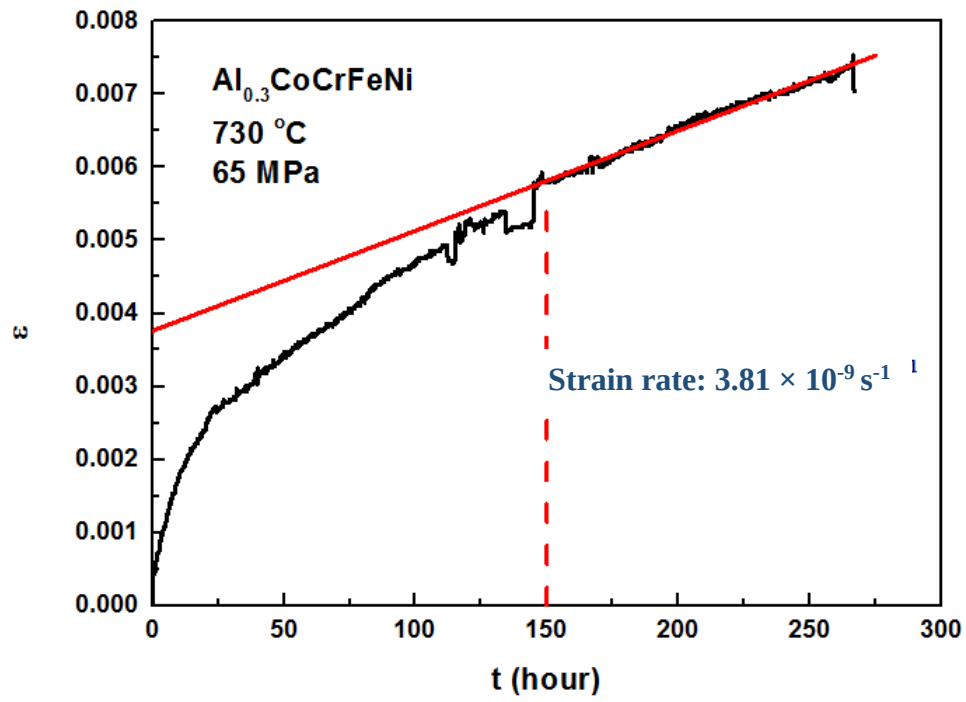
(l)



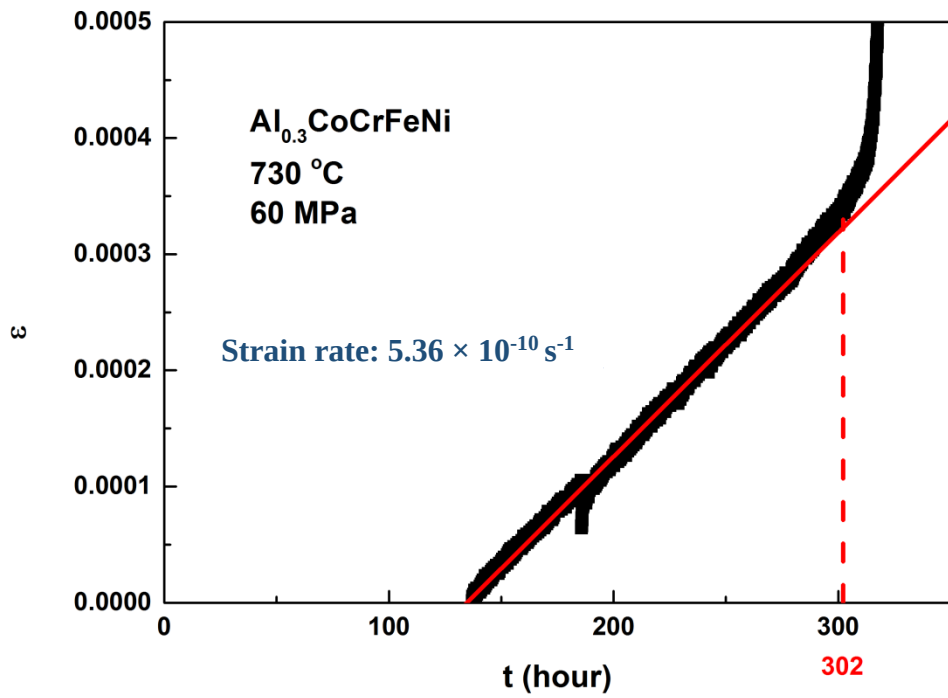
(m)



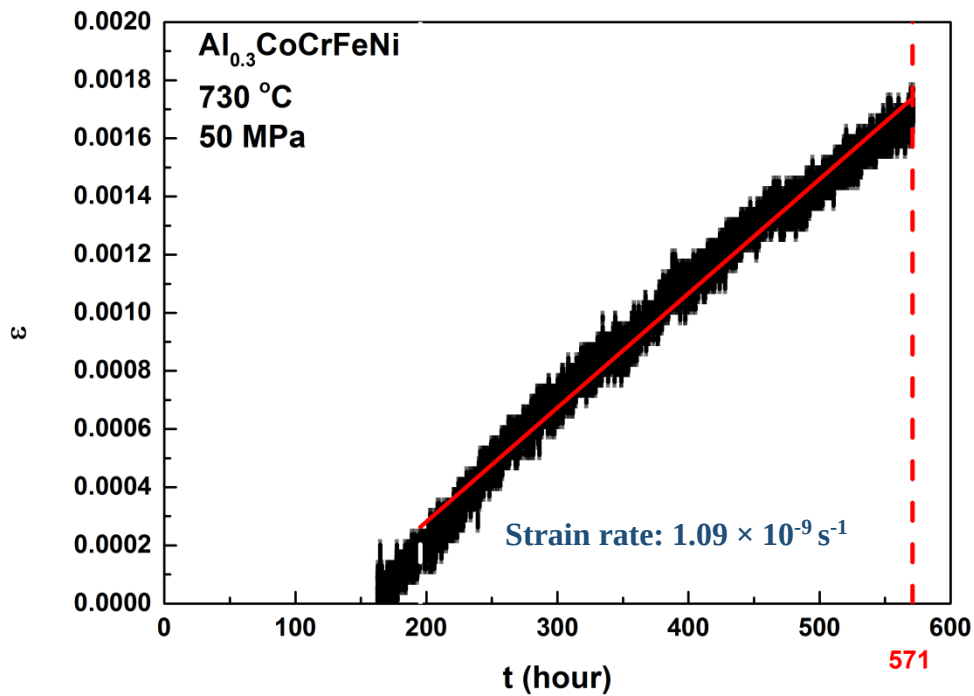
(n)



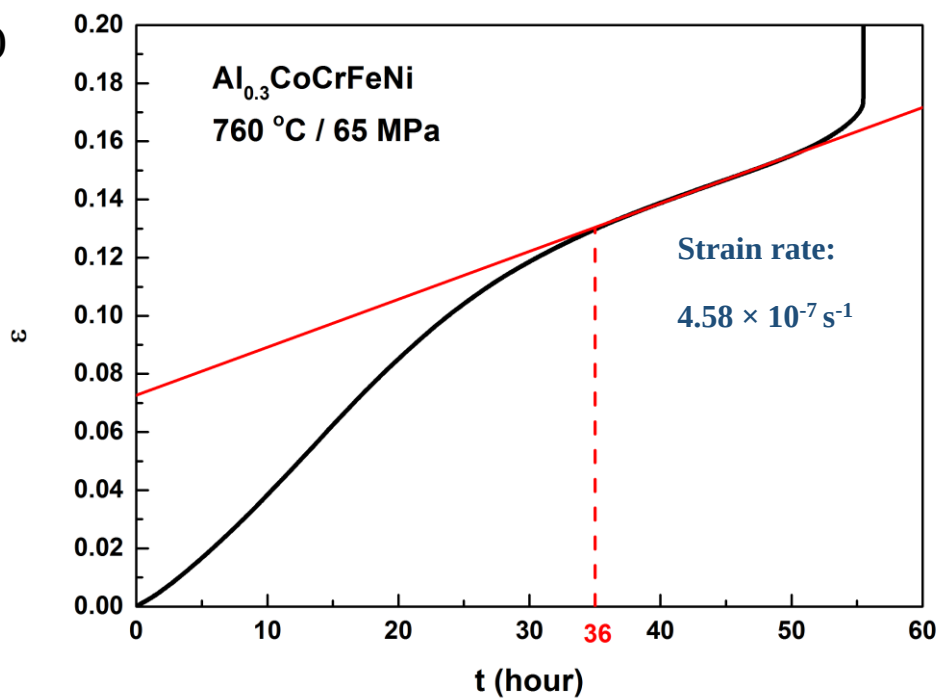
(o)



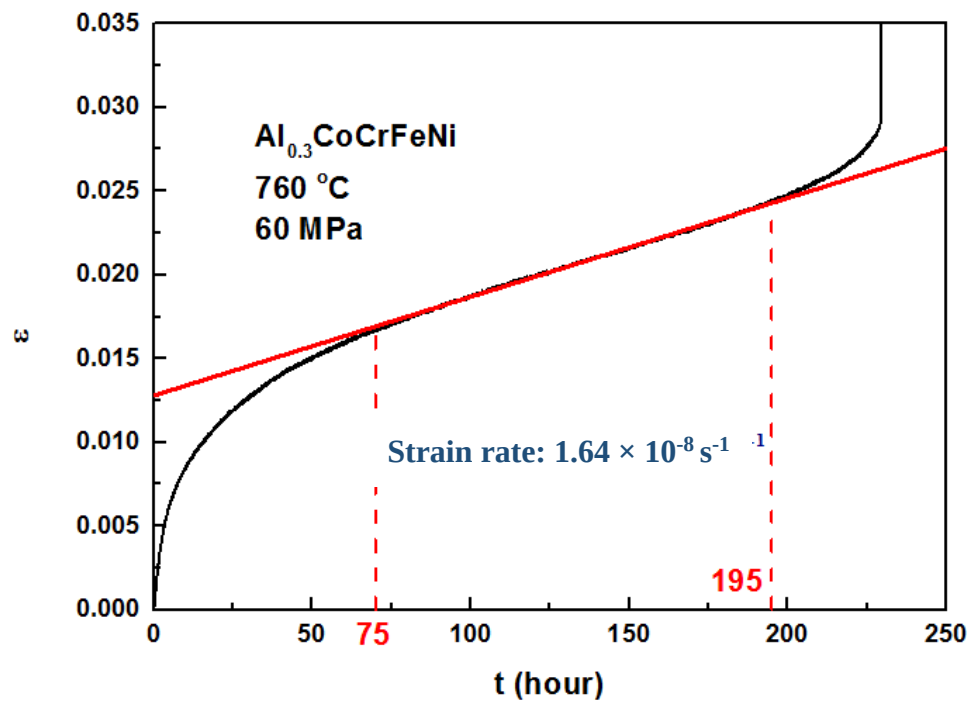
(p)



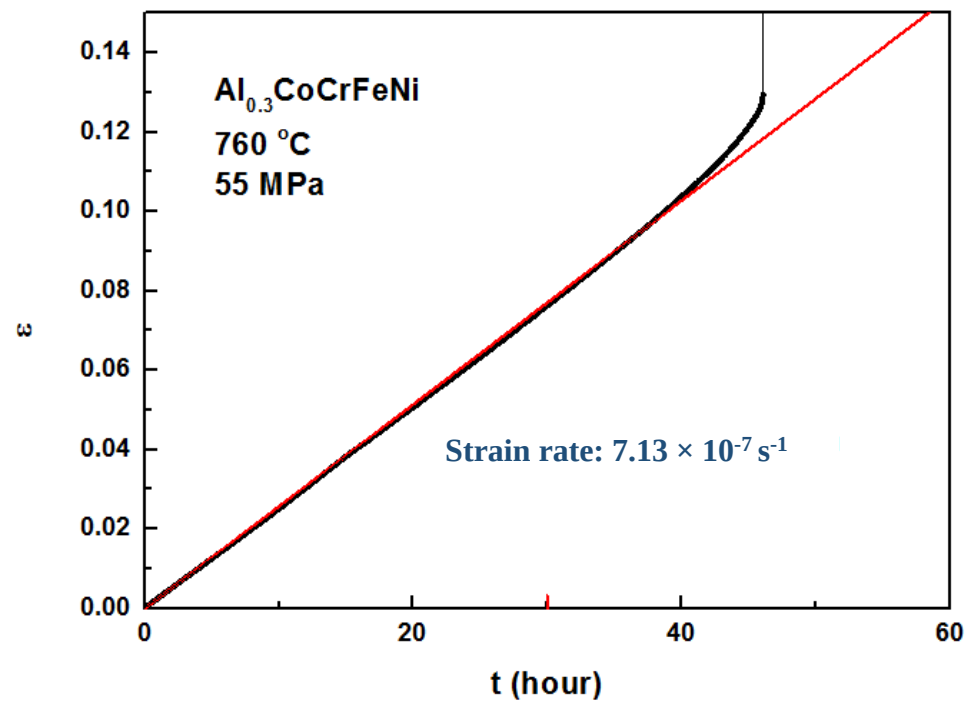
(q)



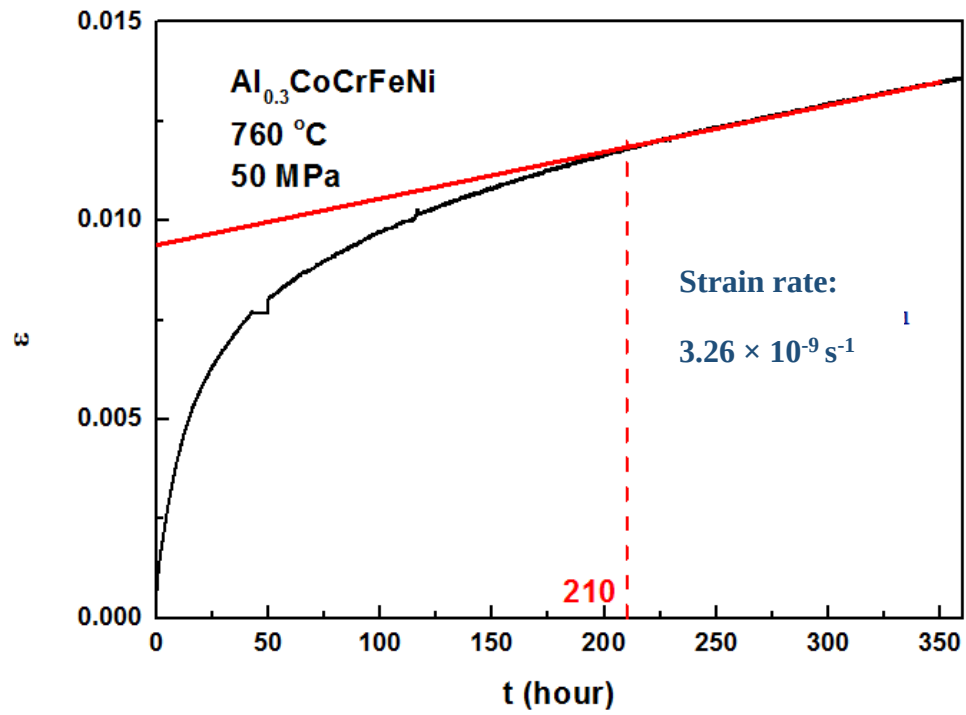
(r)



(s)



(t)



(u)

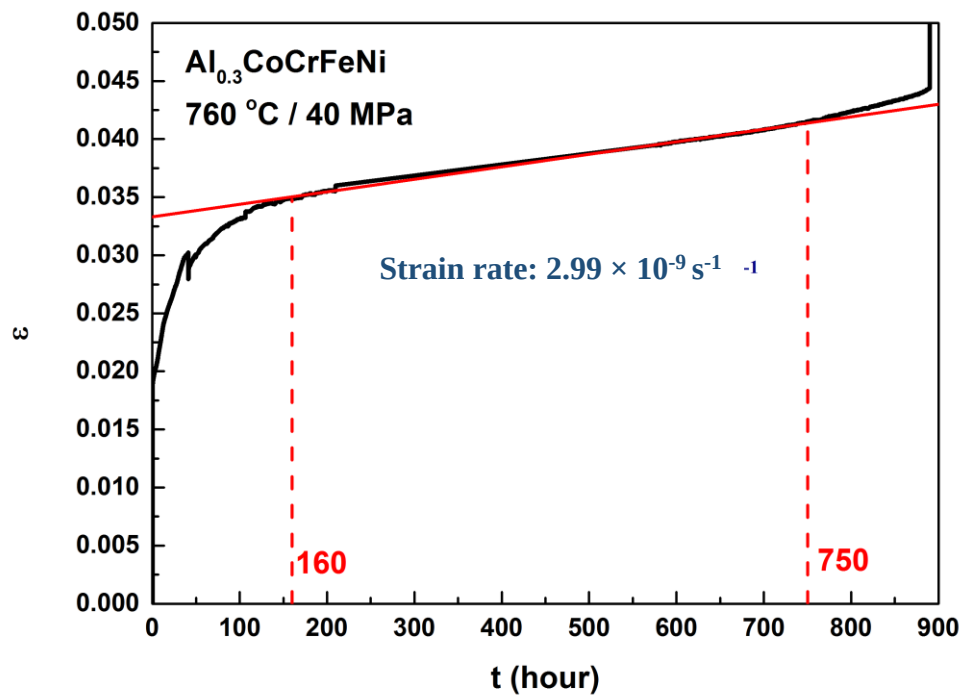


Figure 83 (a) Typical creep curves; Macroscopic tensile-creep curves (b) at 550 °C under 100 MPa, (c) at 600 °C under 100 MPa, (d) at 700 °C under 100 MPa, (e) at 700 °C under 85 MPa, (f) 700 °C under 80 MPa, (g) 700 °C under 75 MPa, (h) 700 °C under 70 MPa, (i) 700 °C under 65 MPa, (j) 700 °C under 60 MPa, (k) 700 °C under 55 MPa, (l) at 700 °C under 50 MPa, (m) at 730 °C under 70 MPa, (n) at 730 °C under 65 MPa, (o) at 730 °C under 60 MPa, (p) 730 °C under 50 MPa, (q) 760 °C under 65 MPa, (r) 760 °C under 60 MPa, (s) 760 °C under 55 MPa, (t) 760 °C under 50 MPa, and (u) 760 °C under 40 MPa of the Al_{0.3}CoCrFeNi (as-HIPed)

Creep behavior is characterized by the creep rate as the secondary stage using the following scaling relation:

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} \quad (21)$$

where $\dot{\varepsilon}$ is the creep rate, ε is the tensile displacement, and t is the creep time.

The steady creep-rates are summarized in Table 10. The double logarithmic plot of the stress vs. strain rate is shown in Figure 84.

Table 10 The steady creep-rates of Al_{0.3}CoCrFeNi (as-HIPed)

	550 °C	600 °C	700 °C	730 °C	760 °C
100 MPa	$1.86 \times 10^{-10} \text{ s}^{-1}$	$1.47 \times 10^{-9} \text{ s}^{-1}$	$5.85 \times 10^{-9} \text{ s}^{-1}$	-	-
85 MPa	-	-	$5.09 \times 10^{-9} \text{ s}^{-1}$	-	-
80 MPa	-	-	$2.68 \times 10^{-9} \text{ s}^{-1}$	-	-
75 MPa	-	-	$4.44 \times 10^{-9} \text{ s}^{-1}$	-	-
70 MPa	-	-	$1.99 \times 10^{-9} \text{ s}^{-1}$	$4.59 \times 10^{-9} \text{ s}^{-1}$	-
65 MPa	-	-	$2.09 \times 10^{-9} \text{ s}^{-1}$	$3.81 \times 10^{-9} \text{ s}^{-1}$	$4.58 \times 10^{-7} \text{ s}^{-1}$
60 MPa	-	-	$5.00 \times 10^{-9} \text{ s}^{-1}$	$5.36 \times 10^{-10} \text{ s}^{-1}$	$1.64 \times 10^{-8} \text{ s}^{-1}$
55 MPa	-	-	$1.14 \times 10^{-8} \text{ s}^{-1}$	$1.32 \times 10^{-8} \text{ s}^{-1}$	$7.13 \times 10^{-7} \text{ s}^{-1}$
50 MPa	-	-	$2.04 \times 10^{-9} \text{ s}^{-1}$	$1.09 \times 10^{-9} \text{ s}^{-1}$	$3.26 \times 10^{-9} \text{ s}^{-1}$
45 MPa	-	-	-	-	$9.85 \times 10^{-8} \text{ s}^{-1}$
40 MPa	-	-	-	-	$2.99 \times 10^{-9} \text{ s}^{-1}$

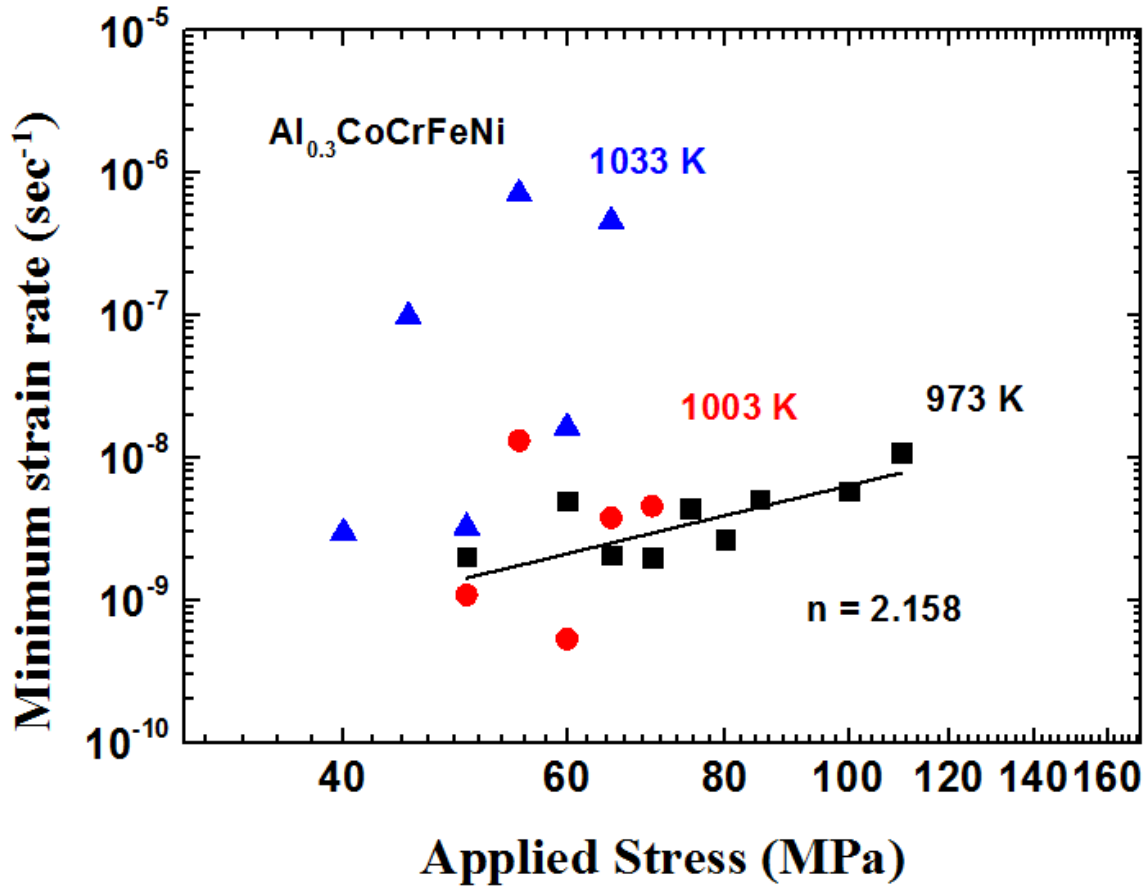


Figure 84 Minimum strain rate as a function of applied stress for the Al_{0.3}CoCrFeNi (as-HIPed) at 700 °C, 730 °C, and 760 °C, respectively.

The stress vs. strain rate of Al_{0.3}CoCrFeNi (as-HIPed), compared with conventional alloys, on a double logarithmic scale at 700 °C is shown in Figure 85. The creep behavior of Al_{0.3}CoCrFeNi (as-HIPed) is superior to conventional alloys. For the case at 100 MPa for example, the creep rate of Al_{0.3}CoCrFeNi (as-HIPed) is two orders slower than P92 and P122 alloys.

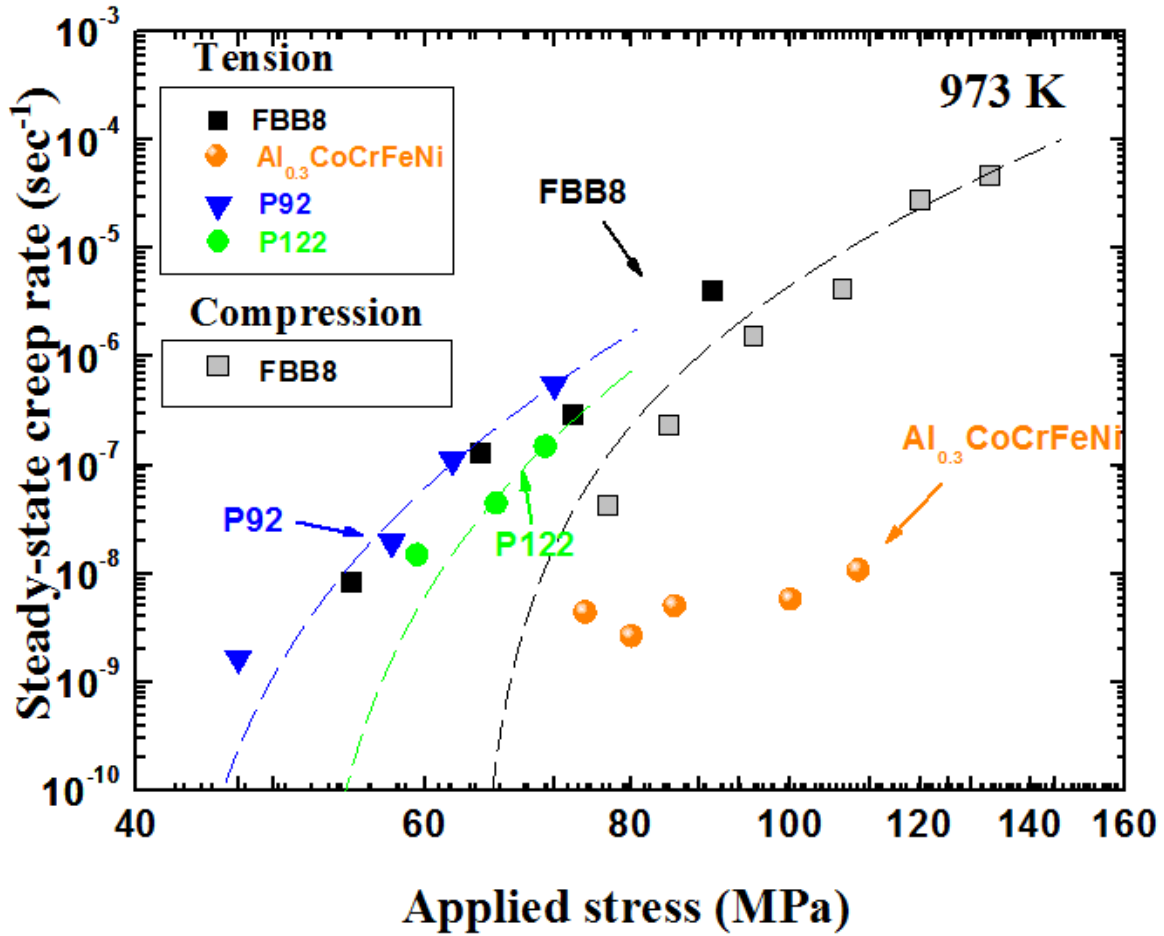


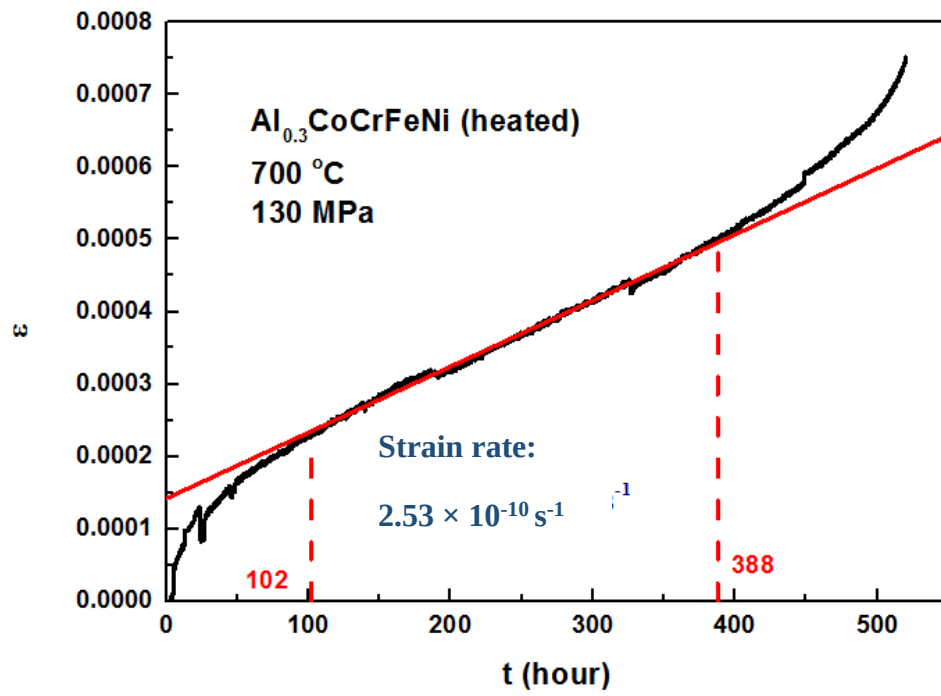
Figure 85 Minimum strain rate as a function of applied stress for the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) at 700 °C, compared with conventional alloys

6.4.1 Heat Treatment (700 °C for 500 h) Effects on the Creep Properties of $\text{Al}_{0.3}\text{CoCrFeNi}$

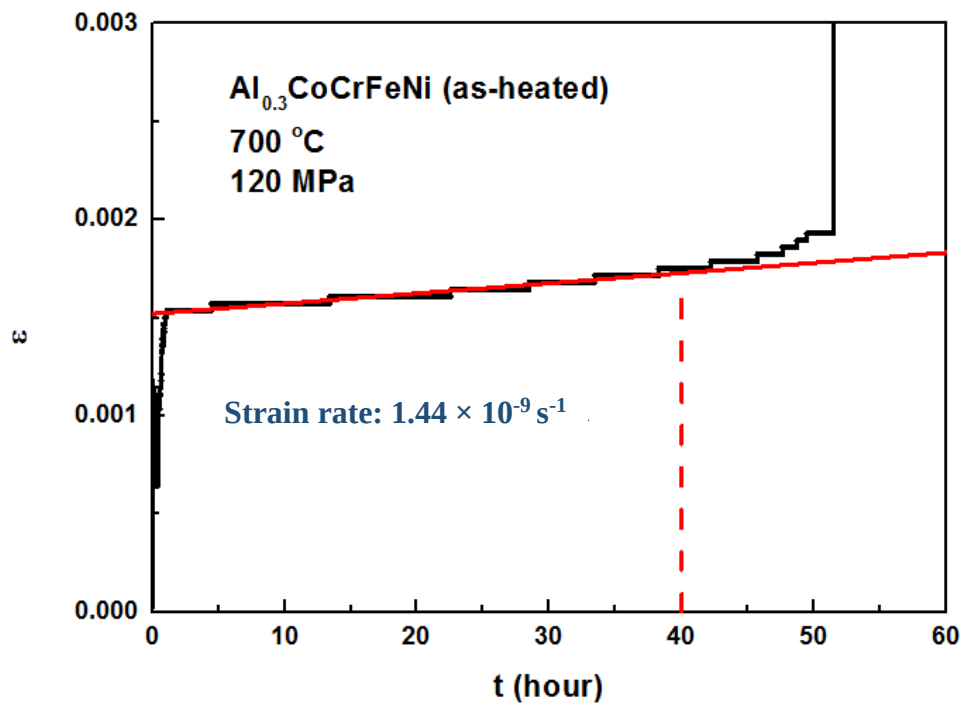
The effect of heat treatment at 700 °C for 500 h on the creep properties is also studied.

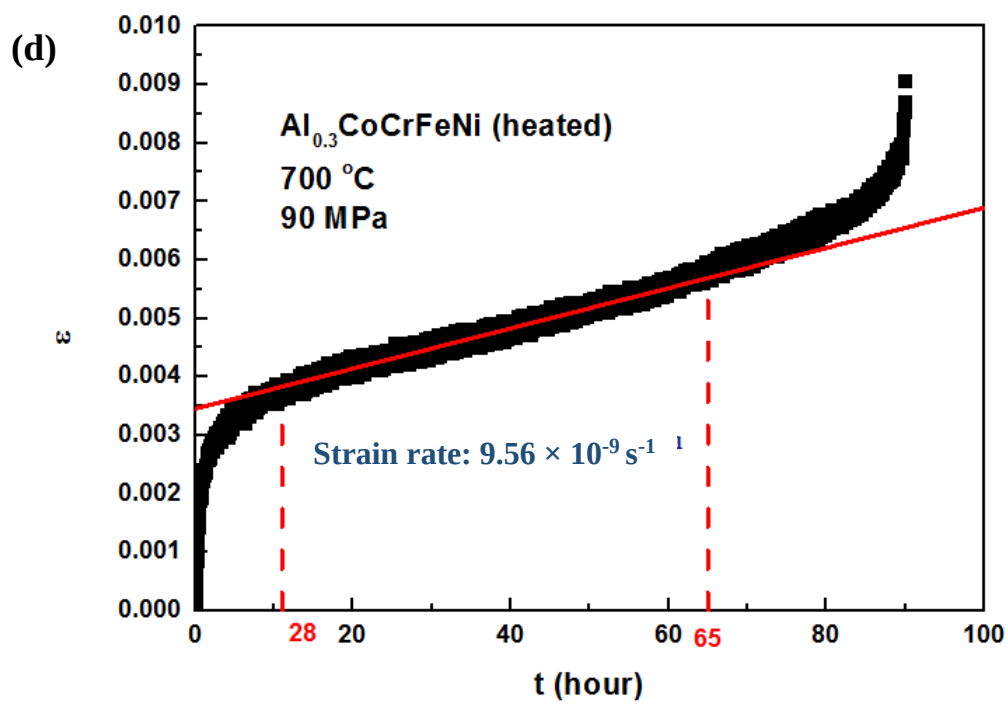
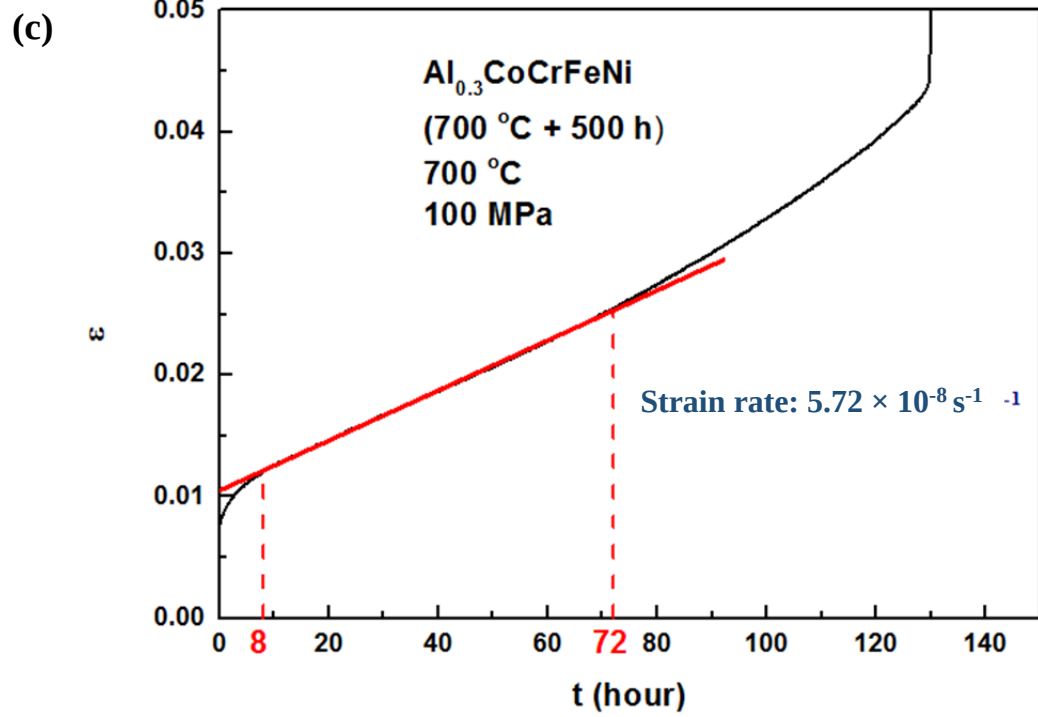
Figure 19 shows the macroscopic tensile-creep curves at 700 °C under 100 MPa of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (annealed at 700 °C for 500 h) HEA. There are obvious three stages in the creep curve. The primary stage takes around 8 hours, while the secondary stage takes around 72 hours.

(a)



(b)





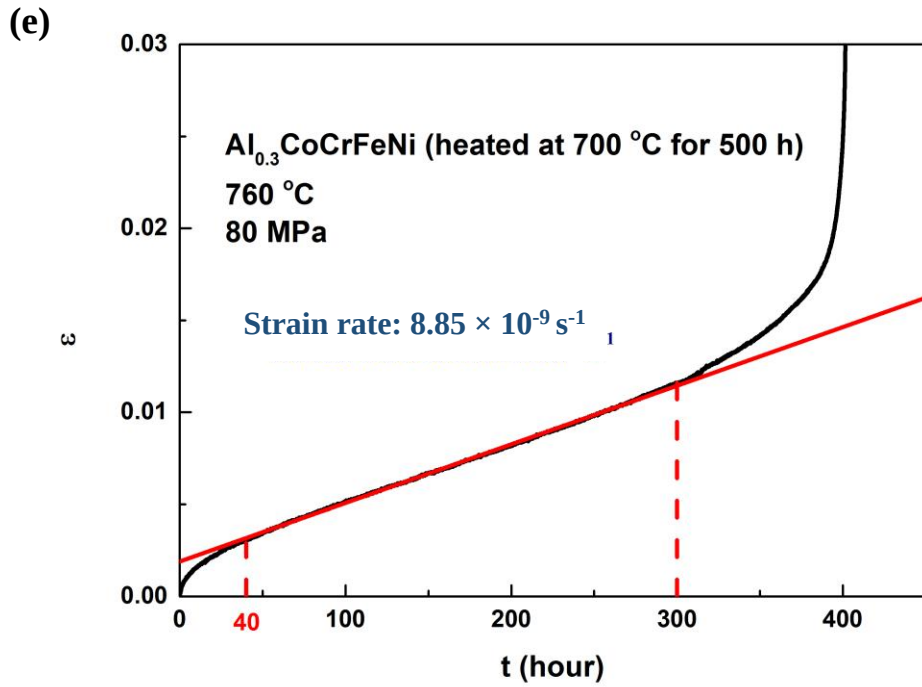


Figure 86 Macroscopic tensile-creep curves of the Al_{0.3}CoCrFeNi (as-heated) HEA. (a) at 700 °C under 130 MPa, (b) at 700 °C under 120 MPa, (c) at 700 °C under 100 MPa, (d) at 700 °C under 90 MPa, and (e) 760 °C under 80 MPa

The comparison between Al_{0.3}CoCrFeNi (as-HIPed) and Al_{0.3}CoCrFeNi (as-heated) is shown in Figure 87. At 700 °C and 100 MPa, the creep rate after the heat treatment is lower than that of a single-phase HEA. However, at 730 and 760 °C, the Al_{0.3}CoCrFeNi (as-heated) can go to higher stress level and has a lower creep strain rate than Al_{0.3}CoCrFeNi (as-HIPed).

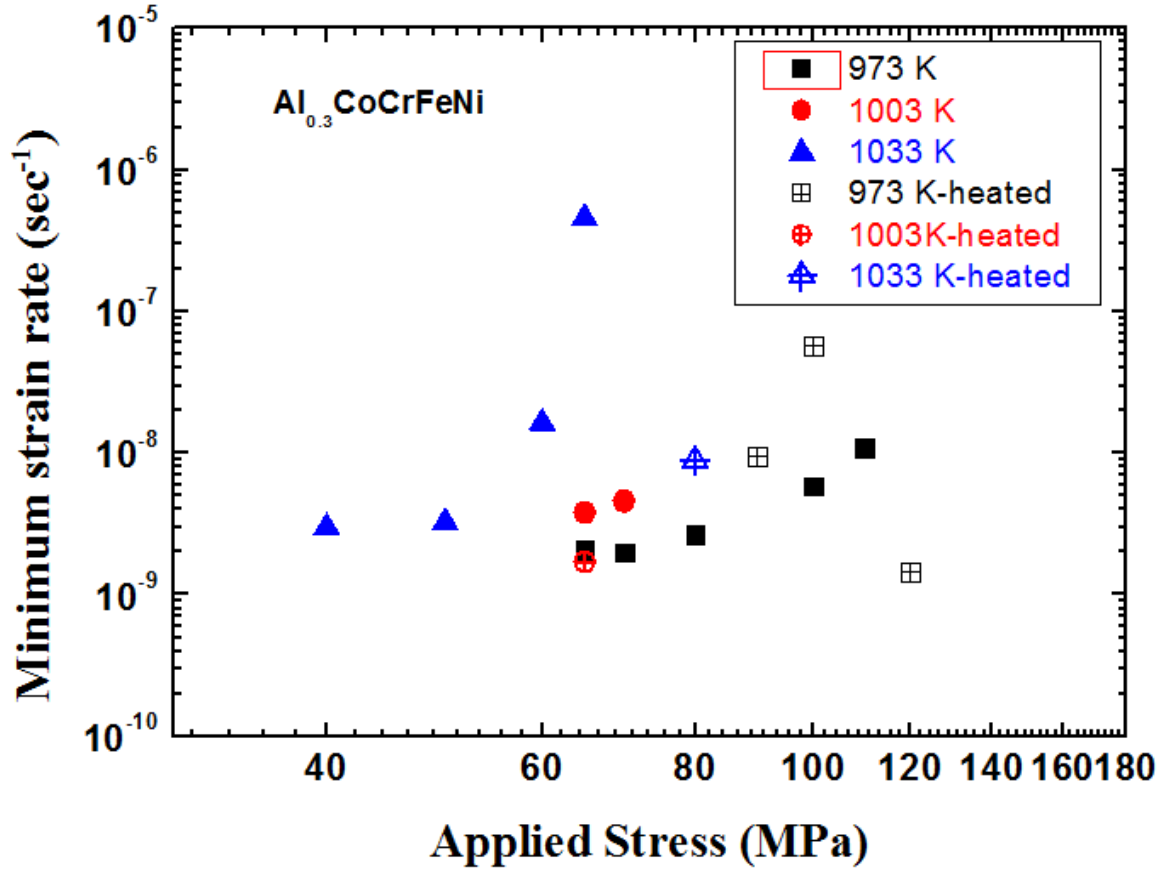


Figure 87 Minimum strain rate as a function of applied stress for the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) at 700 °C, 730 °C, and 760 °C, compared with $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed)

6.5 In-situ Synchrotron Diffraction Patterns during Tension of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-forged)

In contrast to the residual stress/strain state measured with ex situ characterization techniques, in-situ measurements under loading probe the dynamic lattice strain evolution during deformation. Because diffraction allows the precise determination of interplanar spacings, it can be used to measure the elastic-lattice strains. On the contrary, diffraction is not directly sensitive to plastic deformation because the shear strain parallel to crystallographic planes induced by slip deformation cannot be detected directly by diffraction. However, the local plastic strain of differently oriented grains is generally incompatible and, thus, is compensated by elastic strains, which create local residual stresses. Therefore, the effects of plastic deformation on the elastic lattice

strain can also be revealed by analyzing the measured elastic-lattice strain. The schematic of the in-situ tension diffraction experiment is shown in Figure 88.

The stress-strain curve of the in-situ tension diffraction experiment is shown in Figure 89. The red points indicate where diffraction patterns are collected. The diffraction patterns as the elastic region, yielding region, and plastic region are shown in Figure 90a, 90b, 90c, and 90d, respectively.

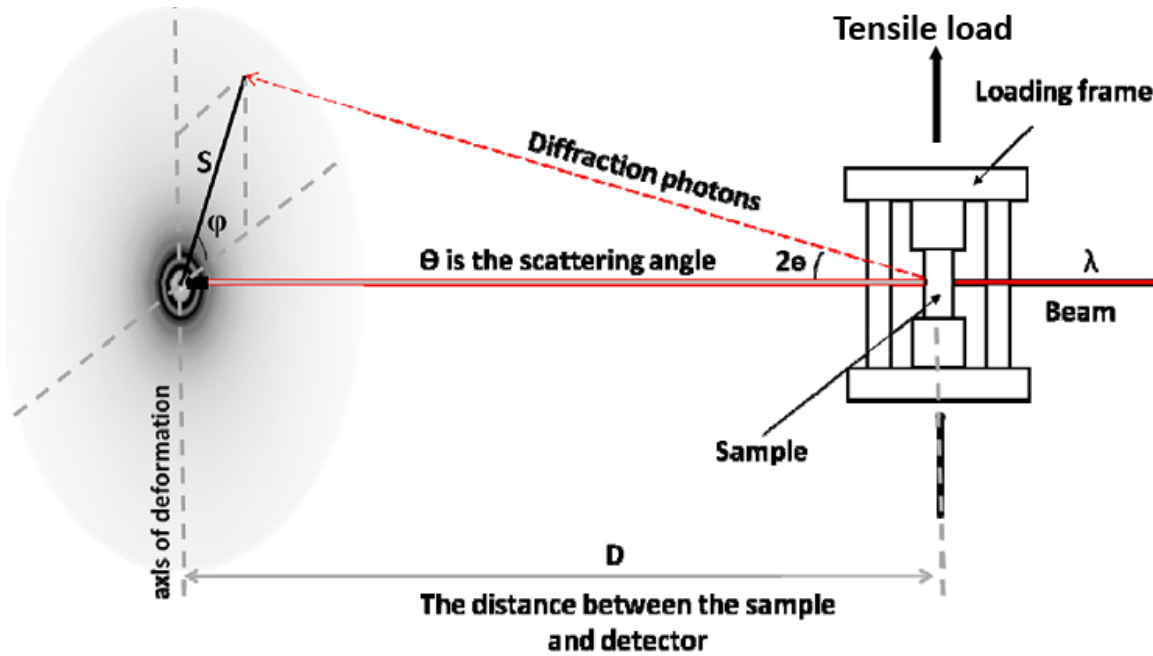


Figure 88 Schematic of the in-situ tension diffraction experiment

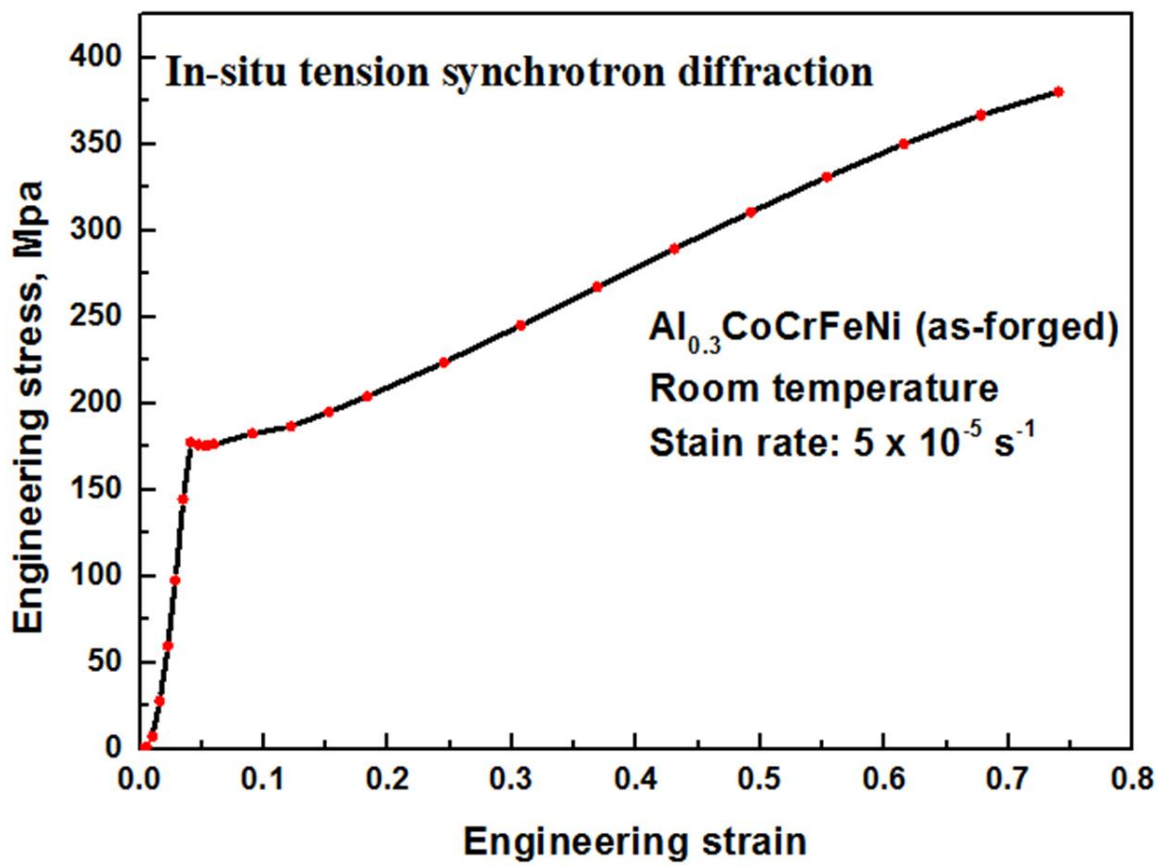


Figure 89 Stress-strain curve of the in-situ tension diffraction experiment. The red points indicate where diffraction patterns are collected

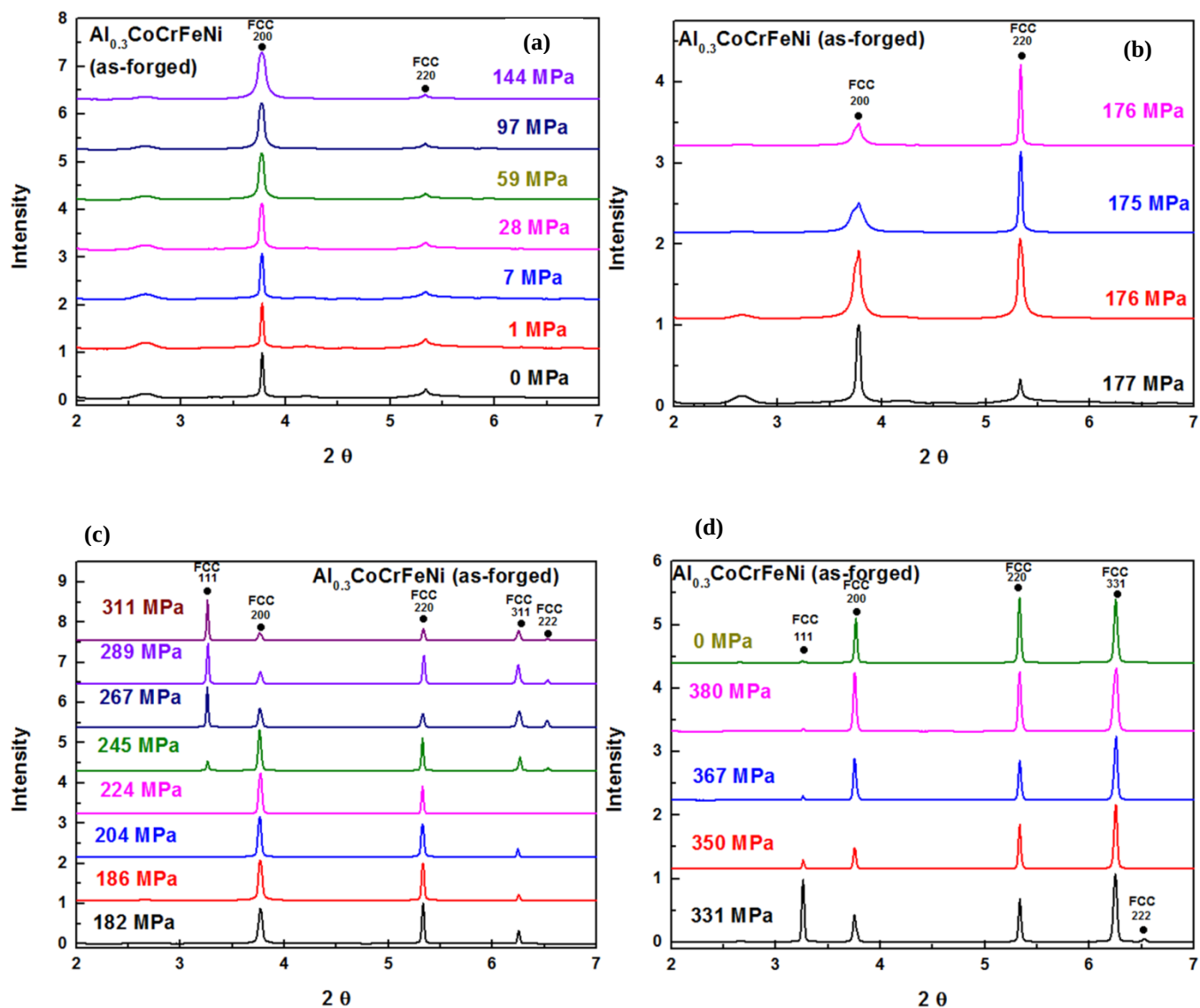


Figure 90 Synchrotron diffraction patterns at different points during the in-situ tension synchrotron diffraction experiment

6.6 In-situ Neutron Diffraction Patterns during Tension of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) and $\text{Al}_{0.3}\text{CoCrFeNi}$ (after heat treatment) HEAs

In the present work, we utilize in-situ neutron diffraction to investigate the lattice-strain evolution during tensile deformation of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) and $\text{Al}_{0.3}\text{CoCrFeNi}$ (after heat treatment) HEAs at the temperatures from room temperature (RT) to 760 °C. The neutron-diffraction

experiments were conducted at the ENGIN-X, ISIS Facility, Rutherford Appleton Laboratory, UK. ENGIN-X is a time-of-flight (TOF) neutron diffractometer, which is optimized to measure elastic strains at precise locations in bulky specimens. Fast counting times, together with a flexible and accurate definition of the instrumental gauge volume are the main requirements of neutron strain scanning and have been addressed on ENGIN-X through the design of a novel TOF diffractometer with a tunable resolution and interchangeable radial collimators. Further, the routine operation of the instrument has been optimized by creating a virtual instrument, i.e. a three-dimensional computer representation of the diffractometer and samples, which assists in the planning and execution of experiments. On comparing ENGIN-X with its predecessor ENGIN, a 25 X gain in performance is found, which has allowed the determination of stresses up to 60 mm deep in steel specimens. For comparison with constant-wavelength diffractometers, special attention has been paid to the absolute number of counts recorded during the experiments. A simple expression is presented for the estimation of counting times in TOF neutron strain scanning experiments[141].

The experimental loading rig is mounted with its loading axis oriented horizontally and at 45° to the incident beam, with two detectors oriented at 90° to this beam. Strain components are thus determined parallel and perpendicular to the applied load, using extensometer. The incident beam height and width were defined as 5×5 mm using slits, while the diffracted beam width is defined to be 1.5 mm using radial collimators. The typical measurement time per load level was 10-15 minutes. The experimental setup is shown in Figure 91.

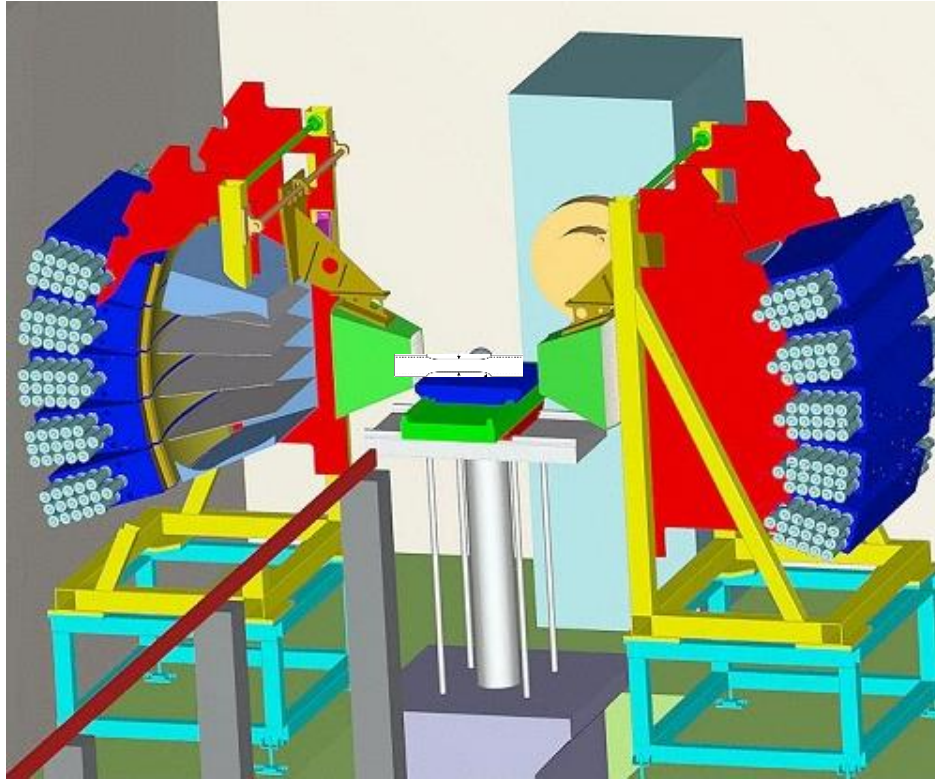


Figure 91 Experimental setup showing that a sample loaded on the grip with its loading axis oriented horizontally and at 45° to the incident beam, two detectors oriented at 90° to this beam, and furnace placed along the axial direction around the sample.

The screw-threaded cylindrical samples for neutron-diffraction experiment at ISIS, with a gage length of 34 mm and a gage diameter of 8 mm were machined. The related sample geometry is shown in Figure 92.

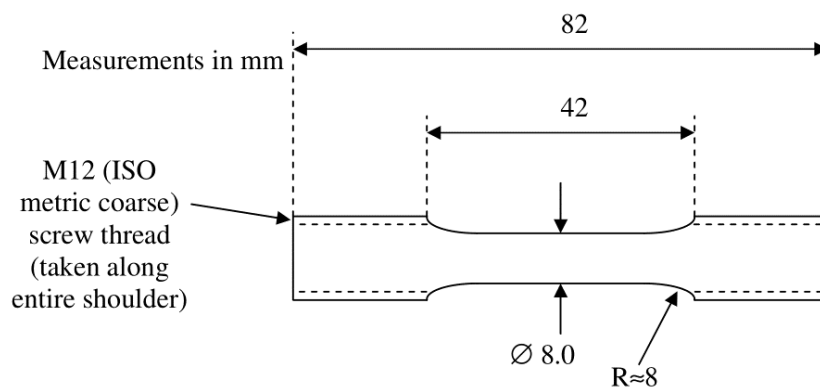


Figure 92 The tensile sample geometry for neutron-diffraction experiments at ISIS

6.6.1 In-situ Tensile Neutron Diffraction Analysis of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) at Room Temperature

1) Neutron-diffraction analysis of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) at room temperature under the unloaded state

HEAs [5, 6, 90] are loosely defined as solid-solution alloys that contain more than five principal elements in equal or near equal atomic percent (at. %). The concept of high entropy introduces a new path of developing advanced materials with unique properties, which cannot be achieved by the conventional micro-alloying approach based on only one dominant element. They are candidates for elevated-temperature structural applications, because of their high-temperature softening resistance. In-situ neutron-diffraction techniques [31, 142] subjected to continuous tension are used to study lattice-strain changes, elastic constants, and elastic moduli as a function of temperature in the single-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ (FCC) and dual-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ (FCC + B2) HEAs. Figure 4 shows a typical diffraction pattern of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) HEA measured at room temperature with a 15-minute data collection.

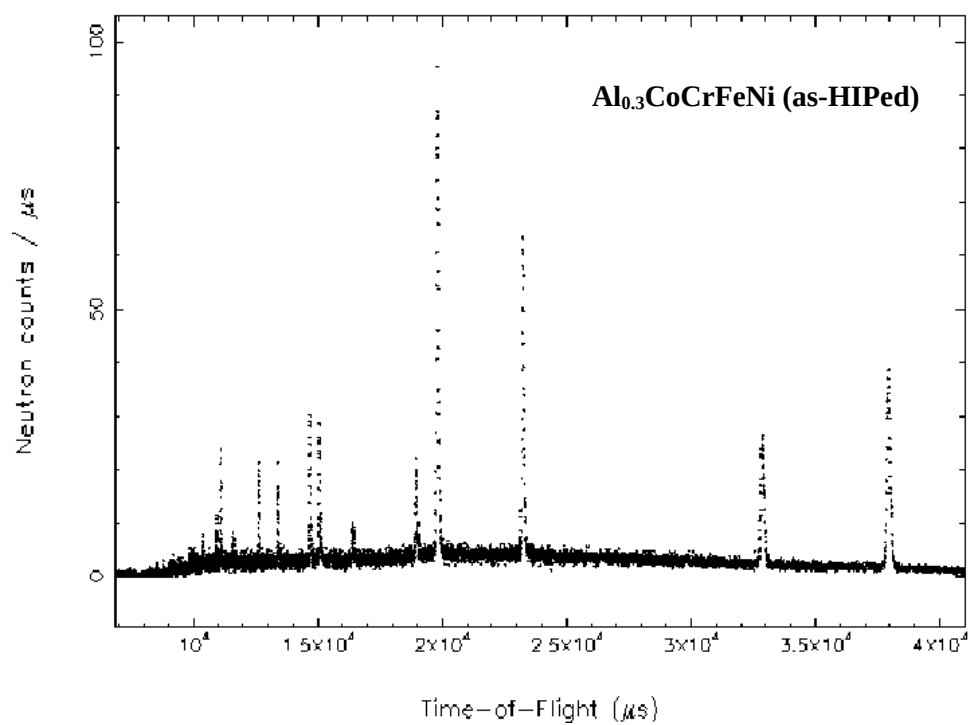


Figure 93 A typical diffraction pattern of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) HEA measured at room temperature as a function of time-of-flight (microsecond)

All peaks are indexed to the FCC structure and related results are shown in Figure 5. The average lattice parameters are obtained from the whole-pattern Rietveld refinement using the General Structural Analysis System (GSAS). The d-spacing of specific planes is obtained from single-peak refinement using Engin-X Routines Software.

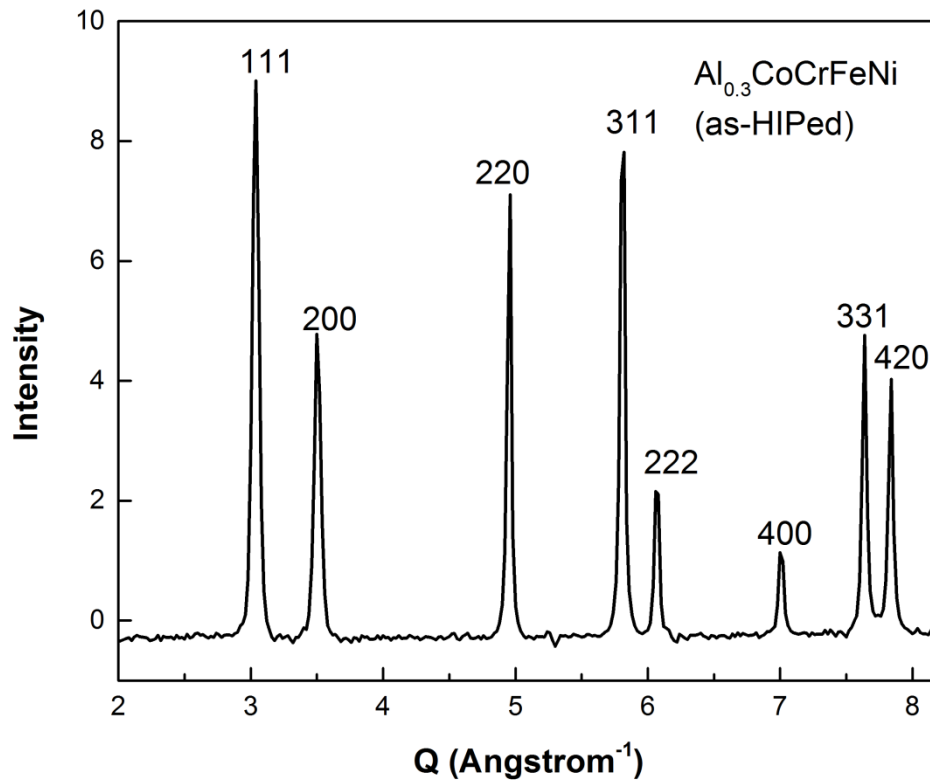


Figure 94 A typical diffraction pattern of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) HEA measured at room temperature as a function of Q-spacing.

The neutron scattering geometry allows for simultaneous measurements of two scattering vectors, Q_1 and Q_2 , which are parallel and perpendicular to the tensile axis, respectively. Diffraction from the crystal lattice of grains whose plane normal (that is, $\langle hkl \rangle$) is parallel to Q_1 or Q_2 and satisfies Bragg's law will be detected, and the lattice spacing (d_{hkl}) can thus be measured from the diffraction peak corresponding to the (hkl) reflection.

The lattice parameter and d-spacing of $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$, and $\langle 311 \rangle$ of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) are calculated and the related values are listed in Table 11. These values are used as reference for the lattice strain calculation.

Table 11 The reference lattice parameter and d-spacing values of $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$, and $\langle 311 \rangle$ for the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed)

	Lattice parameter	d₁₁₁	d₂₀₀	d₂₂₀	d₃₁₁
Values (Angstrom)	3.5847	2.06808	1.79269	1.26725	1.08102

2) Macroscopic stress-strain behavior of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) at room temperature

The macroscopic stress-strain behavior during in-situ tension at room temperature using the ENGIN-X engineering diffractometer was measured. In the elastic region, the machine is under stress-control mode, i.e., the tension tests are interrupted and hold for 15 minutes at 10, 30, 50, 70, 90, 110, 130, 150, and 170 MPa, respectively. Then the machine is under strain-control mode, i. e., the tension tests are interrupted and hold for 15 minutes at 1%, 2.5%, 4%, 5.5%, and 7%, respectively. The macroscopic stress-strain curve is shown in Figure 6. The yielding stress is around 170 MPa.

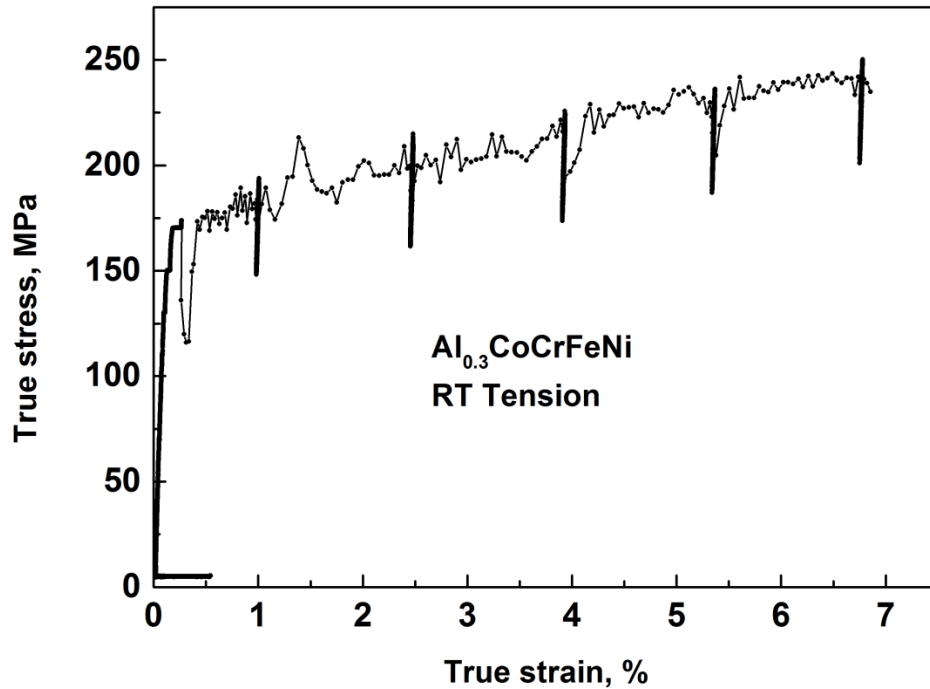


Figure 95 True stress–true strain curve for tensile loading of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) at RT measured by ENGIN-X engineering diffractometer. In the elastic region, the machine is under stress-control mode, i.e., the tension tests are interrupted and hold for 15 minutes at 10, 30, 50, 70, 90, 110, 130, 150, and 170 MPa, respectively. Then the machine is under strain-control mode, i. e., the tension tests are interrupted and hold for 15 minutes at 1%, 2.5%, 4%, 5.5%, and 7%, respectively.

3) Lattice strain evolution of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) during tensile deformation at room temperature

Three types of elastic lattice strains, average phase strains, hkl plane-specific lattice strains, and intragranular phase strains, can be calculated from neutron-diffraction measurements in the polycrystalline-multiphase material. In this report, average phase strains and hkl plane-specific lattice strains are analyzed as a function of applied axial stress. The average phase strain is referred to as the lattice strain of an individual phase volume averaged by all its diffracted aggregates, which represents the bulk behavior of the phase in the constrained state. The average phase strain is determined by the following formula,

$\varepsilon = (a - a_0) / a$, where a_0 is the reference lattice parameter before deformation under unloaded state, and a is the lattice parameter as a function of the applied stress, for the respective phases. The average FCC phase strain of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) during tensile deformation at room temperature is shown in Figure 7. From the Bank 1, it shows the lattice is under tension and tend to yield around 100 MPa at macroscopic level, even though the yielding stress from stress-strain curve is around 170 MPa. From the Bank 2, it shows the lattice is under compression and tend to yield around 170 MPa, which is close to the yielding stress from stress-strain curve.

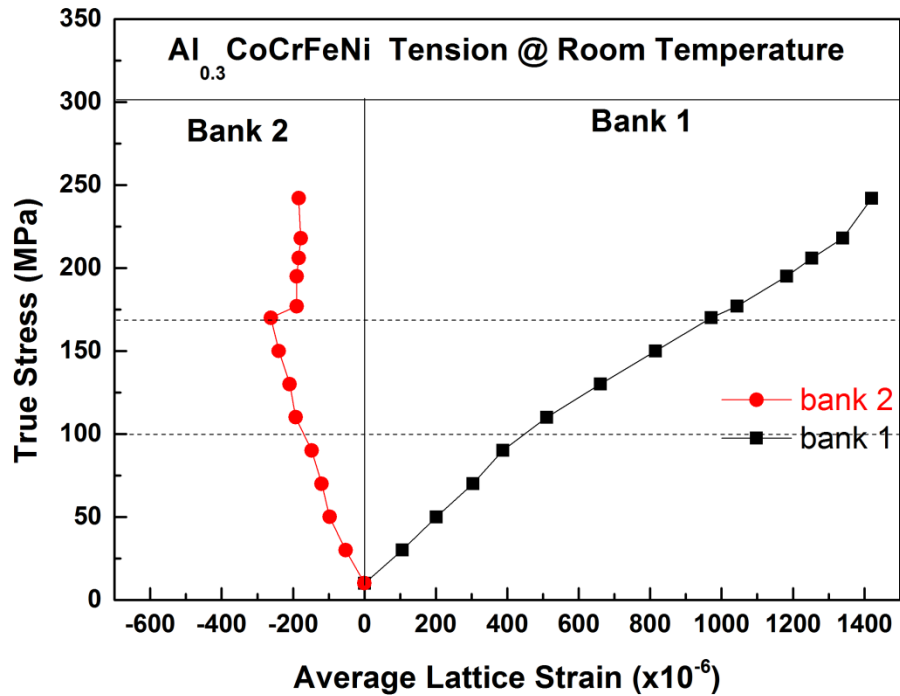


Figure 96 The average lattice strain evolution as a function of stress during tensile test at room temperature of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed).

The hkl plane-specific lattice strain is grain-orientation dependent and described as the average lattice strain accumulated in the diffracted grains whose hkl plane normal are parallel to the diffraction vector, Q . In a polycrystalline material, the response of differently-

oriented grains under an applied stress varies due to the effects of the elastic and plastic anisotropies. The elastic anisotropy arises from the fact that the elastic modulus depends on the grain orientation, which is manifested by the difference in the slopes of the applied stress vs. lattice strain in the elastic region. The origin of the plastic anisotropy is that plastic deformation occurs on certain preferential slip systems and the sequence of grain yielding relies on the magnitude of the Schmid factor determined by grain orientation. The plastic anisotropy is usually characterized by the non-linear behavior of the hkl plane-specific lattice strain and the tensile/compressive strain shift, relative to its elastic slope. Examinations of elastic and plastic anisotropies are important to understand the interactions between grains of different orientations during creep deformation, because they provide a measurement of the internal stress, even in the plastic region. The hkl plane-specific lattice strain is determined by Engin-X routine software single-peak fitting, as

$$\varepsilon_{hkl} = (d_{hkl} - d_{hkl}^0) / d_{hkl}^0 \quad (22)$$

Where ε_{hkl} is the lattice strain in the hkl-oriented grains, d_{hkl}^0 is the reference lattice spacing before deformation under unloaded state, and d_{hkl} is the d spacing as a function of the applied stress, for the respective phases.

The d spacing of <111>, <200>, <220>, and <311> within the Al_{0.3}CoCrFeNi (as-HIPed) during tensile deformation at room temperature is shown in Figure 8. The results illustrate that the lattice strain change is strongly dependent on the grain orientations, indicative of strong elastic anisotropy. The {200} grains exhibit the largest elastic strain along the loading direction and a significant shift relative to their linear elastic response, which manifests the elastic-plastic transition. The {311} grains have the second largest

elastic strain but maintain nearly a linear response. The {220} and {111} grains, on the other hand, have a lower elastic strain, indicating that they have a larger elastic stiffness.

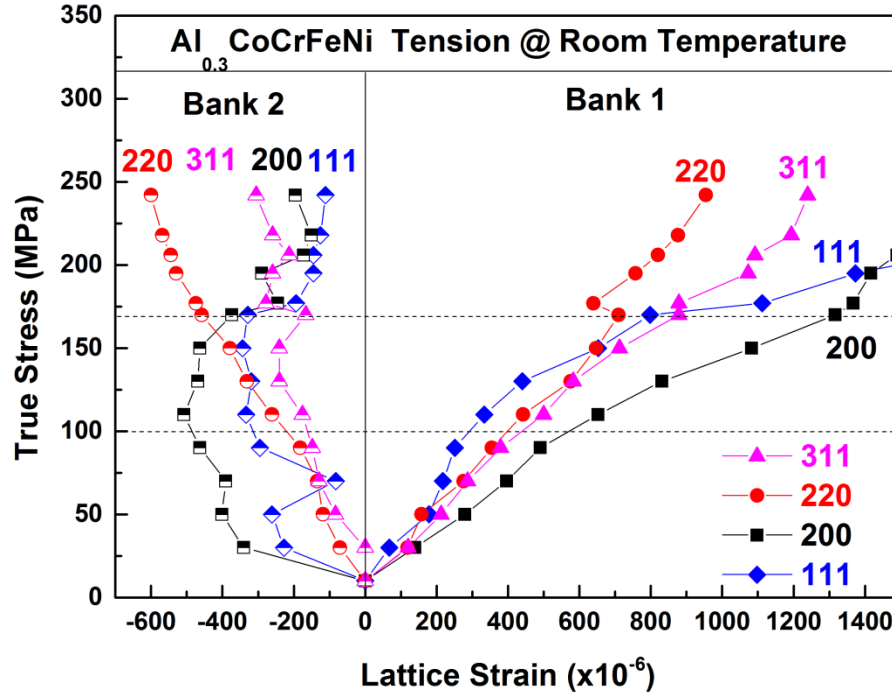


Figure 97 The response of hkl plane specific lattice strain along axial direction as a function of stress during tensile test at room temperature for the Al_{0.3}CoCrFeNi (as-HIPed).

6.6.2 In-situ Tensile Neutron Diffraction Analysis of Al_{0.3}CoCrFeNi (as-heated) at Room Temperature

As we reported in former quarterly reports, the Al_{0.3}CoCrFeNi alloy is a FCC single-phase HEA and exhibits low yielding strength (around 170 MPa). In order to increase the yielding stress of the Al_{0.3}CoCrFeNi HEA, we tried different heat treatments, with the assistance of thermodynamic modeling. The microstructure before and after ageing at 700 °C for 500 h and related secondary-phase characterization is summarized in Figure 42 and Figure 43. A second Al-Ni riched B2 phase appears in the FCC matrix.

The mechanical property studies show that the yielding strength of the Al_{0.3}CoCrFeNi (as-heated) at room temperature increases from 177 MPa to 349 MPa. Thus, it is essential to use in-situ

neutron-diffraction techniques [31, 142] subjected to continuous tension to study lattice-strain changes, elastic constants, and elastic moduli as a function of temperature in the dual-phase $\text{Al}_{0.3}\text{CoCrFeNi}$ (FCC + B2) HEAs.

1) Neutron diffraction analysis of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) at room temperature under unloaded state

Figure 10 shows a typical diffraction pattern of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) HEA measured at room temperature with a 15-minute data collection. Besides FCC peaks, at least three peaks, $\langle 110 \rangle$, $\langle 200 \rangle$, and $\langle 211 \rangle$ of secondary phase are shown in Figure 98.

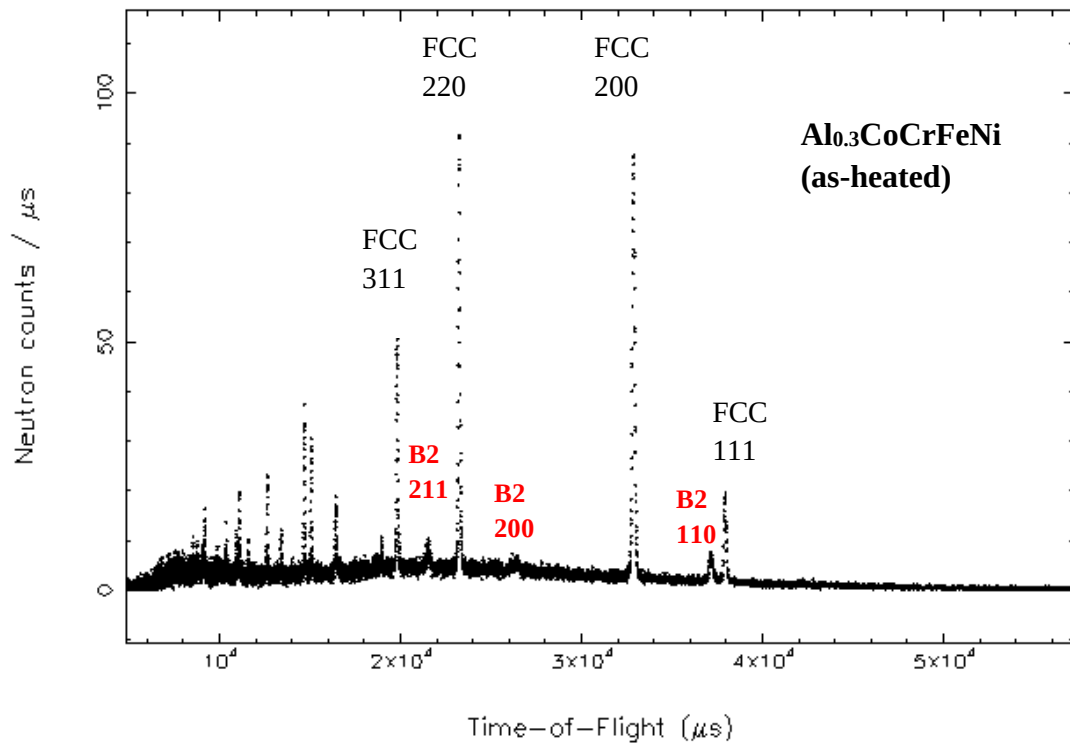


Figure 98 A typical diffraction pattern of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) HEA measured at room temperature as a function of time-of-flight (microsecond)

.The lattice parameters and d-spacing of <111>, <200>, <220>, and <311> of the FCC phase and d-spacing of <110> and <211> of the BCC phase are calculated and the related values are listed in Table 12, respectively. These values are used as reference for the lattice strain calculation.

Table 12 The reference lattice parameter and d-spacing values of <111>, <200>, <220>, and <311> for the FCC phase and <110> and <211> of the BCC phase for the Al_{0.3}CoCrFeNi (as-heated) HEA

Parameters Phases	Lattice parameter	d₁₁₁	d₁₁₀	d₂₀₀	d₂₂₀	d₂₁₁	d₃₁₁
FCC (Angstrom)	3.58466	2.06881	-	1.79279	1.2672	-	1.08082
B2 (Angstrom)	-	-	2.0261	-	-	1.17379	-

2) Macroscopic stress-strain behavior of the Al_{0.3}CoCrFeNi (as-heated) at room temperature

The macroscopic stress-strain behavior during in-situ tension at room temperature using the ENGIN-X engineering diffractometer was measured. In the elastic region, the machine is under stress-control mode, i.e., the tension tests are interrupted and hold for 15 minutes at 10, 60, 110, 160, 210, 260, and 310 MPa, respectively. Then the machine is under strain-control mode, i. e., the tension tests are interrupted and hold for 15 minutes at 2 %, 3.5 %, 5 %, and 6.5 %, respectively. The macroscopic stress-strain curve is shown in Figure 99. The yielding stress is around 350 MPa.

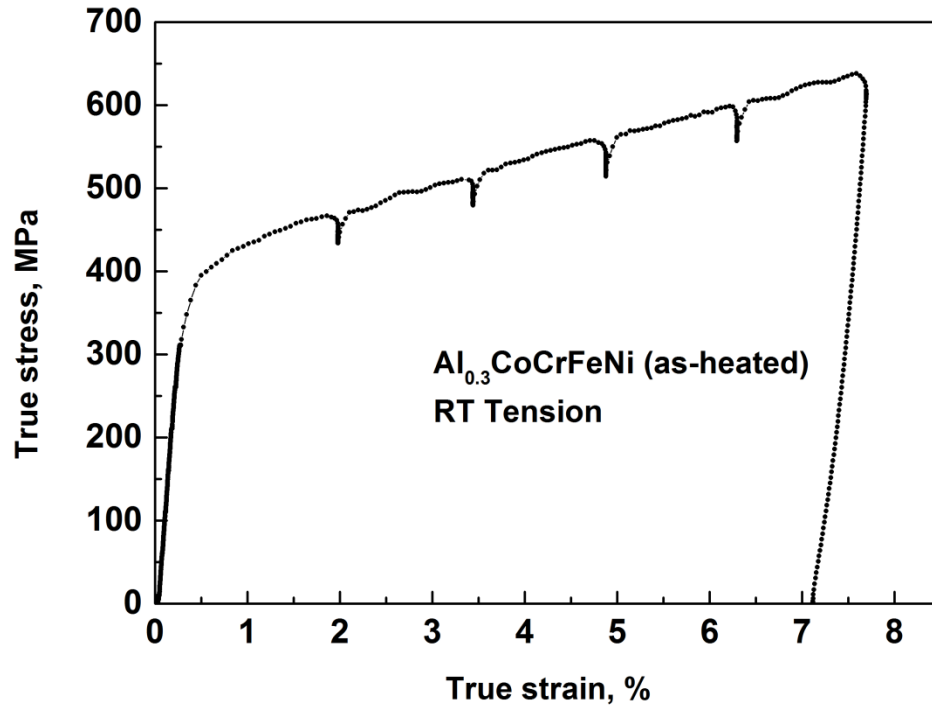


Figure 99 True stress–true strain curve for tensile loading of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) at RT measured by ENGIN-X engineering diffractometer. In the elastic region, the machine is under stress-control mode, i.e., the tension tests are interrupted and hold for 15 minutes at 10, 60, 110, 160, 210, 260, and 310 MPa, respectively. Then the machine is under strain-control mode, i. e., the tension tests are interrupted and hold for 15 minutes at 2 %, 3.5 %, 5 %, and 6.5 %, respectively.

3) Lattice strain evolution of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) during tensile deformation at room temperature

Three types of elastic lattice strains, average phase strains, hkl plane-specific lattice strains, and intragranular phase strains, can be calculated from neutron-diffraction measurements in the polycrystalline-multiphase material. In this report, average phase strains and hkl plane-specific lattice strains are analyzed as a function of applied axial stress.

The average phase strain is referred to as the lattice strain of an individual phase volume averaged by all its diffracted aggregates, which represents the bulk behavior of the

phase in the constrained state. The average phase strain is determined by the following formula,

$$\varepsilon = (a - a_0) / a \quad (23)$$

Where a_0 is the reference lattice parameter before deformation under unloaded state, and a is the lattice parameter as a function of the applied stress, for the respective phases.

The average FCC phase strain of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) during tensile deformation at room temperature is shown in Figure 100. It is difference from the FCC phase in the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed). The lattice does not yield until 300 MPa at macroscopic level.

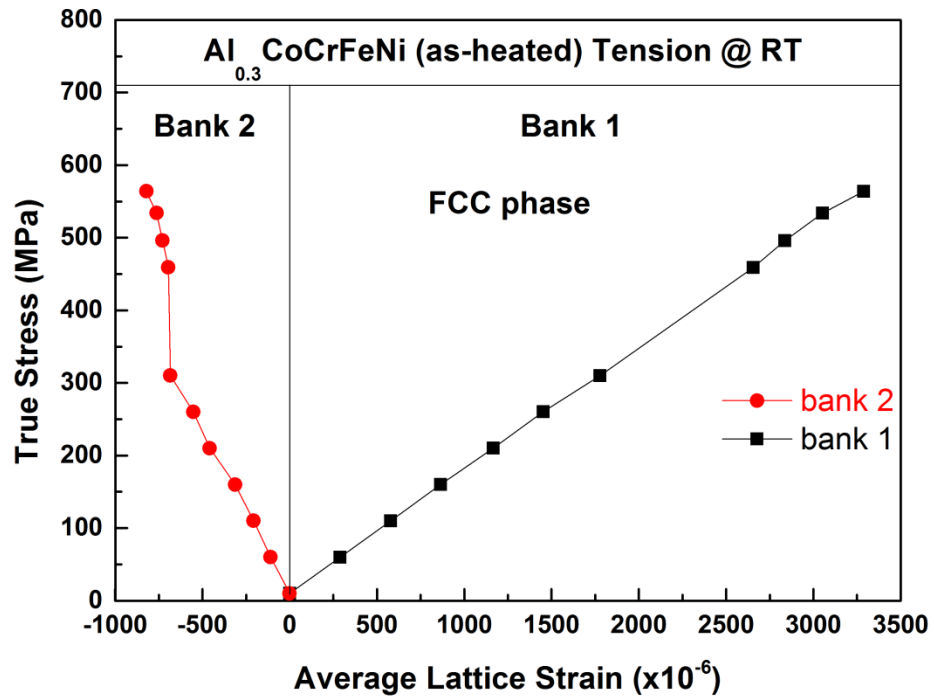


Figure 100 The average lattice strain evolution of FCC phase as a function of stress during tensile test at room temperature of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated).

The hkl plane-specific lattice strain is grain-orientation dependent and described as the average lattice strain accumulated in the diffracted grains whose hkl plane normal are parallel to the diffraction vector, Q . In a polycrystalline material, the response of differently-oriented grains under an applied stress varies due to the effects of the elastic and plastic anisotropies. The elastic anisotropy arises from the fact that the elastic modulus depends on the grain orientation, which is manifested by the difference in the slopes of the applied stress vs. lattice strain in the elastic region. The origin of the plastic anisotropy is that plastic deformation occurs on certain preferential slip systems and the sequence of grain yielding relies on the magnitude of the Schmid factor determined by grain orientation. The plastic anisotropy is usually characterized by the non-linear behavior of the hkl plane-specific lattice strain and the tensile/compressive strain shift, relative to its elastic slope. Examinations of elastic and plastic anisotropies are important to understand the interactions between grains of different orientations during creep deformation, because they provide a measurement of the internal stress, even in the plastic region. The hkl plane-specific lattice strain is determined by Engin-X routine software single-peak fitting, as

$$\varepsilon_{hkl} = (d_{hkl} - d_{hkl}^0) / d_{hkl}^0 \quad (24)$$

Where ε_{hkl} is the lattice strain in the hkl-oriented grains, d_{hkl}^0 is the reference lattice spacing before deformation under unloaded state, and d_{hkl} is the d spacing as a function of the applied stress, for the respective phases.

The d spacing of $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$, and $\langle 311 \rangle$ of the FCC phase within the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) during tensile deformation at room temperature is shown in Figure 13. The results illustrate that the lattice strain change is strongly dependent on the grain orientations, indicative of strong elastic anisotropy. The $\{200\}$ grains exhibit the largest elastic strain along the loading direction and a significant shift relative to their linear elastic response, which manifests the elastic-plastic transition. The $\{311\}$ grains have the second largest elastic strain but maintain nearly a linear response. The $\{220\}$ and $\{111\}$ grains, on the other hand, have a lower elastic strain, indicating that they have a larger elastic stiffness.

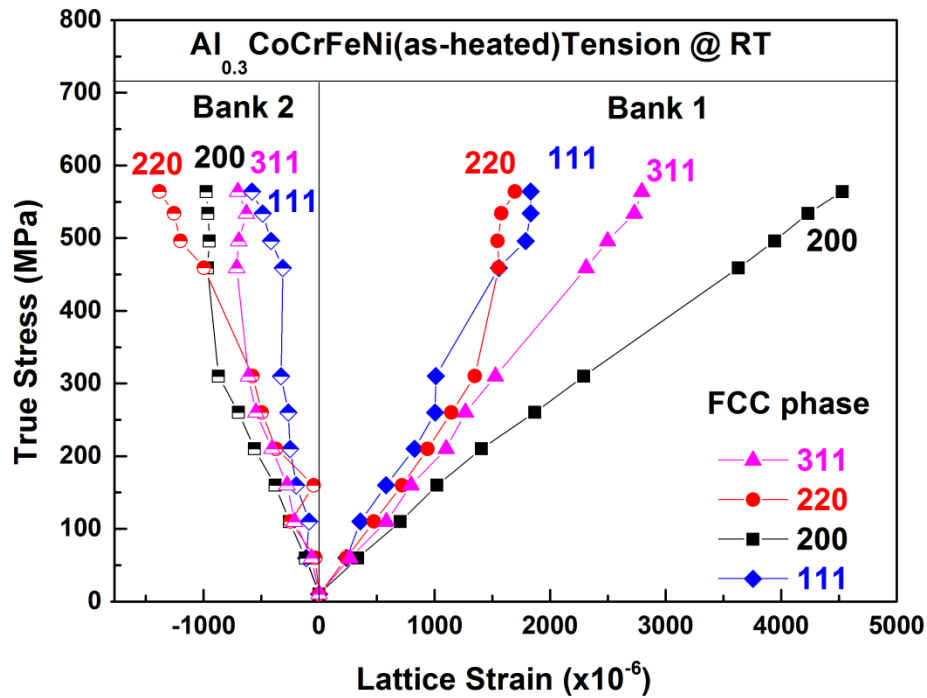


Figure 101 The response of hkl plane specific lattice strain along axial direction as a function of stress during tensile test at room temperature for the FCC phase within $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated).

The d spacing of <110> and <211> of the B2 phase within the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) during tensile deformation at room temperature is shown in Figure 102. The results illustrate that the lattice strain change is strongly dependent on the grain orientations, indicative of strong elastic anisotropy. The {110} and {211} grains exhibit nearly elastic response along the loading direction.

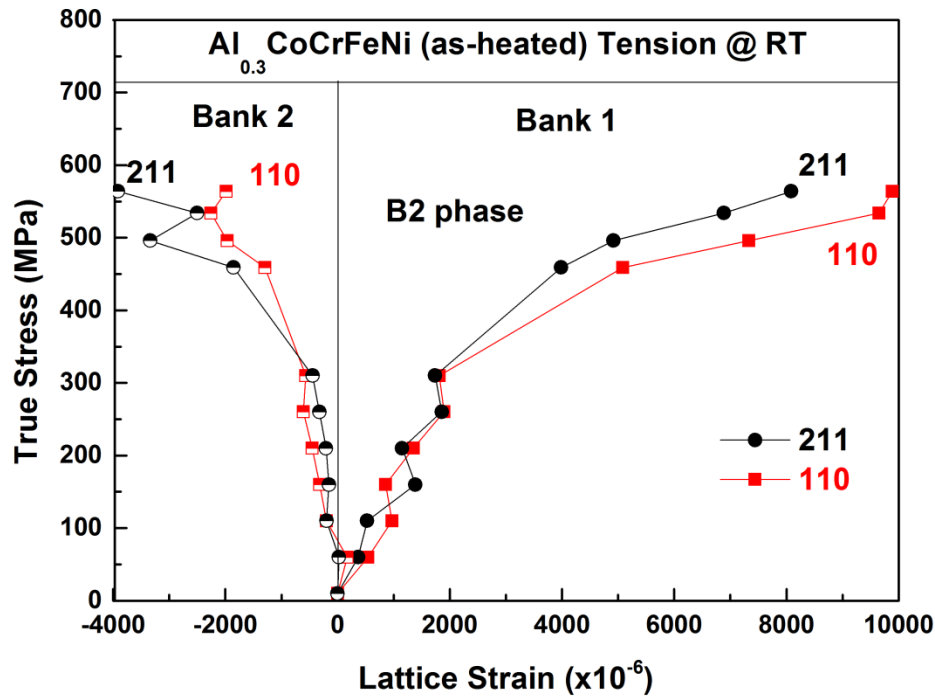


Figure 102 The response of hkl plane specific lattice strain along axial direction as a function of stress during tensile test at room temperature for the B2 phase within $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated).

6.6.3 In-situ Mechanical-behavior Characterizations using Neutron Diffraction of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) and $\text{Al}_{0.3}\text{CoCrFeNi}$ (after heat treatment) HEAs

In the present work, we utilize in-situ neutron diffraction to investigate the lattice-strain evolution during tensile deformation of $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) and $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated)

HEAs at the temperatures from room temperature (RT) to 760 °C. The neutron-diffraction experiments were conducted at the VULCAN, oak ridge national laboratory. VULCAN is a time-of-flight (TOF) neutron diffractometer, which is optimized to measure elastic strains at precise locations in bulky specimens. Fast counting times, together with a flexible and accurate definition of the instrumental gauge volume are the main requirements of neutron strain scanning and have been addressed on VULCAN through the design of a novel TOF diffractometer with a tunable resolution and interchangeable radial collimators. Further, the routine operation of the instrument has been optimized by creating a virtual instrument, i.e., a three-dimensional computer representation of the diffractometer and samples, which assists in the planning and execution of experiments.

The experimental loading rig is mounted with its loading axis oriented horizontally and at 45° to the incident beam, with two detectors oriented at 90° to this beam. Two detectors, Bank 1 and Bank 2, were employed to collect the diffracted beams from polycrystalline grains with lattice planes, which are parallel and perpendicular to the axial direction, respectively. Therefore, the axial and transverse lattice strains of differently-oriented grains can be measured simultaneously by Bank 2 and Bank 1, respectively. Strain components are determined by an extensometer. The incident beam height and width were defined as 5×5 mm using slits, while the diffracted beam width is defined to be 1.5 mm using radial collimators. The typical measurement time per load level was 10 ~ 15 minutes. The experimental setup is shown in Figure 5.

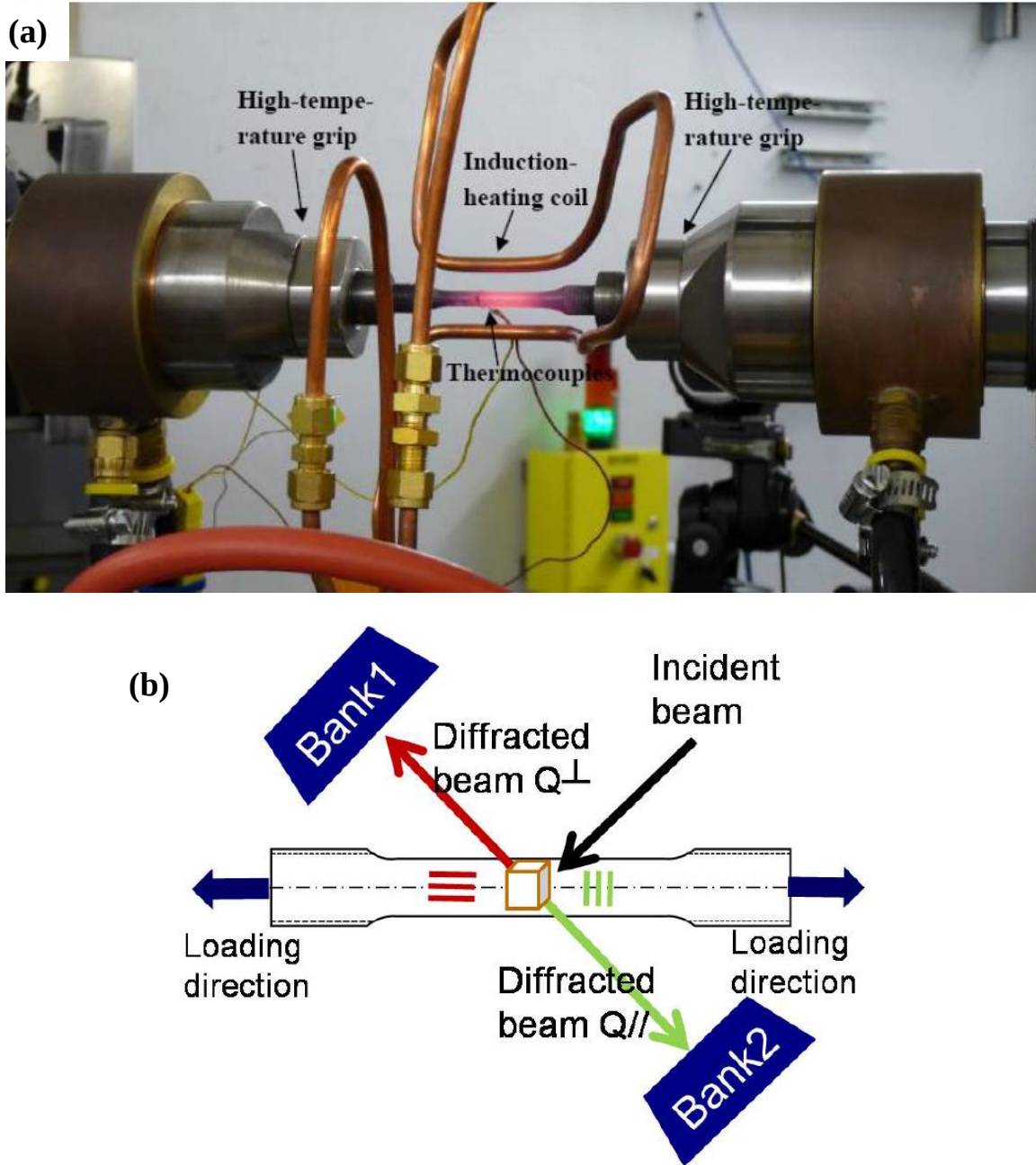


Figure 103 Experimental setup of in-situ tensile tests (a) showing that a sample loaded on the grip with its loading axis oriented horizontally and an electric induction heating coil placed along the axial direction around the sample, and (b) showing that the sample loaded at 45° to the incident beam, and two detectors oriented at 90° to this beam.

The screw-threaded cylindrical samples for the neutron-diffraction experiment at ISIS, with a gage length of 34 mm and a gage diameter of 8 mm, were machined. The related sample geometry

is shown in Figure 6.

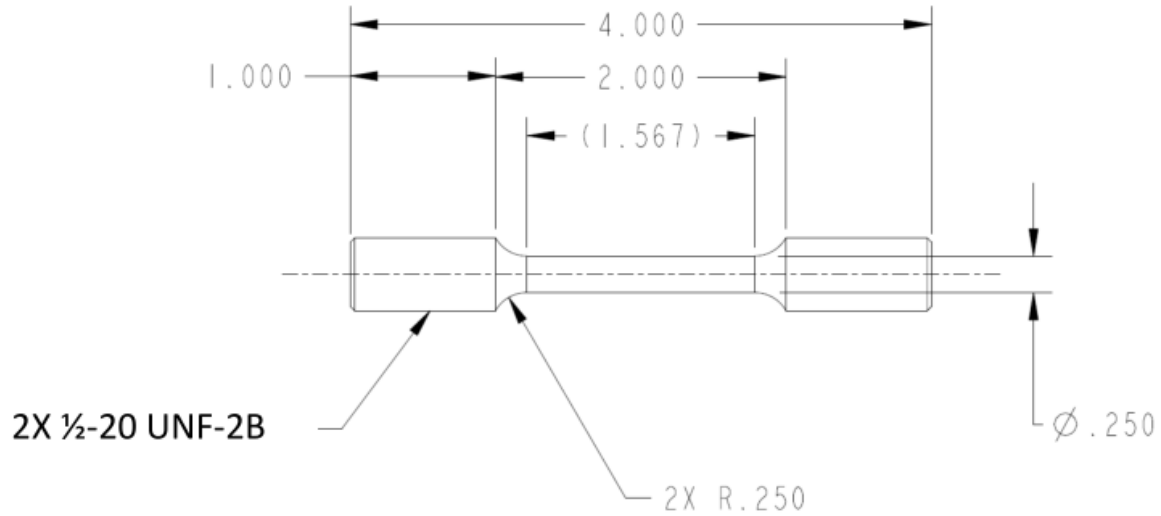


Figure 104 The tensile sample geometry for neutron-diffraction experiments at VULCAN

A crystal-plasticity finite-element model is developed to predict the lattice-strain evolution during the tensile test of HEAs. This constitutive model has been implemented into ABAQUS using the user-defined material model (UMAT) subroutine, which allows us to study the lattice evolution of HEAs.

The composition of the $\text{Al}_{0.1}\text{CoCrFeNi}$ (as-HIPed), $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed), and $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-heated) HEAs were determined by atom probe tomography (APT). To prepare the samples for APT, a thin blank with a dimension of $0.25 \times 0.25 \times 10$ mm was cut from the bulk material by electrical-discharge machining (EDM) for the polishing. After that, a sharp needle tip was obtained, it was focused-ion beam (FIB) milled to remove any surface irregularities, ensure a circular cross-section, a taper semiangle of 10 and an apex between 50 and 150 nm in radius. The local electrode atom-probe analysis was performed on a Cameca Instruments LEAP 4000X HR in a voltage-pulsed mode with a pulse repetition rate of 200 kHz and a voltage pulse fraction of 0.2, and at a specimen temperature of 60 K.

6.6.4 In-situ Tensile Neutron-Diffraction (ND) Analysis of the Al_{0.3}CoCrFeNi (as-HIPed) at Room Temperature

In situ, full-field, non-destructive measurement of lattice strain (which relies on the inter-granular interactions of the inhomogeneous deformation fields in neighboring grains) by neutron-diffraction techniques has been performed for the tensile tests of Al_{0.3}CoCrFeNi (as-HIPed). These microscopic grain-level measurements provided the unprecedented information on the further creep mechanisms.

ND provides the crucial structural information at mesoscopic scales, specifically the accurate deformation of lattice strains in differently-oriented grains and/or multiple phases. The large beam size and great penetration of neutrons into matters enable the illumination on a substantial quantity of grains, from which structural mechanisms in the bulk can be determined with good statistics. In contrast to the residual stress/strain state, as measured by ex-situ characterization techniques, in-situ measurements under loading at high temperatures probe the dynamic lattice-strain evolution during deformation. Since diffraction allows the precise determination of interplanar spacings, it can be used to measure elastic lattice strains. On the contrary, diffraction is not directly sensitive to the plastic deformation, since the shear strain parallel to crystallographic planes induced by slip deformation cannot be directly detected by diffraction. However, the local plastic strain of differently-oriented grains is generally incompatible and, thus, is compensated by elastic strains, which create local residual stresses. Therefore, effects of plastic deformation on the elastic lattice strain can also be revealed by analyzing the measured elastic lattice strain.

Figure 105 shows a typical diffraction pattern of the $\text{Al}_{0.3}\text{CoCrFeNi}$ (as-HIPed) HEA measured at room temperature with a 15-minute data collection. All peaks, including 111, 200, 220, 311, 400, 331, and 420, are indexed to the FCC structure. The d-spacing of different specific (hkl) planes is obtained from the single-peak fitting, using the Data Reduction and Interactive Visualization Software for Event Mode Neutron Diffraction (VDRIVE).

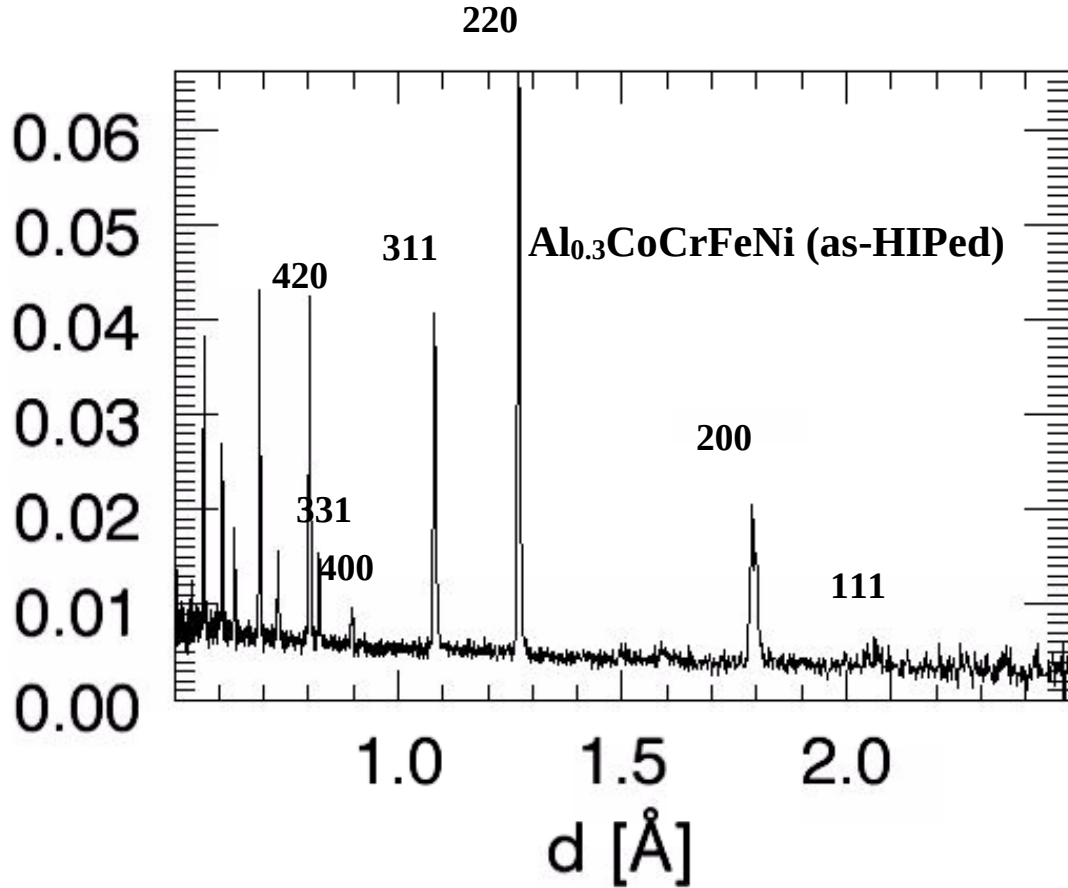


Figure 105 Typical diffraction pattern measured at VULCAN at room temperature with the normalized intensity on a logarithmic scale. The fundamental reflections, including 111, 200, 220, 311, 400, 331, and 420, are present.

The macroscopic stress-strain curve is displayed in Figure 8 for the in situ tension experiments, with strains measured from an extensometer. In the elastic region, the machine is under a stress-control mode, i.e., the tension tests are interrupted and hold for 15 minutes at 20, 40, 60, 80, 100, 120, and 140 MPa, respectively. Then the machine is under a strain-control mode, i.e., the tension tests continue until the strain is 11%. Then force is unloaded. The yielding stress is around 150 MPa.

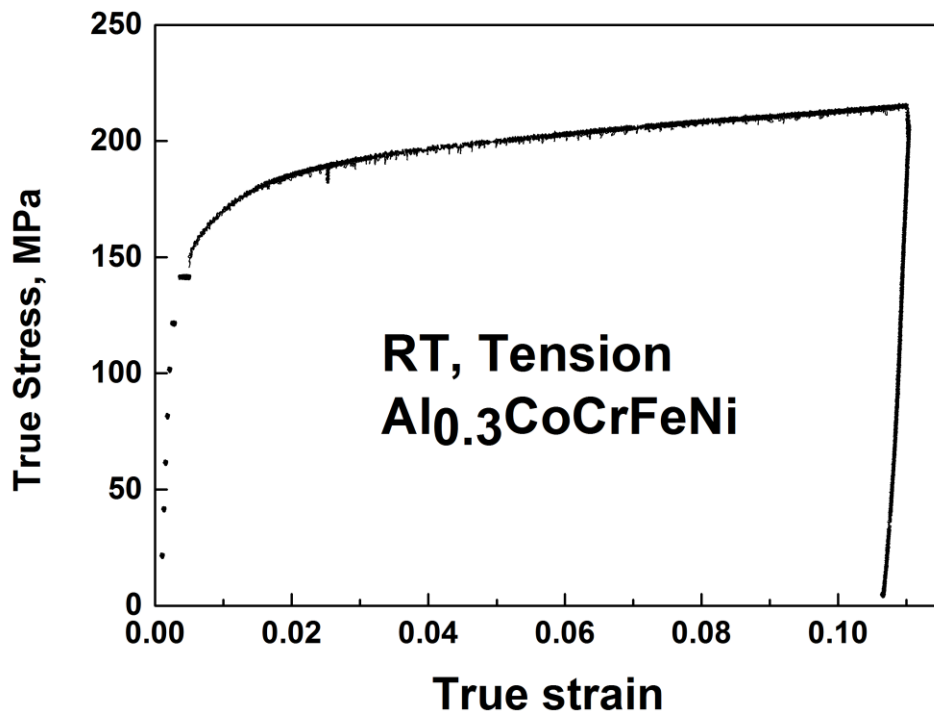


Figure 106 Macroscopic stress-strain curves of $\text{Al}_{0.3}\text{CoCrFeNi}$ for tension at room temperature with unloading.

Three types of elastic lattice strains, average phase strains, hkl plane-specific lattice strains, and intragranular phase strains, can be calculated from neutron-diffraction measurements in the polycrystalline-multiphase material. In this report, (hkl) plane-specific lattice strains are analyzed as a function of the applied axial stress.

The hkl plane-specific lattice strain is grain-orientation dependent and described as the average lattice strain accumulated in the diffracted grains, whose hkl plane normal are parallel to the diffraction vector, Q , ($Q = \frac{4\pi \sin \theta}{\lambda}$, where λ is the wavelength of the synchrotron X-ray, and 2θ is the scattering angle). In a polycrystalline material, the response of differently-oriented grains under an applied stress varies due to the effects of the elastic and plastic anisotropies. The elastic anisotropy arises from the fact that the elastic modulus depends on the grain orientation, which is manifested by the difference in the slopes of the applied stress vs. lattice strain in the elastic region. The origin of the plastic anisotropy is that plastic deformation occurs on certain preferential slip systems and the sequence of grain yielding relies on the magnitude of the Schmid factor determined by grain orientation. The plastic anisotropy is usually characterized by the non-linear behavior of the hkl plane-specific lattice strain and the tensile/compressive strain shift, relative to its elastic slope. Examinations of elastic and plastic anisotropies are important to understand the interactions between grains of different orientations during creep deformation, because they provide a measurement of the internal stress, even in the plastic region. The hkl plane-specific lattice strain is determined as

$$\varepsilon_{hkl} = (d_{hkl} - d_{hkl}^0) / d_{hkl}^0 \quad (1)$$

where ε_{hkl} is the lattice strain in the hkl-oriented grains, d_{hkl}^0 is the reference lattice spacing before deformation under the unloaded state, and d_{hkl} is the d spacing as a function of the applied stress, for the respective phases.

The lattice strain evolution of <200>, <220>, <311>, and <331> within the Al_{0.3}CoCrFeNi (as-HIPed) during tensile deformation at room temperature is shown in Figure 9. The results illustrate that the lattice-strain change is strongly dependent on the grain orientations, indicative of the strong elastic anisotropy. The {200} grains exhibit the largest elastic strain along the loading direction and a significant shift relative to their linear elastic response, which manifests the elastic-plastic transition. The {311} grains have the second largest elastic strain but maintain nearly a linear response. The {220} and {331} grains, on the other hand, have a lower elastic strain, indicating that they have a larger elastic stiffness. This trend indicates that the current HEA exhibits the elastic behavior similar to that of simple face-centered cubic (FCC) metals.

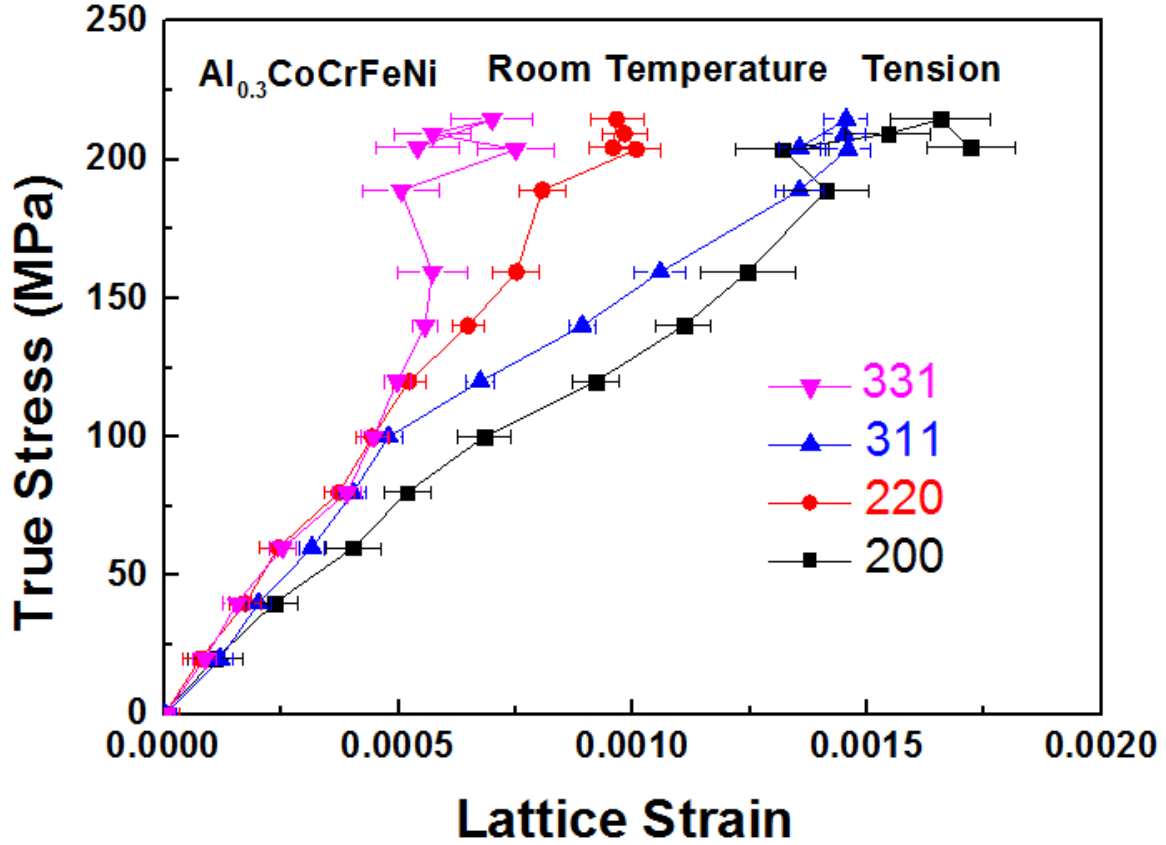


Figure 107 The response of the hkl plane specific lattice strain along the axial direction as a function of stress during the tensile test at room temperature for the Al_{0.3}CoCrFeNi (as-HIPed).

6.7 Crystal-plasticity Finite-element Simulations

A crystal-plasticity finite-element model (CPFEM) is developed to predict the lattice strain evolution during the tensile test in polycrystalline materials. The slip-based crystal-plasticity model considered the slip deformation inside each grain, and the yielding sequence of different grains is governed by the grain orientation, elastic modulus, and Schmid factor of specific slip systems. The constitutive parameters include elastic constants, C_{11} , C_{12} , and C_{44} , the critical resolved shear stress, τ_0 , and those describing the strain-rate dependence and hardening behavior. This model has been implemented in ABAQUS, which

is a commercial finite-element software, through the user-defined material (UMAT) subroutine. The finite-element simulation is conducted on a tension specimen with cubic elements in the ABAQUS model, shown in Figure 108. The system was a polycrystalline aggregate containing $22 \times 22 \times 66$ cubic grains with a random texture. There were $3 \times 3 \times 3$ grids, or equivalently representing 27 elements, in each grain. The calculated $\{hkl\}$ lattice strain was a volume average of the projected elastic strains in a subset of grains, whose $\{hkl\}$ plane normal direction was parallel to the diffraction vector. Input material parameters for CPFEM included stiffness, C_{11} , C_{12} , and C_{44} , the stress exponent, n , the initial hardening modulus, h_0 , the initial slip strength, τ_s , and the latent hardening parameter, q , for the $Al_{0.3}CoCrFeNi$.

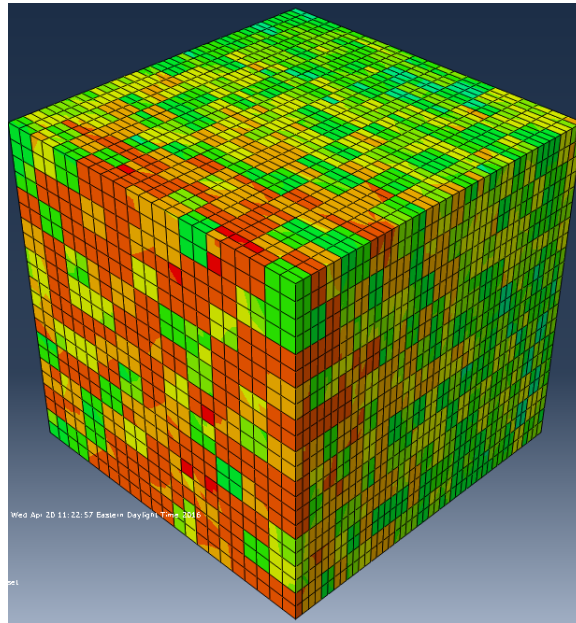


Figure 108 The finite-element simulation is conducted on a tension specimen with cubic elements in the ABAQUS model.

Since there were no available experimental data for the single-crystal elastic constants of the $Al_{0.3}CoCrFeNi$, we estimated their elastic constants from the experimental

polycrystalline diffraction data. This calculation is of practical importance, because single-crystal elastic constants are usually not available for newly-designed alloys. Voigt, Reuss, and Kroner models are widely used to calculate the isotropic elastic properties of a polycrystalline bulk material from the single-crystal elastic constant of its individual grains. To obtain the single-crystal elastic constant from the polycrystalline diffraction data is an inverse problem. From the diffraction-peak specific elastic constants, E_{hkl} and ν_{hkl} , we determined constants, $S_1(hkl)$ and $S_2(hkl)$, as follows,

$$s_1(hkl) = -\nu_{hkl} / E_{hkl} \quad (25)$$

$$\frac{1}{2} s_2(hkl) = [1 + \nu_{hkl}] / E_{hkl} \quad (26)$$

The least-squares fitting covered the different measured hkl directions, ranging from the (200), (220), (311), and (331). Further refinement of single-crystal elastic constants was performed by tuning the values of input stiffness in CPFEM to the ND measurements.

The macroscopic stress-strain curve predicted by CPFEM is shown in Figure 10, in comparison to the experimental measurement during in situ tension at room temperature. The red line in Figure 11 is predictions while the black line is the experimental data. A quantitative agreement within the elastic deformation regime and plastic regime is observed. Next, the parameter, n , H_0 , and q , will be further tuned.

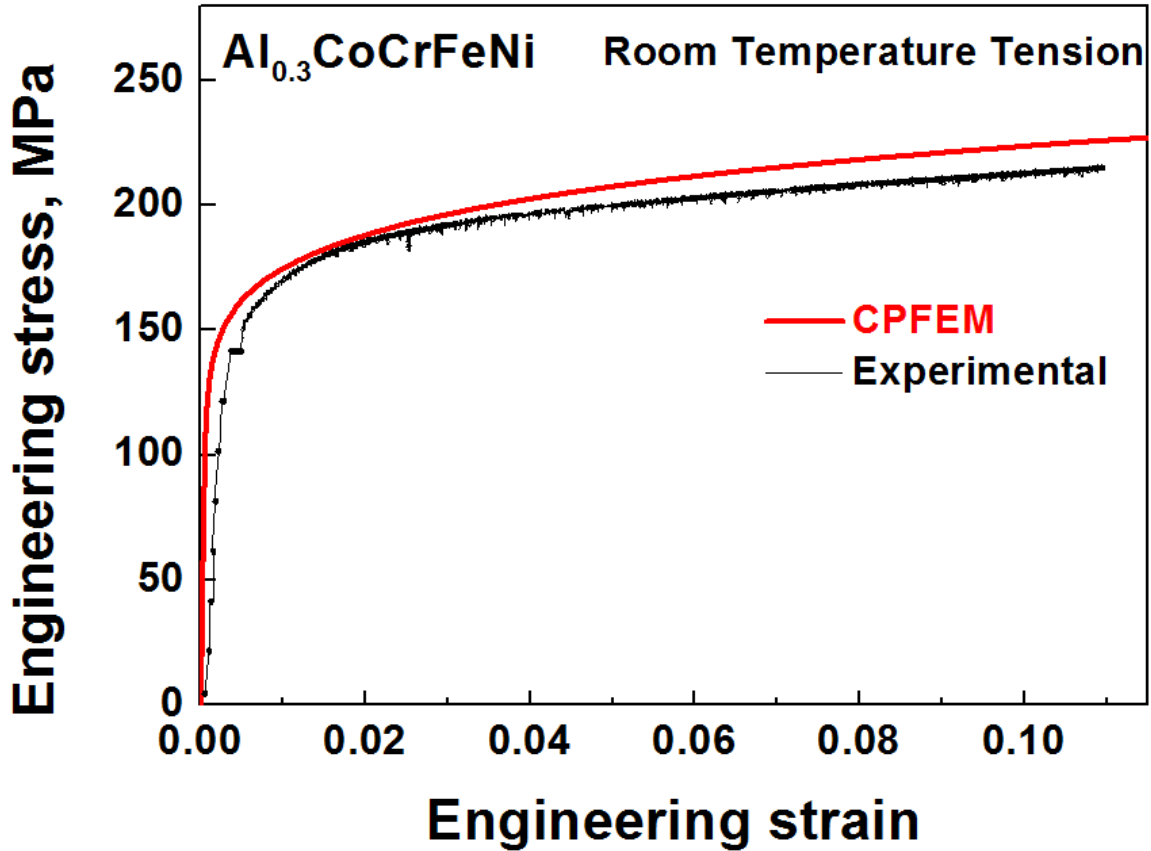


Figure 109 Simulated stress-strain curve by the crystal plasticity finite-element method, in comparison with in-situ neutron tensile experimental data.

The lattice-strain evolution as a function of stress predicted by CPFEM is shown in Figure 110, in comparison to the experimental measurement during in situ tension at room temperature. The solid lines in Figure 110 are predictions while the symbols are experimental data. A quantitative agreement within the elastic deformation regime for (220), (331), and (311) is found. There is some difference between the simulated and experimental results in the (200) specific lattice strain. Next, the parameter, C_{11} , C_{12} , and C_{44} , will be further tuned.

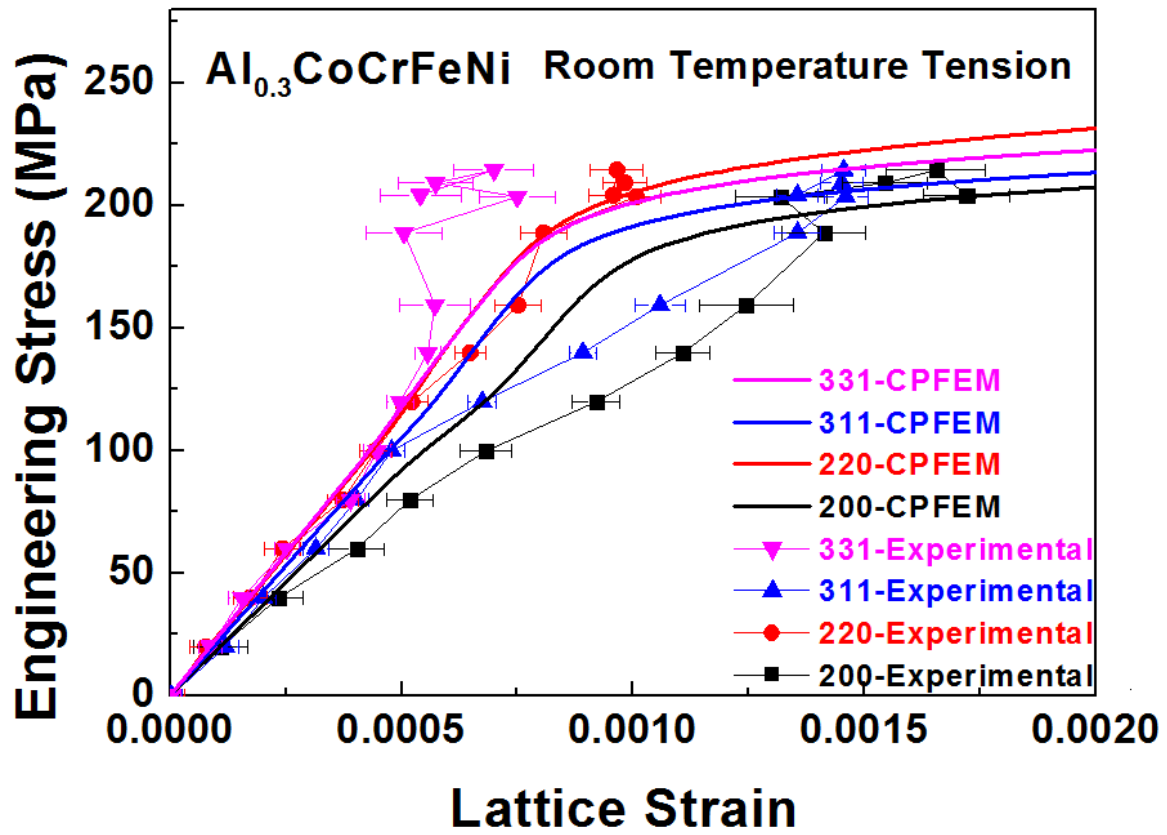


Figure 110 Simulated lattice strain evolution as a function of stress by the crystal-plasticity finite-element method, in comparison with in-situ neutron tensile experimental data.

7. CONCLUSIONS

Above all, fundamental studies have been conducted, using (1) thermodynamic calculations to quantify the phase compositions, phase fractions, and phase stability versus temperature and composition, (2) mechanical tests (hardness, tensile, compression, nanoindentation, and creep) for the ductility investigation and the creep-resistance examination, (3) neutron diffraction to reveal the deformation mechanisms of both single-phase and precipitate-strengthened HEAs, during plastic (tensile and creep) deformation, (4) characterization techniques (atomic-probe tomography, transmission-electron microscopy) to verify the predictions by thermodynamic calculations and study the creep deformation mechanisms, and (5) crystal-plasticity finite-element modeling (CPFEM) to further verify the lattice evolution of lattice strains during high-temperature deformation.

In the first task, all the constituent binary and ternary systems of the Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems were thermodynamically modeled within the whole composition range. Comparisons between the calculated phase diagrams and literature data are in good agreement. The multi-component thermodynamic database of the Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems were then obtained via extrapolation. The current Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni thermodynamic database enables us to carry out the calculations of phase diagrams, which can be used as useful guidelines to identify the Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni HEAs with desirable microstructures and creep properties.

In the second task, seven types of HEAs were fabricated from Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems. The $\text{Al}_x\text{CrCuFeMnNi}$ HEAs have disordered (FCC + BCC) crystal structures, not FCC or BCC single structure. But the constituent phases vary for different aluminum concentration. The $\text{Al}_{0.1}\text{CrCuFeMnNi}$ has two kinds of FCC phases and one kind of the BCC phase, while $\text{Al}_{0.8}\text{CrCuFeMnNi}$ has one kind of the FCC phase and two kinds of BCC phases. 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 constitute phases, and (3) existing temperatures of all six phases. After homogenization, the $\text{Al}_{0.3}\text{CoCrFeNi}$ material is pure face-centered-cubic (FCC) solid solution. After aging at 700 °C for 500 hours, the optimum microstructure combinations, FCC matrix, needle-like B2 phase within grains, and granular σ phase along grain boundary, is achieved for $\text{Al}_{0.3}\text{CoCrFeNi}$. Cold-rolling process is utilized to reduce the grain size of $\text{Al}_{0.1}\text{CoCrFeNi}$ and $\text{Al}_{0.3}\text{CoCrFeNi}$.

In the third task, the chemical elemental partitioning of FCC, BCC, B2 and σ phases at different temperatures, before and after mechanical tests, in Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems are quantitatively characterized by both synchrotron X-ray diffraction, neutron diffraction with levitation, scanning electron microscopy (SEM), advanced atom probe tomography (APT), and transmission electron microscopy (TEM). The physical metallurgy of HEAs, i. e., the structure-property relationship, coupled with alloy design in task 1 and mechanical properties in task 4, is investigated.

In the fourth task, the mechanical properties are studied by hardness, compression, and tensile tests. As the Al ratio increases, the yielding stress increases, while the ductility decreases in both Al-Cr-Cu-Fe-Mn-Ni and Al-Co-Cr-Fe-Ni systems. In-situ neutron diffraction experiments were conducted to study the strengthening effect of B2 phase on tensile properties of $\text{Al}_{0.3}\text{CoCrFeNi}$ HEAs directly. The results show the creep behavior of $\text{Al}_{0.3}\text{CoCrFeNi}$ is superior to conventional alloys, and the heat treatment introduces secondary B2 phase into the FCC matrix, which increase the yielding strength, decrease the ductility, diminish the serrated flow during compression tests at high temperatures.

In summary, the outcomes of the development of the HEAs with creep resistance include: (1) Suitable candidates, $\text{Al}_x\text{CrCuFeMnNi}$ and $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloy (HEA) systems, for the application to boilers and steam and gas turbines at temperatures up to 760 °C and a stress of 35 MPa. (2) Fundamental understanding on the precipitate stability and deformation mechanisms of

both single-phase and precipitate-strengthened alloys at room and elevated temperatures, and (3) The demonstration of an integrated approach, coupling modeling [thermodynamic calculations and crystal-plasticity finite-element modeling (CPFEM)] and focused experiments, to identify HEAs that outperform conventional alloys for high-temperature applications, which will be applicable for the discovery and development of other high-temperature materials in the power-generating industry.

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Structures, Phase Transformations and Elastic Properties of High-Entropy Al_xCoCrCuFeNi Alloys: Ab Initio Molecular Dynamics Simulation, M. Gao, L. Santodonato, and P. K. Liaw.
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Disordered and Weakly-Ordered Solid-Solution Phases in the High-Entropy Alloy System of Al-Co-Cr-Cu-Fe-Ni, L. Santodonato, Z. Tang, A. Chuang, and P. K. Liaw.
- [3] 2012 TMS Meeting, Orlando, March 11-15, 2012 (Invited)
Accumulation and Recovery Processes in a High-Entropy Alloy Irradiated with 2.5 MeV Electrons, Y. Petrusenko, A. Bakai, V. Borysenko, E. Mayevsky, P. K. Liaw, G. Wang, and J.-W. Yeh.
- [4] 2012 American Conference on Neutron Scattering, June 24-28, 2012 (Invited)
The Evolution of Local and Long-range Order in a High-Entropy Alloy, as it Solidifies from the Liquid Phase, Louis J. Santodonato, Yang Zhang, Mikhail Feygenson, J. Neuefiend, Zhi Tang, Richard JKR Weber, Michael C. Gao, and Peter K. Liaw.
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Experimental Study of Local and Long-Range Atomic Ordering in the High-Entropy Al_xCoCrCuFeNi Alloys during Solidification, Louis Santodonato, Yang Zhang, Mikhail Feygenson, Joerg Neuefiend, Zhi Tang, Richard Weber, Michael Gao, and Peter Liaw.
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Single Phase CrCoCuFeNi High-entropy Alloy Films: Microstructure, and Mechanical Behaviors, Zhinan An, Yueying Wu, Philip Rack, and Peter K. Liaw.
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First-Principles Simulations and Neutron Scattering Studies of High-Entropy Bulk Metallic Glasses, Michael Gao, Michael Widom, Louis Santodonato, and Peter Liaw.
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High-Entropy Alloys FeCoNiAl_xSi_x with High Saturation Magnetization and Electrical Resistivity,

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Electron-Irradiation Induced Defects and Recovery Kinetics in a High-Entropy Alloy, Yuri Petrusenko, Alexander Bakai, Valeriy Borysenko, Denys Irzhevskiy, Peter K. Liaw, Gongyao Wang, and Jien-Wei Yeh.
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Relaxation Behaviors of Al_xCoCrFeNi High-Entropy Alloys by Dynamic Mechanical Analyzer, Shengguo Ma, Yong Zhang, and Peter Liaw.
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Elevated-Temperature Corrosion Resistance of CoCrCuFeNiAl High-Entropy Alloys, Omer Dogan, Jeffrey Hawk, David Alman, and Peter Liaw.
- [12] 2012 Materials Science & Technology, Pittsburgh, October 07-11, 2012 (Invited)
A Combinatorial Approach to Investigations of High Entropy Alloys, Brian Welk, Peter Liaw, Mark Gibson, and Hamish Fraser.
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Mechanical Behavior of High-Entropy Alloys, Yong Zhang, Zhi Tang, Louis Santodonato, Michael Hemphill, Gongyao Wang, Michael Gao, and Peter Liaw.
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Low Temperature Mechanical Behavior of the Al_{0.5}CoCrCuFeNi High-Entropy Alloy, Marina Laktionova, Elena Tabachnikova, Zhi Tang, and Peter Liaw.
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Fatigue Behavior of Al_{0.5}CoCrCuFeNi High-Entropy Alloys, Michael Hemphill, Zhi Tang, Tao Yuan, Gongyao Wang, Jien-Wei Yeh, CheWei Tsai, Andrew Chuang, and Peter Liaw.
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Tensile Behavior and Fracture Mechanism of AlCoCrFeNi High-Entropy Alloy Subjected to Hot Isostatic Pressing and Annealing, Zhi Tang, Oleg Senkov, Daniel Miracle, Louis Santodonato,

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First-Principles Simulations of High-Entropy Al_xCoCrCuFeNi Alloys, Michael Gao, Louis Santodonato, and Peter Liaw.
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Thermodynamic and Elastic Properties of High Entropy Alloys: Atomistic Molecular Dynamics Simulations, De Nyago Tafen, Michael Gao, Louis Santodonato, and Peter Liaw.
- [19] The 9th International Conference on Bulk Metallic Glasses, Xiamen, China, December 16-20, 2012 (Invited)
Computational Thermodynamics Aided High-Entropy Alloy Design, C. Zhang, F. Zhang, S. L. Chen, W. S. Cao, Z. Tang, and P. K. Liaw.
- [20] 2013 TMS Meeting, San Antonio, TX, USA, March 3-9, 2013 (Invited)
Automatic Fabrication of High-Entropy Alloys and Their Properties, Y. Yokoyama, X. Xie, J. Antonaglia, M. Hemphill, T. Zhi, T. Yuan, G. Wang, C. Tsai, J. Yeh, A. Chuang, K. Dahmen, and P. K. Liaw
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Non-Equilibrium and Equilibrium Phases in AlCoCrFeNi High-Entropy Alloys, Z. Tang, O. Senkov, C. Parish, L. Santodonato, D. Miracle, G. Wang, C. Zhang, F. Zhang, and P. K. Liaw
- [22] 2013 TMS Meeting, San Antonio, TX, USA, March 3-9, 2013
Ordering Behavior in the Al(x)CoCrCuFeNi High-Entropy Alloys, L. Santodonato, Y. Zhang, M. Gao, C. Parish, M. Feygenson, Z. Tang, J. Neuefeind, R. Weber, and P. K. Liaw
- [23] 2013 TMS Meeting, San Antonio, TX, USA, March 3-9, 2013 (invited)
Computational Modeling of High-Entropy Alloys, M. Gao, D. Tafen, J. Hawk, Y. Wang, M. Widom, L. Santodonato, and P. K. Liaw
- [24] 2013 TMS Meeting, San Antonio, TX, USA, March 3-9, 2013 (Invited)
Computational Thermodynamics Aided High-Entropy Alloy Design, C. Zhang, F. Zhang, S. Chen,

W. Cao, J. Zhu, Z. Tang, and P. K. Liaw

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Statistical Fatigue-Life Modeling for High-Entropy Alloys, T. Yuan, M. Hemphill, Z. Tang, G. Wang, A. Chuang, C. Tsai, J. Yeh, and P. K. Liaw
- [26] 2013 TMS Meeting, San Antonio, TX, USA, March 3-9, 2013 (Invited)
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M. Gao, M. Widom, L. Santodonato, A. Takeuchi, Z. Tang, M. Hemphill, and P. K. Liaw
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A Combinatorial Approach to the Investigation of Metal Systems that Form Both High Entropy Alloys and Bulk Metallic Glasses, B. Welk, P. K. Liaw, M. Gibson, and H. Fraser
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Minor Phase and Defect Effects on Fatigue Behavior of Wrought Al_{0.5}CoCrCuFeNi High-Entropy Alloys, Z. Tang, M. Hemphill, T. Yuan, G. Wang, J. Yeh, C. Tsai, and P. K. Liaw
- [29] 2013 TMS Meeting, San Antonio, TX, USA, March 3-9, 2013 (Invited)
Phase Separation and Intermetallic Formation in "High-Entropy" Alloys, C. Parish, M. Miller, L. Santodonato, Z. Tang, and P. K. Liaw
- [30] University Coal Research/Historically Black Colleges And Universities And Other Minority Institutions Contractors Review Meeting, The Wyndham Grand Pittsburgh Downtown, Pittsburgh, USA, June 11-13, 2013 (Invited)
Experimental and Computational Investigation of High-Entropy Alloys (HEAs) for Elevated-Temperature Applications, H. Y. Diao, C. Zhang, F. Zhang, and P. K. Liaw.
- [31] SES 50th Annual Technical Meeting and ASME-AMD Annual Summer Meeting. Brown University, Providence, RI, USA, July 28-31, 2013 (Invited)
Extracting Materials Properties from Crackling Noise and Slip-Avalanche Statistics of Slowly-Sheared Materials, K. A. Dahmen, X. Xie, J. Antonaglia, M. Laktionova, E. Tabachnikova, Z.

- Tang, J. W. Qiao, J. W. Yeh, C. W. Tzai, Y. Zhang, J. Uhl, and P. K. Liaw.
- [32] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014
Modeling Plastic Deformation and the Statistics of Serrations in the Stress Versus Strain Curves of Bulk Metallic Glasses, K. Dahmen, J. Antonaglia, X. Xie, J. W. Qiao, Y. Zhang, J. Uh, and P. K. Liaw.
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Aluminum Alloying Effects on Lattice Types, Microstructures, and Mechanical Behavior of High-entropy Alloys Systems, Z. Tang, M. Gao, H. Y. Diao, T. F. Yang, J. P. Liu, T. T. Zuo, Y. Zhang, Z. P. Lu, Y. Q. Cheng, Y. W. Zhang, K. Dahmen, P. K. Liaw, and T. Egami.
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The Influence of Cu and Al on the Microstructure, Mechanical Properties and Deformation Mechanisms in the High Entropy Alloys CrCoNiFeCu, CrCoNiFeAl_{1.5} and CrCoNiFeCuAl_{1.5}, B. Welk, B. B. Viswanathan, M. Gibson, P. K. Liaw, and H. Fraser.
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Ultra-Grain Refinement in High Entropy Alloys: N. Tsuji, I. Watanabe, N. Park, D. Terada, A. Shibata, Y. Yokoyama, P. K. Liaw.
- [36] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014
Nanostructure Evolution through High-pressure Torsion and Recrystallization in a High-entropy CrMnFeCoNi Alloy, N. Park, A. Shibata, D. Terada, Y. Yokoyama, P. K. Liaw, and N. Tsuji.
- [37] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014
Mechanical Behavior of an Al_{0.1}CoCrFeNi High Entropy Alloy, M. Komarasamy, N. Kumar, Z. Tang, R. Mishra, and P. K. Liaw.
- [38] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014

- Using the Statistics of Serrations in the Stress Strain Curves to Extract Materials Properties of Slowly-sheared High Entropy Alloys, Karin Dahmen, X. Xie, J. Antonaglia, M. Laktionova, E. Tabachnikova, J. W. Qiao, J. W. Yeh, C. W. Tsai, J. Uh, and P. K. Liaw.
- [39] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014
Characterizing Multi-Component Solid Solutions Using Order Parameters and the Bragg-Williams Approximation, L. Santodonato, and P. K. Liaw.
- [40] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014
The Oxidation Behavior of AlCoCrFeNi High-entropy Alloy at 1023-1323K (750-1050°C), Wu Kai, W.S. Chen, C.C. Sung, Z. Tang, and P. K. Liaw.
- [41] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014
Strain-rate Effects on the Structure Evolution of High Entropy Alloys, X.Xie, J. Antonaglia, J. P. Liu, Z. Tang, J. W. Qiao, G. Y. Wang, Y. Zhang, K. Dahmen, and P. K. Liaw.
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Neutron diffraction studies on creep deformation behavior in a high-entropy alloy CoCrFeMnNi under high temperature and low strain rate, W. C. Woo, E. W. Huang, J. W. Yeh, P. K. Liaw, and H. Choo.
- [43] 2014 TMS Meeting, San Diego, CA, USA, February 16-20, 2014
The Hot Corrosion Resistance Properties of Al_xFeCoCrNi, S. Y. Yang, M. Habibi, L. Wang, S. M. Guo, Z. Tang, P. K. Liaw, L. X. Tan, C. Guo, and M. Jackson.
- [44] Workshop on Deformation, Damage and Life Prediction of Structural Materials, National Institute of Materials Science, Japan, June 23-24, 2014 (Keynote)
Fatigue Behavior of Bulk Metallic Glasses and High Entropy Alloys, Peter K. Liaw.
- [45] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
On the Friction Stress and Hall-Petch Coefficient of a Single Phase Face-Centered-Cubic High Entropy Alloy Al_{0.1}FeCoNiCr, Nilesh Kumar, Mageshwari Komarasamy, Zhi Tang, Rajiv Mishra, and Peter Liaw.

- [46] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
Strength and Deformation of Individual Phases in High-Entropy Alloys, A. Giwa, Haoyan Diao, Xie Xie, S, Y, Chen, Zhi Tang, Karin Dahmen, and Peter Liaw.
- [47] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015
- [48] Al-Co-Cr-Fe-Ni Phase Equilibria and Properties, Zhi Tang, Oleg Senkov, Chuan Zhang, Fan Zhang, Carl Lundin, and Peter Liaw.
- [49] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015
Fatigue Behavior of an Al_{0.1}CoCrNiFe High Entropy Alloy, Bilin Chen, Xie Xie, Shuying Chen, Ke An, and Peter Liaw.
- [50] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
Flow and Fracture Behavior of a High Entropy Alloy, Yong Zhang, Peter Liaw, and John Lewandowski.
- [51] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
Deformation Twinning in the High-Entropy Alloy Induced by High Pressure Torsion at Room Temperature, Gong Li, P.F. Yu, P.K. Liaw, and R.P.Liu.
- [52] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015
Microstructures and Mechanical Behavior of Multi-Component Al_xCrCuFeMnNi High-Entropy Alloys, Haoyan Diao, Zhinan An¹; Xie Xie, Gongyao Wang, Chuan Zhang, Fan Zhang, Guangfeng Zhao, Fuqian Yang, Karin Dahmen, and Peter Liaw.
- [53] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015
The Characterization of Serrated Plastic Flow in High Entropy Alloys, Shuying Chen, Xie Xie, James Antonaglia, Junwei Qiao, Yong Zhang, Karin Dahmen and Peter Liaw.
- [54] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
A Model for the Deformation Mechanisms and the Serration Statistics of High Entropy Alloys, Karin Dahmen, Bobby Carroll, Xie Xie, Shuying Chen, James Antonaglia, Braden Brinkman, Michael LeBlanc, Marina Laktionova, Elena Tabachnikova, Zhi Tang, Junwei Qiao, Jien Wei Yeh,

Chi Lee, Che Wei Tsai, Jonathan Uhl, and Peter Liaw.

- [55] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
Segregation and Ti-Zr-Hf-Ni-Pd-Pt High Entropy Alloy under Liquid State, Y. Yokoyama, Norbert Mattern, Akitoshi Mizuno, Gongyao Wang, and Peter Liaw.
- [56] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
Computational-Thermodynamics-Aided Development of Multiple-Principal-Component Alloys, Chuan Zhang, Fan Zhang, Shuanglin Chen, Weisheng Cao, Jun Zhu, Zhi Tang, Haoyan Diao, and Peter Liaw.
- [57] 2015 TMS Meeting, Orlando, FL, USA, March 15-19, 2015 (Invited)
Sputter Deposition Simulation of High Entropy Alloy via Molecular Dynamics Methodology, Yunche Wang, Chun-Yi Wu, Nai-Hua Yeh, and Pete Liaw.
- [58] 2015 Chinese Materials Research Society (C-MRS) Conference, Guiyang China, 2015 (Invited)
Characterization of Intermittent Behavior in Bulk Metallic Glasses and High Entropy Alloys, Peter Liaw, Xie Xie, Shuying Chen, James Antonaglia, Junwei Qiao, Gongyao Wang, Yoshihiko Yokoyama, and Karin Dahmen.
- [59] 2015 Chinese Materials Research Society (C-MRS) Conference, Guiyang China, 2015 (Keynote)
Deviation from High-Entropy Configurations in the $\text{Al}_{1.3}\text{CoCrCuFeNi}$ Alloy, Louis J. Santodonato, Yang Zhang, Mikhail Feygenson, Chad M. Parish, Michael C. Gao, Richard Weber, Joerg C. Neuefeind, Zhi Tang, and Peter K. Liaw.
- [60] The Shanghai University, China, July 6, 2015 (Invited)
Characterization of Serrated Flows Bulk Metallic Glasses and High Entropy Alloys, X. Xie, S. Y. Chen, J. Antonaglia, J. P. Liu, J. W. Qiao, Y. Zhang, G. Y. Wang, Y. Yokoyama, G. Wang, J. L. Ren, M. W. Chen, K. A. Dahmen, and Peter K. Liaw.
- [61] The Shanghai Jiao Tong University, China, July 6, 2015 (Invited)
Characterization of Serrated Flows Bulk Metallic Glasses and High Entropy Alloys, X. Xie, S. Y.

Chen, J. Antonaglia, J. P. Liu, J. W. Qiao, Y. Zhang, G. Y. Wang, Y. Yokoyama, G. Wang, J. L. Ren, M. W. Chen, K. A. Dahmen, and Peter K. Liaw.

[62] The Zhengzhou University, China, July 8, 2015 (Invited)

Characterization of Serrated Flows Bulk Metallic Glasses and High Entropy Alloys, X. Xie, S. Y. Chen, J. Antonaglia, J. P. Liu, J. W. Qiao, Y. Zhang, G. Y. Wang, Y. Yokoyama, G. Wang, J. L. Ren, M. W. Chen, K. A. Dahmen, and Peter K. Liaw.

[63] The China Academy of Science Institute Mechanics Group, July 16, 2015 (Invited)

Characterization of Serrated Flows Bulk Metallic Glasses and High Entropy Alloys, X. Xie, S. Y. Chen, J. Antonaglia, J. P. Liu, J. W. Qiao, Y. Zhang, G. Y. Wang, Y. Yokoyama, G. Wang, J. L. Ren, M. W. Chen, K. A. Dahmen, and Peter K. Liaw.

[64] The Beihang University, Chian, July 17, 2015 (Invited)

Deviation from High-Entropy Configurations in the Atomic Distributions of a Multi-Principal-Element Alloy, L. J. Santodonato, Y. Zhang, M. Feygenson, C. M. Parish, M. C. Gao, R. J. K. Weber, J. C. Neufeind, Z. Tang, Y. Zhang, X. Xie, S. Y. Chen, H. Y. Diao, T. N. Tran, K. A. Dahmen, and Peter K. Liaw.

[65] The University of Science and Technology Beijing, China, July 17, 2015 (Invited)

Deviation from High-Entropy Configurations in the Atomic Distributions of a Multi-Principal-Element Alloy, L. J. Santodonato, Y. Zhang, M. Feygenson, C. M. Parish, M. C. Gao, R. J. K. Weber, J. C. Neufeind, Z. Tang, Y. Zhang, X. Xie, S. Y. Chen, H. Y. Diao, T. N. Tran, K. A. Dahmen, and Peter K. Liaw.

[66] The Navy Surface Warfare Center, Maryland, USA, August 12, 2015 (Invited)

Deviation from High-Entropy Configurations in the Atomic Distributions of a Multi-Principal-Element Alloy, L. J. Santodonato, Y. Zhang, M. Feygenson, C. M. Parish, M. C. Gao, R. J. K. Weber, J. C. Neufeind, Z. Tang, Y. Zhang, X. Xie, S. Y. Chen, H. Y. Diao, T. N. Tran, K. A. Dahmen, and Peter K. Liaw.

[67] The ALCOA Company, Pittsburg, August 27, 2015 (Invited)

Deviation from High-Entropy Configurations in the Atomic Distributions of a Multi-Principal-

- Element Alloy, L. J. Santodonato, Y. Zhang, M. Feygenson, C. M. Parish, M. C. Gao, R. J. K. Weber, J. C. Neuefeind, Z. Tang, Y. Zhang, X. Xie, S. Y. Chen, H. Y. Diao, T. N. Tran, K. A. Dahmen, and Peter K. Liaw.
- [68] The Carnegie Mellon University, Pittsburg, August 18, 2015 (Invited)
Deviation from High-Entropy Configurations in the Atomic Distributions of a Multi-Principal-Element Alloy, L. J. Santodonato, Y. Zhang, M. Feygenson, C. M. Parish, M. C. Gao, R. J. K. Weber, J. C. Neuefeind, Z. Tang, Y. Zhang, X. Xie, S. Y. Chen, H. Y. Diao, T. N. Tran, K. A. Dahmen, and Peter K. Liaw.
- [69] 2015 Materials Science & Technology Conference (MS&T), Columbus, OH, October 4-8, 2015
The Serrated Flows in High Entropy Alloys, Shuying Chen, Xie Xie, James Antonaglia, Junwei Qiao, Yong Zhang, Karin Dahmen, and Peter Liaw.
- [70] 2015 Materials Science & Technology Conference (MS&T), Columbus, OH, October 4-8, 2015
The Serration Behavior and Pop-in Phenomena in $\text{Al}_x\text{CrCuFeMnNi}$ High Entropy Alloys, Haoyan Diao, Xie Xie, Shuying Chen, Fuqian Yang, Karin Dahmen, and Peter Liaw.
- [71] 2015 Materials Science & Technology Conference (MS&T), Columbus, OH, October 4-8, 2015 (Invited)
The Grain Boundary on the Nanoindentation Creep Behavior of $\text{Al}_{0.3}\text{CoCrFeNi}$ High-entropy Alloy, Gong Li, Lijun Zhang, Pengfei Yu, and P.K Liaw.
- [72] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Deviation from High-Entropy Configurations in the $\text{Al}_{1.3}\text{CoCrCuFeNi}$ Alloy, Louis Santodonato, Yang Zhang, Mikhail Feygenson, Chad Parish, Michael Gao, Richard Weber, Joerg Neuefeind, Zhi Tang, and Peter Liaw.
- [73] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
A Bragg-Williams Model of Ordering in High-entropy Alloys, Louis Santodonato, and Peter Liaw.

- [74] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Structure Evolution during Cooling of Al_{0.1}CrCuFeMnNi High-entropy Alloy, Haoyan Diao, Chuan Zhang, Louis Santodonato, Mikhail Feygenson, Joerg Neuefeind, Xie Xie, Fan Zhang, and Peter Liaw.
- [75] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016 (Invited)
Atomic and Electronic Basis for Viscous Flow Mediated Avalanches of Ultrastrong Refractory High Entropy Alloys, William Yi Wang, Shunli Shang, Yi Wang, Yidong Wu, Kristopher Darling, Xie Xie, Oleg Senkov, Laszlo Kecskes, Karin Dahman, Xidong Hui, Peter Liaw, and Zi-Kui Liu.
- [76] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016 (Invited)
Microstructure and Mechanical Properties of YxCoCrFeNi High Entropy Alloys, Gong Li, Huan Zhang, Lijun Zhang, Pengfei Yu, Hu Cheng, Qin Jing, Mingzhen Ma, Peter Liaw, and Riping Liu.
- [77] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016 (Invited)
Fracture Toughness and Fatigue Crack Growth Behavior of High Entropy Alloys, Mohsen Seifi, Dongyue Li, Zhang Yong, Peter Liaw, and John Lewandowski.
- [78] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Microstructures and Properties of CoFeMnNiX (X = Al, Ga, Sn) High Entropy Alloys, Ting Ting Zuo, Xiao Yang, Michael Gao, Shu Ying Chen, Peter Liaw, and Yong Zhang
- [79] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Deviation from High-Entropy Configurations in the Al_{1.3}CoCrCuFeNi Alloy, Louis Santodonato, Yang Zhang, Mikhail Feygenson, Chad Parish, Michael Gao, Richard Weber, Joerg Neuefeind, Zhi Tang, Peter Liaw.
- [80] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
A Statistical Study of the Potential-scan-rate and Al-content Dependent Metastable Pitting (Serration) Behavior of Al_xFeCoCrNi High-entropy Alloys, Yunzhu Shi, Bin Yang, Xie Xie, Zhi Tang, Karin Dahmen, and Peter Liaw.
- [81] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016

- Serrated Plastic Flow in CoFeMnNi, CoCrFeMnNi, and CoCrFeNi High Entropy Systems, Joseph Licavoli, Karin Dahmen, Paul Jablonski, Michael Gao, Peter Liaw, and Jeffrey Hawk.
- [82] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Microstructural Characterization and Phase Evolution of Al_{11.5}CrFeMnTi and Al₁₂CrFeMnTi, Rui Feng, Chanhoo Lee, Peiyong Chen, Michael Gao, Chuan Zhang, Fan Zhang, and Peter Liaw.
- [83] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Serrated Flows in High Entropy Alloys (HEAs), Shuying Chen, Peter Liaw, Xie Xie, Karin Dahmen, Yong Zhang, and Junwei Qiao.
- [84] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Deformation and Structural Modeling of a Quenched Al_{0.1}CrCoFeNi Multi-principal Element Alloy under High Strains, Aayush Sharma, Peter Liaw, and Ganesh Balasubramanian.
- [85] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016 (Invited)
A Model for the Deformation Mechanisms and the Serration Statistics of High Entropy Alloys, Karin Dahmen¹; Robert Carroll, Xie Xie, Shuying Chen, Michael LeBlanc, Jien Wei Yeh, Chi Lee, Che Wei Tsai, Peter Liaw, and Jonathan Uhl.
- [86] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016 (Invited)
Computational-Thermodynamics-Aided Development of Lightweight High Entropy Alloys, Chuan Zhang, Jun Zhu, Fan Zhang, Shuanglin Chen, Chuan Zhang, Rui Feng, Shuying Chen, Haoyan Diao, and Peter Liaw.
- [87] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016
Computational High-Entropy Alloy Design and Phase Equilibria of an Al-Co-Cr-Fe-Ni System, Zhi Tang, Oleg Senkov, Jonathon Poplawsky, Chuan Zhang, Fan Zhang, Carl Lundin, and Peter Liaw.
- [88] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016 (Invited)
Understanding High-Entropy Alloys Using a Cluster-based Structural Model, Qing Wang, Wen Lu, Chuang Dong, and Peter Liaw.
- [89] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016

- A Novel, Single Phase, Refractory CrMoNbV High-entropy Alloy, Rui Feng, Michael Widom, Michael Gao, and Peter Liaw.
- [90] 2016 TMS Meeting, Nashville, TN, USA, February 14-18, 2016 (Invited)
Effect of Zr and Si Addition on Microstructure and Properties of AlFeNiCuCrTi High Entropy Alloys, Dai-hong Xiao¹; P.F. Zhou¹, and Peter Liaw.
- [91] Lunch Lecture, Knoxville, TN, USA, February 26, 2016 (Invited)
Deviation from High-Entropy Configurations in the Al_{1.3}CoCrCuFeNi Alloy, Louis Santodonato, Yang Zhang, Mikhail Feygenson, Chad Parish, Michael Gao, Richard Weber, Joerg Neuefeind, Zhi Tang, and Peter Liaw.
- [92] The Joint Institute for Neutron Sciences (JINS) Invited Lecture, Knoxville, TN, USA, March 21, 2016 (Invited)
Deviation from High-Entropy Configurations in the Al_{1.3}CoCrCuFeNi Alloy, Louis Santodonato, Yang Zhang, Mikhail Feygenson, Chad Parish, Michael Gao, Richard Weber, Joerg Neuefeind, Zhi Tang, and Peter Liaw.
- [93] International Workshop on Advanced Material, Yangzhou, China, March 29, 2016
Deviation from High-Entropy Configurations in the Al_{1.3}CoCrCuFeNi Alloy, Peter Liaw.
- [94] NETL Crosscutting Research & Rare Earth Elements Portfolios Review Meeting, Pittsburgh, PA, USA, April 18-22, 2016
Experimental and Computational Investigation of High Entropy Alloys for Elevated High Temperature Applications, Peter Liaw.
- [95] Neutron Imaging: Application to Materials Science Workshop, Oak Ridge, TN, USA, May 25, 2016
High Entropy Alloys, Peter Liaw.
- [96] QuestTek Inovation LLC, Evanston, IL, July 25, 2016
Deviation from High-Entropy Configurations in the Al_{1.3}CoCrCuFeNi Alloy, Peter Liaw.
- [97] Osaka University, Osaka, Japan, July 29, 2016

Serration Behavior of Bulk Metallic Glasses and High Entropy Alloys, Peter Liaw.

[98] Kyoto University, Kyoto, Japan, August 1, 2016

Serration Behavior of Bulk Metallic Glasses and High Entropy Alloys, Peter Liaw.

[99] Pacific Rim International Conference on Advanced Materials and Processing (PRICM9),
Kyoto, Japan, August 3, 2016

Deviation from High-Entropy Configurations in the Al_{1.3}CoCrCuFeNi Alloy, Louis Santodonato,
Yang Zhang, Mikhail Feygenson, Chad Parish, Michael Gao, Richard Weber, Joerg Neumeier, Zhi
Tang, and Peter Liaw.

[100] Pacific Rim International Conference on Advanced Materials and Processing (PRICM9),
Kyoto, Japan, August 3, 2016

Characterization of Shear-Band Dynamics by Thermography for Bulk Metallic Glasses: Xie Xie,
Junwei Qiao, Yenfei Gao, K. Dahmen, P. Liaw.