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In-situ neutron diffraction analysis of deformation behavior of ductile rare-earth intermetallic YCu

Scott H. Williams
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In-situ neutron diffraction analysis of deformation behavior of ductile rare-earth intermetallic YCu

by

Scott H. Williams

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

Program of Study Committee:
Alan Russell, Co-major Professor
Karl Gschneidner, Jr., Co-major Professor
Gordon Miller
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Iowa State University
Ames, Iowa
2009

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To my friends who have supported me in so many ways, and my family who has loved me always.

To my mom, for spending so much of her life to create so much of mine.
**Introduction and Background**

Intermetallic compounds offer great promise for engineering applications. Many intermetallic compounds possess high strength and high stiffness at elevated temperature, excellent corrosion resistance, and low density, making them potentially useful in a wide range of applications. However, several drawbacks, limited ductility in particular, have prevented these compounds from achieving wide-spread application. If intermetallic compounds are ever to realize their full potential, these limitations must be better understood and overcome. This investigation, then, is representative of the most fundamental concept of materials science, the relationship between a material’s structure and its properties.

A rare-earth metal (R) which is stoichiometrically combined with a late transition metal (M) and possesses the CsCl-type (B2) crystal structure is designated as RM-B2. A number of these compounds have been shown to exhibit significant tensile ductility. This thesis describes a series of experiments to study the relation between crystal defects and the high ductility of YCu, an RM-B2 compound.
Intermetallic Bonding

The name *intermetallic* refers to the bonding between the constituent elements of a material system. Specifically, these substances are described to have “mixed bonding”, being partially covalent, partially ionic, and partially metallic. Descriptions of these different types of bonding may be found in chemistry textbooks such as those by Masterton and Hurley [1] or Hill et al. [2], or the introductory materials text of Callister [3]. Covalent bonding refers to a sharing of electrons between atoms within a material. The hydrogen molecule, H₂, is an example of a covalently bonded material. In the gaseous state, two electrons are shared equally between two H atoms, bonding the two atoms together. Each atom has thus achieved a filled 1s valence electron shell. Many other materials also exhibit this type of behavior. Covalent bonding is not limited to gaseous compounds and also occurs in condensed matter, typically when the difference in electronegativity between atoms, \( \Delta \chi \), is small or zero, and for atoms with a high individual electronegativity, \( \chi > 2 \). An example would be tetrahedrally bonded carbon (C) in the diamond structure.

Ionic bonding occurs between a metal atom and a non-metal atom. A common example would be sodium chloride, NaCl, ordinary table salt. The metal Na has a single valence electron, like the rest of the alkali family. The non-metal Cl has a valence shell of 7 electrons, similar to the rest of the halogen family. When the two atoms are brought into close proximity, the Na will give up its single s-shell electron, leaving a full 2p valence shell and taking a charged ionic state of +1. Correspondingly, Cl will accept the additional electron, filling its valence 3p shell to eight electrons and having an ionic charge of -1. The two charged ions will now be electrostatically drawn towards one another and strongly bonded. This bond is said to be highly localized, as the electron given up from the Na has a high probability of being found around the Cl nucleus. As with covalent bonding, many different molecules and compounds exhibit this type of bonding. The localization of the transferred electron(s) within an ionic bond is dependent upon the
electronegativity of the bonding atoms. A very common scale of electronegativity of atoms defines the *relative* affinity for electrons when compared with other elements, simply given in Pauling units. Using this scale, it is commonly accepted that $\Delta \chi \geq 1.7$ is used as the working definition of ionic bonding.

The third bonding type is metallic bonding. A solid with metallic bonding has large numbers of electrons that are not bound to any particular atom or location in the crystal. Rather, the crystal lattice of nuclei (and inner-shell electrons) is said to be surrounded by a “sea of electrons”, which may be described as completely non-localized. Metallic bonding is also described as non-directional. The nature of this bonding gives rise to many of the properties characteristic of metals, such as, most obviously, high electrical conductivity. Common metals such as iron (Fe) or aluminum (Al) exhibit this type of bonding.

Intermetallic bonding is a mixture of these three types of electron bonding behaviors, partially localized (ionic and/or covalent) and partially de-localized (metallic), between atoms that would exhibit metallic bonding in their pure elemental forms. To illustrate this description, Figure 1 shows van Arkel-Ketelaar diagram from Burdett [4], page 160. Along the bottom axis of the diagram are all elements plotted as a function of increasing electronegativity. The representative type of bonding for a binary compound is found by taking the horizontal axis to be the sum of the electronegativities of the constituent elements, and the vertical axis is the difference between the electronegativities.
Figure 1: Graphical representation of bonding type in a van Arkel-Ketelaar diagram
**Intermetallic Crystal Structures**

Pure Al and Fe both exhibit metallic bonding. A binary alloy of these two elements exhibits various crystal structures, dependent on the atomic composition. The Al-Fe system provides a good example of several fundamental intermetallic crystal structure properties and behaviors. Crystal structure information is summarized in the temperature-composition phase diagram from the ASM Handbook [5] seen in Figure 2.

![Phase diagram for the binary Fe-Al system](attachment:figure2.png)

**Figure 2: Phase diagram for the binary Fe-Al system (from ASM Handbook)**

At room temperature, several equilibrium phases exist across the composition gradient from 100 at.% Fe-0 at.% Al to 0 at.% Fe-100 at.% Al. Starting from the pure Fe side of the diagram, the addition of Al will create a solid solution of $\alpha$-Fe with the body-centered cubic (BCC) crystal structure. Within this phase, Fe and Al exhibit metallic bonding, a delocalization of the valence bonding electrons. Around the composition of 25 at.% Al, there exists the Fe$_3$Al
As indicated by the non-zero width of the Fe$_3$Al phase field on the diagram, Fe$_3$Al is stable within a compositional range around the stoichiometric ratio. Fe$_3$Al also exemplifies the phenomenon of atomic ordering. In various sources, this phenomenon is also referred to as long-range order, or the formation of a superlattice or superstructure. According to Pearson’s *Handbook of Intermetallics*, by Villars et al. [6], Fe$_3$Al can exist as either the ordered D0$_3$-type structure or the disordered W-type structure, depending on the processing history of the sample. The existence and formation of the ordered and disordered phases are well documented in the literature (e.g., Krymov [7], Oguma [8]), as are the effects on the properties of the compound. Fan et al. [9] studied the difference between the ordered and disordered Fe$_3$Al through the use of non-equilibrium preparation methods. The ordered D0$_3$-type structure is present at lower temperatures, while the B2 structure exists above the critical temperature of 550°C. This transformation from one to the other is also described by McKamey et al. [10].

With increasing Al content, four additional intermetallic phases occur within the binary equilibrium Fe-Al phase diagram; FeAl, FeAl$_2$, Fe$_2$Al$_5$ and FeAl$_3$. The Fe-Al binary phase diagram contains no fully stoichiometric intermetallic phases (also called *line compounds*) which exist in the single-phase form only at a specific atomic ratio.
Various naming conventions exist for describing intermetallic phases. A number of the more common schemes for several example intermetallic phases are given in Table 1.

**Table 1: Structure types for some common intermetallic compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Prototype</th>
<th>Strukturbericht</th>
<th>Pearson</th>
<th>Space Group</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlFe</td>
<td>CsCl</td>
<td>B2</td>
<td>cP2</td>
<td>Pm-3m</td>
<td>221</td>
</tr>
<tr>
<td>AlFe₃</td>
<td>AlFe₃</td>
<td>D₀₃</td>
<td>cF16</td>
<td>Fm-3m</td>
<td>225</td>
</tr>
<tr>
<td>Al₃Fe</td>
<td>Al₃Fe</td>
<td>--</td>
<td>mC102</td>
<td>C2/m</td>
<td>12</td>
</tr>
<tr>
<td>AlNi</td>
<td>CsCl</td>
<td>B2</td>
<td>cP2</td>
<td>Pm-3m</td>
<td>221</td>
</tr>
<tr>
<td>AlNi₃</td>
<td>AuCu₃</td>
<td>L₁₂</td>
<td>cP4</td>
<td>Pm-3m</td>
<td>221</td>
</tr>
<tr>
<td>AlTi</td>
<td>AuCu</td>
<td>L₁₀</td>
<td>tP2</td>
<td>P4/m/mmc</td>
<td>123</td>
</tr>
<tr>
<td>AlTi₃</td>
<td>Ni₃Sn</td>
<td>D₀₁₉</td>
<td>hP8</td>
<td>P6₃/m/mmc</td>
<td>194</td>
</tr>
<tr>
<td>AuTi</td>
<td>AuCd</td>
<td>B₁⁹</td>
<td>oP4</td>
<td>Pnma</td>
<td>51</td>
</tr>
<tr>
<td>BFe</td>
<td>BFe</td>
<td>B₂⁷</td>
<td>oP8</td>
<td>Pnma</td>
<td>62</td>
</tr>
<tr>
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<td>CFe₃</td>
<td>D₀₁₁</td>
<td>oP16</td>
<td>Pnma</td>
<td>62</td>
</tr>
<tr>
<td>CeNi</td>
<td>BCr</td>
<td>B₃₃</td>
<td>oC₈</td>
<td>Cmcm</td>
<td>63</td>
</tr>
<tr>
<td>CuZn</td>
<td>CsCl</td>
<td>B2</td>
<td>cP2</td>
<td>Pm-3m</td>
<td>221</td>
</tr>
<tr>
<td>NiTi</td>
<td>CsCl</td>
<td>B2</td>
<td>cP2</td>
<td>Pm-3m</td>
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</tr>
<tr>
<td>NiTi</td>
<td>NiTi</td>
<td>--</td>
<td>mP4</td>
<td>P₂₁/m</td>
<td>11</td>
</tr>
</tbody>
</table>

FeAl exhibits the CsCl-type (B2) structure, one of the more commonly studied ordered intermetallic structures. This arrangement resembles the body-centered cubic (BCC) structure, but rather than having random filling of the lattice sites, B2 exhibits long-range order. A cesium (Cs) atom is located at each of the 8 corner sites of the unit cell, considered to be 1/8th contained within the cell. In the body-centered position of the unit cell sits a chlorine (Cl) atom. Together, this gives a total of 2 atoms per unit cell. The basic B2 unit cell is shown in Figure 3 [11].
Figure 3: B2 unit cell

Since the positioning of the unit cell within a repeating lattice structure is arbitrary, the choice of atoms at the respective corner and center sites is also arbitrary. If the cell were shifted half of the lattice parameter in each of the x, y and z dimensions, the Cl atom would fill the corner sites, with the Cs atom at the center. Within the ordered cell, each Cs atom has 8 heteroatomic Cl nearest neighbors, and then 6 next nearest neighbor Cs atoms. As previously described, the nature of the intermetallic bond is partially directional and electron positions are localized when compared with dissociated metallic bonding. This can lead to higher bond strength between nearest neighbors, but can also frustrate dislocation slip. Example compounds with this ordered structure include CuZn (β-brass), AgZn, FeCo, AlCo, and β-NiAl.

Just as the ordered B2 structure shares lattice points with the BCC structure, the L1₂ (AuCu₃-type) ordering structure is based upon the FCC lattice. Atomic positions are represented by the eight corners of the cubic unit cell (for 8*1/8 atoms within the unit cell, 1 total), and the six faces of the cube (for 6 *1/2 atoms within the unit cell, 3 total). The L1₂ structure can occur for compounds with an A₃B atomic ratio. The ordering fills cube corner positions with one species, while the faces are populated by the other, as seen in Figure 4 [11].
In addition to relatively simple ordered structures such as B2, numerous intermetallics possess more complex structures. Examples include the previously mentioned Fe$_3$Al-type D0$_3$ structure, which is a more complex ordering of the BCC lattice, the lower symmetry FeB-type B27 structure, and the anisotropic CrB-type B33. These are but a few of the many possible binary compound structures. Ternary and more complex alloys often possess large, low symmetry unit cells containing scores or even hundreds of atoms per unit cell.
**Intermetallic Properties**

The existence of intermetallic phases in the majority of alloy systems makes them an obvious subject of scientific interest. The varied and often favorable properties of intermetallic compounds have led to significant engineering interest as well, and numerous studies are available in the literature. Indeed, publications such as *Journal of Alloys and Compounds* (ISSN: 0925-8388), contain a large fraction of articles related to structure, processing and properties, and *Intermetallics* (ISSN:0966-9795) is devoted entirely to the study of these materials.

Some of the greatest challenges in materials science in recent decades have come from aerospace applications. Airframes need to be both strong and lightweight to deliver the best performance. Turbine engine requirements are especially demanding; turbine blades require high-strength, creep-resistant alloys that can withstand high-temperature, corrosive environments for extended periods. Presently, the most often selected materials are nickel superalloys, consisting of directionally grown single crystal Ni with second- and even third-phase particles. The properties of intermetallic materials make them well suited for this particular application. Indeed, much study has gone into intermetallics for this application.

The directional nature of intermetallic bonding can create high bond strengths. Cottrell [12] finds the cohesive energy of Ni-Al to be 8.45eV, compared with the constituent metals having bond energies of 4.44eV for FCC Ni and 3.43eV for FCC Al. As a result, intermetallic compounds can possess high strengths and high melting temperatures. According to Okamoto [13], stoichiometric NiAl melts congruently at 1630°C. As would be inferred from the bond strength, this is higher than Ni, 1455°C and much higher than Al, 660°C.

Other less-common intermetallics are known to have even higher melting temperatures. Tantalum carbide (TaC) has a melting point near 3950°C, and hafnium carbide (HfC) is known to melt at about the same temperature. Since C is a non-metallic element, there is some question about whether carbides should be considered true intermetallics. Kaufman and Stepakoff [14]
and Deadmore [15], report that alloying the three elements together produces the highest melting
temperature material known, tantalum hafnium carbide (Ta₄HfC₅), which melts at 4215°C.

The high bond strength of intermetallics also leads to higher material strength. FeAl has
a yield strength of over 1000 MPa. Bowman et. al. [16] found the yield strength of
polycrystalline NiAl sample at room temperature to be about 350 MPa, depending on grain size.
The partially directional nature of intermetallic bonding also frequently leads to materials with
highly anisotropic properties. Courtney [17] p. 56 states that the anisotropy ratio, A, of a cubic
material can be found from the three independent elastic constants of the elastic stiffness tensor
Cₘₙ according to Equation 1

**Equation 1: Anisotropic ratio, expressed in terms of elastic stiffness
constants**

\[ A = \frac{(C_{11} - C_{12})}{2C_{44}} \]

Wasilewski [18], states that NiAl has an anisotropy ratio of \( A = 3.28 \). Payne and Desai
[19] offer a good summary of properties of some of the more common and heavily studied
intermetallic compounds. The review by Miracle [20] of the physical and mechanical properties
of NiAl has been cited hundreds of times.

The favorable mechanical properties of intermetallic compounds, including good high
temperature strength and stiffness, are particularly appealing for practical application because of
their relatively low densities. The work of Walston and Darolia from 1993 as summarized by
Stoloff and Sikka [21] compares various physical properties of stoichiometric NiAl, NiAl alloys,
and an advanced superalloy. The densities for each of these three are 5.9, 6.3 and 8.6
g/cm³ respectively. Hence, the specific properties, (specific strength, specific stiffness, etc.) for
intermetallic compounds are often superior to the alloys widely used today. Lower density
turbine blades of a similar design would be of lower weight, thus improving the overall efficiency of the turbine in operation.

Many studies have investigated the properties of various intermetallic compounds under diverse testing conditions, including elevated temperature and corrosive atmospheres. García-Alonso et al. [22] studied the corrosion resistance of Fe₃Al in a chloride solution, and found corrosion rates comparable to those of 316L stainless steel which is commonly used in corrosive applications. Klöwer et al. [23] stated that nickel aluminides at high temperatures showed “excellent resistance in air, in carburizing gases, and in chlorinating/oxidizing atmospheres, while its corrosion resistance in oxygen-deficient chlorinating gas atmospheres and in sulphidising atmospheres is poor”. Additions of zirconium to Ni₃Al were found to significantly alter the corrosion-resistant properties, favorably in some conditions and unfavorably in others, whereas chromium additions had little effect. Brill [24] states that Ni₃Al shows improvements over common commercial alloys in a number of challenging corrosive environments.

An important advancement in the understanding of intermetallic properties was the insight into the susceptibility to environmental embrittlement, first noted by Liu et al. [25]. FeAl samples tested in room air failed after only 1-2% elongation. However, samples tested in environments which minimize the presence of water vapor showed significant ductility, with a maximum value of 14% elongation recorded in dry oxygen. This result is startling due to the number of prior investigations which had reported the compound to be brittle. Liu et al. concluded that FeAl is actually intrinsically ductile, and a mechanism of the decomposition of water vapor to produce atomic hydrogen weakens the compound to the point of premature failure in most situations.
**Intermetallic Ductility**

The major impediment to much wider usage of intermetallics is their lack of ductility. In general, the inability to demonstrate even small amounts of plastic deformation makes intermetallics difficult to fabricate and prone to failure by fracture. Common methods of forming such as bending and swaging are impossible, thus cost to manufacture is increased. In many cases fracture is considered catastrophic failure and can have costly and even life-threatening consequences. As a result, designing with this inherent constraint of intermetallics is difficult or impossible for numerous applications.

Despite their brittle tendencies, intermetallics’ numerous favorable properties have led to intensive study in this field. Numerous ductilizing strategies have been investigated and found to improve ductility in varying amounts. A few intermetallics have already found niche applications, but most intermetallics would require major breakthroughs in ductility improvement to have much utility in engineering designs.

In general, materials with simpler, higher-symmetry crystal structures are more likely to exhibit ductility. This can be generally associated with the von Mises criterion for yielding [26], which is summarized nicely by Atkinson [27] as follows. “An individual crystal grain in a polycrystalline aggregate undergoing deformation can only sustain an arbitrary deformation by dislocation glide and thus conform to the shape changes of its neighbors if it has five independent slip systems available.” The multiplicity of high-symmetry structures tends to lead to a greater number of independent slip systems available for dislocation motion.

Due to this tendency, intermetallic compounds with high symmetry systems such as B2 and L12 have been most intensely studied. Ductility is most commonly achieved by dislocation glide. Russell [28] provides a good overview of the dislocation behavior relevant to ductility in these structures. NiAl, a compound representative of the B2 structure, is composed of Al and Ni, both of which take the FCC structure in their elemental form. Due to the difference in lattice
positions between B2 and FCC, $\frac{1}{2} <10-1> \{111\}$ slip along the face diagonal, which is dominant in FCC, is geometrically impossible in B2. The similarity between B2 and BCC structures (B2 is composed of the same lattice positions as BCC, with superlattice atomic ordering) would suggest that BCC type slip systems of $\frac{1}{2} <-111>\{110\}$, $\frac{1}{2} <-111>\{211\}$, or $\frac{1}{2} <-111>\{321\}$ may be active in B2. However, this is not usually the case due to atomic ordering energy. If B2 NiAl were to slip along the $<111>$ direction, Ni atoms would be next to similar Ni atoms, and Al would be next to Al. This is a considerably higher energy state for the lattice, and is thus unlikely to occur. This type of disruption within the lattice is termed an *anti-phase boundary* (APB). The mechanism by which the crystal would be returned to the lower energy state would be the propagation of a second dislocation traveling through the crystal within the same crystallographic slip system. This combination of two dislocations gliding together through the crystal is termed a “superdislocation”. Two dislocations of the same orientation will tend to repel one another due to lattice strain energy; therefore, the pair of dislocations can lower crystal energy by maintaining a wide separation from one another. However, the APB region lying within the superdislocation has an energy term associated with it as well, and this is minimized by reducing the distance between the two dislocations. As a result, intermetallic structures will tend to minimize the sum of the lattice strain energy and APB energy terms. Systems in which APB energy is low tend to show larger superdislocation separation, whereas systems with high APB energy show relatively small distances between dislocations.

Bayer et al. [29] provide an experimental study of dislocation deformation mechanisms observed to be active in NiAl through testing of bicrystals at various temperatures. The orientation of the crystals was such that $<110>$ slip would be the sole slip direction. When tested at temperatures above the brittle-to-ductile (BTD) transition temperature, $\{110\} <110>$ slip dominates, and at higher temperatures the authors describe a transition from $<110>$ slip to $<100>$ climb.
Plastic deformation due to dislocation motion is not the only mechanism known to operate in intermetallic compounds. A well-studied example of an alternative deformation mode would be the shape-memory effect observed in NiTi, also known as nitinol. These Shape-Memory Alloys (SMA) can accommodate deformation due to stress-induced martensitic phase transformation. The crystal structures of NiTi undeformed, as well as after straining, have been the subject of numerous studies, as well as theoretical first principles calculations such as those by Huang [30], and more recently using in-situ diffraction by Bourke [31] and Swallowe [32].

Just as deformation of intermetallics can occur through various mechanisms, so too are there numerous possibilities for failure. In tension, intergranular fracture, transgranular fracture, and cleavage have all been observed to operate in various systems. Alternatively, no driving force for crack opening or crack propagation exists in compression, and these failure modes are replaced with buckling or microcrack coalescence. As a result of this difference in dominant failure mechanisms, intermetallics with limited tensile ductility can sometimes show substantially greater amounts of plastic deformation under compression.

During deformation, the various mechanisms of plasticity are energetically competitive with the mechanisms of failure. This has led to studies focusing on different aspects of tensile failure. The commonly observed preference in intermetallics for intergranular crack propagation (as opposed to plastic deformation) is generally attributed to weakness of grain boundaries. Investigations by groups such as George, et. al. [33] and Liu [34] describe studies of grain boundary failure, as well as attempts towards mitigations such as with boron doping and modified-environment testing.

While some intermetallics exist only as fully-stoichiometric phases, or line compounds, others show stability of the single phase over a range of compositions around exact atomic ratios, including Fe$_3$Al, and Co$_3$Ti. This second example is interesting because Takasugi et al. [35]
showed that while Co–25 at% Ti exhibits essentially zero ductility, Co–20 at% Ti maintains the L1_2 structure and elongates to 58%.

Although improving ductility in intermetallics by shifting from stoichiometric to non-stoichiometric compositions sounds appealing from an engineering perspective, slight changes in composition tend to affect other properties of intermetallics in undesirable ways. The yield strength of ordered Fe-50 at% Al is around 1000 MPa, but Fe-45 at% Al has a yield strength of only 250 MPa. This is a heavy detriment considering that the negligible ductility for the equiatomic alloy is increased to only around 2% elongation for the Fe-rich alloy. Additionally, deviations in chemical composition also decrease high-temperature performance for most compounds by adding defects that accelerate diffusion. While the ordering energy of the B2 structure is sufficiently high that diffusion-related phenomena are energetically unfavorable, this advantage is lost in off-stoichiometric compounds.

Numerous studies have examined the effects of other alloying additions. Payne and Desai [19] summarize work on additions to TiAl and Ni_3Al and NiAl so succinctly that it is reprinted here at some length.

“Sikka has provided an excellent review of the effects of alloying additions on various intermetallics. Many alloying additions have been examined for γ-TiAl. Niobium and vanadium are two of the most common additions. Niobium increases the oxidation resistance and enhances the creep resistance of the alloy. While 1-3 at.% vanadium additions generally decrease the oxidation resistance, they increase the ductility of duplex alloys. Additions of >0.5 at.% boron improve the strength and workability of the alloy while refining the grain size. In fine-grained material, the addition of molybdenum improves the strength and ductility while increasing the oxidation resistance. Tungsten additions greatly improve the oxidation resistance. The addition of tantalum improves the oxidation and creep resistance, but also increases susceptibility to hot cracking. Additions of 0.5-1 at.% silicon have similar effects, but while silicon increases the
fluidity of the material, the susceptibility to hot cracking is increased. Carbon additions have been found to increase creep resistance, but reduce ductility. Manganese additions of 1-3 at.% increase the ductility of the duplex alloy. Chromium additions of 1-3 at.% also increase the ductility of the duplex alloy. Additions of chromium greater than 2 at.% enhance the workability and superplasticity of TiAl alloys. At levels of greater than 8 at.%, chromium additions greatly improve the oxidation resistance of the material.”

“Several alloying additions to Ni$_3$Al and NiAl have been examined. Some of the most effective additions for Ni$_3$Al are Cr, Zr, Hf, Mo and B. Boron is known to ductilize Ni$_3$Al, reduce moisture-induced hydrogen embrittlement and enhance grain boundary cohesive strength. Chromium additions reduce oxygen embrittlement at high temperatures. Zirconium is a solid solution strengthener of Ni$_3$Al. It improves castability by reducing macroporosity and shrinkage through the formation of a low-melting-point eutectic. The oxidation resistance of zirconium doped Ni$_3$Al is also greatly improved by increased scale adherence. The addition of hafnium increases high temperature strength and prevents mold-casting interactions between zirconium additions in the Ni$_3$Al and the ceramic shell mold. Molybdenum additions have been found to improve strength.”

“Microalloying NiAl with 0.1 at.% zirconium has been found to decrease ductility, but greatly improve both the strength and the DBTT. Microalloying with molybdenum, lanthanum, rhenium and hafnium has similar effects. Macroalloying with Mn, Cu, Fe, Co, Ru, Rh, Pd, Os, Ir, or Pt could have a beneficial effect as all these elements are soluble in NiAl. V, Re, Cr, Mo and W are slightly soluble and may also provide some benefit. Se, Y, Ti, La, Zr, Hf, Nb, and Ta form ternary phases, and may help strengthen NiAl, but will probably lower the ductility.”

The effect on properties of intermetallics due to testing in different environments is described by Liu et al. [36]. The authors describe earlier results indicating that while FeAl had been considered intrinsically brittle, “the low tensile ductility and cleavage fracture were caused
mainly by environmental embrittlement involving moisture in air”. When tested in air at room
temperature, FeAl suffered brittle cleavage fracture after only 2.2% tensile elongation. Tested in
a conventional vacuum, the same alloy showed elongation of around 8%. Finally, when tested in
an environment of dry oxygen, elongations as high as 18% were achieved. Similar effects of
environmental embrittlement have been shown to occur in single-crystal FeAl by Lynch et al.
[37], and Nathal and Liu [38].

As previously described, the properties of some intermetallics are known to be highly
anisotropic. In the collective work edited by Stoloff and Sikka [21], Noebe et al. in Chapter 7
summarize results showing that single-crystal specimens of NiAl of the “hard” [100] orientation
have a room temperature yield stress of about 1400 MPa. “Soft” orientations (non-[100]) have
significantly lower values; [123] single crystals yield at around 600 MPa, and [110]- and [111]-
oriented crystals yield below 200 MPa. Several studies have examined this great variation in
properties, and the work of Skrotzki et al. [39] and others examines the possibility of creating
favorable polycrystalline performance through control of texture, or preferred orientation of
grains within the aggregate.

Khadkikar et al. [40] examined the preferred orientation of powder-extruded and cast
extruded nickel and iron aluminides. NiAl showed a [111] texture for both types of samples, as
did powder-extruded FeAl, all of which remained unchanged with annealing. Cast and extruded
FeAl showed a [110] texture, which was replaced by a [211] texture upon annealing. Compared
with the previously described B2 compounds, the L12 Ni3Al showed only a minor preference
towards [111] texture as-extruded, which became a nearly random preferred orientation after
annealing.

High-temperature forging experiments were conducted by Zhao et al. [41], along with
subsequent annealing and recrystallization. Significant peak intensity changes were recorded in
x-ray spectra, which indicate changes in the preferred orientation. TEM was used to collect
statistical information about dislocation types within the deformed specimens. From these observations, the authors concluded that \{110\}<111> and \{112\}<111> slip systems were active at low temperatures, while \{001\}<100> and \{011\}<100> slip systems were dominant at high temperatures.

The work of Ahzi [42] examines active slip systems and resulting texture development of NiAl due to tensile and compressive loading, and compares these to experimental results from compressive loading at elevated temperatures, where plastic deformation is known to occur. From numerous earlier works, Ahzi concludes that “plasticity in NiAl polycrystals, at room or elevated temperature (up to 800°C), is mainly due to the three independent slip systems formed by the sets \{110\} <001> and \{100\} <001>. Contributions to plasticity by slip in the <110> direction seems to be very limited or totally absent.”

Ahzi concludes that under uniaxial loading conditions, while \{110\} <001> and \{110\} <110> slip systems contribute to plastic strain, neither contribute to lattice rotation because each of these slip systems is comprised of pairs of orthogonal slip systems with opposing resolved shear stress and shear rates. Additionally, since each pair has antisymmetric Schmid tensors of opposite signs, the result is no plastic spin (crystal reorientation), which matches the macroscopic reorientation behavior due to the conditions of uniaxial loading. Plastic spin effects on texture are further investigated in the work of Paulun and Pecherski [43], as well as Pranti et al. [44].

With projection modeling developed earlier by Parks and Ahzi [45], pole figures were developed to show calculated preferred orientation within polycrystalline NiAl under both tensile and compressive loading. Ahzi points out that, as previously described by Khadkikar et al. [40], if extrusion takes place below 1100 K, <110> fiber texture develops, but if extrusion is done above 1300 K, the result is dominated by recrystallization, and the result is a <111> fiber texture.
The effect of polycrystalline texture on mechanical properties is well documented in metal alloys, and put into application in numerous engineering situations. Skrotzki et al. [39] studied the effect of initial texture on the deformation of NiAl samples in compression. Cast NiAl was extruded at elevated temperatures (1100°C and 1200°C), and samples with preferred orientations of <100>, <110> and <111> were cut from the extruded rods. However, the authors overlook the previous work by Ahzi, which points out that extrusion at this temperature will result in a recrystallization texture. While the authors do acknowledge that the microstructure is recrystallized, it is unclear whether this is the type of texture desired. It is possible that as samples were cut from the extruded bars to choose “certain preferred orientations… with respect to the compression axis”, the underlying type of texture was considered irrelevant. Additionally, the intensity of preferred orientation was not particularly strong, with maximum values of 3.9, 2.4 and 2.7 times random for the three orientation samples. Typically, a “highly textured” sample could have a distribution maximum of 10 or more times random.

The samples were compressed under gas confining pressure to mitigate microcrack formation and encourage activation of hard secondary slip systems. Results exhibited a significant degree of plastic anisotropy, with the <100>-textured samples behaving much harder than the <110>- and <111>-textured samples. The authors conclude that “strongly plastic anisotropic crystals do not deform homogeneously as required by the Taylor theory, at least at the beginning of deformation.” It is likely that slip occurs within crystallites whose orientation is favorable for primary slip. As these crystallites would be less frequent in hard oriented <100>-textured samples, the flow stress tends to rise much faster than in the soft oriented samples. It is likely that if, as previously described, the samples had started with stronger initial texture, these trends would have been more pronounced.
**RMB2 studies**

In the search for improved ductility in intermetallics, a recent finding from an Ames Laboratory group has opened a new area of research. Gschneidner et al. [46] reported on an entire family of compounds possessing the B2 structure which exhibit room temperature tensile ductility. These materials do not require third-element additions, off-stoichiometric chemistry, disordering, or elaborate environmental testing conditions to enhance ductility.

Studies in the initial work focused on YAg, YCu, and DyCu, although other compounds were reported to show preliminary signs of ductility. Grain sizes were reported to be on the order of 0.1-0.3µm, as determined from TEM. Specimens received a relatively long, hot annealing treatment, 60 hrs at 1075 K. YAg tensile test specimens were reported to exceed 20% elongation when tested, while YCu showed only 6 to 11% elongation. The yield strength of polycrystalline YCu was reported to be between 175 and 300 MPa. One possibility suggested for the lower ductility observed in YCu was a stress-induced transformation to the lower symmetry B27 structure, which has been described by Ritter et al. [47] previously to occur at low temperatures.

Fracture toughness testing reported $K_{IC}$ values to be relatively high compared with other intermetallic compounds. Single-crystal specimens of YCu were tested with tension along the [142] axis, with the yield strength reported to be 45 MPa. Slip line traces revealed the active slip systems to be $\{100\}<010>$ and $\{101\}<010>$, which matches previous findings for NiAl. Another single crystal was tested with the compression axis along the $<001>$ direction to try to promote $<111>$ slip, after 300 MPa the sample showed no slip and began deforming by either a twinning or kink-band process. It was suggested that the rare-earth element may inhibit hydrogen embrittlement, a known cause of failure in other intermetallics when tested in tension.

Single crystal specimens of YAg were tensile tested with the [110] direction parallel to the tensile axis. Slip lines showed the active slip system to be $\{110\}<010>$, with a critical
resolved shear stress (CRSS) of 13 MPa. Some evidence of secondary slip on \{100\} \langle011\> was also reported. A specimen with the \langle001\> parallel to the tensile axis did not show any slip activity, and began to fracture at 300 MPa. TEM examination showed dislocations to be predominantly of \langle111\> type. This was noted as surprising because slip line traces showed no indication of \langle111\>-type slip, and the high ordering and APB energies of the compound suggest that \langle111\> slip would be unlikely. Dislocation decomposition was listed as a possible explanation for these observations. Results were reported for shear acoustic measurements and \textit{ab initio} calculations conducted to determine elastic constants for YAg and YCu. Calculations of APB energies and unstable stacking fault energies tended to agree with single-crystal slip findings.

The initial work published in 2003 suggests some possible mechanisms responsible for deformation and ductility, and numerous studies have taken place since that time to study the underlying causes for this behavior. Russell et al. [48] further examined the mechanical properties of single-crystal YAg. Findings regarding slip lines were similar to that of earlier work. The $\tau_{\text{CRSS}}$ of the \{110\} \langle010\> slip system was reported to be 13 MPa.

Similar studies on YCu were reported by Russell et al. [49]. The CRSS values for two slip systems were given to be about 17 MPa for \{100\}\langle010\> and 18 MPa for \{110\} \langle010\>. Single crystals compressed parallel to the [100] direction (such that there exists no resolved shear stress on either \{100\} \langle010\> or the \{110\} \langle010\> slip systems) showed yielding at approximately 300 MPa. While not given in the paper, from the $\sigma$-$\varepsilon$ plots the Young’s modulus appears to be about 16 and 19 GPa for the two samples tested in this “hard” orientation. Results of discontinuous yielding and acoustic emission were attributed to the possibility of twinning, kink-band formation, or stress-induced phase transformation. Differential scanning calorimetry (DSC) data for a compressed sample showed an exothermic event at 455 K, which may correspond to the transformation from the B27 phase back to the B2 phase, known to be stable at
higher temperatures. DSC results from one untested and one tensile tested specimen showed no exothermic events. An SEM surface micrograph was presented to further support the conclusion of phase transformation.

Zhang et al. [50] studied the fracture toughness in polycrystalline samples of YCu, DyCu, and YAg by means of standard $K_{IC}$ and $J_{IC}$ testing. The results were found to be 12.0 MPa·m$^{0.5}$ for YCu, 25.5 MPa·m$^{0.5}$ for DyCu, and 19.1 MPa·m$^{0.5}$ for YAg. These values are relatively high compared with other stoichiometric B2 intermetallics (typically below 6 MPa·m$^{0.5}$), and several possible explanations were suggested. The operation of multiple slip systems discussed in previous work was highlighted. Fine grain size (about 0.2µm) was brought forth as effecting ductility due to minimizing dislocation pile-up stress. Specimen fracture surfaces displayed no indication of intergranular fracture. The rare earth counteraction of environmental embrittlement was also described.

The active slip systems in DyCu are further described by Cao et al. [51]. Single-crystal results support earlier work, and the CRSS of the \{110\} <001> slip system is reported to be 18 MPa. The \{100\} <010> system seen previously in YAg and YCu was not observed. TEM studies revealed numerous <100> and <111> type dislocations, consistent with slip line trace analysis. The more energetically difficult <111> slip was suggested to be possible through a combination of $\frac{1}{2}$ <111> + APB + $\frac{1}{2}$ <111> superdislocation pairs. This was not directly observed, although the relatively high APB energy may render these features too small to be resolved with the TEM magnifications employed. The fact that a crystal oriented with the [001] along the compression axis, which would have a favorable Schmid factor for \{011\} <111> slip, showed limited elongation remained an open question in this research.

The substitution of Ni for Dy in DyCu was studied by Xie et al. [52]. Diffraction patterns showed that Dy$_{50}$Cu$_{45}$Ni$_{5}$ was found to be single-phase B2, while Dy$_{50}$Cu$_{40}$Ni$_{10}$ contained some B27 phase. The orientation relationship between the B2 and B27 phases was determined by
TEM observations and selected area electron diffraction (SAED). From lattice parameter shifts, the solubility limit of Ni in the B2 DyCu phase was estimated to be about 7 at.%. Lattice parameters for the B27 phase were reported, similar to previous literature. Mechanical testing revealed ~4% elongation for both Dy$_{50}$Cu$_{50}$ and Dy$_{50}$Cu$_{45}$Ni$_{5}$, with the Ni-substituted alloy exhibiting a slight solid solution strengthening effect. Dislocations of <001> and <111> type were reported from TEM observations. Dy$_{50}$Cu$_{40}$Ni$_{10}$ showed much higher strength, attributed to second phase hardening, but essentially no plastic deformation.

Investigations have also been made into other properties of RM B2 intermetallics. Stumphy et al. [53] reported on the oxidation resistance of rare-earth magnesium intermetallic compounds. Results included oxidation products and reaction kinetics, compared with the pure rare earth metal component counterparts. Morris et al. [54] studied the bulk and defect properties of several rare earth intermetallics by means of ab initio calculations. Calculated properties tended to agree with experimental results, and included lattice parameters, elastic constants, phase stability, and anti-phase boundary energies. Chen and Biner [55] have reported on the stability of perfect dislocations, interaction energy of kink pairs, cross-slip behavior of screw dislocations and the instability of pinned dislocations in YCu, YAg and YZn. Xie et al. [56] made excellent use of high resolution TEM to examine dislocation behavior in YAg, and observed dissociation of superlattice dislocations into two superpartials bound to either a stacking fault or an antiphase boundary.
Studies of YCu

Prior to the recent experiments on the ductility with this family of rare earth intermetallics, many of these compounds had been the subject of previous study. In particular, YCu had been studied from a crystallographic and structural perspective, before the ductility of the material was discovered.

The work of Chakrabarti and Laughlin [57] gives a thorough description of the Cu-Y phase diagram and the numerous compounds found therein, building on earlier and less complete work by Domagala et al. [58], as well as the unpublished work of Beaudry. Chakrabarti and Laughlin make specific reference to the fact that rare-earth Y is very reactive and may contain contamination by hydrogen and/or oxygen. Stoichiometric CuY is identified to have a cubic structure with a lattice parameter of 3.48 Å, and remains stable up to the congruent melting temperature of 935 ± 15°C. The two neighboring eutectic points are given as 67 at.% Y and 760 ± 15°C between CuY and Y on the Y-rich side, and 42 at.% Y and 830 ± 15 °C between Cu₂Y and CuY on the Cu-rich side. The phase diagram of Cu-Y is shown in Figure 5.
Figure 5: The Cu-Y phase diagram according to the work of Chakrabarti and Laughlin
Similar to other rare earth metals, much of the research into YCu has been focused on magnetic structure and properties. YCu is described in various literature references to be Pauli paramagnetic, unlike copper compounds with other lanthanides. Walline and Wallace [59] identify YCu as Pauli paramagnetic, along with ascribing the CsCl structure, in agreement with earlier work of Chao [60], and Gschneidner [61]. However, Walline and Wallace focus their studies on other lanthanide—copper compounds with more complex magnetic structures.

Hohnke and Parthé [62] studied other rare earth compounds, and in particular those with the FeB-type (B27) first described by Bjurström and Arnfelt [63], and CrB-type (B33) structures. Cable et al. [64] studied the magnetic ordering of rare-earth intermetallic compounds including TbCu. Pierre [65] studied the specific heat of YCu at low temperatures. Von Meerwell et al. [66] investigated nuclear relaxation of magnetic materials, including a sample of YCu received from Pierre. Belakhovsky et al. [67] used calculations to examine the electronic structure of YCu and YZn. Results give the density of states at the Fermi level for YCu to be 1.9 +/- 0.2 electrons / eV unit cell which showed close agreement with the experimental value of 1.32 electrons / eV unit cell obtained from specific heat measurements.

Balster et al. [68] first discovered that YCu (along with several other similar CsCl-type compounds) undergoes a martensitic crystal structure transformation upon cooling. Data from electrical resistivity measurements as a function of temperature for a polycrystalline sample show an irregularity at about 150K with a very large hysteresis. In order to recover the CsCl structure with the same resistivity values at room temperature as those before cooling, the sample required heating above 500°C. The authors attempted to use x-ray reflection to identify the new phase, but in the first attempt no new peaks were observed. They concluded, “The polishing before cooling obviously prevented the phase transition within the surface layer accessible to X-rays. This sensitivity of the phase transition to structural defects and distortions is consistent with
the observed large hysteresis loop”. While the authors did not ascribe a structure to the new phase, they specifically excluded FeB or CrB.

Kadomatsu et al. [69] further investigated the structural transformation of YCu at low temperature through studies of the electrical resistivity, thermal expansion, X-ray diffraction, pressure effects on the transition temperature, and compositional substitution of other transition metals for Cu. Samples were prepared by means of arc melting and annealing at 800°C for one week. Electrical resistivity results confirmed the earlier findings by Balster et al. [68], including the existence of a large hysteresis width of ~400K, given by $\Delta T = T_H - T_L$, where $T_H$ represents the transition temperature to the high temperature phase, and $T_L$ is the transition temperature to the low temperature phase.

When attempting to examine the transformed structure, an annealed sample powdered at room temperature was cooled to liquid helium temperature and its X-ray pattern was taken at room temperature. The sample pattern was no different than the initial CsCl pattern. This was attributed to the fact that the strain from filing at room temperature suppressed the transformation. A bulk sample was cooled to liquid nitrogen temperature, and the pattern taken again at room temperature showed little change. Surface strain in the transformation was considered to be the reason for no observed change in this case. In an attempt to observe “the inner part of the sample grain which had not suffered from the surface strain in transformation”, the bulk sample was cooled to liquid helium temperature, and then filed at room temperature. The pattern compares quite closely with that of NdCu, which is known to be of the orthorhombic FeB structure. Similar results were obtained for a sample cooled to and filed at liquid nitrogen temperature. From this, it is concluded that the low temperature phase is likely to be of the FeB type.

Since it was concluded that the shear stress due to filing acted to suppress the transformation, the authors investigated the effect of uniform hydrostatic pressure on several
samples cooled through the transition temperature. With increasing pressure, $T_L$ was shown to decrease, vanishing in the samples tested above 4 kbar. Using the Clausius-Clapeyron equation applicable to the first-order transformation and the change in volume from linear thermal expansion measurements, the latent heat was found to be 0.89 cal /g. Compositional substitution was used to further support the conclusion of the transformed FeB structure. From an electronic perspective, Kadomatsu et al. state “the cubic-orthorhombic transition is also expected to arise from the d band Jahn-Teller effect… the d band widening effect is dominant over the s-d transfer effect.” Finally, the authors describe the transition as “accompanied by a very large thermal hysteresis. This indicates that large driving forces, which are equal to the interface and elastic deformation energies in the transition process, are necessary”.

The most recent studies of YCu transformation have been done by Ibarra et al. [70-74]. These papers focus mainly on the magnetic structure of the compound. In a short paper written with Ritter et al. [47], the low temperature transformed structure was described to be FeB-type. A neutron diffraction thermograph demonstrates the onset of the second phase, but does not offer any insight into quantitative analysis of phase fractions transformed. The lattice parameters of the B27 phase are given, and compared with prior work on similar compounds exhibiting transformation. The authors make note that the transformation is observed to take place in bulk samples cooled below the transformation temperature, but not for crushed or filed powders. It is concluded that “the internal stress induced in the sample by the crushing or filing of the bulk sample hinders the martensitic transformation”.

While limited research has been conducted regarding mechanical properties of YCu, Ibarra et al. [74] does specifically state “The samples were so malleable that it was necessary to file them in order to obtain powder”. However, none of the authors appear to have followed up on this observation to any extent.
**Diffraction**

Diffraction has been a powerful investigation tool since the influential work of von Laue in 1912 demonstrated that x-rays could be used to study the periodicity of a crystal lattice. Crystallographers have uncovered detailed descriptions of countless compounds through the use of diffraction, including such famous examples as the work of Watson and Crick [75], and Franklin and Gosling [76] into the double-helix structure of DNA. A vast array of sources exists describing every aspect of diffraction, from the history of development to the fundamentals of the underlying principles to the intricate detail of specific methods of analysis. Some good general references include: Cullity [77], Pecharsky and Zavalij [78] as a significant portion of work devoted to practical application, particularly with computer-assisted full-pattern refinement methods, Warren [79], Cowley [80], and Guinebretiere [81].

Even the earliest works regarding diffraction described the phenomenon for different types of radiation, including x-rays, electrons, and neutrons. While the fundamentals are similar and previous references do touch on multiple forms of radiation, with advancing technology, these fields have become respectively more complex, requiring individual coverage. Flutz and Howe [82] offer good coverage of the topics regarding electron diffraction along with their coverage of TEM. Neutron diffraction specifically has been addressed in an historical perspective by Bacon [83], and in theory and practice by Bacon [84] and the collection edited by Dachs [85].

The power of the technique of diffraction was greatly extended in the 1930’s with the advent of phase identification from powder diffraction data based on works of Hanawalt, Rinn, and Frevel. Since that time, a huge database of crystal structure information has been collected and maintained as the Powder Diffraction File (maintained by the International Center for Diffraction Data).
Another major advancement was the result of the work by Rietveld [86-88], eventually leading to the technique which now bears the author’s name. The Rietveld method for full profile powder diffraction refinement [89] employs the least-squares approach to minimize the difference between a calculated diffraction pattern based on physical parameters and collected diffraction data. By refining the values of the calculated model through cycles of small steps, the parameters are found to have physical significance in representing the investigated structure. This method has been greatly extended with the development of modern computer processing power, making calculations of very accurate refinements possible in seconds or minutes.

Diffraction experiments are often analyzed based on the assumption that interaction of the incident and diffracted beams within the crystal are negligible. This is the “kinematic theory of diffraction”, and is well applied in most engineering situations. Even before the initial work of von Laue and Bragg, theory about scattering and diffraction from crystal lattices included treatments for cases where the kinematic theory is not applicable. The resulting effect on experimental data is termed “extinction”. Cullity [77] gives the definition of extinction as “the decrease in the integrated intensity of the diffracted beam as the crystal becomes more nearly perfect”. Chandrasekhar [90] describes extinction to be “the screening of the lower layers of the crystal at the reflecting angle”. Pecharsky and Zavalij [78] state, “Primary extinction is caused by back-reflection of the scattered wave into the crystal, and it decreases the measured scattered intensity”.

The first general treatment of this condition for practical application was put forth by Zachariasen [91]. Since that time, others have expanded the theory to include various additional theoretical cases that more closely approximate real experimental conditions. Notably, the work of Sabine [92] is the foundation of the extinction treatment used in the General Structure Analysis System (GSAS) software package. Experimental work with extinction and treatment thereof has been done by Gomez-Gasga [93] for textured aluminum samples, and more recently
by Tomov [94] in electrodeposited silver. The dynamical theory of diffraction has been expanded and described in great detail by Authier et al. [95, 96]. Through all of these resources, with theoretical treatment for a large number of cases, a specific description of the degree of lattice coherency necessary to transition from kinematic to dynamical diffraction has yet to be found within literature.

The Rietveld method of full profile refinement is particularly well suited to work with another more recent advancement in diffraction techniques, namely the use of pulsed source neutron radiation. From Bragg’s Law, the condition for diffraction is satisfied when a particular wavelength is incident upon crystallographic planes from a particular angle. A very common approach then is to vary the angle of incidence. High voltage x-ray excitation used in desktop scale X-ray diffraction units is inherently monochromatic (with slight physical considerations) due to the nature of x-ray sources. By modifying the angle of the source and the detector, entire profiles can be quickly and easily collected. Neutron reactor sources are also monochromatic, and instruments based on angular modulation have been used very successfully. Conversely, spallation neutron sources create a "white" beam of radiation at various energies. A linear particle accelerator (linac) can accelerate protons to appreciable fractions of the speed of light. Pulses are then compressed and directed towards a heavy metal target such as tungsten or mercury. When a high-energy proton strikes the target, the atomic structure of the metal atoms is ripped apart, releasing neutrons of various energies through the process of spallation. About 20 neutrons are emitted for every incident proton. Through moderation, the range of neutron energies can be tailored for use with a wide variety of experiments.

While x-rays interfere with the electron cloud, and thus show an increasing interaction with increasing atomic number, neutrons interact with atomic nuclei, and the scattering does not show periodic trends. Different isotopes of the same atom often exhibit vastly different neutron behaviors, and this can be both an advantage and a detriment to neutron diffraction. The
scattering cross-section of hydrogen makes water a suitable choice for moderation. With water at about 290 K, the resulting Maxwell-Boltzman distribution of neutrons of energies around 0.025 eV (v = 2.2 km/s) are termed thermal neutrons. This gives neutrons with wavelengths on the order of a few Ångstroms, which are convenient for studying condensed matter crystal structures. The topic of thermal neutron scattering is covered in detail by Squires [97].

In contrast to the angular modulation used with monochromatic x-rays, a white beam of neutrons requires a different measurement technique. Given the following relationships

\[
E = \frac{hc}{\lambda} = \frac{1}{2}mv^2
\]
\[
v = \frac{d}{t}
\]

there exists a direct relationship between the energy (or wavelength) of a neutron and the time it takes to travel a given distance. By measuring the time it takes for a neutron to travel from the moderator source to the detector, a measurement of the wavelength of the neutron is accomplished. Thus, neutrons of various energies within the white beam represent various wavelengths all traveling together within a single pulse. With this Time Of Flight (TOF) technique, the sample and detector geometry remain stationary, and the entire diffraction profile is collected. Due to this relationship TOF data can be represented as a function of time (µsec), or d-spacing (Å). A much more complete description of the TOF technique can be found in Reichelt and Rodgers [98] and Schwartz [99].

A software implementation of the Rietveld method of full profile refinement specifically created to be used with TOF data is the GSAS as described by Larson and von Dreele [100].
This package is based on the theoretical and experimental work of many different sources, which are cited at length in the GSAS manual provided with the package.

X-ray diffraction can be done on a desktop scale, but the nature of linear accelerator spallation sources means that TOF neutron diffraction is feasible only at large user facilities. A number of such engineering instruments are available throughout the world, including ENGIN-X at ISIS in Oxfordshire, England [101], SMARTS at LANSCE in New Mexico, USA [31], SAFE at J-PRAC in Tokai, Japan [102] (augmenting the earlier generation RESA at JAERI), VULCAN at SNS in Tennessee, USA [103], and likely a similar instrument at European Spallation Source still in planning stages. A brief discussion of current instruments, with a focus on the ESS, is given by Argyriou and Bordallo [104].

The Spectrometer for Materials Research at Temperature and Stress (SMARTS) is a neutron diffractometer optimized for the study of engineering. A T-zero chopper and a path length of ~31m deliver high time-of-flight resolution (about 0.4%). The inside of the SMARTS cave, along with a schematic depiction of the instrument are shown in Figure 6 and Figure 7.
Figure 6: View of the inside of the SMARTS cave

Figure 7: Schematic representation of the diffraction geometry of SMARTS
For in-situ uniaxial tension/compression testing, a load frame is positioned at 45° from the incident neutron beam. Two separate banks of $^3$He detector tubes are situated at -90° and +90° from the beam, which correspond to scattering vectors parallel and perpendicular to the axial direction of the sample. The banks are referred to as +90° / Bank 1 / perpendicular / transverse, and as -90° / Bank 2 / parallel / axial, respectively. Each bank is composed of 192 independent detector tubes in three rows covering about 15° in real space. The hardware and software of the data acquisition system (DAQ) used throughout LANSCE are described in further detail by Nelson et al. [105]. Data from banks of tubes are “binned” together to represent two single point detectors through the use of calibration sample measurements and computer software.

The Instron load frame is controlled through a panel located outside the cave. The panel can either be controlled manually, or through scripting via connection with a desktop computer. Sample data are collected using a 250 kN load cell, along with a two-prong type extensometer with a gauge length of 25mm. Strain gauges may also be applied directly to the surface of specimens. Ancillary equipment is shielded from both incident and diffracted neutrons with gadolinium oxide, either in the form of curtains, placards, or a mixed slurry applied as a paint. The entire load frame is mounted directly on a translator table which can move in approximately 100 micrometer intervals in x, y, and z, as well as rotating within the horizontal plane. For compression samples, a minimum stress of about 5MPa is required to hold the specimen accurately within the path of the beam.

Mechanical testing is accomplished with feedback control of either displacement or load, referred to as position control or load control, depending on specific material properties.

When displacement is held constant, samples may undergo changes in stress vis-à-vis relaxation. If load is held constant, then a sample may undergo changes in strain vis-à-vis creep. In general, if neither effect is expected to be significant, load control is preferred. With constant
stress macroscopically applied, the intergranular stress distribution within particular grain orientations remains fixed, and as a result corresponding grain strains can be measured more accurately that with constant macroscopic strain and possible fluctuations in stress.

Sample positioning is accomplished through a high-precision locating system within the cave. Architectural theodolites are positioned in two corners of the cave to allow triangulation of the specimen. Reference positions throughout the cave are precisely marked, including each piece of the linear collimators that make up the incident neutron beam. Slit collimators allow the cross-section of the incident beam to be controlled.

The incident neutron beam created by the spallation target is measured in several ways. The current of the charged proton beam is constantly measured and reported throughout LANSCE in μA. SMARTS data computers automatically collect this data over time and record micro amp hours, μAh, or MAH. The T-zero spin chopper within the beam line reports counts in terms of T-ZEROs. In addition, a neutron detector is placed after the chopper down in the beamline, monitoring a representative fraction of neutron flux and reporting monitor counts as MON.

In-situ neutron diffractometers like SMARTS provide the capability of collecting diffraction profiles for particular changes in sample environment including load, temperature, and magnetic field. When load data are collected simultaneously with diffraction data, macroscopic information and microstructural information are directly correlated. Figure 8 and Figure 9 show a representative microstructure and diffraction pattern.
Figure 8: Microstructure highlighting subsets of particular orientation
Figure 9: Diffraction pattern highlighting orientation peaks
The subset of particular grains in the microstructure whose orientation is such that the plane normals lie parallel to the scattering vector of the detector bank are represented in the diffraction pattern by the peak at the corresponding lattice d-spacing. In the case of SMARTS, this is equally true for either detector bank, representing grain orientations that are parallel or perpendicular to the axis of load. The parameters of the diffraction peak have significance in representing the properties and behavior, on average, of all grains of a particular subset of the microstructure within the sample. The subset of grains of the \{111\} orientation, highlighted with the higher d-spacing, are represented in the diffraction pattern by the peak with a position corresponding to \{111\} d-spacing. If the lattice spacing within grains of the \{111\} orientation changes due to the macroscopic application of load, a change will be observed in position of the \{111\} diffraction peak. This relationship between particular grains and diffraction profile does not imply that diffraction data alone can fully describe the microstructure, and assumptions are required.

One specific limitation of this two-detector arrangement comes from the fact that plane normals do not uniquely identify a grain orientation within the sample coordinate system. Grains with \{111\} plane normals scattering into the axial bank may still have an orientation distribution of \{100\} plane normals within the subset. In some instances, this may be addressed through assumptions of radially symmetric orientation distribution. More complete texture measurements can be used to validate this assumption. The other possible method of addressing this indistinguishability would be to add a third detector with a scattering vector perpendicular to the other two. No instruments currently exist with this capability, due mainly to the logistical complexity. For SMARTS, the panel would need to be overhead of the load frame, a location devoted to a retractable roof for crane access.

Diffraction peaks are characterized by the basic parameters of position, width, intensity and profile, as represented in Figure 10.
Peak position is the lattice interplanar d-spacing about which the peak is centered, measured in Å. In theory, this would represent the exact value at which Bragg’s law is satisfied. In practice, conditions such as compositional variation, strain inhomogeneities and dislocation density, as well as instrumental parameters, tend to create a range over which the diffraction peak is recorded. The width of the peak is characterized by the full width of the peak taken at half the peak maximum value (FWHM), also recorded in Å. The peak dimension of height can be observed, but is more frequently accounted for in integrated intensity, a function of both height and breadth, which represents the entire area under the peak (typically no units are ascribed to this measure). As height and width do not fully describe recorded diffraction data, the shape of the peak, the peak profile is also commonly characterized. Many of the same factors that affect peak width also affect the profile of a peak. Different mathematical
representations of peaks frequently bear the names of those who proposed them, such as Pearson, Voight and Chebechev profile functions or a Gaussian distribution.

Countless studies using diffraction have created a stock of literature which describes the effects of many different materials behaviors and phenomena. Examples of these effects include the work of Bourke [106] and Swallowe [32] on NiTi shape memory alloys through study of elastic lattice strains. Benson et al. [107] observed deformation-induced phase development in cobalt alloys. Twinning in magnesium alloys is described by Wu et al. [108].

The behavior of peak intensities during deformation and the underlying indications of preferred orientation in an FeAl alloy were studied by Zhao et al. [41]. These results in particular nicely exemplify the effects of preferred orientation changes on diffraction patterns and are duplicated in Figure 11 and Figure 12.

Figure 11: FeAl forged at 800°C
Figure 12: FeAl forged and then annealed at 800°C

The forged sample alloy of Fe-41Al-2Cr was forged at high temperature, resulting in the diffraction pattern seen in the Figure 11. After annealing for only 10 min at 800°C, the pattern in Figure 12 was collected. Significant peak intensity changes are noted between the two patterns. The \{111\} displays a reduction of nearly 90\%, while the \{200\} more than triples in intensity. Through the recrystallization process, a significant volume fraction reorients from one direction to another. Overall, this reorientation is a zero-sum process and the total pattern integrated intensity is conserved.

While peak profiles are a complex relationship, work by Ungar [109] has shown that useful information may be deconvoluted relative to physical parameters describing dislocation effects within the sample. Particle size broadening, strain and dislocation density each exhibit different functional relationships, and as such with a significantly high resolution instrument, the nature of these changes may be detected within deformed samples.
A more detailed method of tracking the changes in individual peak parameters of the sample is accomplished by performing single peak fit (SPF) analysis. A model based on numerical values of position and peak profile is refined using computer-assisted methods of least squares. This type of analysis can be scripted and computed rapidly for multiple peaks through a sequence of multiple patterns. The SMARTSware software package is designed to accomplish this and other related tasks particularly for use with SMARTS data by Clausen [110]. Full details of the principles and operation of the package are available in the software manual.
Motivation, and User Facility Proposals

In-situ neutron diffraction was selected as a means of investigating the deformation mechanisms operating within the RM B2 family of ductile intermetallics. Thanks in part to the suggestion of Dr. E. Üstündag, the present author applied and was selected to attend the LANSCE Winter Neutron School in March of 2005. Seminars included nine days of lecture and laboratory instruction on TOF neutron diffraction, the Rietveld method, and the capabilities of SMARTS. This course also afforded the opportunity to discuss in detail the possibilities of using in-situ measurement techniques with instrument scientist Dr. Donald Brown. The capabilities of SMARTS are well suited to detect twinning and/or phase transformation. Proposals were written and submitted to the LANSCE User Program for several days of beam time. Upon scientific review by the selection committee, beam time was granted in two separate periods, once in September of 2005, and the second in December of the same year. In this way, an opportunity was provided to analyze the first sets of data and make any necessary modifications to samples and testing methods to ensure the highest likelihood of success.
Sample Preparation

High purity yttrium, as prepared by the Materials Preparation Center (MPC) of Ames Laboratory [111], and OFHC copper of appropriate weights to achieve stoichiometry were arc-melted into fingers in an argon environment by Arne Swanson. The buttons were flipped and re-melted 6 times to ensure homogeneity. These buttons were wrapped in tantalum foil and welded under inert argon gas in a stainless steel container. Hot swaging at 720°C reduced the thickness of the sample buttons by approximately a factor of three, resulting in large elongated discs 8mm in thickness x 120mm in length. From these discs, two dog-bone geometry tensile samples were cut using electron discharge machining. One compression sample was also prepared with a diameter of 10mm and a height of 20mm. This is the minimum cylindrical specimen size that would allow the incident and diffracted neutron beams to clear the compression platens of the SMARTS load frame.

All three samples were wrapped again in tantalum foil, and sealed in quartz tubes under argon at a pressure of approximately 5 psi below atmospheric pressure. Some inert gas is required within the quartz tube to facilitate thermal convection during heat treating. The lower pressure is necessary to ensure that the tubes do not over-pressurize and burst upon heating. The samples were then annealed at 720°C for 100 hours in electric resistance tube furnaces. The temperature of hot processing and annealing was selected to be ~50°C below the lower eutectic temperature of YCu and Y.

For the second round of test samples, slight modifications to the sample preparation process were made. Due to problems with chipping from EDM, as well as fracture outside the gauge length of the tension samples, a round tensile geometry was selected. Initial alloying was carried out as previously done with arc-melting. However, after several re-melts, the buttons were finally melted into finger tray molds 9.5 mm in diameter.
These fingers were then placed inside a Ta tube with a Ta disc welded into one end to form a bottom. The long, slender can, 12.7 mm diameter and approximately 25 cm length, was annealed at 900° for 1 hour to outgas any impurities in the metal. With the YCu fingers inside, the can was hung from a Ta wire within the coils of a vacuum induction melting furnace. Under vacuum of $10^{-5}$ Torr, the sample was heated to 1100°C to melt the compound. Temperature was checked from outside the quartz vacuum chamber using optical pyrometry. To avoid significant shrinkage piping within the melt upon cooling, the sample was slowly lowered through the induction coils, to emerge out the bottom, creating a simplified directional solidification effect.

After melting, the Ta tube, with the YCu compound melted directly inside, was placed into a stainless steel tube. The outer tube was then TIG welded under inert gas with tapered and plugged ends. The entire SS-Ta-YCu rod was hot swaged at 720°C to achieve a final YCu diameter of ~11 mm. Using a lathe, the exterior SS and Ta cans were machined off the YCu rod. Cylindrical samples of YCu were created with dimensions of 10 mm diameter and 20 mm length. These samples consisted of the smallest dimensions for compression cylinders that could maintain unshielded neutron diffraction within the SMARTS mechanical testing apparatus while still avoiding compression cylinder buckling. For final processing, the samples were annealed as before, at 720°C for 100 hours.
Experimental Results – Low temperature phase transformation

From the initial findings of Balster, and the later characterization by Ibarra and Ritter, a transition to a low temperature phase is known to exist within stoichiometric YCu. The calculations of Morris show that the difference in phase energies between B2 and B27 may be small for this compound. Based on these facts, the possibility of stress-induced phase transformation had been suggested as a possible mechanism of deformation. To study the onset of the new phase, experiments were first conducted to detect the known temperature induced transformation. Diffraction patterns were collected using the HIPPO instrument on LANSCE Flight Path 04 for a sample with compression cylinder geometry for a temperature range of 300K down to 50K. Representative pattern results for the highest and lowest studied temperature are shown in Figure 13 and Figure 14.

Figure 13: YCu diffraction profile at 300K, showing high temperature B2 phase
Figure 14: YCu diffraction pattern at 50K, showing high temperature B2 and low temperature B27 phases

Diffraction profiles were refined throughout the range of cooling temperatures. Initial lattice parameters for the low temperature B27 phase were taken from Ritter, and then allowed to be refined. Refinements were carried out sequentially, passing parameters from one pattern to the next using the SmartsRunRep software. This procedure can have difficulty achieving convergence for patterns exhibiting the appearance of a phase with a low volume fraction, as would exist at the onset of the transition during cooling, so the sequence proceeded from low temperature to high temperature. Based on the scattering of the sample studied and the signal-to-noise response available in HIPPO, the lower limit of detection is about 5% by volume. Phase fraction parameters were extracted from refinements and examined as a function of temperature, the results of which are shown in Figure 15.
Figure 15: Phase volume fraction for high temperature (B2) and low (B27) temperature phases of YCu as a function of decreasing temperature
Discussion

Diffraction results show the transition of the YCu sample from the B2 phase to the low temperature B27 phase previously described in literature. The onset temperature of the transition is about 150K. Multiple patterns were collected at several temperatures, and the results exhibit the time-dependent of the transition not previously reported in literature. For example, the data at 100K in Figure 15 may appear streaked in the vertical direction, but this is due to multiple data points at that specific temperature. After reaching the desired temperature, patterns were collected for approximately 8 min, with about 45 seconds between patterns for data accumulation. It is possible that the time-dependent nature of the transformation is a result of the time required for the sample to reach thermal equilibrium. Temperature measurements were taken from a thermocouple within the sample container very near the specimen. While this is likely to give a very close measurement of the temperature of the actual sample, some discrepancy may exist. However, it is unlikely for a 10mm diameter cylinder to require nearly 30 min to reach equilibrium after the container reached the desired temperature. With only three patterns collected, and the resolution considerations of HIPPO, calculations regarding the transformation kinetics would be challenging and unlikely to yield concise results, and thus were not attempted.

The onset of the transformation as a function of temperature is observable in Figure 15. The transition to the low temperature phase begins at approximately 150K, and by 50K about 25% volume of the sample transformed. Due to the limited beam time available, only one pattern was collected once the sample reached 50K. As suggested earlier, it is possible that with additional hold time at 50K, the sample would have achieved further transformation. The general trend in the data between 150K and 100K suggest that a higher volume fraction transformed at 50K may be likely.
Experimental Results – In-situ Diffraction in September 2005

Initial in-situ neutron diffraction experiments were carried out in September of 2005. Two dog-bone tensile samples and one cylindrical compression sample were examined. Measurements of an initial pattern showed YCu to be a strong scatterer. The necessary count times were determined by collecting diffraction patterns with increasing count times and plotting the error in peak position. During stable beam current, this translated to count times of about 30 minutes per load.

The mechanical loading of samples was conducted under the condition of position control through the use of computer-assisted scripting. Samples were strained until the specified displacement was achieved and held for the collection of diffraction data. Engineering stress was determined using data from the load cell integrated within the load frame in the beam path and measurement of initial cross-sectional area. Engineering strain was measured with a surface extensometer with a gauge length of 25mm. As a result, a stress-strain plot of the tests shows incremental steps (Figure 16, Figure 17, Figure 18). Several unloading cycles were also completed during loading of the compression sample.
Figure 16: Macroscopic stress-strain plot for tension sample 1

Figure 17: Macroscopic stress-strain plot for tension sample 2
Samples tested in tension failed at a stress of 158 MPa and 168 MPa, respectively. In both samples the failure was a result of fracture through the head of the dog-bone, with cracks formed radially from the pin hole and perpendicular to the direction of loading. After mechanical testing, sample fracture surfaces were examined using scanning electron microscopy (SEM) in Ames. A representative image of the fracture surface is shown in Figure 19.

Figure 18: Macroscopic stress-strain plot for compression sample
Figure 19: SEM photomicrograph of fracture surface of a tension sample showing evidence of brittle fracture
Full profile refinement using the Rietveld method and the GSAS software package was completed for each diffraction pattern collected. Refined parameters were histogram scale factor, background function, lattice parameter, atomic position, thermal scattering factor, absorption and sigma-1 using peak profile type no. 1. The measured data showed close agreement with the calculated B2 structure. Figure 20 and Figure 21 show the results; recorded diffraction data are displayed as red pluses (+), calculated B2 structure peak positions are indicated with black hash marks ( | ), and the calculated and refined profile is displayed as a continuous green line (which runs more or less directly through the data points). The difference between the collected data and the refined profile gives an indication of the agreement between the two, and is displayed below the data as a solid purple line.
Figure 20: Refined diffraction profile (Bank 2, longitudinal) for tension sample 1, undeformed

Figure 21: Refined diffraction profile (Bank 2, longitudinal) for tension sample 1, after deformation
In-situ diffraction profile data is collected at numerous points throughout the experimental run. Figure 22 and Figure 23 display the data collected before deformation and at a stress level of 160 MPa. The horizontal axis represents d-spacing (converted from µs TOF data), and the vertical axis displays the normalized intensity at that particular d-spacing (µs TOF).

**Figure 22:** Diffraction pattern collected for compression sample (Bank 2, longitudinal), undeformed

**Figure 23:** Diffraction pattern collected for compression sample (Bank 2, longitudinal), at a stress level of 160 MPa
Patterns were further analyzed using single-peak fit analysis for the strongest diffraction peaks. Resulting data include (among other data) peak position, peak width recorded as FWHM and integrated peak intensity, for numerous peaks in each pattern through the testing cycle. The agreement of fit between refined profile and collected data along with the difference curve between the two for several representative peaks is shown in Figure 24, Figure 25 and Figure 26. Similar to earlier diffraction patterns, the horizontal axis is in units of TOF µs, and the vertical axis indicates normalized intensity.

Figure 24: Single peak fit result for tension sample 1, undeformed, \{110\} peak
Figure 25: Single peak fit result for tension sample 1, undeformed, \{211\} peak

Figure 26: Single peak fit result for tension sample 1, undeformed, \{310\} peak
Several fundamental peaks within each pattern, collected at varying stress/strain states, were analyzed using SPF routines. From these results, the integrated peak intensities of numerous peaks can be plotted as a function of stress. Integrated peak intensity data are normalized by the value recorded in the initial diffraction pattern in the unloaded condition, such that all peak intensity measurements start with a value of 1. Through this type of analysis, trends in the behavior of diffraction profiles are much more readily observed, as seen in Figure 27 and Figure 28. Normalized peak intensity (in arbitrary units), shown on the vertical axis, and stress in MPa (either positive or negative) is displayed along the horizontal axis.

![Normalized peak intensity vs stress](image)

**Figure 27:** Normalized peak intensity (Bank 2, longitudinal) plotted as a function of applied stress for tension sample 2
Figure 28: Normalized peak intensity (Bank 2, longitudinal) plotted as a function of applied stress for compression sample
Peak width data, reported as FWHM, was analyzed through a method of SPF analysis similar to peak intensity. The peak width results collected from axial detector bank for tension sample 1, as a function of stress, is shown in Figure 29. FWHM data are normalized by the initial peak width, and unloading results are included. The figure legend is sorted relative to the order of most significant observed effect.

Figure 29: Peak width (Bank 2) plotted as a function of stress
Peak position data were also collected through SPF methods. The principles of analysis are similar to peak intensity and peak width data, but additional calculations were performed with peak position data. Diffraction peaks are representative of a particular subset of grains within the sample whose plane normals point parallel to the scattering vector of one of the two detector banks. The strain on those particularly oriented grains can be calculated by studying changes in peak position. Strain at a particular level is found according to $\varepsilon_{hkl} = (d_{hkl} - d_0) / d_0$, where $\varepsilon_{hkl}$ is the strain of a subset of grains of a particular orientation $hkl$, $d_{hkl}$ is the peak position, and $d_0$ is initial peak position. The trends in these data were observed by calculating and plotting the grain-specific microstrain as a function of applied stress for multiple grain orientation subsets as shown in Figure 30 and Figure 31. The data for the transverse detector bank in Figure 30 is plotted on a smaller horizontal axis, which takes into account the relationship between axial and transverse loading as described by Poisson’s ratio.
Figure 30: Grain-specific strain (Bank 1, transverse) as a result of applied load for tension sample 1

Figure 31: Grain-specific strain (Bank 2, longitudinal) as a result of applied load for tension sample 1
Lattice strain data were collected, calculated, and studied for each sample. The results of these studies for one representative tension sample compared to the results for the compression sample are shown in Figure 32 and Figure 33.

Figure 32: Grain-specific microstrain for tension sample 2 showing $hkl$-specific lattice strains
Figure 33: Grain-specific microstrain for compression showing $hkl$-specific lattice strains
**Discussion**

The motivation for in-situ neutron diffraction experiments was to investigate the possibility of twinning and or phase transformation as mechanisms of plastic deformation in RM B2 intermetallic compounds. The accumulated results give insight into this possibility, as well as revealing numerous other interesting aspects of deformation behavior.

The stress-strain plots shown in Figure 16, Figure 17 and Figure 18 show a significant degree of work hardening for both of the tension specimens as well as for compression. Since displacement control was used for the tests, the diagrams display some degree of relaxation during diffraction pattern collection. This is not necessarily indicative of the serrated yielding sometimes observed in other studies. All three samples seemed to yield at about 15 MPa, which is quite low for metal or intermetallic materials in general, as well as compared to earlier experiments with YCu. From single-crystal tests, the critical resolved shear stress for the dislocation mechanisms expected to be operating within YCu was cited by Russell and by Zhang to be about 18 MPa. Schmid’s Law states

**Equation 2: Schmid's Law for polycrystalline yield stress**

\[ \sigma_y = \tau_{\text{CRSS}} \cos \varphi \cos \lambda \]

where \( \sigma_y \) is the yield stress, \( \tau_{\text{CRSS}} \) is the critical resolved shear stress, \( \varphi \) is the angle between the tensile axis and the slip plane normal, and \( \lambda \) is the angle between the tensile axis and the slip direction. This would imply that even a polycrystalline specimen containing some grains ideally oriented for slip, thus minimizing the values of \( \cos \varphi \) and \( \cos \lambda \) would not yield until at least twice the value of \( \tau_{\text{CRSS}} \). For a recorded yield stress of 15 MPa, the critical resolved shear stress would be about 7.5 MPa, noticeably lower than recorded by Russell, and by Zhang. Possibilities for this difference in results include variation in specimen composition and/or purity, thermomechanical history prior to testing, and physical sample preparation methods. The use of
electro-discharge machining (EDM), both in Russell's and Zhang's studies as well for the tension samples studied here, could also have affected the samples in unforeseen ways. The high-energy nature of EDM, combined with H-rich cutting fluids, may create an environment for H to permeate the structure, and this in turn could affect the properties of the samples. Single-crystal studies did not report annealing treatments after crystal growth, although these may indeed have occurred. If unannealed, these samples may have displayed some pre-strained behavior during testing.

The degree of work-hardening detected, particularly within the compression sample, is very large relative to most plastically deforming materials. With $\sigma_y$ of 15 MPa, the compression specimen achieved 180 MPa easily without any indication of failure. From the work hardening rate observed, it is likely that the sample would have been able to be stressed to a still higher level had the test continued. If that is indeed the case, the ratio of $\sigma_{UTS} / \sigma_y$ would be extraordinarily large indeed.

The two tensile specimens showed similar work hardening behavior. In compression, the sample seems to have demonstrated somewhat lower strength. This may be an indication that different deformation mechanisms are operating in tension, as compared with compression. Certainly, failure mechanisms are different; while the tension samples failed at about 160 MPa, the compression sample showed every indication of continuing to deform extensively to much higher levels of stress. The SEM micrograph in Figure 19 shows that failure in tension was due to brittle fracture, although the intergranular or transgranular nature of the fracture surfaces is somewhat ambiguous.

The unloading results of the compression sample display a value of Young’s modulus that supports the early onset of yielding. The modulus between stress levels of 5 MPa and 15 MPa is very similar to that observed upon unloading after 0.5% strain and 3.0% strain. This is complicated by the fact that the unloading cycles display non-linearity, which may be indicative
of Bauschinger-type behavior. The unloading and reloading hysteresis after 3.0% strain is quite large. This possibility would offer an interesting study for future investigation.

Failure of the tension samples occurred as a result of fracture directly through the pin-holes. The dog-bone sample geometry proved to be less than ideal for testing a material with somewhat limited ductility. In addition, EDM sample preparation left significant undesirable chipping around every edge of the tension samples. These chips may have served as crack initiation sites to expedite failure. In an attempt to avoid these problems, future samples were prepared via a different method.

Diffraction profile refinement was successful in matching the expected B2 structure as seen in Figure 20 and Figure 21. Several relatively minor features do occur in the difference curve, and these are addressed in greater detail later. Between Figure 22, which was collected in the unstressed state, and Figure 23 collected at 160 MPa, the B2 structure prevalence is nearly equivalent. No new peaks are observed, and the intensities of the B2 peaks remain quite similar, as do the ratios of the peak intensities. These two figures in general show conclusively that neither twinning nor phase transformation occurs in significant volumes within the bulk of the samples. While SMARTS is a high-resolution instrument, and the patterns collected are quite well defined, the limit of detection of changes within the polycrystal remains about 5% by volume. Therefore, while there are no indications of significant twinning or phase transformation, it is possible that either of these may occur in small volume fractions. For example, assuming APBs with a 1.4nm width and 1nm thick, with two dislocations per APB having lengths of 100nm, and dislocation density of $10^{10}$ mm$^{-2}$, the structure would have volume of 140 nm$^3$ within a single APB region, and $5*10^{12}$ APBs / mm$^3$. This corresponds to only 0.07% of the volume of the sample would be contained within APB regions. This would be far below the limit of detection.
The profiles of the compression sample collected at the unstressed state (5 MPa holding the sample) and at 165 MPa and seen in Figure 22 and Figure 23, respectively, also show no indication of twinning or phase transformation within measurable volume fractions. However, peak intensities clearly changed between the two patterns. A simple visual estimation of the most intense peak, the \{110\} at 2.48Å, shows a change of approximately 200%. An increase by about 50% occurs for the second strongest peak, corresponding to \{211\} at 1.42Å. Not only do peak intensities show significant increase, but the ratio of intensities between the peaks seems to be changed as well. Whereas the \{110\} peak is about twice as intense as the \{211\} peak in the initial pattern, it is more than three times as intense after deformation. The cause of this phenomenon was not readily explained during experimental runs, nor for quite some time afterward.

Peak intensity changes, even of this magnitude, are not uncommon during in-situ diffraction experiments. Either twinning or phase transformation may exhibit effects on peak intensity, as would texture development from twinning or dislocation slip with grain reorientation. However, twinning behavior would cause some peaks to increase in intensity, while others correspondingly decreased in intensity, as would any texture development. Phase transformation would be marked by peaks of the initial phase diminishing in intensity as peaks for the new structure increase. These behaviors are not observed in the experimental results.

Single peak fit (SPF) analysis results give further insight into the behavior of YCu. Results of SPF for three peaks in the pattern of the first tension sample in the undeformed condition are shown in Figure 24, Figure 25 and Figure 26. Agreement between the fit model and the collected data is quite good, and difference curves are very low. Similar analysis was conducted through computer-scripting for numerous peaks in each of the patterns collected with comparable results.
Plots of the integrated peak intensity (normalized to initial pattern values) as a function of stress are shown in Figure 27 and Figure 28. This type of analysis provides a quantitative description of the trends observed and estimated from the patterns in Figure 20 and Figure 21 for tension, and Figure 22 and Figure 23 for compression. It is immediately obvious that integrated peak intensities increase significantly with relatively small stress. This is observed for both tension and compression, although to a much greater degree for the compression sample. While compression testing was conducted to a higher stress, facilitated by the lack of failure, this does not explain the peak intensity change behaviors. As seen from the plots, and particularly in compression, most of the peak intensity increase occurs before a level of about 125MPa. The increasing behavior tends to level off after this point. Similar trends were observed in both axial and transverse detector banks.

During analysis of this peculiar trend, it was observed that changes in peak intensity tended to be dependent on d-spacing. From Figure 28 it is seen that during compression, the \{110\} peak shows the largest normalized integrated peak intensity increase, followed by \{200\}, \{211\}, \{220\}, \{310\} \{222\} and finally \{321\}.

One possible method of increasing peak height would be for peaks to become narrower as they become taller. The peak widths for several fundamental peaks are shown in Figure 29. The widths of each peak are noticed to increase slightly with increasing stress. This indicates that the increases noticed in peak intensity are not coming from a narrowing effect. Additionally, the possibility of peak intensity increases as a result of peak narrowing is addressed by the fact that intensity information is presented as \textit{integrated} peak intensity, taking the entire area under each diffraction peak into account, rather than strictly peak height. Further discussion of peak intensity changes are provided with results from later experiments.

The grain-specific strain results, as calculated from SPF, for a number of peaks in each different pattern for both diffraction detector banks are shown in Figure 30 and Figure 31.
{222} orientation (and similar) is seen to show very little increase in lattice strain with increasing applied stress, indicating the onset of early yielding within grains of this soft orientation. Alternatively, grains of the {200} orientation display the hardest response, taking on the most significant lattice strain with increasing macroscopic loading. From these data alone it is not possible to draw any conclusions about the absolute amount of plastic strain occurring within any particular grain orientation subset. SMARTS is incapable of directly measuring grain-specific plastic strain. It is possible to state that in a relative sense, the grains of the {222} orientation are yielding plastically to a much greater extent than those of a {200} orientation. The particular relationship of this load partitioning, the intergranular strain, is indicative of the underlying mechanism(s) responsible for deformation, although it was not directly evident what this might be.

Additional lattice strain data are provided in Figure 32 and Figure 33 to illustrate the comparison between tension and compression. The same intergranular strain behavior is observed in both samples. In the compression data at about 150 MPa, there is a slight change in the behavior of several orientations. The soft {222} orientation shows a greater degree of yielding as the amount of strain for increasing stress becomes slightly less, i.e., the slope becomes steeper. At the same point, the hard orientations {200} and {310} show a slight change in behavior. This same level of stress is the point at which the tension sample fails. It is reasonable to conclude that this may indicate the onset of a second mechanism of deformation which is available in compression, but either unavailable in tension, or overtaken by fracture.
Experimental Results – In-situ Diffraction in December 2005

The accepted proposal for beam time included two experimental periods, the second of which was conducted in December, 2005. From the results of the prior experiments, several testing modifications were made. Samples were prepared through swaging and turning, rather than through rolling and EDM. The dog-bone tensile geometry was replaced with a threaded tensile sample geometry. The new preparation method resulted in much less chipping and porosity observable on the surface of the samples. Compression cylinders were 10mm diameter and 20mm in length, and tension samples were 6.35mm diameter with 42mm gauge length.

Figure 34: Tension and compression samples prepared for December by swaging and lathe turning
Mechanical testing results for tensile loading are summarized by the stress-strain plots seen in Figure 35, Figure 36, and Figure 37.

Figure 35: Macro stress-strain plot for tension sample 1
To facilitate comparison of the work hardening rate between tension and compression, Figure 36 shows the compression behavior plotted on the same scale as Figure 35 for tension. This does not allow the entirety of the data collected to be viewed, but does bring the region with the onset of plastic yielding to a magnified view.

![Macro Stress-strain plot for compression sample (enlarged)](image)

**Figure 36:** Macro Stress-strain plot for compression sample (enlarged)
The entire stress-strain data conducted at constant load is displayed in Figure 37, showing a large degree of plastic deformation and work hardening. The mechanical unloading cycles performed on the sample are shown in this figure.

Figure 37: Macro Stress-strain plot for compression sample (full)
From Figure 37, a discontinuous stress-strain response can be observed at higher strain levels. This behavior is highlighted in the magnified plot in Figure 38.

Figure 38: Macro Stress-strain plot for compression sample, enlarged to show strain jumps
Tensile samples failed at 138MPa and 134 MPa. The fracture surfaces were studied by SEM, and representative photomicrographs are depicted in Figure 39 and Figure 40.

Figure 39: SEM photomicrograph of the brittle fracture surface of a tensile sample, 150x
Diffraction data analysis was similar to that conducted for samples studied in September and described previously. Briefly, this included full pattern refinement, single peak fit analysis, SPF data normalization to initial values, and representation of orientation-specific data as a function of macroscopic strain (or stress) to show trends. Grain-specific strain results for the compression sample tested to a higher strain and stress than previously studied are displayed in Figure 41. Legend labels are presented in order of increasing lattice strain response, right to left across the figure. The data for \{110\} / \{211\} / \{220\} / \{321\} lay almost directly on top of each other.

**Figure 40: SEM photomicrograph of the brittle fracture surface of a tensile sample, 500x**
Figure 41: Lattice strain (Bank 2) as a function of applied stress for compression sample
Peak widths were evaluated via normalized FWHM measurements for the compression sample. The higher stress achieved during deformation allows for examination of peak width behavior with unloading as seen in Figure 42. Since the vast majority of strain within the sample was non-recoverable plastic deformation, data is plotted as a function of stress rather than strain. The figure legend is ordered to correspond with degree of change recorded for different specific grain orientations.

Figure 42: Peak width (Bank 2) plotted as a function of stress
Integrated peak intensities calculated from SPF as a function of applied stress are plotted in Figure 43 and Figure 44. The intensity data are plotted as a function of stress, rather than strain, to show the unloading response, observed as approximately horizontal lines, after loading to 50 MPa. If the data were plotted as a function of applied strain, these unloading data would be obscured due to the fact that the sample exhibited permanent plastic deformation very early on, and strain values did not recede with unloading. Therefore, the intensity data points plot essentially on top of one another, and do not exhibit a clear trend.

![Figure 43: Normalized peak intensity (Bank 1, transverse) changes as a function of strain during compression](image)
Figure 44: Normalized peak intensity (Bank 2, longitudinal) changes as a function of strain during compression
A correlation between peak intensity increases (as a function of applied load) and lattice interplanar spacing was observed in earlier data, and is again clearly evident in Figure 43 and Figure 44. This trend is summarized in Figure 45 by plotting the normalized change in integrated peak intensity for peaks as a function of d-spacing after 2% strain. Two peak values in particular are highlighted with plane orientation labels.

Figure 45: Integrated peak intensity changes as a function of d-spacing after 2% strain
To ensure that the observed peak intensity changes were not an instrumental phenomenon, a simple piece of software was used to sum the area underneath the first five fundamental peaks. The measured intensity data throughout the entire diffraction pattern were normalized by two different measurements of flux of the incident neutron beam, monitor counts (MON) and T-Zero chopper counts (T0), to account for fluctuations in the spallation neutron source. The results of this calculation for all diffraction patterns in a single mechanical test are plotted as a function of strain in Figure 46. Three or four data points show anomalous results just below 2% strain, with jumps in the MON pattern and corresponding drops in the T0 pattern. These fluctuations are the result of inconsistent accelerator current and variations in the way that flux is recorded between the two methods (MON vs. T0) during those particular diffraction collection periods.

Figure 46: Integrated peak intensity for first 5 fundamental peaks
It was suggested that the changes in peak intensity could be due to incomplete Debye rings. If this were the case, individual tubes within the detector banks would show variation in collected diffraction intensity. Typically, all detector tubes within a given detector bank are “binned” together to represent a single detector. It is this binned data that is used to study trends for most in-situ experiments. To address this possibility, the data for individual detector tubes was graphically prepared and examined. The data is represented in Figure 47. Individual detectors are represented along the horizontal axis, and the vertical axis plots TOF values. Diffracted intensity for a particular tube / TOF combination is displayed by color gradient.

Figure 47: Individual detector tube data for entire detector array
Higher strain portions of Figure 43 and Figure 44 show that this behavior levels off, but intensities still fluctuate. A similar plot of intensity as a function of changing applied strain is shown in Figure 48, with intensity data normalized to the values recorded at 2% strain (140 MPa), the point at which initial change behavior is concluded. The legend labels are sorted to match the order of the data trend; the \{222\} peak behavior shows the largest increase (towards the top of the graph), and the \{310\} peak undergoes the greatest decrease (the bottom trend line of the graph).

Figure 48: Peak intensity changes after normalizing to values at 2% strain for compression
The effect of texture development within the sample as a result of deformation was examined by collecting complete orientation distribution function (ODF) information for the compression specimen before and after loading using the HIPPO diffractometer. Texture information can be graphically represented through the use of pole figure plots, as seen in Figure 49 and Figure 50. Each circle depicts a top-down view of a semi-sphere superimposed symmetrically about the cylindrical axis of the specimen. The distribution of six particular plane normal pole orientations about the semi-sphere is given independently in terms of an intensity gradient with units of “times random”, which describes the comparison to a homogenous distribution of a random texture. Regions of the semi-sphere in which higher density of poles are clustered are represented by the gradient with intensity greater than random. The scale of this gradient is shown on the right of the figure.

![Pre-Deformation Pole Figures](image)

**Figure 49: Pole figures representing sample texture before deformation**
Figure 50: Pole figures representing sample texture after compression deformation
The GSAS software used to implement the Rietveld method of full profile refinement has a numerical treatment for the existence of extinction within a sample. This parameter can be refined, and is reported in terms of the mosaic block size with units of µm. This parameter was refined sequentially by passing refinement results from one pattern to the next for each pattern through the compression test. The sequence was conducted starting at high strain, where it was assumed that extinction was not a factor, and proceeding to lower strain. The parameter refinement results are plotted as a function of strain in Figure 51.

![Figure 51: Mosaic block size as a function of applied strain during compression](image-url)
Discussion

Mechanical testing displayed similar results to those recorded in September. Tension samples yielded plastically at slightly higher levels of about 25 MPa. The compression sample, alternatively, began plastic deformation after only about 12 MPa. Unloading, in tension and in compression, showed a nonlinearity hysteresis. Tension samples failed due to fracture within the gauge length just after 135 MPa.

As the first round of tests provided the realization that compression would likely sustain much higher stress levels, this test was conducted up to 325 MPa. The degree of work hardening was even higher than previously measured, with $\sigma_{UTS} / \sigma_y$ calculated to be more that 25:1. Even at this high stress, it is likely that the compression sample could have sustained still higher stress, and beam time limitations cut short the experiments before any signs of failure.

The behavior of serrated yielding, which was only just noticeable during September testing, is much more pronounced in the compression data. An initial conclusion might be that the jumps occur corresponding with diffraction pattern hold times. However, this is not the case, as can be seen in the enlarged image of strain jumps shown in Figure 38. The clustered data points at 220 MPa, 240 MPa, and 260 MPa represent the diffraction pattern waiting periods. The jumps in the data occur during the continuous loading between pattern holds. Strain jumps of nearly a full percent are observed to occur at intervals. Examination of the extensometer after testing confirmed that these jumps are not instrumental mistakes caused by blade slippage. It is likely that the fact that this experiment was conducted in load control, as compared with the position control of testing in September, may at least partially explain why this behavior was not recorded in earlier tests. One possible explanation for this behavior may be a dynamic strain aging effect. It has been proposed from other studies on YCu and similar compounds that dislocations may be pinned within the lattice, such as by dissolved impurity atoms. With
increasing strain, these dislocation pile-ups may be able to break away, causing large macroscopic effects to be recorded.

Fracture surfaces for failed tensile samples appeared similar to those recorded earlier, both in September, as well as in prior studies. No evidence of traditional ductile pitting exists and failure appears to be caused by brittle fracture.

Grain-specific strain data for the compression sample were the best collected for any YCu specimen. At just 13 MPa, the intergranular strain increase dramatically as the soft \{222\} orientated grains begin yielding, and the hard \{200\} and \{310\} grains take additional load. This behavior is nearly linear between 13 MPa and about 150 MPa. The extended testing of this sample confirms earlier conclusions about a change in deformation mechanism. At this stress level, tensile samples give way to fracture, and under compression, the deformation behavior tends to change. The diffraction elastic constants of all recorded grain orientations seem to curve back away from the divergent behavior of lower stress levels. Grains of the \{200\} and \{310\} orientation appear to begin to soften, while the \{222\} grains take on additional strain with increasing stress.

The higher quality data highlighted a trend that had been previously overlooked. Grain-specific strain distribution between different orientations is correlated with the crystallographic orientation parameter $A_{hkl}$, which is defined by Equation 3.

**Equation 3: Crystallographic orientation term $A_{hkl}$**

$$A_{hkl} = \frac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2}$$

This term is sometimes represented in the literature as $\Gamma$, and should not be confused with the anisotropic ratio, A. The value of this term for various orientations can be summarized with a stereographic triangle representation as seen in Figure 52.
Figure 52: Structure independent stereographic representation of $A_{hkl}$ values for particular orientations

Referring to the lattice microstrain data represented in Figure 41, the \{222\} orientation has the highest $A_{hkl}$ value of 0.33, and also displays the least lattice strain as a function of applied stress. Each of the four orientation peaks clustered in the midrange of the figure, \{110\}, \{220\}, \{211\} and \{321\} all have an $A_{hkl}$ value of 0.25. The \{310\} orientation has a lower value of 0.09, and the \{200\}, which shows the highest increase in microstrain as a result of additional applied stress, has the lowest $A_{hkl}$ of zero.

The term $A_{hkl}$ is also used in relation to grain-specific elastic properties. Following descriptions given by Courtney [17], pages 59-60, and Allen et al. [112] the independent elastic compliance constants ($S_{ij}$) for cubic materials can be related to stiffness according to Equation 4, Equation 5, and Equation 6.
Equation 4: Elastic compliance term $S_{11}$ in terms of elastic stiffness

$$S_{11} = \frac{(C_{11} + C_{12})}{((C_{11} - C_{12})(C_{11} + 2C_{12}))}$$

Equation 5: Elastic compliance term $S_{12}$ in terms of elastic stiffness

$$S_{12} = \frac{-C_{12}}{((C_{11} - C_{12})(C_{11} + 2C_{12}))}$$

Equation 6: Elastic compliance term $S_{44}$ in terms of elastic stiffness

$$S_{44} = \frac{1}{C_{44}}$$

Orientation specific Young’s moduli for cubic crystals can be describe according to Equation 7

Equation 7: Orientation specific Young's modulus

$$\frac{1}{E_{hkl}} = S_{11} - 2(S_{11} - S_{12} - S_{44}/2) (\alpha^2\beta^2 + \alpha^2\gamma^2 + \beta^2\gamma^2)$$

where $E_{hkl}$ represents the modulus for a particular direction $[hkl]$, and $\alpha$, $\beta$, and $\gamma$ are direction cosines of the $[hkl]$ direction and the [100], [010], and [001] directions respectively. The final term in Equation 7 composed of direction cosines is simply an alternative way of expressing $A_{hkl}$, and varies between 0 and 1/3 as previously described.

The anisotropic ratio was previously defined for a cubic material in Equation 1. When the anisotropic ratio is equal to 1, that is to say for an isotropic material, it can be seen that the term $(S_{11} - S_{12} - S_{44}/2)$ will be equal to zero. As a result, the right-hand side of Equation 7 becomes equal to a constant value; all orientations will have the same modulus, which is the definition of an isotropic system.

In an anisotropic system, when $A \neq 0$, for directions $[h00]$ the $A_{hkl}$ term (as represented by direction cosines in Equation 7) will be equal to 0, and $E_{100}$ will be equal to $1/S_{11}$. If $A > 1$, as is the case for YCu, orientations other that $[h00]$ will have $A_{hkl}$ values greater than 0, and will be
correspondingly stiffer than $E_{100}$. With $A_{hkl} = 1/3$, the [111] orientation will exhibit the highest modulus.

A simplified approximation of grain-specific elastic behavior can be made from these mathematical relationships with two additional assumptions. First, the simplified version of Hooke’s Law, $\sigma = E\varepsilon$, allows the relationship between Young’s modulus ($E$), stress ($\sigma$) and strain ($\varepsilon$) for linear elastic deformation. Second, the Sachs assumption of equivalent stress in all grains within the polycrystal can be used to simplify grain-specific stress levels. Further and more rigorous treatment of this method of analysis can be found in works such as Chung and Buessem [113], de Wit [114], and Daymond [115].

Based on these equations and assumptions, the grain-specific elastic strains were calculated as a function of stress and compared with diffraction data, seen in Figure 53.

![Figure 53: Grain specific strain compared to calculated elastic response](image-url)
Several conclusions about the behavior of YCu can be drawn from the figure. For calculated of entirely elastic behavior represented by dashed lines, relatively little variation exists between the behavior of various orientations. This is to be expected, as the anisotropic ratio of YCu is relatively low at $A = 1.15$. Significantly lower levels of the grain-specific micro strain are observed in calculated elastic response as compared with the recorded data. This suggests that elastic behavior alone within the sample would not account for the deformation of the sample, and indeed significant plastic deformation is occurring above 15 MPa to produce the grain specific strains recorded.

The relationship between grain-specific strain responses observed in YCu compared to the crystallographic orientation term $A_{hkl}$ has been briefly previously described. From Equation 7, it is clear that elastic response is proportional to compliance constants, crystal anisotropy, and $A_{hkl}$. From these studies of YCu, there also exists an apparent relationship between grain specific strain response and $A_{hkl}$ for the plastic response. Considering that $A_{hkl}$ describes the relationship of a particular direction relative to the [100] direction, and the active slip system in YCu is {110} <001> it is possible the correlation may be the result of mathematical coincidence between the description relation to the [100] direction and slip in the <001> direction. Then, this correlation may be expected for any cubic system exhibiting slip in the [100]-type direction.

Peak intensity changes show marked increases immediately after the onset of plastic deformation. After only 2% strain, the {110} peak in the axial detector bank had changed by a factor of more than 2.5. Since this trend had been previously observed, several diffraction patterns were collected during an unloading cycle of the compressive testing. This result shows clearly that the change in peak intensity is a function not of the stress state, but the stress history. The increased peak intensities were residual during unloading, and continued to increase with additional increased stress. Some type of dislocation behavior would be one possible
explanation since these lattice disruptions do not (under most circumstances) tend to revert when strain is removed.

The relationship between peak intensity change and d-spacing seen in Figure 45 makes obvious the fact that the \{110\} and \{220\} orientation, while crystallographically representative of the same planes of atoms, do not show the same behavior. If crystallographically equivalent planes exhibit different behavior, it is clear that the underlying cause of this behavior is a diffraction-based phenomenon, rather than a crystallographic one. The Debye-Waller factor of thermal diffuse scattering is related to d-spacing, but shows the inverse exponential functional relationship; the effect is largest for peaks of smallest d-spacing.

When observed together, the results of mechanical testing, lattice strain and peak intensity suggest a compelling description of the deformation behavior of YCu. To illustrate the relationship between these results, all three are shown collectively in Figure 54.
Figure 54: Comparison of results for stress-strain response, lattice strain, and peak intensity, showing distinct regions of behavior
Each of these three plots shows similar characteristic divisions into distinct regions. Initially the sample undergoes linear elastic deformation, with low levels of microstrain recorded for all grain orientation subsets, and little increase in integrated peak intensity. At a strain of 0.02% and a stress of 13 MPa, the sample shows the onset of plastic deformation. The stress-strain response changes dramatically, from the initial linear elastic response to plastic work hardening behavior. At the same point, lattice strain behavior diverges significantly, with the \{200\}-oriented grains accommodating significant microstrain as a result of increased applied stress. Correspondingly, integrated peak intensities jump dramatically, with behavior showing a proportional relationship to interplanar spacing.

When the sample achieved 2.1\% strain, and a stress of 145 MPa, the stress-strain response began to exhibit a different rate of work hardening. This is approximately the point at which all tension samples failed due to fracture. The previously described strain jump behavior also became much more prevalent at strain levels beyond this point. Lattice strain measurements show a change in the diffraction elastic constants, with the \{222\} grains taking additional strain with increased stress, while \{310\} and \{200\} grains accommodate slightly less strain with increased stress. The relatively large increase in integrated peak intensity leveled off and a more modest response is observed with some peaks showing slight increases and some showing slight decreases in integrated intensity.

Factors affecting peak intensity are summarized by the functional relationship in Equation 8, taken from Pecharsky [78]

**Equation 8: Factors which effect diffraction peak intensity**

\[
I_{hkl} = K \times \rho_{hkl} \times L_\Theta \times P_\Theta \times A_\Theta \times T_{hkl} \times E_{hkl} \times |F_{hkl}|^2
\]

where \(I_{hkl}\) = peak intensity, \(K\) = scale factor, \(\rho_{hkl}\) = multiplicity factor, \(L_\Theta\) = Lorenz factor, \(P_\Theta\) = polarization factor, \(A_\Theta\) = absorption factor, \(T_{hkl}\) = texture, \(E_{hkl}\) = extinction, and \(F_{hkl}\) = structure
factor. Of these, the first five are constants of either the instrument or the materials being investigated, and only the final three could potentially show variation during in-situ experiments. As previously discussed, changes in preferred orientation vis-à-vis texture would be indicated by increases in the intensity of some peaks, while others decrease in intensity. The data clearly show that this is not the case. Structure factor changes would be related to either phase transformation or a change in the crystal structure of the initial phase. No new peaks are observed to indicate the onset of a new phase, and peak positions do not show splitting which would characterize a shift away from the cubic unit cell. Only extinction is left as a possible explanation for this behavior.

A simple piece of software was used to calculate the actual area under each of the first 5 fundamental peaks within each diffraction profile. These results were normalized by both monitor counts (MON) and T-Zero counts (T0). Several peaks/spikes occur during the graph, but these are attributed to changes in the accelerator beam current. Indeed, the total area under these 5 combined peaks is seen to increase with applied strain.

Another proposed explanation for changes in peak intensity is due to incomplete Debye rings. A polycrystal with sufficiently large grains may not have the statistical grain distribution to create complete rings, leaving spots of diffracted intensity for the few diffracting grains. This type of spotted or incomplete pattern is routinely observed during diffraction of single crystals, or in SAED when only a few large grains are illuminated with the electron beam. During loading, these spots may have shifted with relation to the detectors, causing detected intensity to increase. The plot shown in Figure 47 demonstrates this not to be the case. Every detector tube is individually represented with the measured signal strength for the full range of TOF describing each pulse. The streaked nature and full coverage of this pattern were described by instrument scientist Dr. Brown to be a clear indication that sufficient numbers of grains within the polycrystal were diffracting, and that diffraction rings were complete. This assessment was
based on examinations of detector tube data for single crystal as well as polycrystal experiments previously conducted using SMARTS.

The peak intensity increases recorded during the first 2% strain are the most significant throughout the in-situ measurements, but additional peak intensity behavior may also be occurring. The plot of peak intensity normalized to values recorded at 2% strain shown in Figure 48 allows observation of trends occurring in the data after the initial changes. There are noticeable increases in {200} and {222} peaks, while the {321} peak stays almost constant. The remaining 4 peaks decrease in intensity, the trend being strongest in {310} and {220}. This distribution of increasing and decreasing intensity is much more typical of the development of deformation texture within a sample. This same behavior may be occurring at lower strain only to be obscured by the marked effects of extinction. With a better understanding of the initial behavior, further insight may be obtained about the deformation texture development.

Diffraction patterns of the compression cylindrical sample collected using HIPPO to measure the full ODF are seen in Figure 49 and Figure 50, shown as pole figures for representative characteristic orientations viewed top-down on the cylindrical axis. In the pre-deformed state, the sample exhibits fiber texture with a maximum distribution of about 1.5 times random for the {111} in the axial direction. This texture is likely the result of the swaging and annealing thermomechanical treatment the sample underwent during preparation. After deformation, the fiber texture is slightly stronger, showing a maximum of about 1.7 times random. This further supports the findings of peak intensity changes after 2% strain indicating deformation reorientation development.

After addressing texture as a possible source of intensity variation from Equation 8, only the parameter of extinction remains. While a process of elimination is not conclusive proof, extinction effects within the sample are a likely possible cause for peak intensity changes.
Literature exists regarding both theoretical treatment and experimental results of extinction, and will be further described. The work of Menon and Fox [116], which deals with the Debye-Waller factor in NiAl studies using XRD, states that “As the volume of the perfect crystals comprising a powder sample increases, the intensity of the diffracted beam decreases from that predicted by the kinematical theory, and this phenomenon is termed extinction”. It is logical, then, to reason that if the volume of perfect crystals were to decrease, that the recorded intensity of the diffracted beam could tend to increase. Again from Menon and Fox, mosaic crystals “depend on both the dislocation density and the distribution”.

The GSAS software package used to refine the diffraction profiles is capable of treatment of an extinction parameter, based on the work of Sabine [92], which is fundamentally concerned only with the physical parameter of mosaic block size, given in units of µm for the diameter of an assumed spherical crystallite. This is not the only factor affecting peak intensity within the fitted model, which complicates the least-squares minimization. The absorption parameter also affects peak intensity, and the two can thus become convoluted. However, the functional behavior of absorption is not particularly complex. Absorption is a well-studied and measured property of most elements. Refined parameters can therefore be easily examined for reasonableness, as well as compared with tabulate values.

The refinement parameters for the treatment of preferred orientation can also become convoluted with the extinction parameter. Texture is addressed mathematically in GSAS using spherical harmonics (SH), including high-order polynomial functional relationships. While this makes SH well-adapted to address complex textures, it also means that by allowing variation in a high number of texture parameters, a physically meaningless fit can easily be achieved for any diffraction pattern.

The YCu patterns were therefore refined for all other relevant parameters, excluding texture, and finally for mosaic block size. These refinements were carried out sequentially, in
reverse, based on the assumption that no extinction is present in the pattern of highest measured strain. This process was accomplished through use of the SmartsRunRep software code. Final refined parameter values from one profile were passed to the next profile in the sequence as to be used as initial values. Due to the potentially convoluted nature of the calculated intensity parameters, the numerical values for the extinction parameter may not be exactly correct. The recorded size range of ~25µm and below is physically reasonable relative to expected grain size within the sample. Even if the numerical values are inaccurate, the trend in parameter value is qualitatively informative.

After the initial onset of plastic yielding, the size of perfect diffracting crystallites decreases rapidly, leveling off to a minimum value of approximately zero after about 2% strain. Unfortunately, direct measurement of the size that is referred to in various literature sources as mosaic blocks / crystallites / diffracting volumes is not easily accomplished. Most techniques are based on interpretations of diffraction data similar to what has been performed here. Thus, it would be difficult to numerically confirm the numbers calculated from diffraction profile refinements with a secondary measurement technique.

The various methods of data analysis when considered together represent a situation not commonly observed in engineering materials studied with in-situ neutron diffraction. Literature does provide the framework to describe the likely mechanisms of behavior occurring within the polycrystalline sample. Figure 55 and Figure 56 are taken from Cullity [77] Sections 5-4 and 5-5, and a paraphrase of the description from the text follows.
Figure 55: Mosaic structure of a real crystal depicting dislocation walls dividing mosaic blocks (from Cullity)
As shown through direct observation using TEM in the 1960s of dislocation structures, all real crystals are known to have a mosaic structure. Single crystals and individual grains of polycrystalline aggregates alike show a substructure defined by the dislocations present. The distribution of dislocations is non-uniform, tending to cluster into boundaries which divide the crystal into regions alternatively referred to in various literature sources as “mosaic blocks”, “sub-grains”, “cells”, “coherent domains” or “diffracting volumes”. Indeed, even the general sounding terms “crystal”, ”crystallite” and “particle” are often used synonymously to describe...
these regions. It is this dislocation structure that is represented, greatly exaggerated, in Figure 55.

Experimental evidence has shown that for real crystals, within these sub-grains, diffraction behavior does not tend to follow the assumptions of the kinematic theory of diffraction. Briefly, these assumptions are that:

- the crystal is “ideally imperfect” consisting of sufficiently small mosaic blocks (10^{-4} to 10^{-5} in thickness)
- the blocks are disoriented such that they are essentially nonparallel

If mosaic blocks are sufficiently large, the resulting effect on peak intensity is termed “primary extinction”, and it is this case which is of interest while interpreting the YCu diffraction results. The case in which coherent diffracting volumes are sufficiently large as to exhibit primary extinction, and the resulting impact on diffraction intensity, is depicted in Figure 56. The description of this figure from Cullity is given below:

“In the discussion which follows it is important to remember that every time a ray is diffracted it undergoes a phase shift of \(\pi/2\) relative to the incident beam. If the incident beam with a wave vector \(K_0\) enters a crystal at the correct angle \(\theta\) for \(hkl\) diffraction, diffracted rays \(K_1\) are produced at angle \(2\theta\) from \(K_0\). The probability of diffraction occurring at any particular plane of atoms is, of course, quite low, but in highly perfect crystals (with thicknesses greater than 1\(\mu\)m) much of the incident intensity is eventually transferred to the diffracted beam.

Suppose diffraction occurs at A, producing an x-ray beam with wave vector \(K_1\) and a phase shift of \(\pi/2\) with respect to \(K_0\). The beam \(K_1\) is incident, however, on another array of scatters (atoms) at angle \(\theta\). At point B, therefore, there is a finite probability that \(K_1\) will be re-diffracted through angle \(-2\theta\), so that the diffracted ray has a wave vector \(K_2\)
parallel to but shifted in phase by $\pi/2 + \pi/2 = \pi$ with respect to $K_0$. Thus $K_2$ will interfere destructively with $K_0$, and because intensity is being removed from the incident beam before it has a chance to diffract from depths below A-A’, the diffracted intensity will be lower than for an ideally imperfect crystal. This process is known as \textit{primary extinction}.

From the description offered by Cullity, it may be understood that a sub-grain structure with sufficiently large mosaic blocks operating within the regime of dynamical diffraction may exhibit extinction effects which serve to decrease the measured diffraction intensity. It is likely that the relatively strong coherent scattering of both Y and Cu, which would make secondary diffraction more probable, facilitate dynamical diffraction within the sample. However, several aspects important to the description of the behavior of YCu are missing from the discussion provided by Cullity. First, the size of mosaic blocks necessary to allow dynamical interference of the incident and diffracted beams is only described as “kinematic diffraction equations… did not apply to the case of highly perfect crystals with dimensions greater than ~ 1-5 µm”. Second, the degree of misorientation which would serve to sufficiently disrupt the condition of dynamical diffraction is not addressed, other than to say “the maximum angle of disorientation between [mosaic blocks] may vary from a very small value to as much as one degree, depending on the crystal”.

The work of Sears [117] is a much more complete description and treatment of the dynamical diffraction, and specifically addresses the case of neutron diffraction. On page 1282, Sears states that “primary extinction is negligible if $d \ll \Delta$. Consequently, the quantity $\Delta$ is called the extinction length”. For the mathematical treatment presented, $d$ represents the thickness of a plane slab. In the case of a polycrystalline aggregate, this may be considered similar to the size of a single diffracting crystal, i.e., the mosaic block size. The equation for calculation of the extinction length in the Bragg case is given in Equation 9
Equation 9: Extinction length
\[ \Delta = \frac{\pi \cdot \Omega_0 \cdot \sin \theta_B}{\lambda \cdot F_{hkl}} \]

where \( \Omega \) is the volume of the unit cell, \( \lambda \) is the wavelength, and \( F_{hkl} \) is the structure factor (including thermal parameter) for a particular plane \( hkl \). For the YCu structure and the most intense \{110\} peak, this calculation gives an extinction length of \( \sim 27\mu m \). As a result, it is reasonable to assume that if the size of mosaic blocks within the YCu approaches \( \sim 27\mu m \), it is possible that dynamical diffractions effects would be observed in the sample. As previously described, refinement of the extinction parameter in YCu in terms of mosaic block size in the undeformed state gave a value of about \( 24\mu m \).

Studies by White [118] give results that confirm that elastic bending of samples indeed show the destruction of a primary extinction mechanism. White summarizes “the increase in diffraction due to bending to be a gross effect, even a factor of 20 or more”. More recently, Üstündag et al. [119] reported “dynamical diffraction processes can cause artifacts, such as double peaks, peaks with shoulders or highly asymmetric peaks for single-crystal or very-large grained polycrystalline specimens examined in TOF neutron powder diffractometers. Unless they are properly identified, such artifacts can cause large errors in data analysis and interpretation.” The results of Üstündag et al. show depth profile scanning which indicates that the intensity of diffraction is directly impacted by the strain within the structure. Neither of these studies specifically addresses how dislocation cell structure would contribute to changes in the dynamical nature of diffraction within a sampled plastically deformed due to dislocation slip mechanisms. Masimov [120] proposed a method of determining substructure characteristics by means of measuring integrated intensities when working with X-rays. Palacios-Gomez [121] describes a simple mathematical description of the relationship between mosaic block size and dislocation density.
The descriptions of Cullity, and the treatments by White, Masimov, and Palacios-Gomez, and the trends from numerous analyses seem to be in agreement as to the underlying mechanism of behavior. With a relatively long, hot annealing treatment, YCu samples developed relatively large regions of nearly perfect crystallinity. The ordering energy of this intermetallic may have contributed to the driving force for the development of relatively large mosaic block size, which is not typically observed in other common engineering materials. The mosaic block size is such that the sample experiences extinction effects, diffracting within the dynamical regime.

With applied strain, the sample undergoes plastic deformation from a low yield point. The relatively low yielding is indicative of a sample which has had most dislocations removed from the lattice. With plastic yielding, dislocations nucleate and glide through the lattice. Only a small number of dislocations are required to disrupt mosaic blocks. As the sample continues to deform, the size of coherently diffracting mosaic blocks decreases, and the interference condition of dynamical diffraction which had artificially lowered diffracted intensity is removed. Peak intensity appears to increase, but a more accurate description is that is peak intensity is recovered. Upon unloading, the deformation done to the lattice is residual, and the recovered peak intensity remains. After about 2% strain, the lattice is sufficiently disrupted that the dynamical condition has been destroyed. At this point in deformation, samples tested in tension give way to the driving forces of fracture. Samples tested in compression have one or more additional modes of deformation available, and continue plastic work hardening. This secondary behavior in compression is described by strain jumps in the stress-strain response, changes in diffraction elastic constants, and a peak intensity behavior which is characteristic of slight reorientation due to the formation of deformation texture.
Results – Elasto-Plastic Self-Consistent modeling of deformation

Experimental measurements of internal microstrains within specific grains can reveal the plastic anisotropy resulting from deformation. Trends in these data can give indications about deformation modes acting within the sample. An inverse modeling approach can be used and compared to complement experimental results. The elasto-plastic self-consistent (EPSC) approach, described by Truner and Tomé [122], has been used for this purpose. The EPSC code uses calculations of deformation mechanisms to produce results for elastic and plastic deformation at the grain length scale, which is in good correspondence with neutron diffraction data collected from an instrument such as SMARTS. Comparison between grain strain results of the model and experimentally recorded data can be used to interpret what deformation mechanism or mechanisms may be operating, as well as physical parameters of those deformation modes. Previous studies have been done using various systems, such as the work on U-Nb by Brown [123], Clausen [124] on Mg, and Holden et al. [125] on Inconel.

A full description of the EPSC approach is provided by Truner and Tomé [122]. Briefly, an ensemble of approximately 1000 grains is assumed which is assigned an initial texture, either random or of a particular preferred orientation distribution. A homogeneous equivalent medium represents the average properties of all grains, which fulfills the externally applied macroscopic boundary conditions. The model treats each grain as an elasto-plastically anisotropic inclusion within the medium, and calculates elastic and plastic strain with an Eshelby approximation. Self-consistency is achieved through matching the values of the grain and those of the matrix across an interface boundary. In this way, the EPSC code produces results that are intermediary to the descriptions of Taylor (constant strain) and Sachs (constant stress).

The model determines which grains would fulfill the Bragg condition for a given wavelength and diffraction vector, and the strain values of these grains are averaged. In this
way, the model produces results similar to the data collection process during diffraction experiments. Both diffraction and EPSC represent average grain information for grains of a particular orientation within a heterogeneous polycrystalline grain neighborhood.

Deformation hardening behavior within the EPSC model is addressed with application of the Voce hardening model

\textbf{Equation 10: Voce hardening law}

\[ \tau^S = \tau_0 + (\tau_1 + \theta_1 \Gamma)(1 - \exp(-\theta_2 \Gamma / \tau_1)) \]

where \( \tau \) is the instantaneous critical resolved shear stress (CRSS) of the \( s \)th slip system, \( \tau_0 \) and \( \tau_0 + \tau_1 \) are the initial and final CRSS, respectively, \( \theta_1 \) and \( \theta_2 \) are the initial and asymptotic hardening rates, and \( \Gamma \) is the accumulated plastic shear within the grain.

The EPSC was implemented to examine the initial deformation behavior of YCu (up to 2\% strain). Elastic constants necessary for input into the model were taken from Gschneidner et al. [46]. Several iterations of modeling calculation were attempted using various active slip systems. Good agreement between neutron diffraction data and model results was found through use of \{110\}<001> type slip, which has been widely reported to occur in B2 systems. A comparison of these results is shown in Figure 57, with data shown as points connected by solid lines, and model results shown as dashed lines.
Figure 57: Lattice strain results for diffraction data and EPSC modeling

The figure represents diffraction data and EPSC results within the region of primary deformation behavior, up to a stress of 140 MPa, and close agreement is seen between the two. Grains of the {222} orientation have relatively little increase in microstrain with increasing stress, whereas {200} grains show the greatest microstrain response. While this does not constitute proof of the active mode of deformation, the close similarity between results from diffraction and modeling using the {110} <001> type slip suggests that this mechanism is active within the YCu sample.
Experimental results – In-situ annealing in June 2006

The results from in-situ deformation experiments on YCu, and the conclusions drawn about the mechanisms operating within the sample, prompted further investigation to confirm or refute the findings. The annealing treatment was believed to create lattice coherency, creating artificially lowered peak intensities and a softer mechanical response. Experiments were designed to measure these effects of annealing.

Compression samples were prepared in the same method as described for the tests in December, but the final steps of quartz tube encapsulation and annealing were omitted. A neutron diffraction profile was collected for the sample in the unannealed state. A portion of these data is represented in Figure 58 (unannealed peak positions have been offset for clarity).

![Figure 58: Three diffraction peaks for patterns of unannealed and annealed samples](image)

Figure 58: Three diffraction peaks for patterns of unannealed and annealed samples
As expected, the unannealed sample demonstrated significantly higher peak intensities across the pattern, as well as a different ratio of peak intensities within the pattern. Of the three peaks seen in the figure, the most intense is for the \{110\} orientation. For this peak, the unannealed pattern shows approximately 2.5 times the peak intensity as compared with the annealed sample data from December.

The stress-strain response in compression of an unannealed sample is compared with the response of the annealed sample, displayed in Figure 59. The yield point of the unannealed samples is about 100 MPa, as compared with the 15 MPa yield strength of the annealed sample. The work hardening rate of the unannealed sample after yielding is also noticeably higher than that of the annealed sample. This relationship suggests that the unannealed sample may exhibit some strain hardening effect either from the lathe turning process, or possibly even from the hot swaging process.

![Graph showing stress-strain behavior](image)

**Figure 59: Macro stress-strain plot showing yielding behavior of unannealed and annealed compression samples**
To address the suggested mechanism of the development of an extinction resulting from annealing, an in-situ annealing experiment was carried out to make direct observations of this process. SMARTS has the capability of performing in-situ experiments based not only on mechanical loading, but on a range of temperatures as well, within a furnace and can be operated under vacuum. An unannealed sample of YCu was placed into the furnace and brought up to a temperature of 720°C, and diffraction patterns simultaneously were collected for the 48 hours. With increasing temperature, the Debye-Waller effect of thermal diffuse scattering decreased the measure intensity by approximately 80% across the entire diffraction profile. To account for this, data were normalized to the values of the first pattern collected at the elevated temperature. A plot of the integrated peak intensity for the most intense \{110\} peak as a function of time is given in Figure 60. The data trend confirms the expected result. The peak intensity was measured to decrease with increasing time at a fixed annealing temperature.

![Normalized peak intensity (Bank 2) for the \{110\} peak as a function of annealing time](Figure 60)

**Figure 60: Normalized peak intensity (Bank 2) for the \{110\} peak as a function of annealing time**
The reduction of intensity measured as a result of the annealing process, about 15% for the strongest peak after 48 hours, is much less than observed change in intensity as a function of applied load, about 250% after 2% strain, but this is due to the aforementioned overall intensity reduction from modified thermal scattering parameter at elevated temperature. A comparison of the patterns collected before and after annealing is nearly identical to Figure 58. The sample before annealing exhibits intensity of about 250% of that of the sample after annealing. This further supports the conclusion that annealing creates a structure within the YCu sample which exhibits extinction of diffracted intensity due to a transition from kinematic to dynamical diffraction behavior.
Additional Experiments

Several additional investigations have been conceived to further investigate the behavior of YCu during deformation, and specifically the transition between dynamical and kinematic diffraction conditions. The degree of lattice coherency necessary for this transition remains uncertain. Direct methods of investigation of this property of a material are uncommon. One possibility for studying this aspect of a sample is through the use of electron back-scatter detection (EBSD) and the technique of orientation imaging microscopy (OIM). The degree of misorientation necessary to disrupt the dynamical condition may be on the order of seconds of arc, and the angular resolution of OIM instruments is usually on the order of about 0.5°. Measurements of this precision could offer evidence that the sample does not possess such a high degree of coherency, or result in further circumstantial evidence that such lattice perfection may exist. The sharpness of the measured Kikuchi pattern, and the numerical value of the Confidence Index, offers another possible quantitative measurement. Discussions with Dr. M. Kramer also led to the interesting idea of subtracting Kikuchi pattern values mapped across the surface of a sample as a way of quantitatively evaluating lattice coherency. These experiments would be well suited to further study and measure the deformation behavior of YCu in the future.

The angular resolution of the EBSD is limited by the instrument geometry, specifically the distance from sample to detector. With the intention of achieving higher angular resolution, experiments using synchrotron microbeam diffraction were proposed and carried out. The experimental concept was very similar to the OIM technique; scanning a microbeam of high-energy x-rays across the surface of one or a few grains, and use diffraction data to calculate the orientation at each location. It would then be possible to determine the lattice misorientation with spatial resolution of a few µm, and the angular resolution was expected to be on the order of 0.005°, or about 18 arc-sec.
This experiment was proposed and accepted for the X13B beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. YCu samples were prepared, and a small in-situ compression apparatus was acquired thanks to Dr C. Aydiner of LANSCE. Unfortunately, numerous problems with data collection and analysis limited potential insights from the results. Diffraction data collection was significantly impeded due to a virus on the data recording computer, and as a result approximately 15% of all diffraction data from the CCD was never recorded.

The most limiting factor in further analysis was the lack of calibration information for the sample and the instrument. Without a reference pattern to determine instrument and detector constants, the recorded diffraction data could not be analyzed to determine crystal orientation. In an attempt to conduct preliminary analysis without calibration parameters, a new data analysis technique was developed to show quantitative information about diffraction patterns. For microbeam diffraction from a single grain within a polycrystal, the CCD detector several diffraction spots. By sequentially examining the same portion of the CCD data, and presenting it as a function of microbeam location on the sample, real-space maps of diffraction spots (of unknown orientation) were generated. One such example is shown in Figure 61.
Figure 61: Real-space map of CCD diffraction spot intensity

The figure represents a grid of diffraction locations across the surface of the sample. For a given micro diffraction position, the intensity of this particular spot suggests that a specific, albeit unknown, orientation. It can be seen from the figure that this particular diffraction spot is present within a given region of the sample, but absent within other locations. In general, it can be inferred that the regions which exhibit similar diffraction spot behavior are of very similar orientation. In other words, the presence of absence of a particular diffraction spot indicates different grains within the sample. It may even be possible, without orientation calibration information, to draw quantitative conclusions about orientation variation within a grain from the diffraction spot profile information, thus addressing the initial query of lattice coherency.
Conclusions

Investigations into the deformation behavior of rare-earth intermetallic YCu, and exhibited ductility, through the use of in-situ neutron diffraction have produced significant insight. The initial motivation for experiments was based on the possibility that twinning or phase transformation could be occurring within stressed samples, contributing the plastic yielding. Mechanical testing confirmed that tests conducted both in tension and compression do show a significant degree of plastic deformation and work hardening, onset at a relatively low yield stress of between about 15 and 25 MPa. Neutron diffraction patterns collected before, during, and after deformation show conclusively that neither twinning nor transformation from the B2 crystal to any other structure is occurring within an appreciable volume of the sample.

Data also indicate that multiple mechanisms may be operating at different stress levels, depending on the method of loading. At levels between about 20 and 150MPa, both tension and compression samples yield plastically. After 150 MPa samples deformed in tension give way to fracture, while compressive samples continue a work hardening behavior that would appear to operate to at least 325 MPa, and possibly well beyond. This is supported by a slight change in nature of load partitioning within the samples, as observed in grain-specific lattice strain data.

Tension and compression samples also exhibit a non-linear unloading behavior indicative of a Bauschinger effect. Compression samples show large jumps in strain, which may be a sign of a dynamic strain aging effect within the sample. Both of these observations may well be worth further investigation.

Results form single peak fit analysis of neutron patterns show an uncommonly observed trend in the intensity of diffraction peaks as a function of deformation. Various means of investigating these changes suggest that the annealing treatment applied to samples created relatively large regions of high lattice coherency within the structure, a mosaic block structure. These areas of crystalline perfection shift the diffraction behavior to a regime dynamical
diffraction behavior, wherein the coupling of the incident and diffracted beams interfere with the result of decreasing diffracted intensity. As deformation of the samples proceeds, the high degree of lattice coherency is disrupted by the build-up and motion of dislocations, mosaic block size is decreased, and the dynamical conditions operating within the sample are destroyed.

This suggested behavior was further validated by in-situ annealing tests intended to observe the creation of this condition. In-situ annealing shows a decrease in the measured peak intensity as a function of annealing time. A before-and-after comparison of the annealed samples shows a reduction in peak intensity on the order of that which was recovered due to deformation. This strong annealing treatment also affected the mechanical response of samples during deformation. The degree of lattice perfection which allowed for the operation of dynamic coupling of diffraction beams within the sample also allow for the easy creation and glide of dislocations within the lattice. As a result, samples show a low yield stress and a high degree of work hardening.

Diffraction results show that the deformation of YCu, and the ductile behavior in particular, is strongly effected by the development of mosaic substructure due to annealing, and the destruction of the same as a result of dislocation slip.
Appendix - Glossary

A – Anisotropic ratio, as defined by elastic stiffness constants

A<sub>hkl</sub> – Crystallographic orientation term for a particular plane with of Miller indices h k l

APB – Antiphase boundary, a planar disruption of crystallographic ordering

EDM – Electrical Discharge Machining

EPSC – Elasto-Plastic Self-Consistent modeling, a method of polycrystalline deformation simulation

FWHM – Full Width Half Maximum, a measurement of the width of a diffraction peak

GSAS – General Structure Analysis System, a software implementation of the Rietveld method of full-profile refinement

HIPPO – High-Pressure-Preferred Orientation, a third-generation in-situ neutron diffractometer, with multiple detector banks to collect crystallographic orientation distribution data

LANSCE – Los Alamos Neutron Science Center

RM-B2 – Family of intermetallic compounds composed of a rare-earth metal (RM) and a transition metal, which possess the B2 (CsCl-type) crystal structure

SMARTS – Spectrometer for Materials Research at Temperature and Stress, a third-generation in-situ neutron diffractometer, capable of using various in-situ sample environments, with a long path length for high resolution

SPF – Single Peak Fit, method of diffraction peak analysis which fits model parameters to collected data through least squares refinement

TOF – Time-of-flight, in reference to diffraction measurements obtained with fixed detector angles and varying energy/wavelength/velocity
References


111. Ames Laboratory, U.S.D.O.E.B.E.S., Materials Preparation Center, Ames, IA, USA.