

Functional Properties of Bulk and Meta-material High Entropy Alloys

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I would like to dedicate this to Emily, Jack and Nellie. You are my world.

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Abstract

High Entropy Alloys (HEAs) are a class of material which is well-known for their high-temperature mechanical strength and corrosion resistance. In these materials, the entropy of mixing is used to encourage alloying between elements which are typically immiscible, sometimes described as alloying beyond the Hume-Rothery Rules. Specifically, the entropy of mixing is increased by including multiple elements on a single lattice site, increasing the free energy cost associated with phase separation. In the HEA community, this ‘high entropy effect’ is typically associated with alloy containing five or more elements. Achieving alloying between immiscible elements generally means the atomic size and/or electronegativity distribution can be large, resulting in extreme local environments, which contribute to strengthening of the alloy for mechanical applications and can also result in unique functional properties. The focus of my current work is electrodeposited HEA nanowires which are used to prepare a low-density metamaterial similar to an aerogel. The other project includes microstructure and spinodal decomposition of bulk HEA, $\text{Al}_x\text{CoCrFeNi}$. The low-density materials have been shown to have impressive mechanical properties and present opportunities for energy, health, and catalytic technologies. Low density metamaterials combined with the high entropy effect of these nanowires create customizable materials associated with highly tough and corrosion resistance characteristics. The five elements in these nanowires, Co, Cr, Cu, Fe and Ni, were chosen for their magnetic responses as well as high toughness found in similar CrCoNi alloys. Magnetic and thermal properties of these materials were measured. A specific target of this project was to determine the response of these materials to gigahertz-frequency electromagnetic radiation. In a parallel work we

have prepared similar metamaterials out of Cu nanowires and have measured their response to electromagnetic radiation and magnetic dynamics. Future work focuses on strengthening the material by sintering the wires and measuring mechanical and thermal properties in the interconnected solid. The $\text{Al}_x\text{CoCrFeNi}$ samples were fabricated with arc melting and have shown higher magnetic responses with higher paramagnetic content. This has been looked at with SANS for a closer look at the microstructure and to help see possible phase separations from the spinodal decompositions.

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Chapter 1

Introduction

Alloys are materials that consist of multiple metal elements that homogeneously combine for the purpose of increasing toughness or corrosion resistance. Alloys have improved strength because the difference of atomic radii making it more difficult to break or slide atomic bonds. The most common example is CuNi. CuNi a combination of copper (Cu) and nickel (Ni). Copper by itself is not as strong as CuNi because there is an advantage to having long range ordering of Cu and Ni atoms, where long range ordering is the repeating pattern of the system over large distances. This distribution helps the material become stronger as well as withstand changes in it's atomic structure at higher temperatures. The process of combining elements is not as easy as choosing two elements at random. If two elements are chosen that do not combine well, they are known as immiscible. Common metals that are immiscible include CuCo and CuAg composites. Knowing which elements alloy is an important step to help further develop materials. William Hume-Rothery came up with a rule to determine the likelihood of elements successfully alloying. Rothery found that if the radii of the different elements had more than a 15% variance to each other, then the metals would create intermetallic phases, which would prevent fully homogeneous alloys. High entropy alloys are a new genre compared to conventional alloys and seem to violate the Hume-Rothery rules, finding stable phases where elements are normally immiscible.

High entropy alloys (HEA) have been heavily investigated for their structural and mechanical properties since their realization in 2004, which was focused on equiatomic compositions. In these materials, the entropy of mixing term in the Gibbs free energy equation is increased with more constituents, thus encouraging alloying between elements which are immiscible. Though HEAs show superior hardness, corrosion resistance, and high temperature toughness, the functional properties of these materials have not been investigated as thoroughly. Often the components of the commonly investigated HEAs are naturally ferromagnetic. Investigating these alloys for their magnetic, electronic, optical and thermal properties will deepen understanding of these functional materials. In some cases, high entropy oxides have been shown to have magnetic saturations of over 9T [34].

To further elaborate on their functional properties, I have realized a way to make high entropy nanowires through electrodeposition, as well as create meta materials from the nanowires. These meta materials are highly porous, have high surface area to volume ratios and have 0.1% density of bulk. These nanowires have a broad array of applications including aerospace, filtration, biomedical and catalytics.

My dissertation research focuses on $\text{Al}_x\text{CoCrFeNi}$ and $\text{Al}_{1.3}\text{CoCrCuFeNi}$, both bulk samples probed with small angle neutron scattering (SANS) and *in-situ* scanning transmission electron microscopy (STEM). My dissertation also focuses on the functional properties of CoCrCuFeNi nanowires and their subsequent meta materials. In this beginning chapter I will go over all the preliminary information necessary to explain the chapters on the specific HEA materials.

1.1 Intro to High Entropy

1.1.1 High Entropy Explanation and Application

High entropy alloys (HEA) are a classification of alloys consisting of 5 or more elements. Initial investigations of these materials were performed with questions regarding phase

stability, and how the increased entropy of mixing contributed to immiscible metals. In 2004, two independent studies from Yeh and Cantor both showed that the high entropy effect resulted in alloying of stoichiometrically equal compositions. Cantor found that the 3d transition metals Mn, Co, Cr, Fe, Ni alloyed together even with slower cooling rates. These findings spurred an investigation of the HEA field and created a new generation of materials. Changing the type and amount of each element can have an impact on the overall performance of the material. In the example of $\text{Al}_x \text{CoCrFeNi}$ at certain amount of Al content the material will successfully alloy. In this work there is a focus on a $\text{Al}_x \text{CoCrFeNi}$ with varying amounts of a Al and also $\text{Al}_{1.3}\text{CoCrCuFeNi}$. Because there are too many variables to keep in consideration for a reasonable phase diagram, often times the phases are organized by referring to the specific composition and amount like can be seen in Figure 1.1.

High Entropy Alloys are given their name from the Gibbs free energy equation.

$$G = H - T\Delta S_{conf} \quad (1.1)$$

Where G is the Gibbs free energy term, H is the enthalpy, T is temperature and ΔS is entropy. Entropy (ΔS) here is known as the entropy of mixing. The more entropy in the system, the less the Gibbs free energy becomes. A lower Gibbs free energy means higher probability of solid solution phases. Thus, if there are more elements in a material the entropy of mixing increases and promotes stability. This is the where the materials get the title 'high entropy'.

This 'cocktail effect' or 'high entropy effect' is further defined with equations to help categorize the materials after their initial surge in popularity. The configurational entropy of a system is defined as:

$$\Delta S_{conf} = k_B \ln \omega \quad (1.2)$$

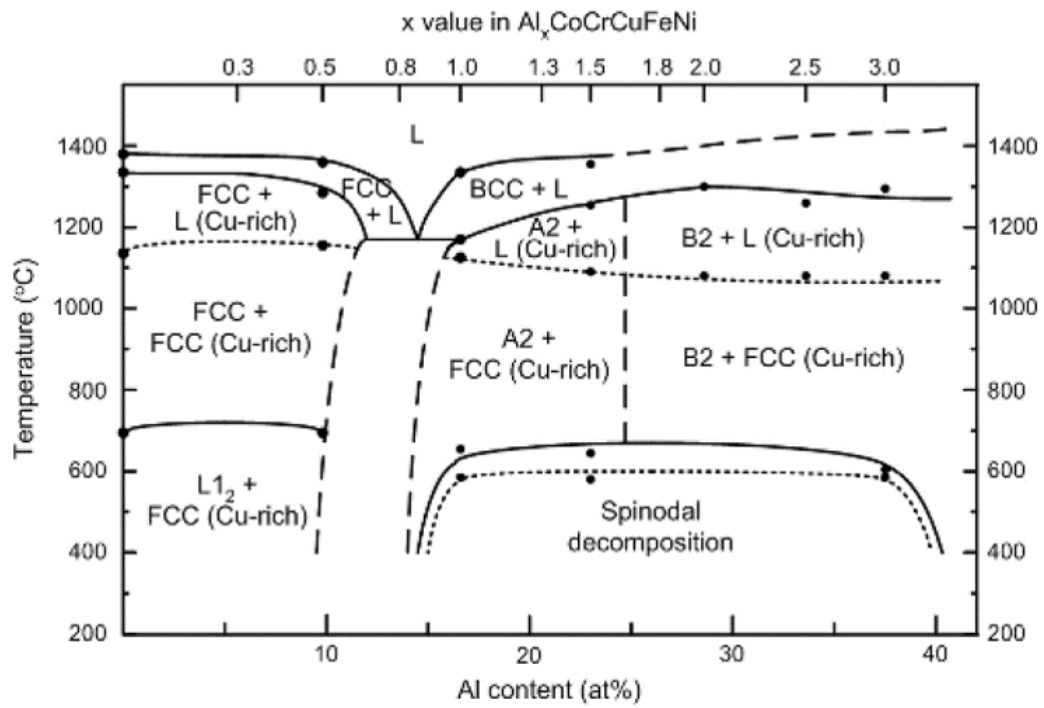


Figure 1.1: A phase diagram for $\text{Al}_x\text{CoCrCuFeNi}$. This work is from Tong, C.J. Metall Mater Trans A 36, 881–893 (2005).

Where k_B is the Boltzman constant and ω is the total configurations for the system. This can be expanded to the equation for the ideal configurational entropy per mole:

$$\Delta S_{conf} = -R \sum_{i=1}^n X_i \ln X_i \quad (1.3)$$

Where R is the gas constant. This equation can be further expanded:

$$\Delta S_{conf} = -k \ln \omega = -R \left(\frac{1}{n} \ln \left(\frac{1}{n} \right) + \frac{1}{n} \ln \left(\frac{1}{n} \right) + \dots \frac{1}{n} \ln \left(\frac{1}{n} \right) \right) = -R \ln \left(\frac{1}{n} \right) = R \ln n \quad (1.4)$$

When n is 5 or more the equation reduces to:

$$\Delta S_{conf} \geq 1.5R \quad (1.5)$$

This is the most succinct definition for what makes a high entropy alloy. Sometimes HEAs are defined simply as having 5 or more elements notice the Figure 1.2. This can often be an efficient method to classify materials, but is not always representative of the category of materials. In the field there are also low entropy materials ($\geq 0.69 R$) and medium entropy materials ($\geq 1.0 R$). An example of a low entropy alloy would be CuNi and is well known but it is never referred to as a low entropy alloy outside of contexts like this dissertation.

Though HEAs have an established nomenclature it is important to recognize that not all HEAs are alloys. The original 2004 study was aimed at finding compositions that alloyed, but the field has evolved to include metals that are also phase separated. For mechanical strength materials, these phase separated compositions have specific intermetallics which would improve and bolster the material. Intermetallics are a type of alloy and are defined as compounds between multiple metals with strong bonding and long range ordering. Often intermetallics have different chemical structures than the compositions that they are made of but are not considered phase separated themselves. Materials with intermetallics are often

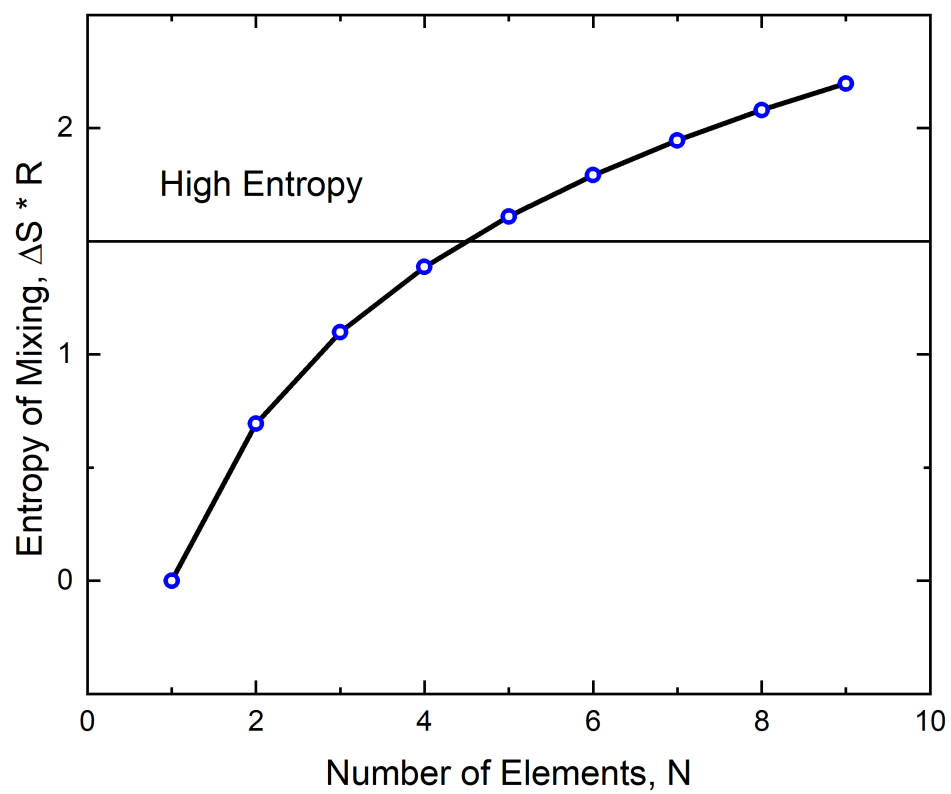


Figure 1.2: Simple curve showing the components of an HEA and what constitutes HEA and what does not.

very hard and brittle but resistant to changes at high temperatures. Other names that HEA materials are referenced to include: Compositionally complex materials and multi component alloys. Regardless of the name, there are usually many elements in the stoichiometry. Even though it may not always be a single phase alloy, the materials as a whole are referred to as HEA.

HEAs have a distribution of atomic radii and bond lengths can make the crystal structure distorted as can be seen in Figure 1.3. Using a ball and spring analogy of the atoms in HEA, larger, heavier atoms dampen phonon propagation. This makes HEAs a unique type of material as normally metals make terrific thermal conductors. Having good electronic conduction with poor thermal conduction is another characteristic of HEAs.

1.1.2 Current High Entropy Scientific Direction

Significant work has been performed on HEA's structural properties and continues currently. Many refractory and rare earth combinations are consistently looked at with different fabrication techniques including additive manufacturing [7, 32, 4, 30]. Since HEA's are made with lower cost material there is a strong emphasis on the recyclability of HEA's with different fabrication techniques. In the infancy of the material there was a broad exploration of the compositions sometimes involving up to fifteen elements in a single material. Different research groups were trying to get a more fundamental understanding of the possibilities that more constituents could provide. Sometimes an unlikely combination of elements would successfully alloy like the AlCoCrFeNi system. With Al having a significantly smaller radius it seemed unlikely that this combination would be permitted under the Hume-Rothery rule, yet it successfully alloyed.

As more work went into the disordered nature of these materials the conversation expanded to other types of materials such as ceramics. Where the high entropy effect can be applied to lattice sites while still maintaining the spinel (AB_2O_4) or perovskite (ABO_3) formula. These materials have already shown to be functional materials[34, 21].

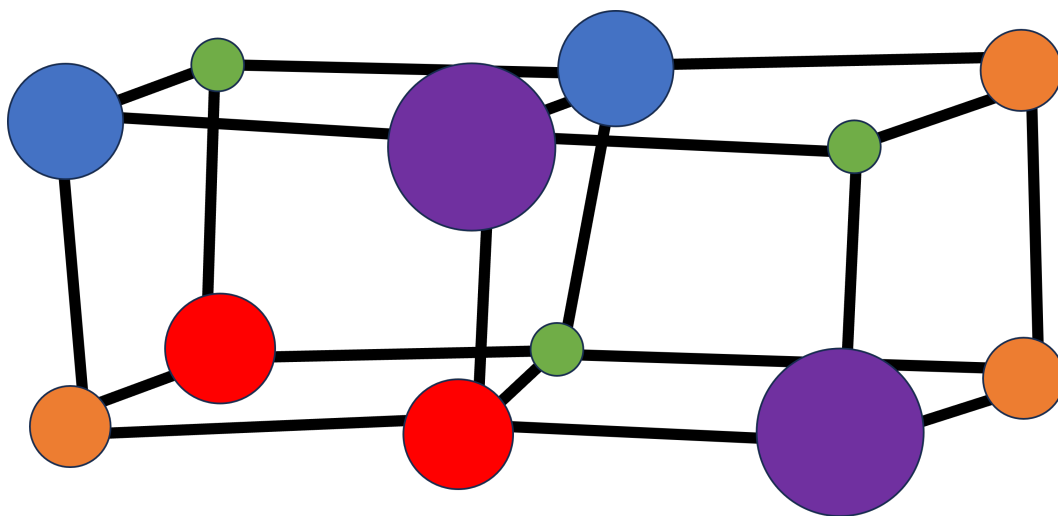


Figure 1.3: A diagram of HEA in similitude of varying lengths and atomic radii.

Understanding the role entropy plays in contributing to these oxides, nitrides and borates has proven to have the same tunability aspect as HEAs with the added benefit of already high temperature resistant material. The fundamental development of the magnetic properties of these materials is not fully understood. Getting a better understanding of the magnetic evolution of these materials will better equip future research regarding other high entropy materials.

1.2 Magnetic Materials

Magnetism in its simplest form is a single spin from an atom. This spin, known as a magnetic moment can interact with other moments. Contributions from individual atoms are rather weak and undetectable, but when many moments are aligned magnetic properties can be observed. There are four categories of magnetic materials: ferromagnetic, antiferromagnetic, paramagnetic, and diamagnetic.

Ferromagnetic materials have all the moments parallel with long range ordering. i.e. the common household magnet. Fe, Co and Ni are the three elements that are naturally occurring ferromagnetic. These three elements are used often in the compositions of HEAs. Hence, there is a likely correlation to magnetism that is worth investigating in these materials inherently from their ferromagnetic elements.

A second type of magnetic ordering arises if the moments are ordered but anti-parallel, called antiferromagnetic. The difference between ferromagnetic and antiferromagnetic ordering can be seen in Figure 1.4. Antiferromagnets have alternating moments of up and down. This alternating pattern means that the sum of the moments comes to zero, as opposed to ferromagnetic which would have a non zero value. Third, paramagnetism means the moments are disordered and not coupled to each other. In paramagnetic systems externally applied fields have a high impact on the the direction of moments. The fourth category is diamagnetism, meaning that in the presence of an external magnetic field, the

moments will align anti-parallel to the field. Having a combination of different magnetic ordering can happen and usually results in a magnetically frustrated system.

There is a way to disorder magnetic systems. Most notably, thermal energy eventually dominates every magnetic system. The Curie temperature (T_C) is the temperature in which the thermal energy is stronger than the energy between moments. Beyond T_C the magnetic ordering behaves like paramagnetism. This magnetic transition is a common measurement of magnetism for any ferromagnetic system. There is a similar magnetic transition for antiferromagnetic systems; which occurs at the Neel temperature (T_N). T_N and T_C are essentially the same thing but are applicable to antiferromagnetic and ferromagnetic systems, respectively.

Magnetic Saturation (M_S) is when an external magnetic field aligns all of the moments in a sample. In low fields, ferromagnetic materials have moment coupling which is strong enough that there is a 'domino effect' that encourages the other moments to align with little energy. In a paramagnetic material the moments are all uncoupled so the applied field is the only motivation for changing the direction of the moments.

Generally, the resultant magnetic properties of a material are not as straight forward as what common intuition may suggest. The presence of ferromagnetic elements are not an indicator that the material itself will be ferromagnetic. There are quantifiable energies and interactions that are important for explaining why and how magnetic properties emerge in these materials and the ferromagnetic elements help with a starting point for those explanations.

1.2.1 Magnetic Energies and Magnetic Exchange

There are multiple competing magnetic interactions in a material. The relevant interactions include the exchange, dipolar, and the anisotropy energies. The exchange interaction is the most prominent interaction and is what determines if a material is antiferromagnetic or ferromagnetic. Direct exchange interactions are only involved in neighboring atoms and are

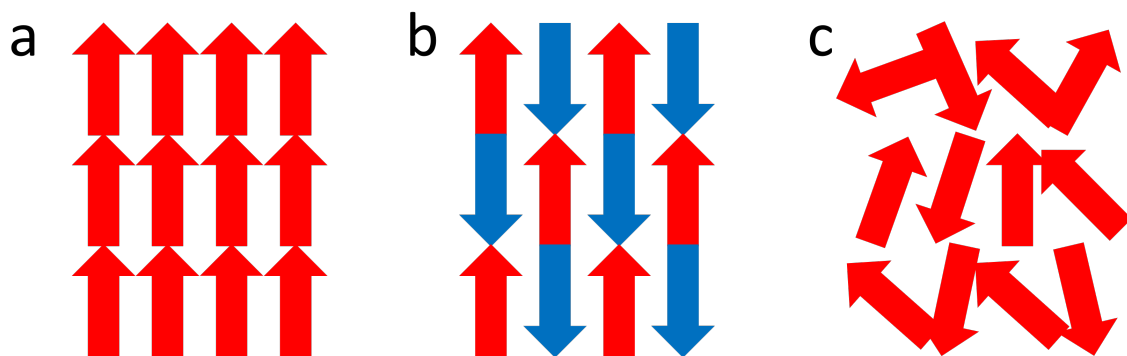


Figure 1.4: Illustrations of (a) ferromagnetic ordering, (b) antiferromagnetic ordering and (c) paramagnetic ordering

dominant over a short distance (several Å). This is what is usually associated to strongly coupled magnetic interactions but is not always the case as demonstrated by Kirby et al. Kirby and Miller explain that itinerant valence electrons still have a coupling that gives rise to magnetism even though interexchange coupling plays a minor role. This quantifiable number is called the exchange interaction constant, known as J . The exchange constant is consistent between specific atoms i.e. 0.0075 eV for two parallel iron atoms. Exchange constants are helpful for determining the coupling strength between magnetic atoms. The angle of the moments contributes greatly to the exchange constant. Parallel spins have the highest exchange constant and the value lessens as the angle increases.

Indirect exchange interactions are not possible in these systems. The metal ionic bonding allows electrons to pass freely between atoms. When electrons are constrained to certain lattice sites then the valence electrons have a stronger influence on the magnetic characteristics. These kind of interactions give rise to super exchange and double exchange interactions which are not part of this work.

1.2.2 Other Magnetic Energies

Crystalline anisotropy is the influence of the geometry to the preferred magnetic orientation. This means that based on the shape of the material (rod, sphere, etc) the moments will behave in a particular way. There are preferred orientations (easy axis) and resistant orientations (hard axis). In the example of a nanowire the easy axis is along the wire as can be seen in Figure 1.5. When moments in the hard axis orientations are in competition with each other, the zeeman energy of the system increases and magnetic systems prefer to be at the lowest energy possible.

Dipole interaction is the energy of two dipoles (polarized molecules) on a much larger scale than the previous examples. The dipole interaction is most prominent at low temperatures (below 20 K). The calculations of these show that the interaction weakens with distance and decays by a power law.

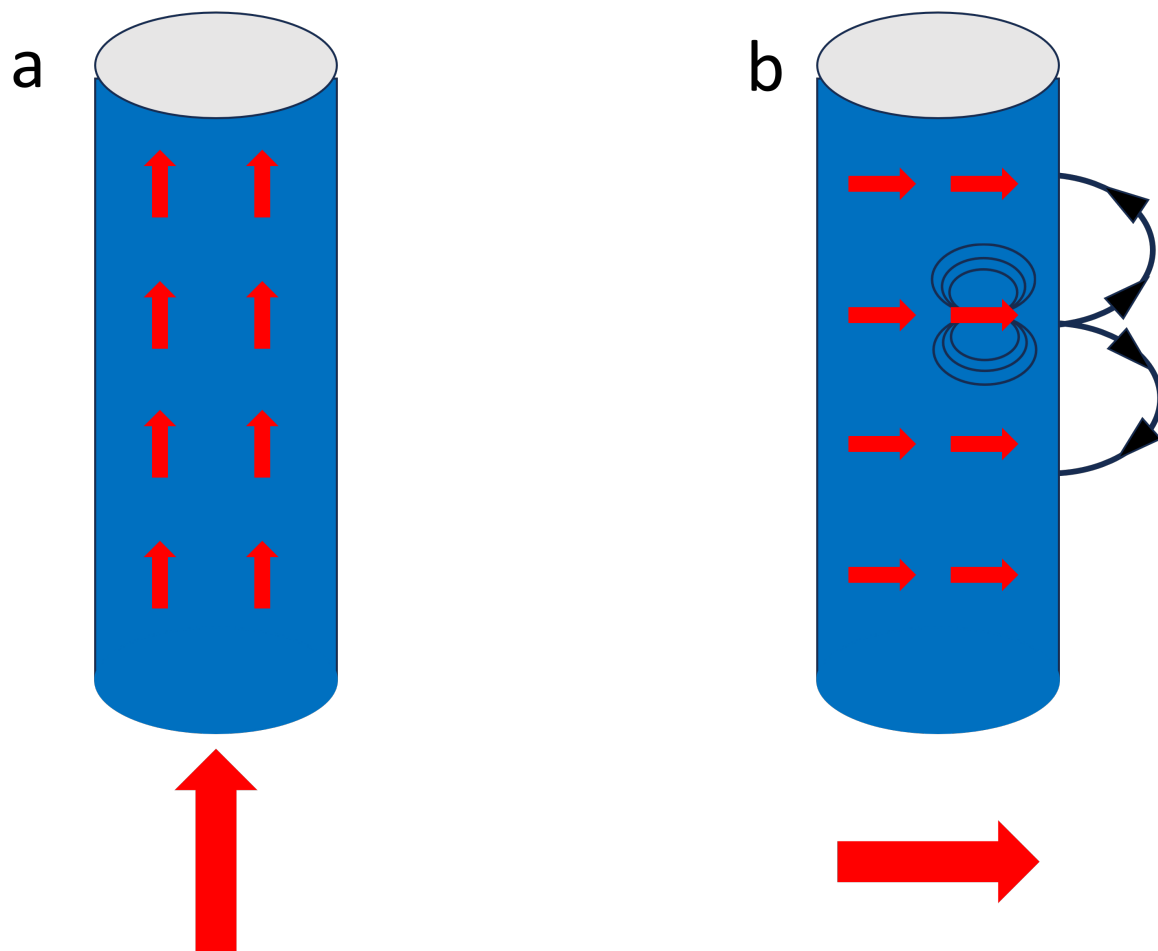


Figure 1.5: Illustrations of shape anisotropy (a) easy axis and (b) hard axis

Thermal energies are calculated with $E = k_B T$. This is the direct calculation for figuring out the Curie temperature, or the temperature in which the magnetic moment becomes dominated by thermal phonons.

In a similar way there is an energy called the Zeeman energy which is correlated to the applied external magnetic field. Magnetism can have an effect on light and specifically when looking at spectroscopy, magnetism can influence the spectral lines. Thermal and Zeeman energies are often starting points for determining basic magnetic information on materials. Curie Temperature and saturation moment are crucial, initial measurements.

1.2.3 Magnetic Domains

Magnetic domains are collections of moments in a material that behave identically and are independent of one another. As can be seen in Figure 1.6 the domains all have the same type of ordering but are collections of different orientations. The white space in between is known as the domain wall. Domain walls are dynamic to external magnetic fields and changing microstructure. Microstructures can align with domains in size, though are not restricted to being congruent with the microstructure. Measurements such as SANS and STEM can help demonstrate the difference between the structure and ordering of the domain walls compared to the microstructure. The domain wall can have an influence on the materials ability to align with the field. Domain wall pinning occurs when domains cannot propagate due to strongly coupled magnetic sites.

1.2.4 State of magnetic HEA work

Magnetic HEA work is underdeveloped compared to it's structural investigations. There is a comprehensive look at the Cantor alloys and some of the underlying magnetic mechanisms that evolve with changing composition.

Tang et al. did combinatorial sputtering of four elements (Cr, Mn, Fe, Ni) getting a thin film of graded elements, then tested the magnetism. This comprehensive look at composition

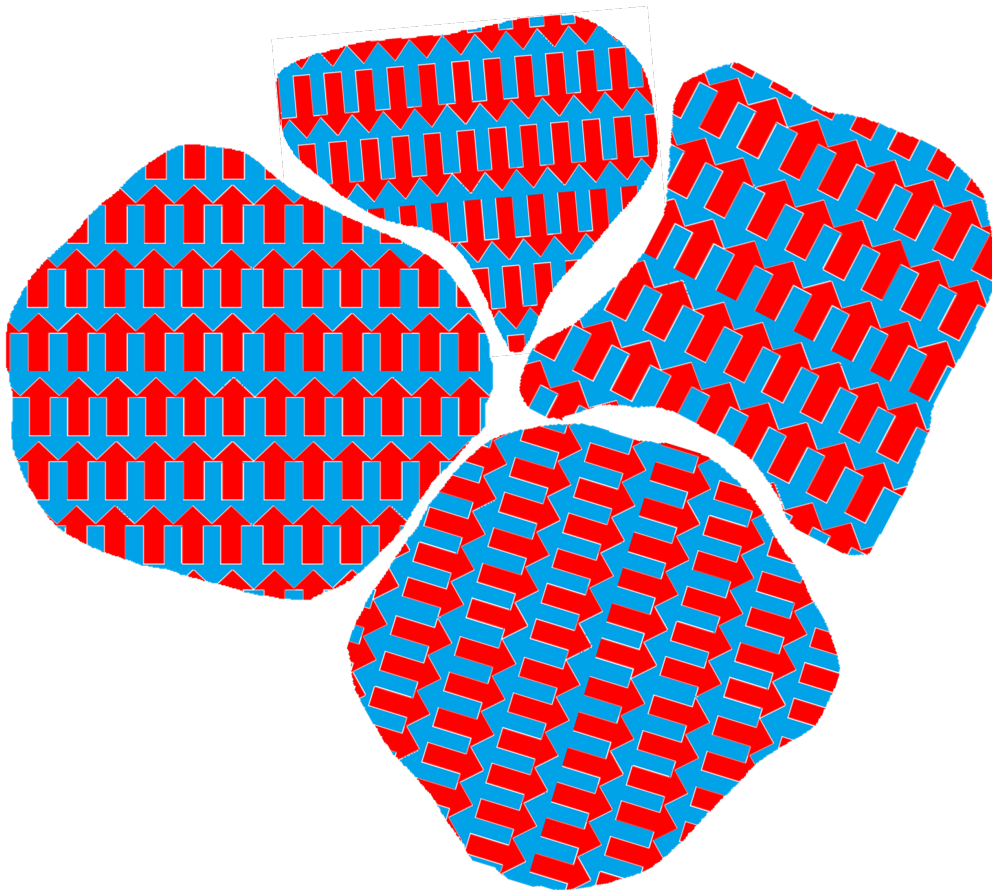


Figure 1.6: Illustrations of domain orientations with the white part as the domain wall

to magnetic properties showed that there can be a large variation in T_C and M_S with little change to composition. [47].

Yeh et al. performed magnetic measurements on $\text{Al}_x\text{CoCrFeNi}$ in 2011. These measurements are low temperature. I investigated the high temperature regime including the spinodal decomposition of the system.

There are high entropy materials that even show super conducting properties with only a fraction of the elements that are normally associated with the actual super conducting features. There are a number of works that each have unique attributes to super conductivity that could show promise [46].

There are other HEA materials including oxides and nitrides that have promising functional applications [34]. While there is significant work in these high entropy materials, the underlying mechanics of magnetism is significantly different from traditional HEAs. These magnetic interactions arise due to how electrons are bound to move within an ionic crystal and polarized orbitals. In high entropy ceramics there are magnetic features caused by super and double exchange interactions which are impossible in metal systems since electrons are itinerant in ionic bonding. Magnetic interactions in metals are not a good comparison for magnetism in ceramics. Musico et al found a spinel of $(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Zn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2})\text{Co}_2\text{O}_4$ that was ferromagnetic and did not saturate in fields up to 9 tesla. This research field is rapidly growing and understanding magnetism in similar systems.

1.3 Neutron Scattering

Neutron scattering is a helpful tool that interacts with atomic nuclei and magnetic moments. Neutrons are a highly penetrating measurement which gives a proper global average for bulk samples. They are low energy thus the radiation is not damaging to more sensitive or delicate materials. The scattering calculations are derived from Bragg's Law of diffraction. Bragg's law applies to neutrons the same way:

$$\lambda = 2d\sin(\theta) \quad (1.6)$$

where d is the inter atomic spacing, λ is the wavelength of the neutron beam and θ is the angle of scattering from the incident beam. The inverse of d is known as q -space and is used often in scattering equations; they are related as $\frac{1}{d} = q$. Using some trigonometry symmetry the equation becomes:

$$q\lambda = 4\pi\sin\left(\frac{\theta}{2}\right) \quad (1.7)$$

Where q is the q -space length on the detector. This equation is most commonly associated with neutron diffraction. Probing materials with neutrons is one of the most effective ways to investigate magnetic materials due to the lack of charge while still having a spin. Neutrons can interact with the magnetic and nuclear structures, which is a powerful aspect to investigating magnetic materials with neutrons. Neutron scattering is the same concept as diffraction, where the spacing between atoms can interfere with incoming radiation (in this case it is neutrons but it could be any form of electromagnetic radiation). Neutrons can "see" the atoms differently than x-rays do. Neutrons interact with atomic nuclei rather than interacting with electrons, like x-rays do. The wavelength of the neutrons helps determine the angle of scattering.

Neutrons can scatter from magnetic or non magnetic atoms. The scattering intensity is related to the atomic size and shape (b_n) and the magnetic scattering lengths (b_m). Inelastic and elastic scattering are different ways the neutrons will interact with the sample. Inelastic scattering is when the neutron energy decreases during scattering. Inelastic scattering generally is associated to different measurements and will not be further elaborated in this work. Elastic scattering is the relationship between the neutron plane wave (wave vector k_i) and the scattered wave from the interacting particle (wave vector k_f). Elastic scattering is only possible when $|k_i| = |k_f|$. The observed scatterer distance (r) is much larger than

the sample radius (r'). When $r \gg r'$, then $r - r' = r$. The detected neutron has an associated angular cross section ($d\Omega$). This cross section is the information regarding atomic position and magnetism. This is difficult to visualize and Figure 1.8 has been provided for clarification.

Neutron scattering is dependant on two terms for calculating the overall intensity of the neutrons, the form factor and the structure factor. Form factor is the particle shape and structure factor is the inter-particle interactions. The intensity of the detected neutrons is a ratio of these different wave vectors $Intensity \approx \frac{|k_f|}{|k_i|} \frac{\Omega}{4\pi}$. The elastic scattering intensity is calculated with $\frac{1}{N} \sum_i^N F_i(q) \exp(iqr_i)$ and $\frac{1}{N} \sum_j^N F_j(q) \exp(-iqr_j)$ where q is the reciprocal space vector, N is the total number of particles, $f_i(q)$ and $f_j(q)$ are form factors of i and j particles respectively. The particles that scatter are the same, so the equation reduces to $F^2(q)S(q)$ where $S(q) = \frac{1}{N} \sum_i^N \sum_j^N \exp(iq[r_i - r_j])$ is the structure factor. The $F(q)$ is the Fourier transform of the scattering, or in other words it is the reciprocal space inversion of the real space scattering potential.

Neutrons are created with either fission or spallation in a controlled environment. Fission occurs when a uranium 235 atom decays, it releases a neutron. These neutrons are gathered and focused into a beam. Spallation is when high energy protons are accelerated into a heavy metal like tungsten. In either case the neutrons have a range of wavelengths and energies. Using a velocity selector the wavelengths are filtered, allowing a specific wavelength through. Scattering is dependant on wavelength, this makes an accurate wavelength crucial for neutron measurements.

1.3.1 Small Angle Neutron Scattering

Neutron scattering provides a structural technique that probes a wide array of length scales. Small angle neutron scattering (SANS) is a method that is very expensive to maintain and run, which is why there are only a handful of them in the United States. The High

Flux Isotope Reactor on the General Purpose beamline (GP-SANS) at Oak Ridge National Laboratory is where this work was performed.

Diffraction scatters at all angles and SANS systems are designed to capture the small angles that normal diffraction systems cannot distinguish. As mentioned previously, scattering angle correlates to real space structure. The scattering angle is directly correlated to the q-space in $q = \frac{4\pi}{\lambda} \sin(\frac{\theta}{2})$. In order to investigate large scale structures (≈ 100 nm) it is required to measure much smaller q values, which is an extremely small scattering angle (θ). When the angle becomes very small there are approximations in the equation that can reduce it further:

$$q = 2\pi/d \tag{1.8}$$

This new equation is the most commonly used on the length scales of SANS measurements for larger structures. Determining large structures is beneficial because magnetic domains can be larger than grain size. SANS instrumentation consists of a fifteen meter long collimator. The collimator converges the neutron beam into a smaller concentric beam. Once the sample is illuminated by the beam, neutrons scatter off the sample into a twenty meter long vacuuated tube with a movable detector, allowing the detector to see the large range of angles the neutrons will scatter off of. The farther back the detector the smaller the detectable angle, which corresponds to larger structures of the sample.

1.3.2 Magnetic Scattering from Neutrons

The neutron detector is comprised of arrays of small neutron detectors, similar to pixels on a screen. These detectors provide q vectors with q_x q_y components. When all arranged together, the final data output is a 2D scattering pattern consisting of intensities in both the x and y direction. Generally materials are anisotropic and the scattering along x and y are very similar and neutron diffraction patterns come out as rings, as can be seen in Figure

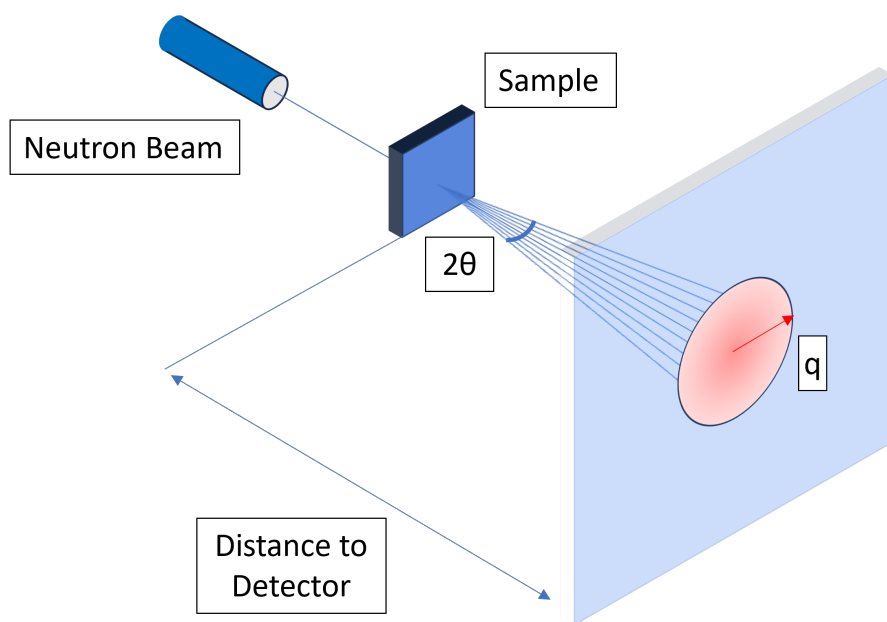


Figure 1.7: A diagram of a neutron beam

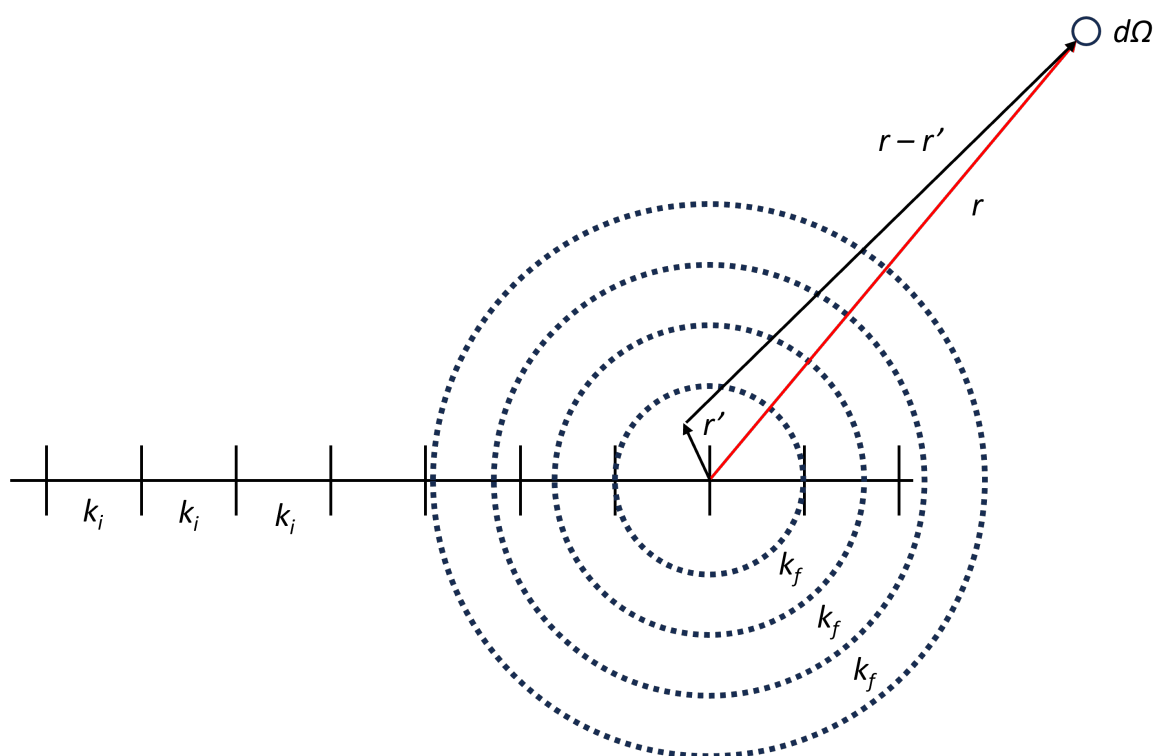


Figure 1.8: diagram of neutron scattering

1.9. The center of the pattern has a lower intensity for two reasons: a beam stop is used to protect the detector from the high intensity of the direct beam and the angle of scattering takes the scattered neutrons away from center. The red line in the 2D data represents the 1D curve in Figure 1.9.

Magnetic scattering is not easily detectable. It must be extracted from the scattering data of the original sample when under an external magnetic field. When a magnetic field is applied to a sample during neutron scattering, the neutrons can interact with the magnetized material and scatter orthogonal to the applied magnetic field. The scattering vector of the neutron must be orthogonal to either the moment of the sample or the spin of the neutron but they cannot be parallel. The previously mentioned equation $\frac{1}{N} \sum_i^N F_i(q) \exp(iqr_i)$ has an additional term of $q \times r_i$ when working with the spin and orbital angular momentum of magnetic atoms. This cross product makes the neutrons scatter orthogonal to the orientation of the spin (i.e. the direction of the magnetic field) Meaning, if the applied magnetic field is horizontal, orthogonal to the beam, then the vertical direction has the magnetic scattering. Do not forget that the vertical and horizontal directions still have nuclear scattering as well. Refer to Figure 1.9 for direct reference to this but imagine that the scattering would not perfectly circular. The vertical and the horizontal direction would be different in a magnetic scattering.

Once the nuclear scattering is achieved it is subtracted from the vertical scattering (which is both magnetic and nuclear) and the resultant data is the magnetic scattering only. This scattering allows for specific information regarding the domain size, shape and periodicity of the magnetic component of the material.

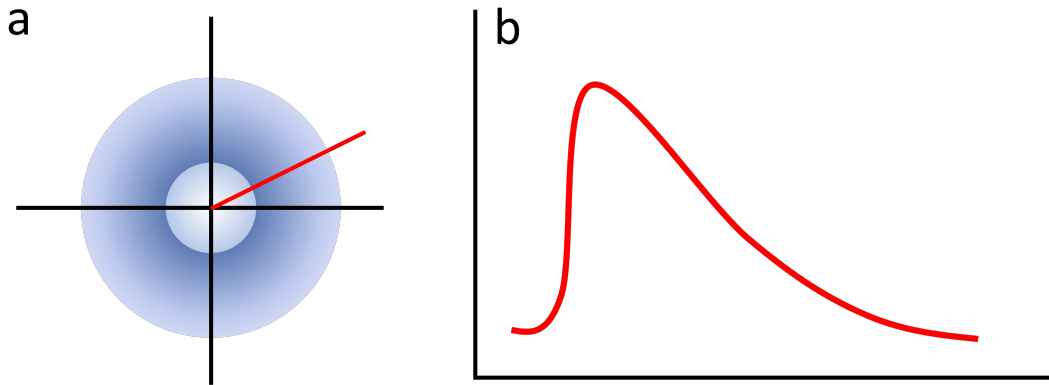


Figure 1.9: Example of 2D (a) and extracted 1D (b) data that would come from the same data set. Where the red line in the 2D corresponds to the 1D curve.

1.4 Characterization

1.4.1 Scanning electron microscopy and electron dispersive x-ray spectroscopy

Scanning electron microscopy (SEM) is a powerful tool that allows for real space images of samples on the length scale of microns to tens of nanometers. Electrons are created by applying a voltage (20 kV) to a filament in a vaccuated chamber. Vaccumed systems are essential for SEM measurements as electrons will interact with the atoms in the air blocking any electrons from the sample. The created electrons are focused into a beam with a charged anode. The beam is converged using a special lens for electromagnetic radiation and then scan coils help make the beam adjustable while being used. When the electrons interact with the sample there are detectors inside the chamber with the beam that can detect them. Electrons probe the material and interact with the atoms of the sample and those atoms will eject different electrons, these electrons are known as secondary electrons. Sometimes the electrons will interact with the sample and the same electrons return, these electrons are known as back scattered electrons. These two different types of electrons are used to create images of the sample in real space. A schematic of a standard SEM is shown in Figure 1.10. These images show the individual grains including the size, shape and any preferred orientations. The interacting volume of the sample is only a few microns so it is crucial to understand that surface effects have a strong influence on the resultant data from an SEM.

When the electrons interact with the sample, the electrons excite the atoms in the sample. The high energy beam knocks the electrons of the sample into higher orbitals. When the electrons drop down from the higher orbital into the vacated energy levels it ejects an x-ray. When the x-rays are ejected from the atom it has a specific energy. The energy of the x-ray will correspond to a specific atomic element. This method is known as energy dispersive x-ray spectroscopy (EDX). Seeing microstructure in combination with the EDX elemental

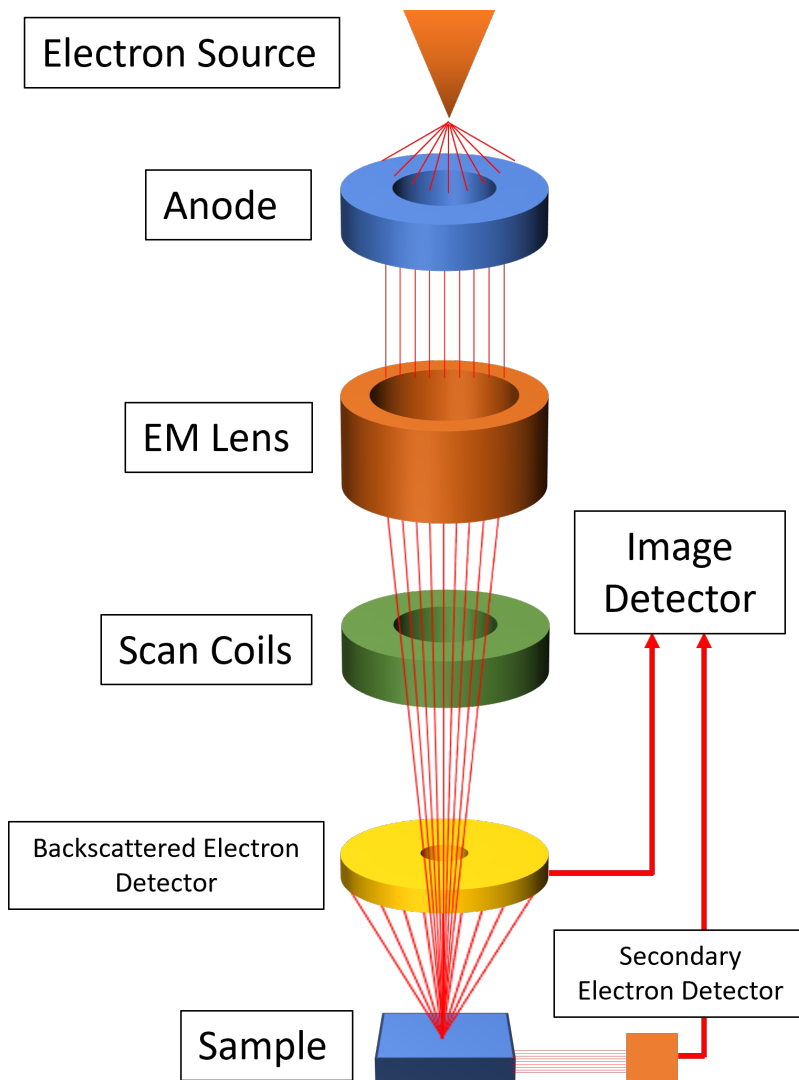


Figure 1.10: Schematic of a scanning electron microscope

maps can help clarify how the distribution of the elements align with the grains and crystal structure.

1.4.2 Scanning Transmission Electron Microscopy

Scanning transmission electron microscopy (STEM) is also a powerful tool that is similar to an SEM but instead of electrons bouncing back, they pass through the material. For this to happen the sample must be thin (100 nm) and a focused ion beam is used to cut the specimen to the appropriate thickness. This setup along with a much higher voltage (300 kV) allows for a significantly higher resolution than SEM and in some cases can even show individual atoms. At the Center for Nanophase Materials Science at Oak Ridge National Laboratory I perform *in – situ* STEM imaging with ramping temperature. This is a powerful tool to see evolution of micrograins with changing temperature. Due to the high energy nature of the $\text{Al}_x\text{CoCrFeNi}$ systems, this *in – situ* measurement was able to capture the phase separation and evolution.

Similar to SEM there is an EDX detector in a STEM that can show the elemental composition of the material. The transmissive nature of STEM is ideal for electron diffraction. Advantages of electron diffraction primarily focus around the extremely small wavelength of electron beams ($2 \text{ } \mu\text{m}$). The small wavelength means high interaction with atoms and also the ability to probe small scale samples.

1.4.3 Magnetometry

Magnetometry can provide valuable information such as T_C and M_S . There are several ways to quantify the magnetism of a material. A vibrating sample magnetometer (VSM) measures the moment of a material with changing external field and temperature. A magnetic sample will oscillate in a series of coils. These coils will induce a current from Lenz’s Law and the resultant current will correspond to a specific moment value. Sweeping the magnetic field and investigating the materials response is commonly referred to as MH measurements.

For ferromagnetic materials this measurement will be hysteretic and the hysteresis loop will provide data whether it is a hard or soft magnet and the magnetic moment saturation.

The ubiquitous measurement from magnetometry is the hysteresis loop. The hysteresis loop is created by first saturating the material and changing the magnetic field incrementally until the material is again saturated in the opposite direction. The major loop of a ferromagnetic hysteresis is shown in Figure 1.11. When the moment no longer increases with magnetic field the material is considered saturated. As the field starts to decrease, there is a slow transition of moments that align once the field reverses. Having a slow trend to the individual moment reversals considers these materials soft magnets. Whereas, if all the moments of the material abruptly align with the field as it begins to reverse direction the material is considered a hard magnet.

The other typical values extracted from hysteresis loops include, coercivity (H_C), bias (H_B), remnance (M_R) and the saturation field (H_S). H_C is the field when the moment is zero and larger values are generally associated to soft magnets. H_B is the shift from center of the major loop at $H=0$. Hysteresis loops that are symmetrical about $H=0$ have a bias of zero and any nonzero value means the system is magnetically frustrated.

A powerful magnetometry measurement is known as the first order reversal curves (FORC). The FORC technique is based on the hysteretic nature of the minor loops. The minor loop range is steadily increased and reversed until it matches the range of the major loop. This build up of minor loops can show smaller reversal behavior that major loops would miss. Each of the minor loops measures a H_C and H_B that is then plotted as a function of the minor loop. The FORC distribution is calculated by taking a second-order derivative of the family of FORCs: $\rho = -\frac{1}{2} \frac{d^2 M}{dH dH_R}$. Recognizing that measurements with increasing magnetic field, e.g. the H axis, are probing magnetic up-switching events from a negative orientation to a positive, while H_R probes down-switching events, the FORC distribution can be re-defined in terms of a coercivity and bias field: $H_C = (H - H_R)/2$ and $H_B = (H + H_R)/2$. Data will be presented in a (H_C, H_B) coordinate space due to the

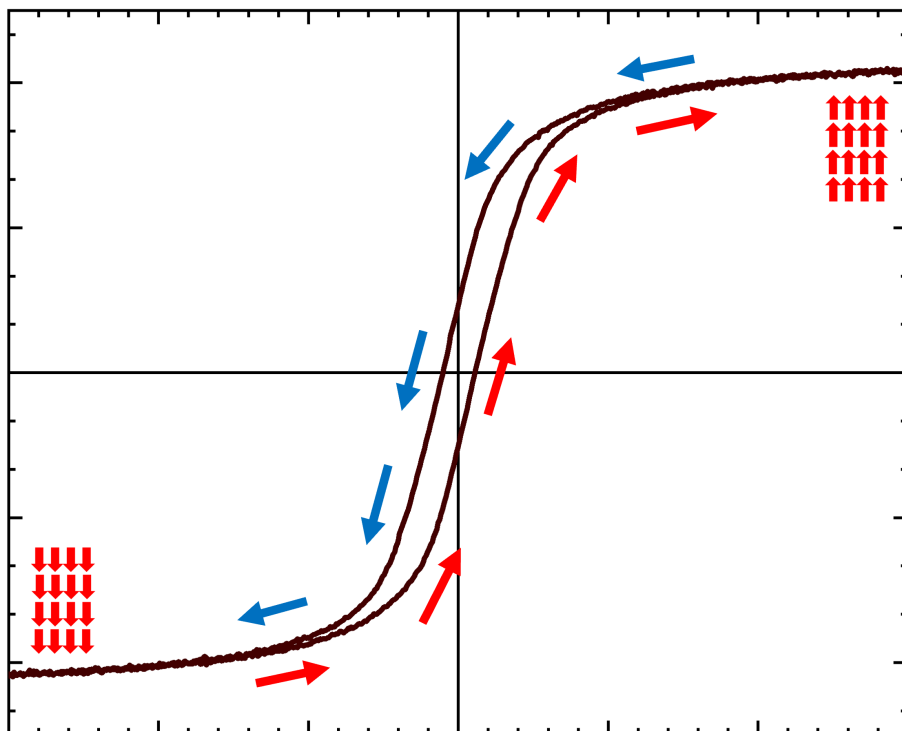


Figure 1.11: Diagram of common hysteresis loop where the x-axis is magnetic field and y-axis is moment. Arrows indicate the formation of the hysteresis loop creation.

improved symmetries in this representation. FORC is a method that can determine multiple magnetic phases in a single material (Assuming they behave differently, i.e. hard and soft magnets). It can use this information to determine magnetic phase fractions. Be careful not to assume things about the phase fraction as it only helps provide insight into the magnetic materials. Non-magnetic materials do not contribute to this.

1.5 Synthesis

1.5.1 Arc Melting

Arc melting is a way to melt metals together. In a vacuuated or inert chamber, the parent ingots are placed in a copper hearth and a large current (10 kA) is applied. This large voltage increases the temperature of the metals very rapidly, causing them to melt. The copper hearth allows for a rapid cool down and helps solidify the sample in a more homogeneous state. The more homogeneous state from arc melting is desirable in order to have a high distribution of magnetic elements. Once the material phase separates, then the magnetic properties will change, irreversibly.

1.5.2 Electrodeposition

Electrodeposition is a method of creating thin films or nanostructures using an electrolyte solution with an applied voltage. Electrodeposition's versatility to deposit individual or multiple ions also make this an attractive high entropy material fabrication method. This method has low costs, easy scalability and ambient atmospheres. An electrolyte solution consists of an ionic salt and an acid. The pH value of this solution is important to track as it can inhibit deposition or strip already deposited ions. A common electrodeposition setup is shown in Figure 1.12 (a). By applying a voltage to the electrolyte solution, the ions will travel to the electrode. The ion exchanges an electron and deposits the atoms on the

working electrode. The reference electrode is an Ag^+/AgCl . This method is primarily used for coatings and platings (i.e. chrome platings on vehicles).

Electrodeposition can also create nanostructures, including nanowires. Replacing the anode with a membrane that still has a working electrode on the backfilled side allows for the ions to fill molds as can be seen in Figure 1.12 (b). The membrane can be removed and the nanowires harvested.

1.5.3 Freeze Casting

Freeze casting is a method for creating a 3D structure from nanowires. In the same way a bird's nest is built from individual sticks, freeze casting is used to turn nanowires into a free standing structure. When freeze casting, the wires must be in water. The water/wire mixture can be molded into any shape that can hold liquid. Once a mold is decided the solution is agitated via ultra sonic sonication to disperse the nanowires. This helps promote disorder to the nanowires, distributing them into a sufficiently disordered state. Then liquid nitrogen is used to flash freeze the water/wire mixture in the dispersed state. The frozen samples are placed in a freeze drier and the ice is sublimated away leaving the free standing nanowire meta material.

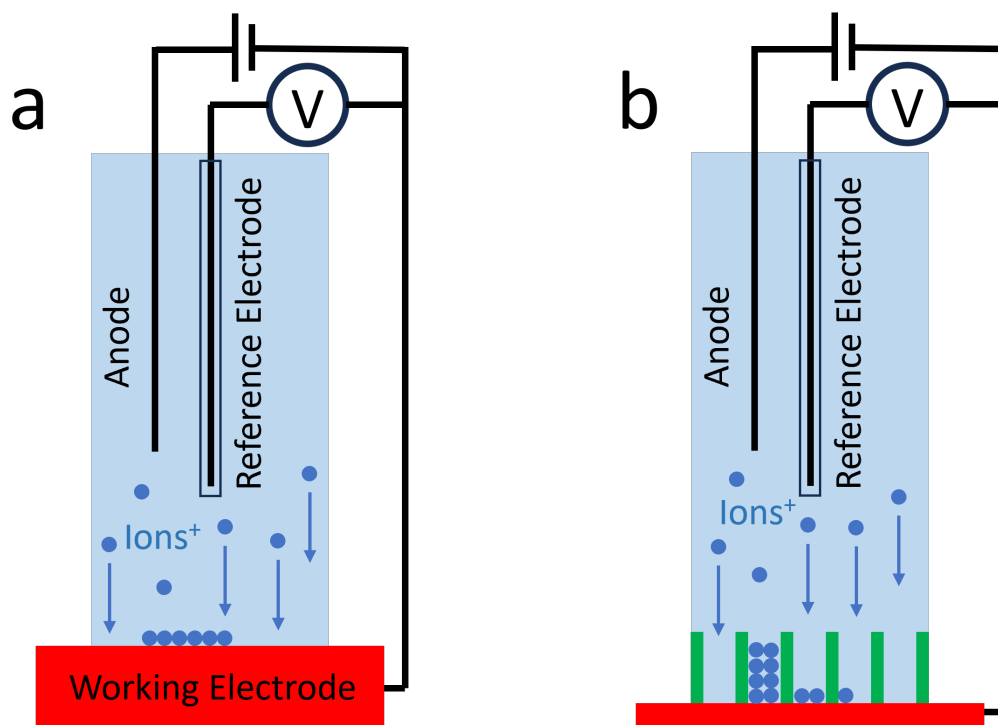


Figure 1.12: Diagram of electrodeposition cell with the blue representing the electrolyte solution and with a anodized alumina membrane in place for the working electrode.

Chapter 2

Al_{1.3}CoCrCuFeNi Spinodal Decomposition Evolution

This chapter investigates the HEA Al_{1.3}CoCrCuFeNi, which has been previously shown to be single-phase at high temperatures, but undergoes phase separation at lower temperatures, transforming the structural and the functional properties. This phase separation is investigated at high temperatures with in-situ small angle neutron scattering (SANS) and scanning transmission electron microscopy (EDX). These techniques show that increasing the temperature up to 800°C, the microstructure of the HEA adiabatically disorders and abruptly homogenizes near 700°C, which is consistent with spinodal decomposition. Overall, the microstructural evolution proceeds mainly by the atomistic redistribution of the constituent elements within simple crystal lattices, producing coherent phase mixtures.

2.1 Introduction

The Al_xCoCrCuFeNi family of HEAs was among the first to be studied, and continues to provide challenges and opportunities for researchers seeking to better understand phase stability, phase separation, and microstructure development in advanced alloys [58, 49, 59, 41, 12, 31, 57, 38]. HEAs were initially recognized for their tendency to form

single-phase solid solutions (e.g., alloys) with excellent mechanical properties such as high yield strength and hardness, which can be systematically varied by changing the aluminum content (x-parameter)[58, 49]. Subsequent studies, particularly by Yeh et al. and Tong et al., have revealed more details about this system, including phase separation between the Al-Ni and Cr-Fe for compositions with percentages $\text{Al} \geq 1$. Commensurate with the phase separation is an enhancement of the hardness and ductility [54, 44, 48]. The interface between these phases has been proposed to be coherent, a feature which strongly contributes to the improved structural performance in modern superalloys [60, 40]. In both the $x = 1$ and $x = 1.3$ compositions, phase separation of Al-Ni and Cr-Fe is reported at room temperature, while at high-temperatures the material is a single homogenized phase. The dissolution of the two phases has been proposed to occur by spinodal decomposition [55, 42]. The high-temperature transformation is determined by the Gibbs free energy, which couples the temperature to the entropy, affirming the role of the HEA paradigm in determining the ordering. The high-temperature, entropically-driven transformation is the focus of the current work. Our previous work has investigated the HEA $\text{Al}_{1.3}\text{CoCrCuFeNi}$ using in-situ diffraction while heating through the transition, capturing changes in the crystal structure [42], but had little sensitivity to the microstructure or chemical ordering. Using differential thermal analysis and room-temperature microscopy, it has been proposed that the transformation occurs by spinodal decomposition (SD) at 600°C. During the SD, the microstructure is proposed to change abruptly, with discrete, well-defined phases merging at higher temperatures into a homogenized alloy. Due to the strong dependence of the macroscopic structural properties on the microstructure and compositional disorder (homogeneity), it is critical to develop a thorough understanding of the structure before, during and after the SD. The present study uses in-situ heating with small angle neutron scattering (SANS) and scanning transmission electron microscopy (STEM) with energy dispersive x-ray spectroscopy (EDS) to investigate the temperature-dependent formation and distribution of phases, confirming the SD transition in $\text{Al}_{1.3}\text{CoCrCuFeNi}$.

2.2 Methods

Samples were fabricated using standard arc melting techniques as described previously [60, 37, 29, 28, 27]. The samples for insitu STEM heating experiments were prepared by first sectioning the as-cast ingots into ~ 5 mm cube-shaped pieces. A Hitachi NB5000 Ga+ focused ion beam (FIB) operated at 40 kV Ga+ was then used to extract and thin (~ 100 nm) specimens, followed by a low 5 kV surface cleaning procedure. An in-situ micromanipulator was subsequently employed to transfer the specimen onto a MEMS fabricated heating microchip device, (Protochips, Inc. Morrisville, NC), following the protocol outlined by Duchamp et al. (2014) FIB milling is an established technique for traditional TEM specimen preparation (Giannuzzi and Stevie, 1999) and it is well known that preparation using this method results in Ga+ implantation (Langford and Petford-Long, 2001). However, the final cleaning at 5 kV reduces the Ga defects in the final specimen (Langford et al., 2001). The in-situ STEM heating experiments were performed from room temperature to 800°C on a Hitachi HF-3300 STEM, operating at 300 kV, ramping the temperature at 5°C per minute then holding the temperature constant for 30 min before imaging. STEM-EDS elemental maps were acquired using a Bruker silicon drift EDS detector at 256×192 pixels, a pixel dwell time of 13 ms, with an overall acquisition time of 11 min.

Small-angle neutron scattering studies were conducted at the High Flux Isotope Reactor (HFIR) on the General-Purpose SANS beamline (GP-SANS) [56]. This technique is sensitive to the microstructure of the material, specifically chemical phase separation and the resulting change in the nuclear scattering length density. The instrument was configured to use a neutron wavelength (λ) of 8 Å with the resolution $\Delta\lambda/\lambda$ of 0.15. The sample-to-detector distance of 19.3 m was chosen to provide a q-range of $0.002 \text{ \AA}^{-1}$ to $0.04 \text{ \AA}^{-1}$ for observing microstructural features in the size range of 160–3,100 Å. A tube furnace exposed to atmosphere was used to control the sample temperature during the SANS measurements, up to 800°C, allowing in-situ measurement of the structure. The temperature was initially heated to 400°C with a ramp rate of 20°C/s and then ramped to higher temperatures by 50°C

every 15 min. The SANS prepared samples were 10 mm diameter disks with a thicknesses of 1 mm.

2.3 Results and Discussion

The first step of the in-situ STEM-EDS study was to reproduce the previously reported room-temperature microstructure of the $\text{Al}_{1.3}\text{CoCrCuFeNi}$ alloy (Santodonato et al., 2018). The as-cast metal has a dendritic microstructure, with Cu-lean dendrites and Cu-rich interdendrites, spanning several hundred microns in scale (not shown). Within the dendrites, a periodic microstructure consisting of Cr-Fe rich plates in a matrix of Al-Ni is observed and shown in Figure 2.1. The Cr-Fe has a body-centered-cubic (BCC) structure, with the plate growth direction normal to the $[1\ 0\ 0]$ vectors [54]; the Al-Ni matrix has an ordered BCC (i.e., B2) structure. These two phases have nearly equal lattice parameters of 2.9 Å, allowing for a coherent interface, characterized previously by Welk et. al. [55]. The Co (not shown) is included in both the Cr-Fe and the Al-Ni phases, with a signal appearing throughout the dendrites. The Cu is shown to form its own plates that are separate from both the Cr-Fe and the Al-Ni, which have a face-centered cubic (FCC) structure [57]. Most of the Cu in the sample forms FCC phases in the inter-dendritic regions [49, 42, 57]. These FCC inter-dendritic zones are stable to temperatures near the melting point of pure Cu (1,085°C). In contrast, the oriented plate microstructure of the dendrite region undergoes significant changes between room temperature and 800°C; which is the main focus of the present in-situ study. The STEM-EDS images in Figure 2.1 show that the microstructure of the sample gradually changes as the alloy is heated from room temperature to 600°C. STEM images showing the microstructure were published in a previous work [42]. As the Cr images emphasize, at 600°C the plates become larger, with an increasingly diffuse boundary. Increasing the temperature to 650°C further degrades the plates, causing them to lose their well-defined structure and coherent orientation. At 650°C the Fe leaves the Cr, entering

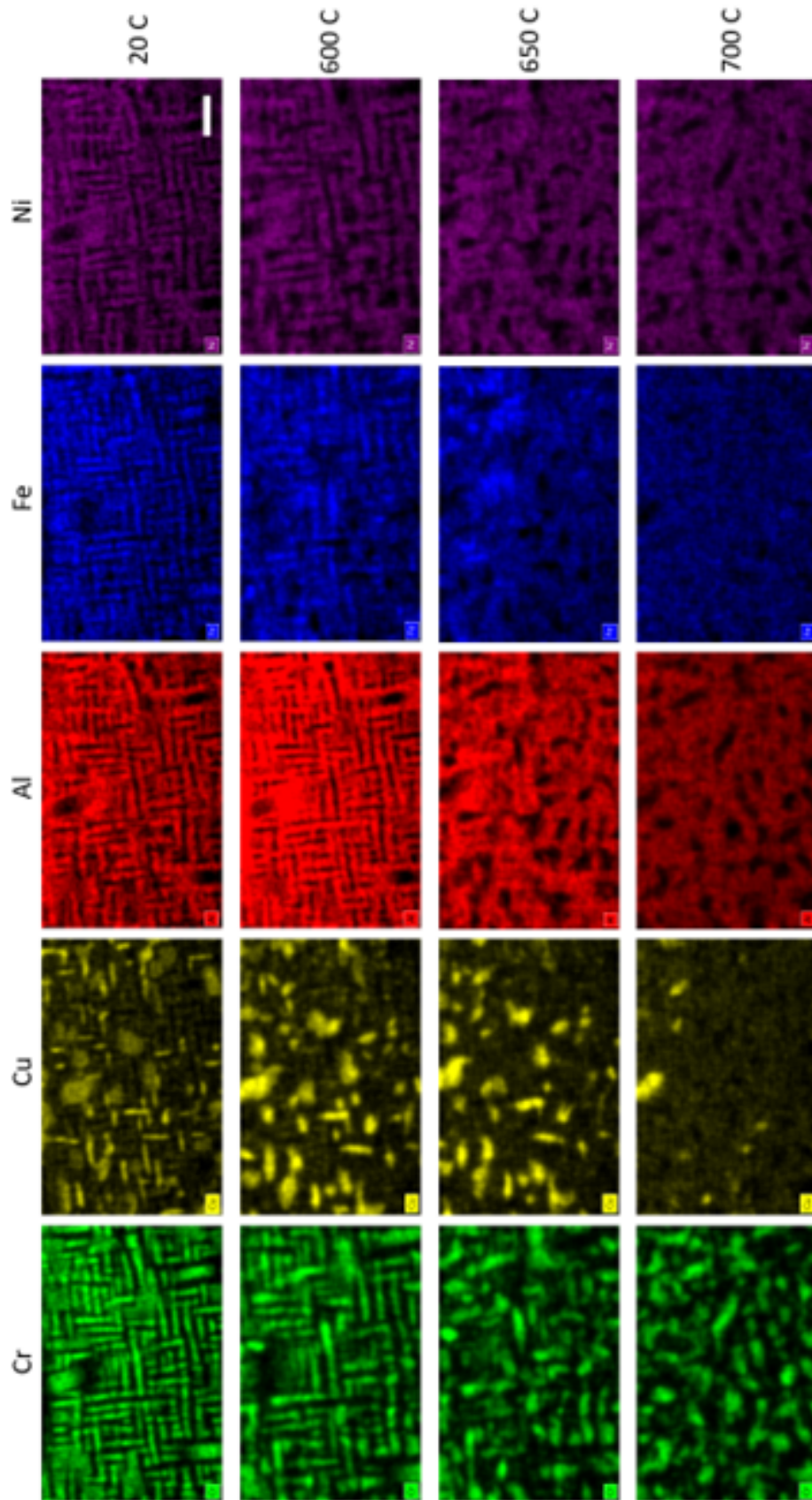


Figure 2.1: EDS elemental maps acquired during in-situ STEM heating experiments of $\text{Al}_{1.3}\text{CoCrCuFeNi}$: (top to bottom) 20, 600, 650, and 700°C. Images show the compositional distributions for (left to right) Cr, Cu, Al, Fe, and Ni. Scale bar is 5,000 Å

the Al-Ni phase, which now forms a matrix with voids for Cr and Cu. Finally, heating to 700°C further homogenizes the sample, resulting in a disordered dispersion of Cr-rich and Cu-rich precipitates. The Co micrograph shows that at high temperatures the Co is intermixed predominantly with the AlFeNi matrix. High-temperature neutron diffraction spectra presented in Santodonato et al [42] shows little change to the underlying crystal structure between room temperature and 1,000°C. Comparing the STEM-EDS results shown here to the diffraction spectra indicates that the microstructural changes occur without significant changes to the underlying crystal structures, consistent with SD. While the STEM images show the local microstructure in the FIB-defined flake sample, a broader perspective of the bulk microstructure is necessary to confirm these results. Small angle neutron scattering is used as a bulk-technique, which is sensitive to microstructural changes in the proposed length scales but is insensitive to the crystal structure. The platelets of the different phases each have a distinct calculated neutron scattering length density: Cr ($3.28 \times 10^{-6} \text{Å}^{-2}$), Cu ($6.55 \times 10^{-6} \text{Å}^{-2}$), and AlFeNiCo ($6.02 \times 10^{-6} \text{Å}^{-2}$). This difference enables the neutron to diffract from the plates, providing the measured signal. Furthermore, the Cu is largely segregated to the inter-dendrite boundary which is sufficiently large in scale ($> 1 \mu m$) that it will not show up in the SANS data. The SANS measurements were performed with in-situ heating from room temperature to 800°C using the $\text{Al}_{1.3}\text{CoCrCuFeNi}$ sample, presented in Figure 2.2 A. The SANS scattering patterns are plotted as a radial average of the intensity as a function of the scattering vector, Q . All of the SANS patterns show a smoothly changing, Porod-like decay. The size distribution of the microstructural phases was determined by analyzing the SANS patterns using the IRENA package [20]. This package uses the cross-sectional scattering formula of:

$$I(Q) = |\Delta\rho|^2 \int |F(Q, r)|^2 (V(r))^2 N_p(r) dr \quad (2.1)$$

Where, $I(Q)$ is the 1D scattering intensity, $\Delta\rho$ is the difference in scattering length density, $F(Q, r)$ is the structure factor, $V(r)$ is the volume fraction, and $N_p(r)$ is the number

of particles. For the calculated analysis method, the experimental scattering pattern can be reasonably well characterized by assuming an average spherical shape, scattering length density difference and contrast for all the particles in this sample. This analysis performs a leastsquares fit to determine the real-space size distribution of features within the sample. The room-temperature data shows a bimodal distribution, with a peak at ≈ 120 Å (Figure 2.2 B), consistent with the periodicity of the platelets in the STEM images. The second, broader peak in the room-temperature curve occurs at ≈ 550 Å. This peak is not present in the 400°C data and is proposed to be a magnetic scattering peak as it agrees well with the expected magnetic transition below 400°C [19]. This indicates that the sample likely contains magnetic domains spanning across areas of the sample much larger than the platelets. Upon increasing the temperature to 600°C, the SANS data shows a continuous shift to larger diameters of the scattering centers. Accompanying this shift is a continuous decrease in the relative volume fraction (Figure 2.2 D). These details are again consistent with the STEM-EDS results, which showed that the plate-like structure became larger upon approaching the SD temperature. At 600°C the STEM images also show that the boundaries of the plates are merging together as seen in the significant increase in the full-width at half-maximum of the size distribution (Figure 2.2 C red curve), increasing their size beyond the range of these measurements and thus decreasing the apparent volume fraction. As the temperature increased to the SD range, at 650°C the distribution of the scattering center sizes increases significantly in width and decreases in their average size. This trend is consistent with a reduction in the periodicity of the plate structure and the merging of the Al, Fe and Ni features seen in the STEM-EDS images in Figure 2.1. Finally, heating above 650°C, the size distribution is largely flat, indicating the loss of long-range regularity of the plate-like structures. To summarize the combined SANS and STEM-EDS results, an expected magnetic transition is observed by SANS between 20 and 400°C due to the loss of the magnetic domain structure present at lower temperatures. Subtle changes in the microstructure occur with increasing temperatures between 400 and 600°C; these gradual changes correspond primarily to structures in the

120–200 Å range. The STEM-EDS images corroborate the growth of the nanoscale plate-like microstructure of the sample. At 650°C the STEM-EDS results show that the plates begin to lose their regularity and structure, then at 700°C the sample transforms from an ordered, quasi-oriented structure to a disordered microstructure. The sequence of gradual elemental redistribution, followed by an abrupt microstructural change, strongly suggests that a spinodal transformation occurs in $\text{Al}_{1.3}\text{CoCrCuFeNi}$, and likely in other similar alloys, as suggested in the early HEA literature [53].

2.4 Conclusion

The microstructure evolution of the high-entropy alloy $\text{Al}_{1.3}\text{CoCrCuFeNi}$ is shown to occur by the precipitation/dissolution of ordered Fe-Cr and Al-Ni nanoplatelet phases. These chemically distinct phases have similar lattice structures and parameters, allowing for a coherent interface between them, but making it difficult to distinguish them by diffraction. current in-situ measurements (SANS and STEM-EDS) are uniquely sensitive to the chemical phase separation and were used to directly probe this phase transition. Using this sensitivity, the present work provides a direct look at the spinodal decomposition previously proposed. In addition to the SD between the Al-Ni and Fe-Cr phases, Cu-rich and Cr-rich secondary phases are observed to persist throughout the matrix at high temperatures. Throughout the transformation and homogenization process, the sample maintains a similar lattice structure and nearly constant size [42], implying the transformation is predominantly chemical ordering, with minimal structural contributions. The current work, together with the previous studies [58, 49, 42, 59, 5, 57], confirms that $\text{Al}_{1.3}\text{CoCrCuFeNi}$ has a unique structure, consisting of a solid-solution matrix with a large fraction of secondary phases at room temperature, and up to 650°C. The secondary phases arise from both spinodal decomposition and the independent precipitation Cu-rich phases, occurring in stages at different temperatures. These phase separation processes may be used to selectively tune heat

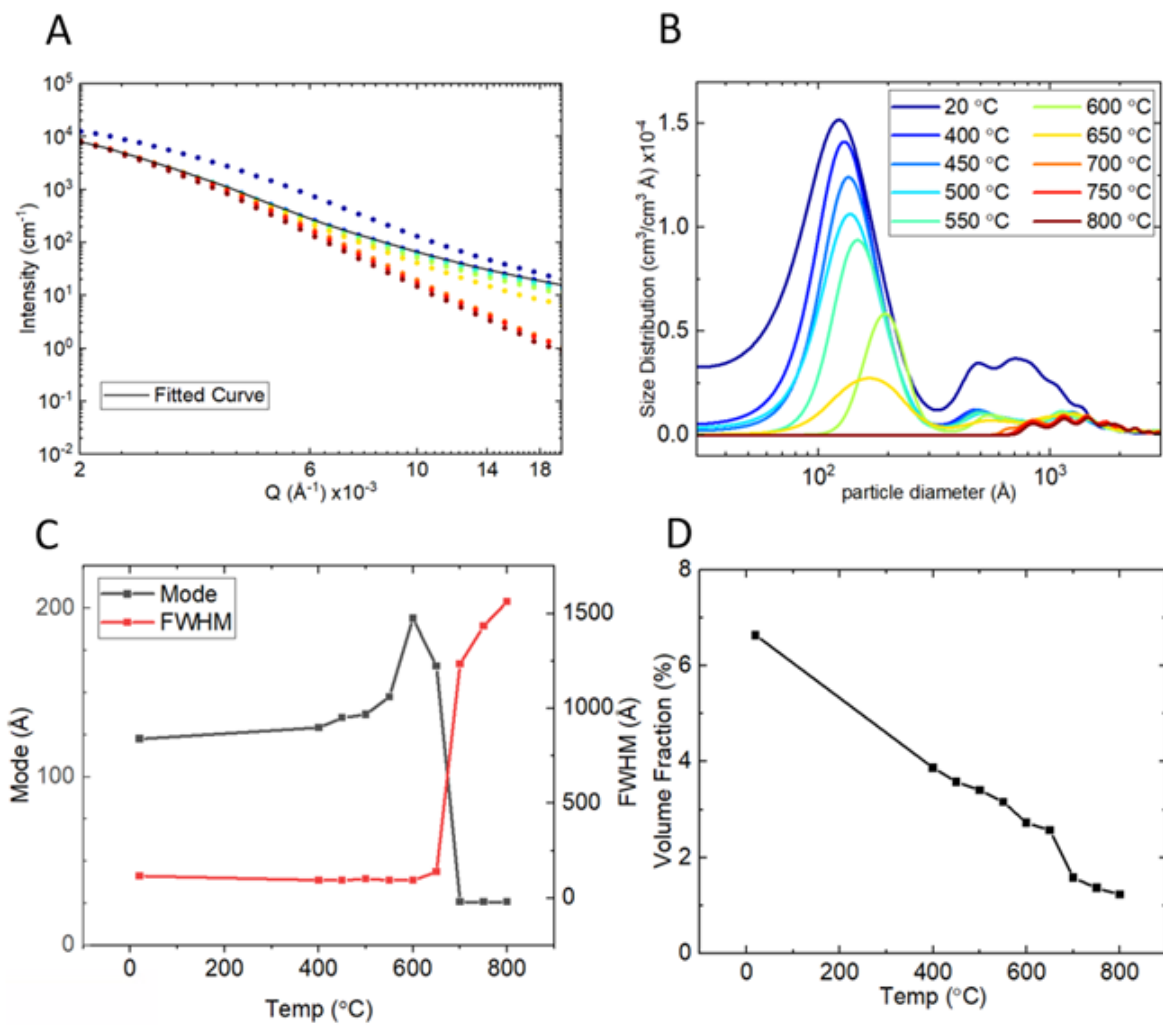


Figure 2.2: Al13 SANS.

treatment for beneficial properties if properly understood and controlled. The coexistence of different formation mechanisms and the coherency of some of the resulting phases provides opportunities to explore property optimization through microstructure control. It has been noted that many important engineering alloys, such as Ni-based superalloys, owe their strength to the presence of coherent precipitates, hence similar features developed in high-entropy alloys may bring extraordinary benefits [42]. It is in this context that the $\text{Al}_x\text{CoCrCuFeNi}$ family of alloys should undergo further scientific and technical study, providing great opportunities for advanced alloy development.

Chapter 3

Bulk $\text{Al}_x\text{CoCrFeNi}$ Magnetic Properties Probed with SANS

3.1 Abstract

High-entropy alloys (HEAs) are materials which utilize the entropy of mixing to encourage immiscible elements to form single-phase solid solutions. These materials have shown superior structural and mechanical properties, especially at high temperatures, but there is increasing interest in their potential in functional applications such as memory storage and energy devices. The current work investigates the magnetic properties of HEAs and proto-HEAs $\text{Al}_x\text{CoCrFeNi}$ ($0 \leq x \leq 2$). These materials form a single phase at $x < 1$, but phase separate at higher concentrations. Interestingly, coincident with the phase separation, the magnetic moment and Curie temperature increases with the inclusion of the non-magnetic Al. The phase separation and the resulting magnetic evolution is investigated at high temperatures with scanning transmission electron microscopy (STEM-EDS) and small angle neutron scattering (SANS). These complementary techniques provide a comprehensive understanding of both the compositional and magnetic phase separation. First order reversal

curve (FORC) analysis is used to correlate the temperature-dependent phase separation with the magnetic coupling and reversal behavior.

3.2 Introduction

High entropy alloys (HEAs) are defined as alloys comprised of five or more stoichiometrically equal elements [58], however, recent allowances for flexibility in composition have motivated the study of new alloys which maintain many of the benefits of the ‘high entropy effect’ while improving specific material properties. These alloys are currently investigated for their mechanical properties [43, 51, 52] and have shown superior toughness and high-temperature behavior. Notably, many HEAs include magnetic transition metals (Fe, Ni, Co, Mn), making it likely that novel magnetic materials may exist in the HEA paradigm. However, conventional magnetic ordering arises from highly localized (several nanometers) interactions in these chemically heterogeneous materials. For this reason, it is not immediately apparent what the magnetic ordering may be in HEAs, and highly likely that the magnetism may change with ordering. Compared to the mechanical properties there have been few investigations of magnetism in HEAs. What works that have been published generally show that HEAs can be magnetic and are magnetically soft[47]. These soft magnetic materials with high-temperature mechanical properties are desirable for energy generation technologies [17]. Complementing the desirable material properties, HEA and P-HEAs are a natural candidate for recycling and are inherently tolerant of impurities, making them low-cost and sustainable to produce [18]. As noted above, the HEAs have generally been demonstrated as magnetically soft, however, recent works have realized HEAs in an L10 structure, resulting in a magnetically hard material [35, 2] with potential applications in motors/generators, sensors, and information technologies. Interestingly, these hard magnetic materials are based on the same Cantor-like alloy[6] as the magnetically soft materials [47, 9, 10] with the inclusion

of Pt. Other high entropy materials have also been shown to be magnetically hard. In particular, Musico et al. identified high entropy oxides with extremely high coercivities, over 9 T, which includes only common rare-earth minerals (e.g. La, rather than Nd and Dy) [34]. Thus, it becomes apparent that the HEA paradigm presents excellent flexibility in the magnetic properties of materials. In the current project the magnetic properties of a Cantor-like [6] HEA $\text{Al}_x\text{CoCrFeNi}$ are investigated using small angle neutron scattering (SANS), scanning transmission electron microscopy (STEM) and magnetometry versus composition, structure and temperature. This material is of particular interest since it forms an alloy at low compositions but undergoes a spinodal decomposition at higher Al content [22], which is expected to impact the magnetic properties. This work follows the phase transition and determines the structure-property (magnetic) relationships. The work complements the seminal work by Yih-Farn Kao et al. [23] which reported the low-temperature magnetic properties of $\text{Al}_x\text{CoCrFeNi}$ alloys, treating them as single-phase systems. Subsequent works have shown that, while these materials are structurally homogenous, they are compositionally phase separated [43, 51, 42, 48]. The current work reports the magnetization between 2 K and 1000 K, focusing specifically on the chemical phase separation, the magnetization of the material as a whole and each of the compositional phases.

3.3 Methods

Arc-melt slabs of HEA were fabricated using arc melting, with source ingots of Al, Co, Cr, Fe and Ni (purity > 99.9%), melting three times to ensure homogeneity, then allowing them to cool passively in the copper hearth. Individual ≈ 200 mg samples were then sectioned from the parent material for measurements. Imaging was performed using scanning electron microscopy (SEM) and compositions were confirmed via energy dispersive X-ray spectroscopy (EDS). Magnetometry measurements, including first order reversal curves (FORC) results, were performed using a vibrating sample magnetometer (VSM) at temperatures between 2 K

and 1000 K. FORC measurements are performed by first saturating the sample in a positive field. Next, the magnetic field is reduced to a reversal field, H_R , then the magnetization, M , is measured as the applied field, H , is increased from H_R back to saturation; this measures a single FORC branch. FORC branches are measured for a range of H_R spanning the range of the hysteretic reversal, collecting a family of FORCs. The FORC distribution is calculated by taking a second-order derivative of the family of FORCs: $\rho = -\frac{1}{2} \frac{d^2 M}{dH dH_R}$. Recognizing that measurements with increasing magnetic field, e.g. the H axis, are probing magnetic up-switching events from a negative orientation to a positive, while H_R probes down-switching events, the FORC distribution can be re-defined in terms of a coercivity and bias field: $H_C = (H - H_R)/2$ and $H_B = (H + H_R)/2$. Data will be presented in a (H_C, H_B) coordinate space due to the improved symmetries in this representation. Details of the FORC measurement procedure and interpretation have been published previously [15, 3].

The as-cast materials were prepared into five cubes. Then, a focused ion beam (FIB) with Ga⁺ ions was used at 40 kV to create ≈ 100 nm thick samples from the cubes. Once the samples were cut with a FIB, 5 kV cleaning of the surface was performed using He. Samples were placed onto a heating microchip device (Protochips, Inc.) for in-situ STEM as outlined by Duchamp [20]. The established method of FIB milling has a tendency for Ga implantation, hence the 5 kV surface cleaning [26, 13]. Scanning transmission electron microscopy (STEM) measurements were performed with in situ heating from room temperature to 1073 K, using an acceleration voltage of 300 kV. The temperature was ramped up at 5 K per minute to the target temperature, then imaging was performed after holding at each temperature for 30 minutes. The STEM-EDS elemental maps were acquired using a dwell time of 13 ms and an overall acquisition time of 11 minutes.

Small angle neutron scattering (SANS) measurements were performed at the High Flux Isotope Reactor (HFIR) on the General Purpose SANS (GP-SANS) beamline [56]. A 4.76 Å wavelength neutron beam was used for high q -ranges and 12 Å for low q ranges, with a wavelength distribution ($\Delta\lambda/\lambda$) of 15%. The detector distances were 18.9 m, 9.6 m, and 2.6

m in order to have the most complete q-range for the system. These different q-ranges were background reduced and stitched together for a complete data set for the samples. This allowed for a q-range of $0.002 \text{ \AA}^{-1}$ to $0.04 \text{ \AA}^{-1}$.

3.4 Results and Discussion

Magnetometry measurements were performed first. Initial expectations of the magnetization were that as the Al content increased the saturation magnetization, M_S , and Curie temperature, T_C , would decrease due to a dilution effect and disruption of the long-range exchange interaction. Magnetization versus temperature (M-T) curves, Figure 3.1 a, indicated this was correct for $x = 0$ and 0.5 which showed a T_C of 125 K and 20 K , respectively. Magnetization versus field (M-H) measured at 2 K (not shown) provide M_S values of 27 emu/g and 9 emu/g for $x=0$ and 0.5 , respectively. Suppression of T_C and M_S often occurs in alloys between ferromagnetic and non-ferromagnetic elements due to a weakening of the long-range exchange interaction and dilution of the ferromagnetic species [24]. However, the trend reverses for $x \geq 0.5$: with increasing Al content, M_S and T_C both increase, with T_C exceeding room temperature. The M-T curves for $x = 1, 1.5$ and 2 show T_C of 860 K , 880 K , and 525 K , respectively. The M-T curves show a strong deviation from conventional, single phase magnetic materials, including anomalous increases and decreases in the magnetization. This behavior may indicate multiple magnetic phase transitions, but more likely indicates structural transitions and associated phase separation events, resulting in phases with different T_C and M_S compared to the preceding phases. Notably, the $x=1$ and 1.5 samples show a strong reduction in the magnetization at $\approx 400 \text{ K}$, a second at $\approx 550 \text{ K}$, then an increase at 600 K and 700 K , respectively, before reaching their ultimate T_C at $\approx 900 \text{ K}$. The $x=2$ sample shows only a single step at 150 K before reaching its ultimate T_C at 525 K . The magnetization versus field (M-H) measurements taken on the as-prepared (arc melted and cooled in hearth) sample $x=1, 1.5$ and 2 , at room temperature, are shown in Figure 3.1

b; the $x=0$ and 0.5 samples are paramagnetic at room temperature and so are not shown. All three plots show a sigmoidal structure with a small coercivity of ~ 100 Oe. Notably, each sample nucleates its reversal well before $H=0$, indicating a demagnetizing factor, such as nanoscale shape anisotropy or competing ferro- and antiferromagnetic interactions. Also notably, M_S increases between $x=1$ and $x=1.5$, then decreases between $x=1.5$ and $x=2$. Previous works have shown that $\text{Al}_x\text{CoCrFeNi}$ alloys have multiple compositional phases, and that increasing the aluminum content promotes phase separation [43, 51, 52, 48, 54]. The current M-T and M-H measurements indicate that several of these phases are magnetic and that the phase separation can be tracked in the magnetic response.

To correlate the compositional/structural phase transitions to the magnetic results, the system is evaluated using STEM, SANS and FORC measurements. Scanning transmission electron microscopy (STEM) imaging with in-situ heating is used to observe the temperature-dependent phase separation, while energy dispersive X-ray spectroscopy (EDS) is used to determine the composition of these phases. The micrographs measured on the $x=1.5$ sample, Figure 3.2, show that the as-prepared sample (which was arc melted then passively cooled in the hearth) has significant phase separation. The EDS maps indicate that the as-prepared sample is largely comprised of Cr-based precipitates ≈ 20 nm in diameter, embedded within an Al-based matrix. In the as-prepared sample, the Co, Ni and Fe are present in each of the phases, although heterogeneously, with the Fe preferentially localizing around the Cr, and NiCo with the Al. As the temperature increases, Co and Fe appear to homogenize while Cr remains segregated from the Al and Ni. The resulting system can be approximately described as chemically similar to $\text{Co}_{0.33}\text{CrFe}_{0.33}$ precipitates in $\text{Al}_x\text{Co}_{0.67}\text{Fe}_{0.67}\text{Ni}$ [45]. Previous works reported that both phases have a body-centered cubic (BCC) structure [54, 45]. The microstructure in the $x = 1.5$ sample also changes with temperature, with the precipitates merging and becoming larger at higher temperatures, especially at $T > 1000$ K. At $x = 0, 0.5$ and 1 there is documentation that the microstructure is highly dendritic and lamellar [48, 36]. At $x = 1.5$ and 2 , the microstructure evolves into these nanoparticles, consistent with our

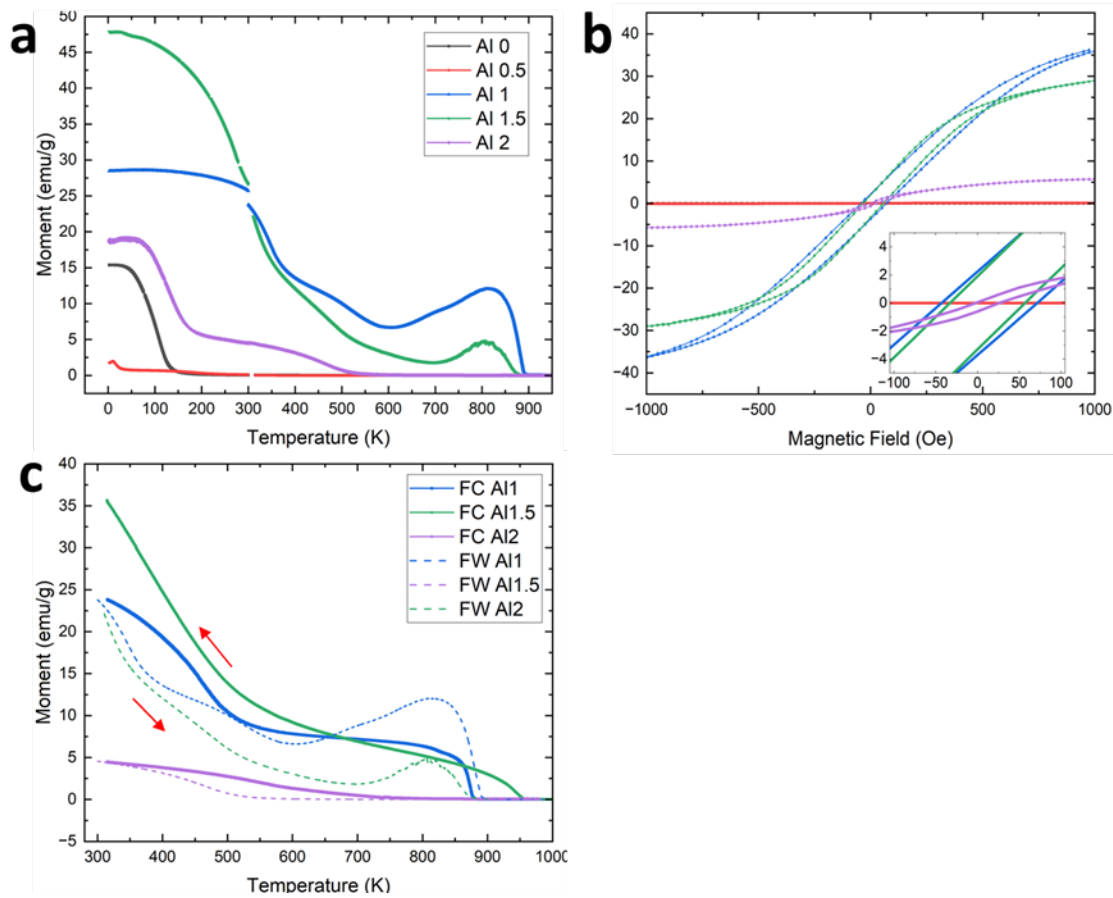


Figure 3.1: (a) Magnetization versus temperature (M-T) measured using a field-cooled procedure in 500 Oe, (b) magnetization versus field (M-H) measured at 300 K, for Al_xCoCrFeNi, and (c) Comparisons of the M-T curves warming and cooling.

observations as can be seen in Figure 3.2 (Cr and Fe at 293 K) [50]. It is expected that the large radius of Al ($r = 1.437 \text{ \AA}$) compared to the other species, and the high enthalpy of mixing for AlNi phase [11] make significant contributions in determining the resultant structure. The STEM results provide critical insights into the temperature dependent chemical structure and microstructure but lack magnetic sensitivity. With magnetic species that are likely coupled in both phases, it is not immediately clear which phase is responsible for this magnetic behavior, if not both.

Small angle neutron scattering, with special sensitivity to both the chemical makeup and magnetic ordering, is an ideal tool to make the connection between the structure and magnetism. SANS is sensitive to variations of the composition and magnetic domains for length scales between $20 \text{ \AA}$ and $1000 \text{ \AA}$. Measurements were taken at room temperature on the $x=1$ and $x=1.5$ samples in the as-cast state, in applied fields of 2.5, 5 and 10 and 15 kOe. At these fields, the material is past its apparent saturation field, e.g. past the hysteretic segment of the reversal, and the moments are oriented generally parallel to the magnetic field. The STEM images reveal that there are small nanoparticle-like precipitates that will experience a significant demagnetizing magnetostatic interaction, e.g. shape anisotropy, which results in a curvature of the moments on the surface of the nanoparticles, particularly at the lower fields. The applied magnetic field competes with the magnetostatic energy, with the former motivating alignment parallel to the field. Choosing these fields allows us to study the magnetic moment and how the magnetic ordering occurs within the composite material.

SANS measurements were performed with a magnetic field in the horizontal direction, orthogonal to the neutron beam. An example of the 2D data, measured on a sample $x=1.5$ at $H=10 \text{ kOe}$, $T=300 \text{ K}$, using a detector distance of 2.6 m with $\lambda=4.76 \text{ \AA}$, is shown in Figure 3.3 a. In this geometry, scattering from the magnetic structure is prohibited in the horizontal direction. Thus, scattering in the horizontal direction is only from the nuclear structure, while scattering in the vertical direction is a combination of nuclear and magnetic structure. Examples of these data were captured for the 2D plot by using narrow wedge-shaped regions

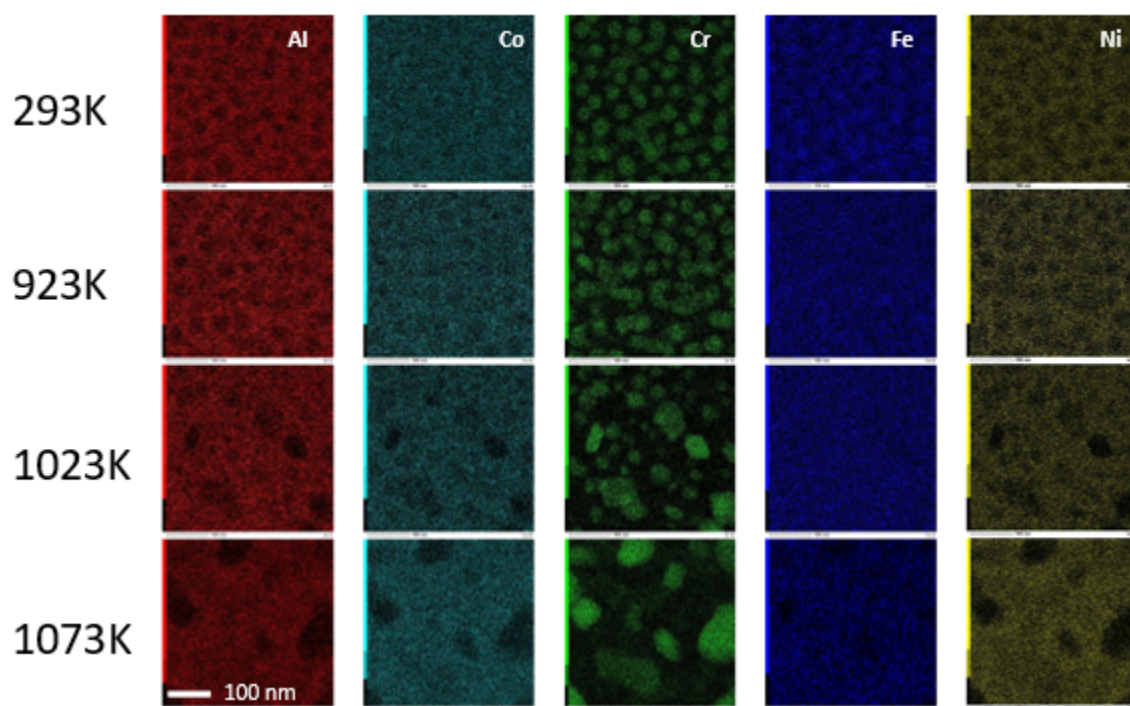


Figure 3.2: EDS elemental maps acquired during in-situ STEM for $\text{Al}_{1.5}\text{CoCrFeNi}$. Temperature progression from top to bottom and chemical distribution from left to right.

of interest in the vertical and horizontal directions, generating an intensity versus q plot shown in Figure 3.3 b. The 1D data for the $x=1$ and 1.5 samples at $H=0$ to 15 kOe are shown in Figure 3.3, with the horizontal (nuclear) cut shown in panels c and d, and the difference (e.g. magnetic) cut shown in panels e and f. Using SASview, a multi-component model was used to fit the data as can be seen in Figure 3.3 b [16, 39, 25]. The model included a polydisperse sphere form factor with hardsphere structure factor, a Gaussian centered at zero representing direct beam, and a power law decay. The converged mode determined that the radius of the spheres for $x=1$ and $x=1.5$ are 34 nm and 16 nm, respectively, with a polydispersity factor of 0.35. The effective radius, which corresponds to the interparticle center-to-center spacing (from the hard sphere structure factor) converged to 50 nm. These values are in good agreement with the STEM results, which showed an average radius of 16 nm for $x=1.5$ and an interparticle distance of 51.5 nm. The correlation of the STEM results with the SANS results suggests that the local measurements (from the STEM) are representative of the global average (measured with SANS). The magnetic scattering length densities (MSLDs) and particle dimensions were extracted from the magnetic scattering data; the particle dimensions here represent the magnetic volume. Neutron scattering in the SANS measurement shows the contrast of different scattering length densities, not an absolute value; using the phase fractions and the saturation moment from the magnetization measurements, the saturation magnetization of each phase will be calculated below. Examples of the nuclear and magnetic fits are shown for the $x=1$ sample, measured at 10 kOe, in Figure 3.3b [33]. The difference of MSLDs in $x=1$ at 2.5 kOe is $0.68 \times 10^{-4} \text{nm}^{-2}$, with the matrix having the larger MSLD. This difference decreases to $0.57 \times 10^{-4} \text{nm}^{-2}$ at 10 kOe. In the $x=1.5$ sample the MSLD difference is $0.68 \times 10^{-4} \text{nm}^{-2}$ at 2.5 kOe and decreases to $0.44 \times 10^{-4} \text{nm}^{-2}$ at 10 kOe. In both materials, the difference in the MSLDs decreases which correlates to the improved polarization of the FeCr spheres and the moments in the Al_xNiCoFe surrounding the spheres. The radius of the spheres determined by fitting the magnetic data was slightly larger than the radius of the nuclear structure, also consistent with curling of the magnetic moments at the sphere-matrix

interface; the curling results in a reduced magnetic polarization in this area, reducing the MSLD. Using the universal units, the comparison of the MSLDs, magnetization, and phase fractions the comparisons between the moments of each phase become clearer. The MSLD – which again corresponds to the contrast between the precipitates and the surrounding matrix – can be converted to emu/cm³ using the relationship $1 \text{ emu/cm}^3 = 2.9 \times 10^{-7} \text{ nm}^{-2}$; using the difference in the magnetization of the two phases, the phase fractions and the total saturation moment (from magnetometry), the magnetization of each phase can be determined. The largest MSLD difference for $x=1$ is $0.68 \times 10^{-4} \text{ nm}^{-2}$ which is equivalent to 234 emu/cm³. Comparing this to the M-H curves and a conversion based on the densities, $x=1$ has an M_S of 247 emu/cm³. The two phases each with their own magnetic moments, the $M_S = 0.66 M_{Matrix} + 0.33 M_{Particles}$, and due to SANS we also know that $M_{Matrix} - M_{Particles} = 234 \text{ emu/cm}^3$. Using SANS in combination with STEM and magnetometry we successfully reduced that the $M_{Matrix} = 325 \text{ emu/cm}^3$ and $M_{Particles} = 91 \text{ emu/cm}^3$ for $x = 1$. This same process yields a $M_{Matrix} = 275 \text{ emu/cm}^3$ and $M_{Particles} = 42 \text{ emu/cm}^3$ for $x = 1.5$. Altogether, the SANS results identify the matrix as the primary magnetic component, although the precipitates also show appreciable magnetic polarization. The SANS results also show appreciable curvature of the moment at the precipitate/matrix interface. Revisiting the M-T curves in Figure 3.1, knowing the magnetization of the two phases, the significant and rapid decline in the magnetization above room temperature can likely be attributed to changes in the AlNi phase.

To further investigate the magnetic features of the phase separated system and its temperature dependent evolution, first order reversal curve (FORC) measurements were performed. FORC measurements allow differentiation of multiple magnetic phases [14], ‘fingerprinting’ reversal mechanisms [8] and quantifying magnetic interactions [1]. From the SANS results, the current system is known to have at two magnetic phases with the larger (both by volume and saturation moment) being the AlNi matrix, and the smaller being Cr-precipitates. These phases are known to change in size and composition with temperature,

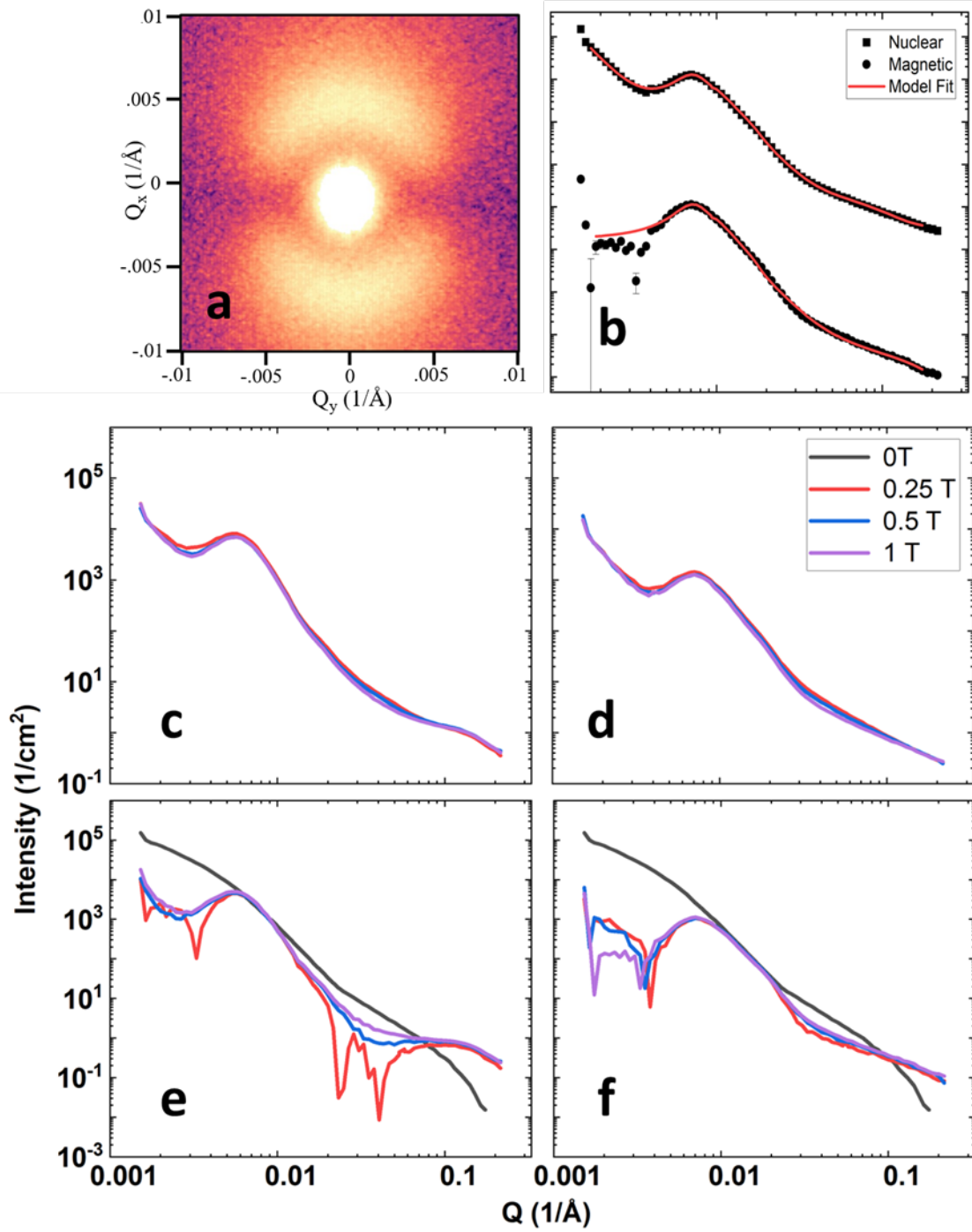


Figure 3.3: (a) 2D SANS image of $\text{Al}_{1.5}\text{CoCrFeNi}$ at 10 kOe, (b) I vs Q 1D data of $\text{Al}_{1.5}\text{CoCrFeNi}$ at 10 kOe with model fits. The magnetic data is shown scaled down by 10^3 for clarity (resulting in a translation in the log scale). I vs Q 1D data from (c, e) AlCoCrFeNi and (d, f) $\text{Al}_{1.5}\text{CoCrFeNi}$, showing nuclear (c, d) and magnetic (e, f) scattering.

and the magnetization is shown to vary in unconventional ways. The FORC analysis will allow the reversal mechanism (as isolated particles, or domain propagation, or vortex reversal etc.) to be identified, the magnetic weight of each phase to be identified, and potentially the interactions between magnetic isolates to be quantified. These features contribute to define the major hysteresis loop (Figure 3.1 b) but generally appear in a convoluted way that makes it challenging to separate. The FORC distributions, Figure 3.4, show the $x = 1$ sample measured at increasing temperature. At 320 K, the primary feature is a long ridge along the H_B axis, indicating the magnetization is predominantly reversible, or nearly reversible. Furthermore, some of these reversible features switch at bias fields of up-to 0.75 kOe, e.g. against the applied magnetic field; this value corresponds to the demagnetizing interaction field within the sample. There is also a fainter ‘boomerang’ shaped feature which corresponds to an irreversible phase. This feature specifically indicates that parts of the sample are reversing as single-domain particles, weakly interacting with a demagnetizing interaction, likely long-range dipolar fields [15]. From the maximal extent of this feature in the H_B axis the interaction field can be quantified and is ≈ 750 Oe at room temperature. The spread along the H_C axis corresponds to the intrinsic switching field distribution, distorted by the interaction field as discussed previously. Accounting for this distortion, the intrinsic switching field extends from ≈ 0 Oe to ≈ 250 Oe, generally falling in the range of a soft to moderate anisotropy ferromagnet. The integrated volume of these two features corresponds to their magnetic weight in the system. As the temperature is increased to 490 K and 600 K, the extent of the reversible feature along H_B is reduced, indicating reduced demagnetizing interactions, and the feature decreases in intensity, indicating the magnetization from this phase is decreasing. This latter observation could indicate the reversible phase is being annealed to a different structure or the measurements are approaching the T_C ; at 490 K atomic diffusion in metals is generally slow, thus T_C is the likely culprit. In comparison, the intensity of the ‘boomerang’ feature grows with temperature, indicating that the irreversible phase is increasing. The spread of this feature in both H_B and H_C is also reduced, indicating

a reduction in the interaction strength and the intrinsic switching distribution. The reduced interactions are a surprise, but the reduced intrinsic switching field is likely the result of tempering mechanics, e.g. annealing out defects and improving local crystalline quality. At 830 K the trend seems to reverse, with the H_B spread of the reversible phase increasing, and the ‘boomerang’ feature becoming more extended. The underlying mechanics can be seen in the FORC diagram, at the merge between the reversible and irreversible phases: in the FORCs measured at 490 K and 600 K the reversible phase has a bifurcation that bridges the two phases, while in the 830 K measurement this is gone. This bridge indicates an exchange coupling between the two phases. In other words, the reversible phase is coupled to the irreversible, resulting in an exchange spring like behavior. In such a system, the reversible phase causes premature switching of the irreversible, reducing the extent along H_C , while the irreversible phase anchors the reversible, reducing its spread along H_B . At 830 K this connection is broken allowing the two phases to reverse independently. Returning to room temperature, the reversible feature is much stronger, and the irreversible phase is altogether absent. It is likely that the annealing improved the microstructure of the material, increasing its magnetization and phase boundaries, and after cooling the phases are strongly coupled, fully suppressing the irreversible phase. The $x = 1.5$ FORC series (not shown) demonstrates a similar set of features and progression.

Together, the STEM, SANS, FORC and magnetometry (M-T and M-H) measurements provide a comprehensive picture of the phase separation in $\text{Al}_x\text{CoCrFeNi}$ ($0 \leq x \leq 2$) and its impact on the magnetic behavior. Broadly, at $x < 1$ the material is chemically homogeneous, and the non-magnetic Al and Cr suppress T_C and M_S , following conventional magnetic dilution effects. Previous works have indicated that in these concentrations the structure is face centered cubic and has low-temperature magnetism, consistent with our observations [23]. At $x > 1$ the STEM and SANS identify two compositional phases, one being Cr-rich precipitates and the other being an Al-rich matrix. Interestingly, this increases the total M_S and the T_C of both phases, with the T_C for each phase in $x=1$ and 1.5 being above room

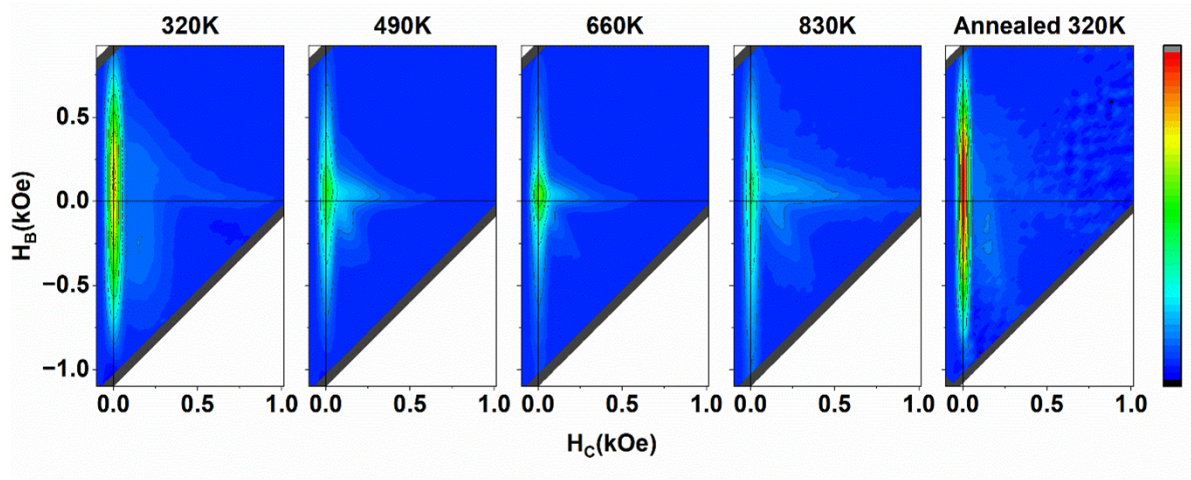


Figure 3.4: FORC diagrams measured on the $x=1$ sample at temperatures between 320 K and 830 K and then a final panel returned to room temperature after annealing.

temperature. The same previous work identified an increase in T_C at these concentrations, attributed to the new body centered cubic structure; this work extended only to room temperature (300 K). The SANS results indicate that the Cr-rich precipitates have a lower moment. The FORC measurements showed that the two phases are both magnetic, with the Al matrix being highly reversible, and the Cr precipitates having sufficient anisotropy to reverse as interacting particles. Exposing the alloy to higher temperatures results in growth of the precipitates, and changes in the Co and Fe distribution, with both moving towards the Al-based matrix.

3.5 Conclusion

By combining SANS, STEM, FORC and conventional magnetometry this work provides a comprehensive understanding of the phase separation in $\text{Al}_x\text{CoCrFeNi}$ alloys and its impact on magnetic properties. At low concentrations ($x < 1$), the addition of paramagnetic Al suppresses M_S and T_C , following conventional dilution behavior, however, at $x \geq 1$ the magnetic behavior changes dramatically, with the M_S increasing and the ultimate T_C increasing to above 900 K; both of these values far exceed the base $x=0$ alloy. The SANS and STEM results show that this behavior can be directly associated with a phase separation into Cr-based precipitates in an Al-based matrix, both of which are magnetic. The reversal behavior of the two phases is explicitly separated using FORC measurements, which indicate the Cr-phase has appreciable anisotropy and at lower temperature are coupled to the Al-matrix, while at higher temperatures they become decoupled, and reverse as single domain particles. With the large number of compositional combinations that exist in HEAs, there is a significant opportunity to design novel functional materials, including magnetic materials. The current work is a valuable step toward improving the field and optimizing the elements chosen for similar materials, and in-particular, highlights a novel deviation of the HEA concept in the transition to two-phase daughter materials.

Chapter 4

Conclusions

This dissertation focuses on high entropy materials and their functional applications. $\text{Al}_{1.3}\text{CoCrCuFeNi}$, $\text{Al}_x\text{CoCrFeNi}$ and the nanowires show valuable application for the tunability of their functional properties. We have investigated using SANS the evolution of $\text{Al}_{1.3}\text{CoCrCuFeNi}$ and $\text{Al}_x\text{CoCrFeNi}$ with increasing temperature. These bulk HEAs both have a spinodal decomposition that occurs at ≈ 900 K. This phase separation gives rise to more exchange interactions and shows rising magnetic moment. The magnetic properties of these bulk systems have shown interesting tunable aspects worth investigating further. We successfully used STEM, SANS, and magnetometry to have a broad overview of the magnetic properties of these bulk HEAs.

The HEA nanowires are fabricated, tested and analyzed showing a low density and high surface to volume ratio. The high entropy effect applied to the meta material structure have shown unexpected results.

In chapter 1 I introduce HEAs with accompanying history. As well as the relationship between electrons, magnetism and the different energies that accompany magnetism. The combination of these different systems is the heart of understanding how multiple magnetic phases interact with each other. I also elaborate on the characterization and the synthesis methods for these different systems including, STEM, EDX, magnetometry, and SANS.

In chapter 2, this study demonstrates that the microstructure evolution of the high-entropy alloy Al_{1.3}CoCrCuFeNi occurs via precipitation/dissolution of ordered Fe-Cr and Al-Ni nanoplatelet phases. These phases, with similar lattice structures, form a coherent interface that is difficult to distinguish by diffraction but can be probed using in-situ SANS and STEM-EDS measurements. These techniques provide direct evidence of spinodal decomposition between Al-Ni and Fe-Cr phases, with Cu-rich and Cr-rich secondary phases persisting at high temperatures. The transformation, primarily through chemical ordering with minimal structural changes, maintains a consistent lattice structure and size. This work, along with previous studies, confirms that Al_{1.3}CoCrCuFeNi consists of a solid-solution matrix with significant secondary phases from room temperature up to 650°C. Understanding and controlling these phase separation processes can allow for selective tuning of heat treatments to enhance properties. The coherency and formation mechanisms of these phases offer opportunities for property optimization through microstructure control, similar to the benefits seen in Ni-based superalloys. The Al_xCoCrCuFeNi family of alloys holds great potential for advanced alloy development and warrants further scientific and technical study.

In chapter 3, this study leverages SANS, STEM, FORC, and conventional magnetometry to provide a comprehensive understanding of phase separation in Al_xCoCrFeNi alloys and its influence on magnetic properties. At low concentrations ($x < 1$), the addition of paramagnetic Al suppresses the M_S and T_C , consistent with conventional dilution behavior. However, at $x \geq 1$, the magnetic behavior changes dramatically, with both M_S and T_C increasing significantly, the latter surpassing 900 K. SANS and TEM results reveal that this behavior is due to phase separation into Cr-based precipitates within an Al-based matrix, both of which are magnetic. FORC measurements further detail the reversal behavior of the two phases, showing that the Cr-phase exhibits significant anisotropy. At lower temperatures, it is coupled with the Al-matrix, while at higher temperatures, it decouples and reverses as single-domain particles.

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Appendices

Vita

Cameron Sparks Jorgensen was born in Idaho Falls, Idaho. He was raised by Joann and Marshall Parker. He pursued his Bachelor's degree at Brigham Young University in Idaho. He is married to his wife Emily and has two children, Jack and Nellie. After his Bachelor's he worked as an intern at the Idaho National Laboratory, then started his PhD at the University of Tennessee in August 2019. He completed his PhD in Materials Science and Engineering in August 2024. He currently works for Arctos, a contractor for the Air Force Research Lab at the Wright Patterson Air Force Base in Dayton Ohio.