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Mechanistic Origins of Damage Tolerance in High-Entropy Alloys

By

David H. Cook

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Engineering – Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Robert O. Ritchie, Chair

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Abstract

Mechanistic Origins of Damage Tolerance in High-Entropy Alloys

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Doctor of Philosophy in Materials Science and Engineering

University of California, Berkeley

Professor Robert O. Ritchie, Chair

High-entropy alloys represent a new paradigm for structural materials in extreme environments; however, these alloys are like their traditional dilute counterparts subject to strength-toughness trade-offs. Whereas alloys with the face-centered cubic (*fcc*) crystal structure have exceptional fracture resistance but low strength, those with the body-centered cubic (*bcc*) structure have exceptional strength but low toughness. To overcome these limitations, a mechanistic understanding of the origin of these properties is required. In *fcc* alloys, high toughness is achieved through a sequence of deformation mechanisms (dislocation glide followed by twinning and a phase transformation) that with increasing strain generate three-dimensional (3D) defect networks that simultaneously arrest and transmit dislocations. This sequence can be repurposed by additive manufacturing, a processing technique that allows carefully tailored microstructures to be inserted into the material that also act to impede and subsequently channel dislocations. This process allows for elevated initial strength, without inhibiting plastic deformation. In *bcc* alloys, on the other hand, toughness can be attained through compositional tuning which enables plastic deformation. In contrast to the *fcc* systems, a softening mechanism—kink band formation—distributes damage from a crack tip despite promoting necking in tension. These alloys can even suppress their ductile-to-brittle transition, inherent to *bcc* systems, by activating an inverted sequence of deformation mechanisms that begins with twinning and a transformation and ends with dislocation glide. This sequence effectively allows the material to rely on temperature-insensitive defects to dissipate damage.

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Chapter 1

Overview of the Dissertation

The work described in this dissertation was carried out as part of the Damage Tolerance in Structural Materials program in the Materials Sciences Division of Lawrence Berkeley National Laboratory. The primary purpose of this program is to understand the mechanical properties of face-centered cubic (*fcc*) and refractory body-centered cubic (*bcc*) high-entropy alloys (HEAs). Emphasis is placed on the salient deformation mechanisms that govern their properties.

Ch. 2 introduces the topic by addressing the inherent strength-toughness trade-offs of the *fcc* and refractory *bcc* systems. These materials exhibit a wide range of properties: while those with the *fcc* structure have exceptional fracture resistance, they often suffer from low yield strength; whereas those with the *bcc* structure possess exceptional strength but have poor fracture resistance. My work has focused on studying the salient deformation mechanisms that can be activated in these systems to overcome these trade-offs. While existing work has been performed on *fcc* HEAs that illustrates this inherent strength-toughness trade-off, little research existed on refractory *bcc* HEAs when I began this research. Therefore, ch. 4 is published as ref. [1], where the properties of a model equiatomic NbMoTaW alloy were investigated in tension to demonstrate that these materials are strong, but very brittle.

Ch. 3 addresses how to strengthen *fcc* HEAs without compromising their strength. These alloys generate exceptional toughness by activating a sequence of deformation mechanisms that create three-dimensional (3D) networks of defects that promote strain hardening, elevate ductility, and delay plastic instability. However, extended strain hardening invariably requires a low yield strength. To overcome this challenge, we demonstrate that additive manufacturing can be used to insert carefully engineered 3D microstructural networks that effectively elevate the yield strength, but also allow for dislocation glide through channels, thus simultaneously generating toughness. This work is published as ref. [2].

The following chapter transitions to the topic of refractory *bcc* HEAs. It is a short chapter intended to introduce a model NbMoTaW system that is very strong, but brittle. Little existing work had been published on the damage tolerance of these systems and so this chapter introduces the challenge of toughening these systems. This work is published as ref. [1].

The following two chapters (ch. 4 and 5) address the problems stated in ch. 3 and chronicle the mechanical behavior of refractory *bcc* NbTaTiHf, an alloy not too dissimilar in composition to NbMoTaW, but with markedly different properties. We found that shifting the composition allows this alloy to activate kink band formation which generates exceptional fracture resistance. These kink bands, despite being a softening mechanism that promotes plastic instability in tension, are very effective at distributing damage at a crack tip. Therefore, unlike in the *fcc* systems, *bcc* refractories do not need to activate extended hardening to generate toughness. This work is published as ref. [3].

Remarkably, this material also does not exhibit a ductile-to-brittle transition, at least at 20 K, as is described in Ch. 5. However, unlike at higher temperatures, kink bands are not the primary driver of this phenomenon. Here, the alloy passes through a slip-twinning transition, resulting in yielding and crack-tip plasticity to be primarily controlled by this temperature insensitive defect.

This deformation pathway allows for continued plasticity at cryogenic temperatures in a crystal structure where dislocation glide is severely restricted. This work is cited as ref. [4].

Chapter 2

Introduction

Structural materials provide the framework of our civilization. For this reason, technological advances in civilization are intimately connected with the discovery and use of new structural materials. Today, the frontier for novel structural materials is in aerospace as well as energy storage and generation where materials must withstand extreme temperatures. Under these conditions, materials must be strong (resist plastic deformation) and fracture resistant. Unfortunately, these two properties are mutually exclusive because strength requires high resistance to plastic deformation (dislocations glide) but high toughness is generated by promoting plasticity, which blunts and dissipates damage from a crack tip [5]. The challenge is thus to create damage-tolerant materials that are fracture-resistant, *i.e.* tough, without compromising strength.

Most structural materials are still metallic in nature. While traditional alloys are predominantly dilute: they have a single principal element and are mixed with small concentrations of other elements; a novel class of materials composed of multiple principal elements commonly known as medium- or high-entropy alloys (M/HEAs) which typically contain 3 to 5 principal elements have become a major field in metallurgy [6].¹ These alloys can crystallize into single phases and display remarkable strength and toughness. The following two sections introduce HEAs with the face-centered cubic (*fcc*) and body-centered cubic (*bcc*) crystal structure, respectively, and examine their inherent strengths and drawbacks.

2.1 FCC HIGH-ENTROPY ALLOYS

One of the initial thrusts into the HEA field began with the investigation of concentrated *fcc* alloys composed of 3d transition metals. Of all the possible alloy compositions, those based on the CrCoNi ternary system have come to the fore. These materials—particularly the CrCoNi alloy which is the subject of the rest of this section—display an exceptional combination of toughness, ductility and ultimate tensile strengths that are enhanced at cryogenic temperatures. Indeed, this material displays the highest toughness on record of 459 MPa√m at 20 K, a twice fold increase from room temperature [7], [8]. These properties are the direct consequence of the combination of deformation mechanisms accessed in this system. With increasing stress and strain, this material sequentially activates dislocation glide, dissociation of dislocations into partials, nano-twinning, and ultimately a phase transformation to hexagonal close-packed (*hcp*) ϵ martensite.[7], [9] As a result, what initially begins as a remarkably simple microstructure of single-phase, equiaxed grains, evolves into a complex three-dimensional (3D) network of defects that elevate strain hardening by impeding and transmitting dislocations.

One caveat of this mechanistic origin of high toughness is that it requires prolonged strain hardening. While this elevates the ultimate tensile strength, it invariably requires a low yield strength to begin with. Thus, although these materials are fracture resistant, they are impeded by

¹ The distinction between a high and medium entropy alloy has been defined to be the magnitude of the mixing entropy. While medium-entropy alloys have a mixing entropy between 1-1.5R, high entropy alloys have a mixing entropy greater than 1.5R. In light of recent studies showing that mixing entropy does not necessarily stabilize a single phase, terms such as “multi-principal element alloys” and “complex concentrated alloy” have come into use.

their low yield strengths [10]. Consequently, large amounts of material are required relative to higher strength alloys to build structural components that do not fail by yielding.

2.2 BCC REFRACTORY HIGH-ENTROPY ALLOYS

The second major class of HEAs that have emerged are single phase *bcc* refractory high/medium-entropy alloys (RHEA/RMEAs)—composed of high concentrations of Group IV, V, and VI elements [11]. These alloys have been identified as a novel design space for high-temperature materials. Unfortunately, RHEAs inhabit the extremes of the strength-toughness trade-off. Depending on the choice of elements, these alloys can either retain their strength at high temperature but have abysmal ductility and toughness [12]; or they can display some tensile ductility but suffer from issues with phase stability at higher temperatures [13], [14]. Specifically, alloys composed of group V-VI mixtures such as NbMoTaW and its derivatives possess impressive compressive strengths up to 1900 K but have limited plasticity as measured in compression [11], [12], [15]. These properties arise from the high intrinsic barrier for dislocation glide in these systems that raise the ductile-to-brittle transition inherent to *bcc* alloys [16]. On the opposite end of this spectrum, the IV-V mixtures (particularly the model HfNbTaTiZr alloy) can exhibit significant tensile plasticity and even high ambient temperature fracture toughness [17]. This is enabled by the group IV elements that reduce unstable stacking fault energies, and phonon frequencies that enable dislocation glide [16]. However, these elements also destabilize the *bcc* phase, which is detrimental to their high-temperature mechanical properties [14], [18], [19], [20]. Therefore, a careful compositional balance must be attained to optimize strength and ductility.

Chapter 3

Additively Manufactured Dual-Phase Al_{0.5}CrCoFeNi

3.1 INTRODUCTION

Conventional strategies to increase the strength in tough and ductile alloys usually follow a “top-down” approach to microstructural manipulation. In low-strength materials, this involves introduction of multi-dimensional defects that impede dislocation motion [5], [21]. First, grain boundary refinement can be employed for increasing strength and in some cases improving toughness when grain boundaries serve as dislocation sources [22], [23], [24]. As a result, refinement alone does not guarantee increased toughness; it requires additional boundary engineering. Second, forest hardening can also be employed to increase strength. Unfortunately, this effectively impedes dislocation motion but does not promote ductility [25]. For this reason, only microstructures that contain a patchwork of fully and non-fully recrystallized grains (termed partially recrystallized) can thread the needle between embrittlement and strength. Finally, precipitates or particles can also be introduced to impede dislocation motion [26]. However, unless dislocations can shear or transmit through precipitates, this strategy can be detrimental for fracture resistance [27].

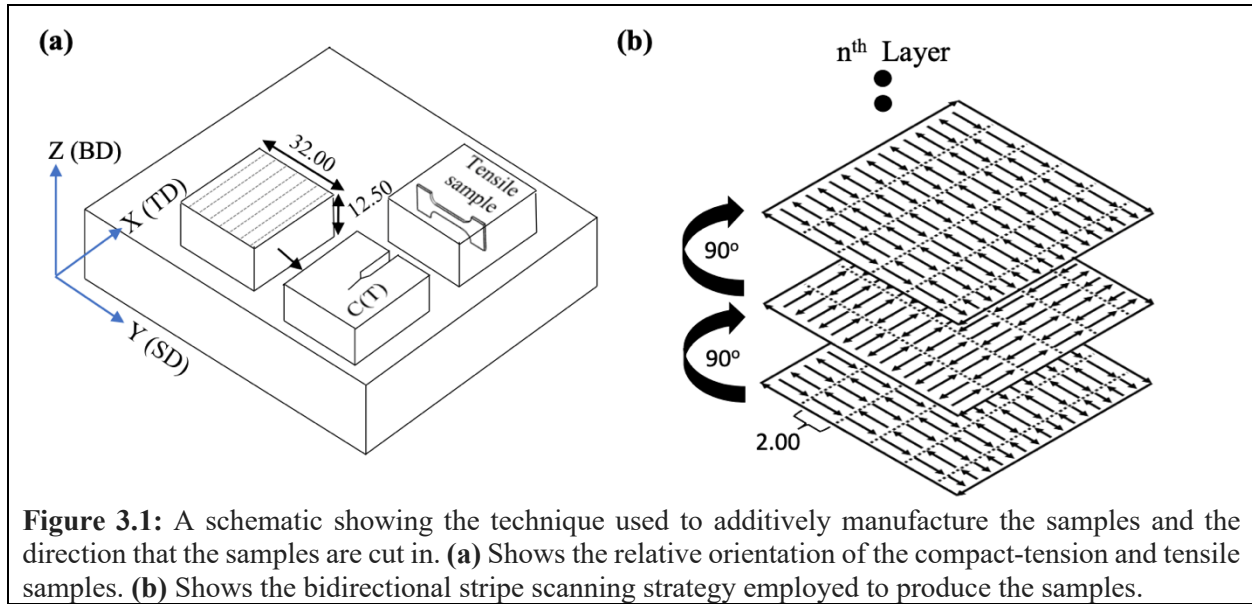
The limitations of “top-down” approaches underscore the need for novel microstructural strategies capable of overcoming this trade-off. Additive manufacturing, particularly laser powder bed fusion (LPBF), offers a promising “bottom-up” route by enabling microstructural design through precise control of laser parameters that influence melt pool size and morphology. The resulting microstructures are hierarchical in nature, comprising melt pool boundaries, cellular dislocation structures, and nanoprecipitates, all arising from the layer-by-layer, line-by-line printing process [28], [29]. When LPBF is employed in a CrCoNi-based alloy with aluminum additions (Al_{0.5}CrCoFeNi), it produces a microstructure mimicking a honeycomb: a soft *fcc* matrix interwoven with a hexagonal network of ordered *bcc* (B2) phase. Notably, the B2 phase does not fully encapsulate the *fcc* matrix. Instead, small “nanobridges” of connected *fcc* regions remain. Thus, instead of generating extended three-dimensional (3D) networks of defects that impinge and subsequently generate dislocations during deformation, this manufacturing process allows one to input 3D networks into the material that elevate the initial strength without compromising toughness.

3.2 PROCESSING AND MICROSTRUCTURE

3.2.1 Materials processing

To produce the material, first a pre-alloyed powder of composition (wt.%) Cr ~22.5%, Co ~24.6%, Fe ~23.2%, Ni ~24.5%, with Al ~5.21% was used in the LPBF process. The pre-alloyed powders were supplied by Vilory Advanced Materials Technology where they were gas-atomized to produce a powder size distribution of ~25–63 μm . The specimens were printed using an SLM280 (SLM Solutions, Germany) machine with an Nd: YAG fiber laser under a protective

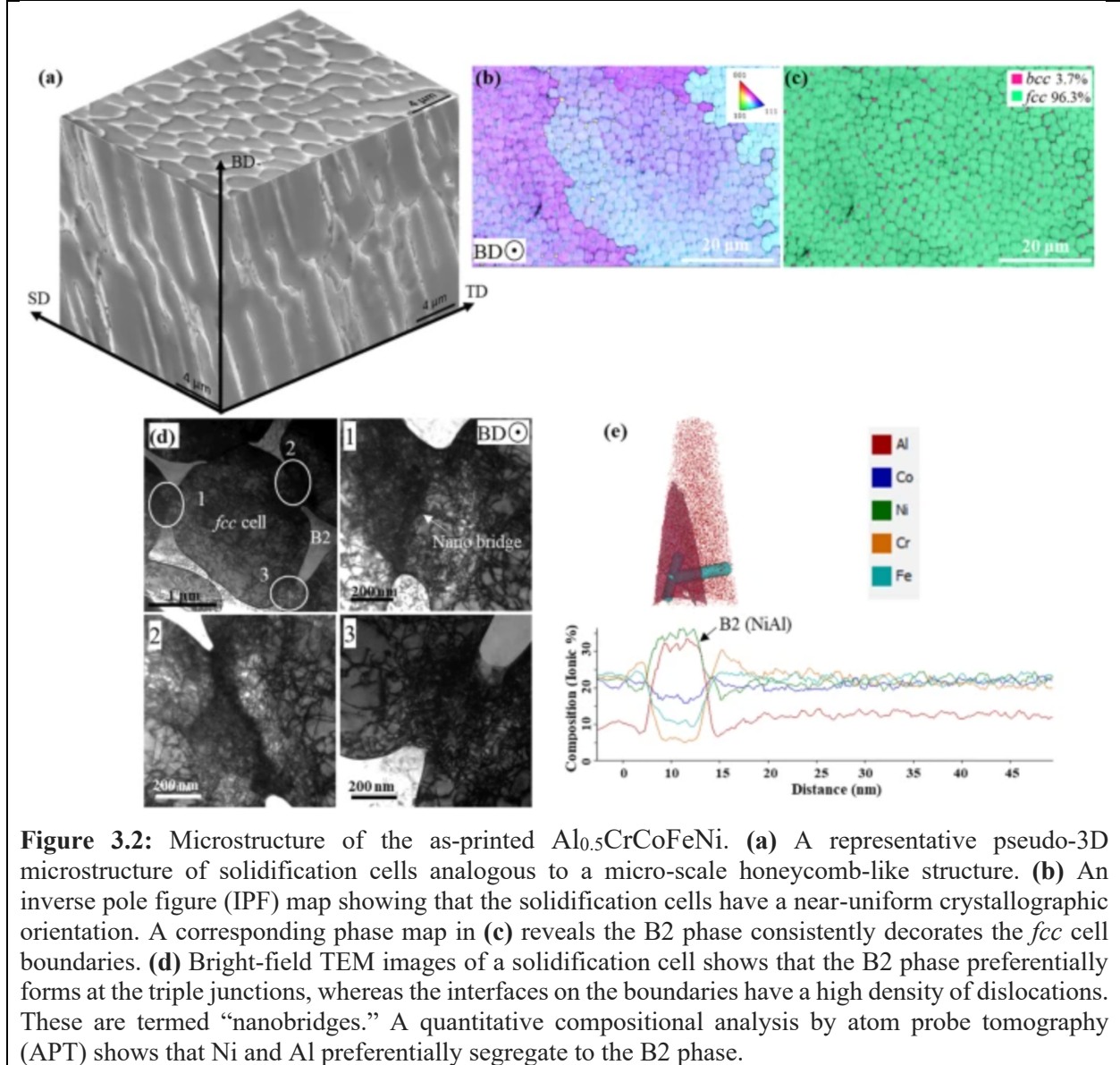
Ar gas environment with a laser power ~ 300 W, layer thickness ~ 50 μm , hatch spacing ~ 90 μm , and a scanning speed ~ 500 mm.s^{-1} with a relative density of $\sim 99.9\%$. Samples were then cut from the as-printed blocks with the orientations with respect to the build platform as shown in Fig. 3.1(a). A bidirectional stripe scanning strategy was employed for the process as is illustrated by the schematic in Fig. 3.1(b). To understand whether this additively manufactured microstructure is unique, four different heat treatments at temperatures 650 $^{\circ}\text{C}$ (20 h), 700 $^{\circ}\text{C}$ (1 and 2 h), and 750 $^{\circ}\text{C}$ (1 h) were performed on as-printed samples. The samples were heat-treated in a box furnace and then water quenched.



3.2.2 Microstructure

This processing technique of the $\text{Al}_{0.5}\text{CrCoFeNi}$ alloy imparted a hierarchical microstructure consisting of melt pool boundaries, cellular structures, and nanoprecipitates [28], [29]. To characterize these structures, the as-printed blocks were mechanically polished to a 0.04 μm finish and then examined by electron back-scatter diffraction (EBSD) or etched by Kalling's reagent for examination with an optical microscope. The plane parallel to the build direction (BD) shows columnar grains of size (area weighted equivalent circle diameter) $\sim 451 \pm 7$ μm . These grains have a primarily $\langle 111 \rangle$ and $\langle 110 \rangle$ texture. During additive manufacturing, the solidification microstructure is controlled by the ratio of thermal gradient, G , and cooling rate, R [30]. Here, the cooling rate, R , during the L-PBF process, is of order $\sim 10^5$ – 10^7 K/s , and the thermal gradient, G , is 10^5 – 10^7 K.m^{-1} [31]; therefore, the additively manufactured alloys generally have a microstructure consisting of a solidification cellular structure [29], [32], [33]. During cellular solidification, solutes with an equilibrium partition coefficient less than unity segregate onto the cell boundaries [30]. Such segregation is driven by the constitutional supercooling (ratio of G and R) and the surface tension of the solute-rich liquid [32], [34], [35]. The solute-rich cell boundaries, after solidification, can also trap dislocations nucleated by thermal cycling during the L-PBF process and form a dislocation cellular structure [36], [37], [38]. In the case of the $\text{Al}_{0.5}\text{CrCoFeNi}$ alloy, the CrCoFe -rich fcc matrix phase rejects Ni and Al onto the cell boundaries, since the equilibrium partition coefficients of Ni and Al are ~ 0.98 and ~ 0.81 , respectively. The

preferential segregation of Ni and Al on the cell boundaries was confirmed by one dimensional (1D) compositional line scans across these boundaries using atom probe tomography (APT) (Fig. 3.2(e)). Moreover, due to the constitutional supercooling, the liquid rich in Ni and Al solutes solidifies last as a supersaturated *bcc* B2 phase on the cell boundaries. The supersaturated prior B2 phase then goes through spinodal decomposition forming an ordered secondary *bcc*-B2 phase and disordered *bcc*-A2 phase of size ~ 10 nm [39]. The APT 1D compositional line scan across the precipitate on the cell boundary confirms the presence of ordered secondary B2 and disordered A2 (Cr-rich *bcc*) phases.



The spinodal mixture of *bcc* phases, hereafter referred to as (prior) B2, preferentially forms at the cell boundary triple points because the flux of solute rejection is highest towards these triple points (Fig. 3.2(c)). The solidification cells grow in a columnar structure, which forms a honeycomb structure in 3D (Fig. 3.2(a)-(b)). The equivalent diameter size of the solidification cells

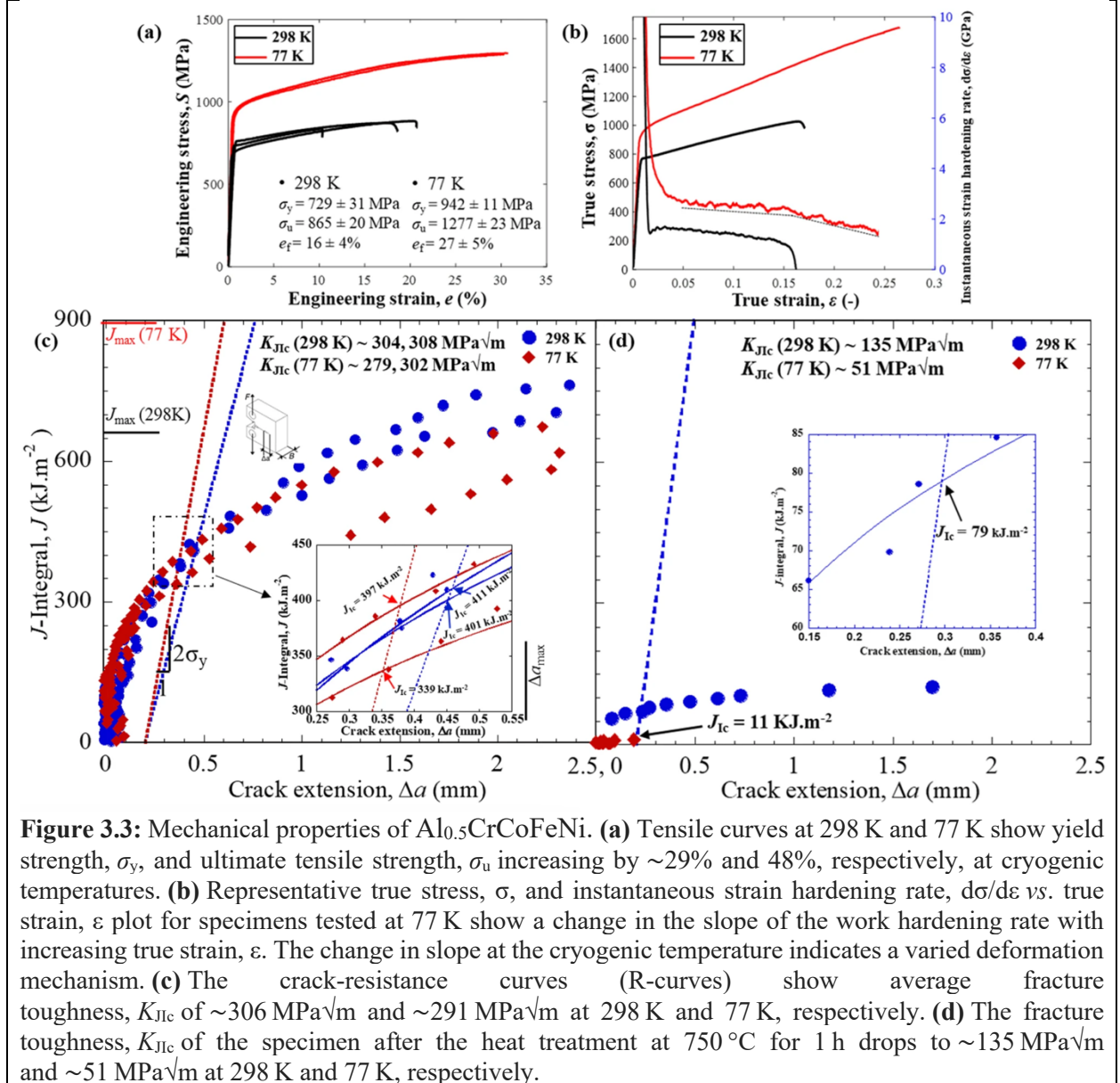
is $\sim 2.7 \pm 0.4 \mu\text{m}$; the corresponding size of the B2 precipitates on the cell boundaries is $\sim 0.54 \pm 0.016 \mu\text{m}$. Transmission electron microscopy (TEM) images show that these B2 phases on the cell boundaries are connected by nano-bridges of high dislocation density (Fig. 3.2(d)). The dislocation nano-bridge form in the regions of the cell boundaries where solutes (Al/Ni) concentration was insufficient to the form B2 phase; however, these solutes trap the dislocations nucleated by thermal cycling during the printing process to form the nano-bridge [40]. The interface of the B2 phase and the *fcc* phase is also incoherent, indicating that the B2 phase on the cell boundaries can effectively strengthen the microstructure.

3.3 MECHANICAL PROPERTIES

The tensile stress-strain curves of as-printed honeycomb microstructure in Fig. 3.3(a) showed yield strengths, σ_y of $\sim 729 \pm 31 \text{ MPa}$ at 298 K and $942 \pm 11 \text{ MPa}$ at 77 K. The elongation to failure, e_f , is $\sim 16 \pm 4\%$ at 298 K, which increases to $27 \pm 5\%$ at 77 K. Along with the yield strength close to $\sim 1 \text{ GPa}$ at 77 K, the representative true stress, σ , vs. true strain, ϵ , plots in Fig. 3.3(b) indicate that the micro-scale honeycomb microstructure can withstand stresses in excess of 1.5 GPa before fracture at cryogenic temperatures. Furthermore, during tensile loading at 77 K at a true strain exceeding 0.15, the change in slope of the instantaneous work-hardening rate suggests a change in the deformation mechanism. Compared to the properties of its wrought counterpart (grain size $\sim 9 \mu\text{m}$) the yield strength of the honeycomb microstructures in the L-PBF $\text{Al}_{0.5}\text{CrCoFeNi}$ alloy at 298 K is $\sim 48\%$ higher [41]. In comparison to other medium- and high-entropy alloys CrCoNi and CrMnFeCoNi, it is respectively $\sim 66\%$ and 78% higher at 298 K, and $\sim 43\%$ and 24% higher at 77 K, although its ductility is reduced [8], [42]. The elongation to failure, e_f , of the L-PBF alloy is ~ 1.5 – 3 times lower than that of its wrought counterpart and the CrCoNi-based high/medium-entropy alloys at these temperatures [8], [41], [42].

The fracture resistance of the honeycomb microstructure was investigated by nonlinear elastic fracture mechanics in the form of *J*-integral-based resistance curves (R-curves) - *J* vs. crack extension, Δa - where *J* accounts for the contribution of both the elastic and plastic deformation to the nonlinear-elastic strain energy release rate during the fracture process. The *J*-based R-curves for the honeycomb microstructure at 298 K and 77 K are shown in Fig. 3.3(c). At 298 K, the average value of the fracture toughness, J_{Ic} , at crack initiation is $\sim 406 \text{ kJm}^{-2}$, which marginally drops by $\sim 9\%$ to $\sim 368 \text{ kJm}^{-2}$ at 77 K. The crack-growth toughness, J_{ss} , is determined as the *J* value at a crack extension of $\Delta a \sim 2 \text{ mm}$ allowed for the C(T) specimen geometry in ASTM E1820 [43, p. 18]. The average crack-growth fracture toughness, J_{ss} , is $\sim 690 \text{ kJm}^{-2}$ and 643 kJm^{-2} at 293 K and 77 K, respectively. All the fracture toughness tests in the present study satisfy the *J*-dominance condition in plane strain, *i.e.*, $B, b \gg 10(J/\sigma_f)$, where *B* is sample thickness, *b* is the width of the uncracked ligament, and σ_f is flow stress ($\sigma_f = (\sigma_y + \sigma_u)/2$), where σ_u is the ultimate tensile stress. In terms of stress intensity factors, the mode-I fracture toughness, K_{Ic} , can be computed through the mode I *J*-*K* equivalence relationship, $K_{Ic} = (J^*)^{1/2}$, where *E* is Young's modulus, and ν is Poisson's ratio determined by ultrasonics method [44]. The average crack-initiation fracture toughness, K_{Ic} , at 298 K is $\sim 306 \text{ MPa}\sqrt{\text{m}}$ which drops marginally by $\sim 5\%$ to $290 \text{ MPa}\sqrt{\text{m}}$ at 77 K. At these temperatures, the average crack-growth fracture toughness, K_{Jss} , are $\sim 399 \text{ MPa}\sqrt{\text{m}}$ and $385 \text{ MPa}\sqrt{\text{m}}$, respectively. Compared to wrought medium-entropy alloy CrCoNi, which is one of the toughest materials on record, and the CrMnFeCoNi Cantor alloy, the fracture toughness, K_{Ic} , of honeycomb microstructure at 298 K is $\sim 47\%$ and 41% higher, respectively. Even at 77 K, the fracture toughness, K_{Ic} , of the present microstructure

is $\sim 6\%$ and $\sim 33\%$ higher, respectively [8], [42]. The enormity of these crack-initiation toughness, K_{JIC} , results becomes apparent only when it is seen in combination with the yield strength, σ_y of the honeycomb microstructure, which is $\sim 66\%$ and 78% higher at 298 K, and $\sim 43\%$ and 24% higher at 77 K compared to the CrCoNi and CrMnFeCoNi alloys [8], [42]. In this regard, the current 3D L-PBF-printed $Al_{0.5}CrCoFeNi$ alloy has superior damage-tolerance, in terms of a combination of strength *and* toughness, than the well-known wrought CrCoNi and CrMnFeCoNi medium- and high-entropy alloys.



To further elucidate the uniqueness of this microstructural design and its role in the intrinsic toughening of $Al_{0.5}CrCoFeNi$, a set of four heat-treatments (outlined in section 2.2) were performed to achieve the optimal combination of yield strength, σ_y , strain hardening, and elongation to failure, e_f . A summary of the tensile properties of this material after every heat

treatment is listed in Table 3.1. Out of the four heat treatments, the material treated at 750°C for one hour (henceforth referred to as HT3) showed the superior combination of tensile properties including strain hardening, *i.e.*, $\sigma_y \sim 1090$ MPa and $e_f \sim 9\%$ at 298 K, $\sigma_y \sim 1376$ MPa and $e_f \sim 6.6\%$ at 77 K. The microstructure of this material, henceforth referred to as HT3, consists of uniformly distributed B2 needles of multiple dimensions (Fig. 3.4). Therefore, C(T) specimens were heat-treated following the HT3 schedule for fracture toughness tests. The J -integral, J , vs. crack extension, Δa , results after the annealing treatment are plotted in Fig. 3.3(d). At 298 K, the HT3 microstructure shows a rising R-curve behavior with crack-initiation fracture toughness, K_{JIC} , of ~ 135 MPa $\sqrt{m}$, and crack- growth fracture toughness, K_{JSS} , of ~ 168 MPa $\sqrt{m}$, which is still reasonable considering the $\sigma_y \sim 1090$ MPa yield strength. However, at 77 K, the crack grows unstably, resulting in an initiation fracture toughness of $K_{JIC} \sim 51$ MPa $\sqrt{m}$. The crack-initiation fracture toughness, K_{JIC} , of the annealed microstructure is less than half at 298 K and ~ 5.7 times lower at 77 K compared to the honeycomb microstructure.

Heat Treatment	σ_y (MPa) 298 K, 77 K	σ_u (MPa) 298 K, 77 K	e_f (%) 298 K, 77 K
HT1 (700°C 1 hr)	1042, 1342	1220, 1536	13.0, 9.0
HT2 (700°C 2 hrs)	1175, 1409	1287, 1504	6.7, 2.2
HT3 (750°C 1 hr)	1090, 1376	1344, 1682	9.0, 6.6
HT4 (650°C 20 hrs)	1204, 1467	1365, 1583	7.2, 4.0

Table 3.1: Ambient and cryogenic (77 K) temperature tensile properties of the Al_{0.5}CrCoFeNi subjected to four different heat treatments.

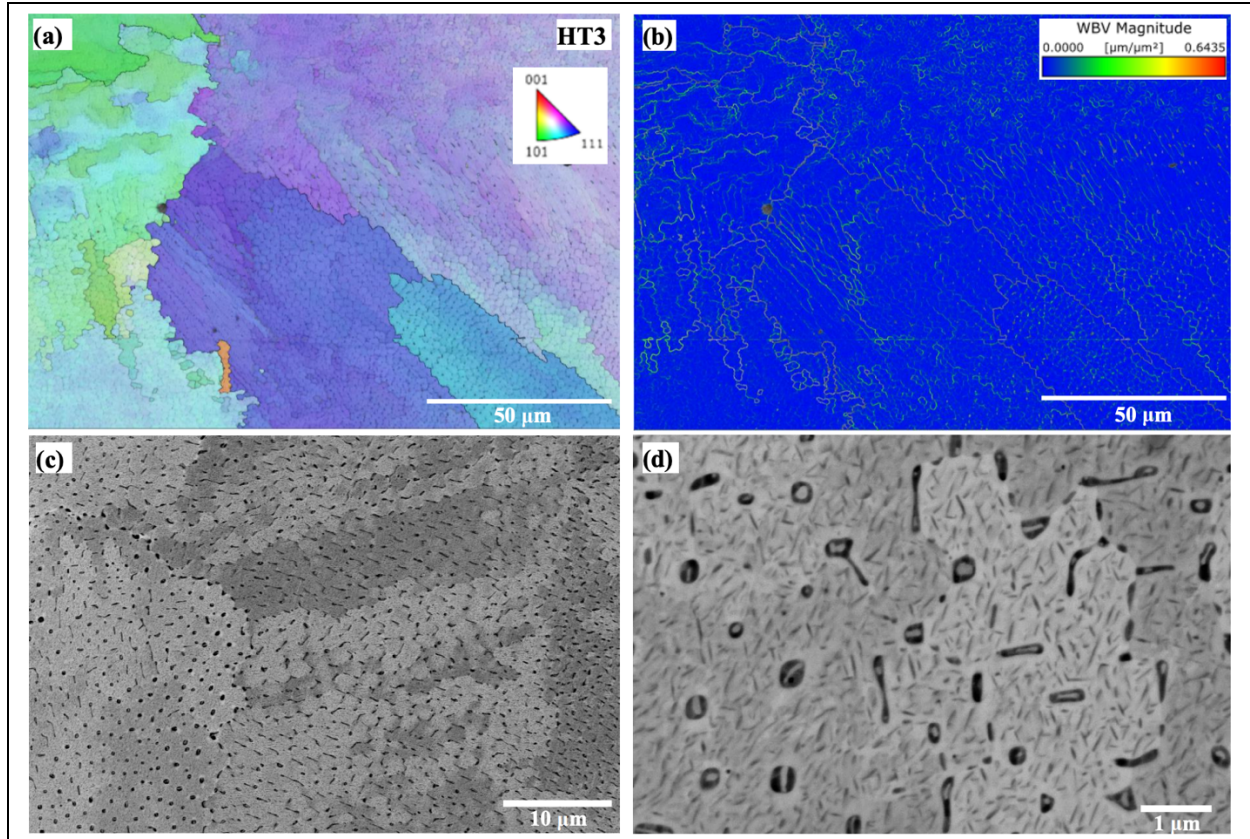
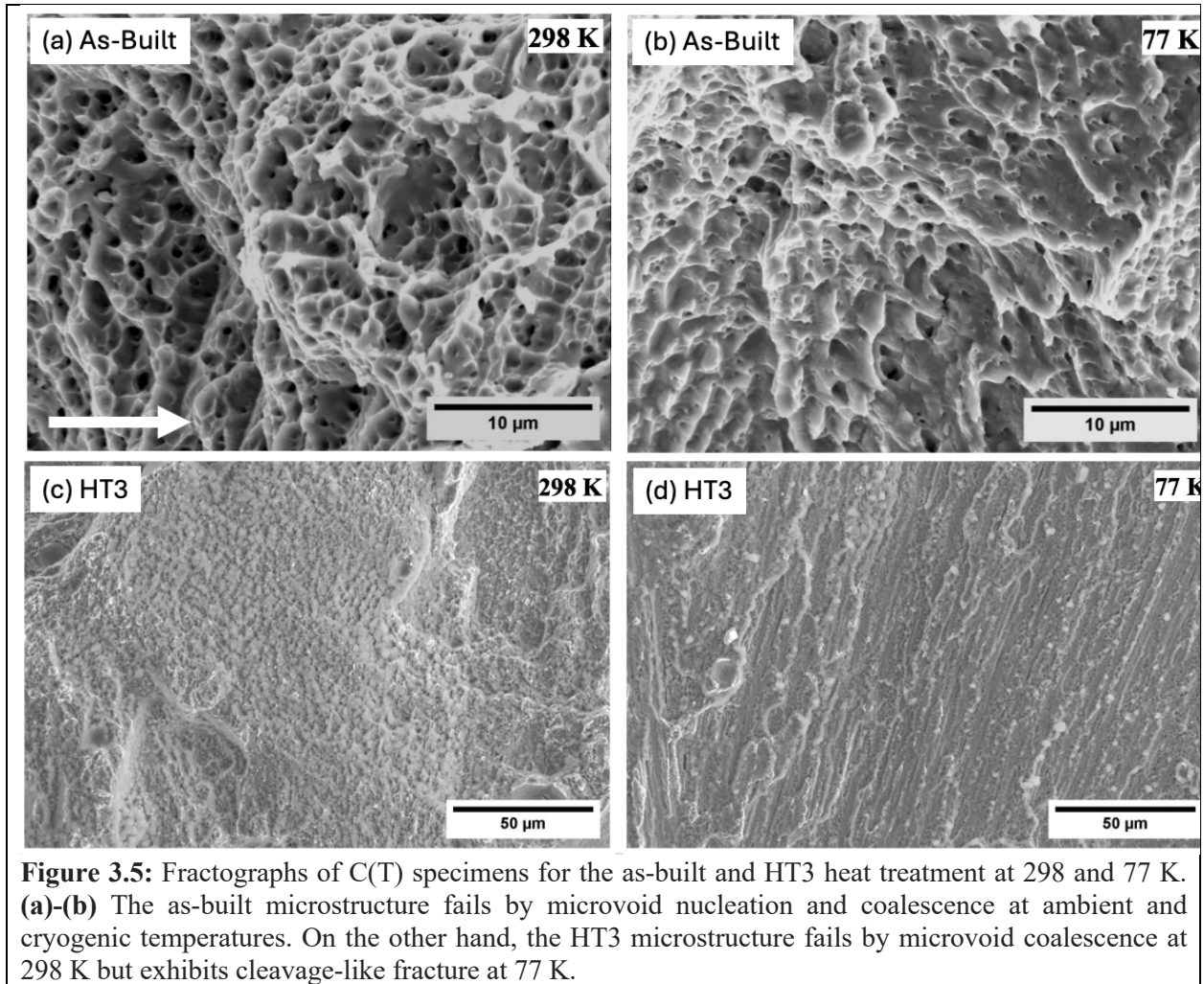


Figure 3.4: Microstructure of the HT3 material. (a) EBSD inverse pole figure (IPF) map of the specimen subjected to heat-treatment HT3 with corresponding weighted Burgers vector map showing dislocation distribution after the heat treatment in (b). (c) An electron-backscattered contrast image obtained by a scanning electron microscope shows the microstructure after the heat treatment. (d) Nanoscale B2 precipitates are uniformly distributed in the microstructure after the heat treatment.

The extreme difference in fracture properties is exemplified by the transition in fracture mode in the C(T) specimens, as seen on the fracture surfaces in Fig. 3.5. Whereas the as-built microstructure has a ductile failure at both ambient and cryogenic temperatures, the HT3 microstructure exhibits cleavage-like fracture at 77 K. This nominally brittle fracture at lower temperatures demonstrates that plastic deformation is restricted in this microstructure compared to the as-built condition, despite the modest increase in strength.



2.4 DEFORMATION MECHANISMS

To understand the reason behind the excellent combination of yield strength, σ_y , and fracture toughness, K_{JIC} , of the honeycomb microstructure as compared to the more traditional top-to-bottom microstructure exemplified by the HT3 microstructure, the post-fracture specimens

were sectioned from mid-thickness to investigate the deformation mechanisms in the fully plane-strain region. An electron backscattered diffraction (EBSD) inverse pole figure map in Fig. 3.6(a) shows the crack propagation path and deformed microstructure around it in a sample fractured at 77 K. The arrows in Figs. 3.6(a)-(b) indicate misorientation bands emanating from the crack. A correlated weighted Burgers vector (WBV) map in Fig. 3.6(c), corresponding to the EBSD map in Fig. 3.6(b), reveals the distribution of dislocations around the crack tip. WBV maps in Fig. 3.7(a) illustrate that the misorientation bands emanating from the crack tip correspond to a band of dislocations moving away from the crack tip; indeed, the dislocation bands spread as far as $\sim 300\text{ }\mu\text{m}$ away from the tip. Moreover, the magnified EBSD IPF and WBV maps in Figs. 3.6(b),(c) show that they pass through the nano-bridges/gaps available in between the B2 phase precipitates on the triple points of the cellular boundaries. A montage of the TEM images in Fig. 3.6(d), from the specimen tested at 298 K, also illustrates that dislocations move through the gaps between the B2 phase (nano-bridges) on the cell boundary. Furthermore, at 77 K, the TEM image from the plastic zone ahead of the crack tip shows deformation-induced nano-twinning (Fig. 3.6(e)). The growth of these nano-twins is restricted by the B2 phase on the *fcc* cell boundaries (Fig. 3.6(f)), which also contributes to the toughness of the microstructure. The change in the slope of the work-hardening rate during tensile deformation at 77 K also indicates activation of twinning above a true strain of $\epsilon > 0.15$ (Fig. 3.3(b)). Post-fracture deformation mechanism near the crack tip in the HT3 microstructure was also investigated. Fig. 3.7(b) shows the EBSD IPF and WBV maps of HT3 microstructure fractured at 298 K and 77 K, respectively. At 298 K, the WBV map shows the deformed region with high dislocation density spreading over a distance of $\sim 50\text{ }\mu\text{m}$ from the crack tip. This is even further reduced at 77 K, where the dislocations only spread $10\text{ }\mu\text{m}$ from the crack tip (Fig. 3.7(c)).

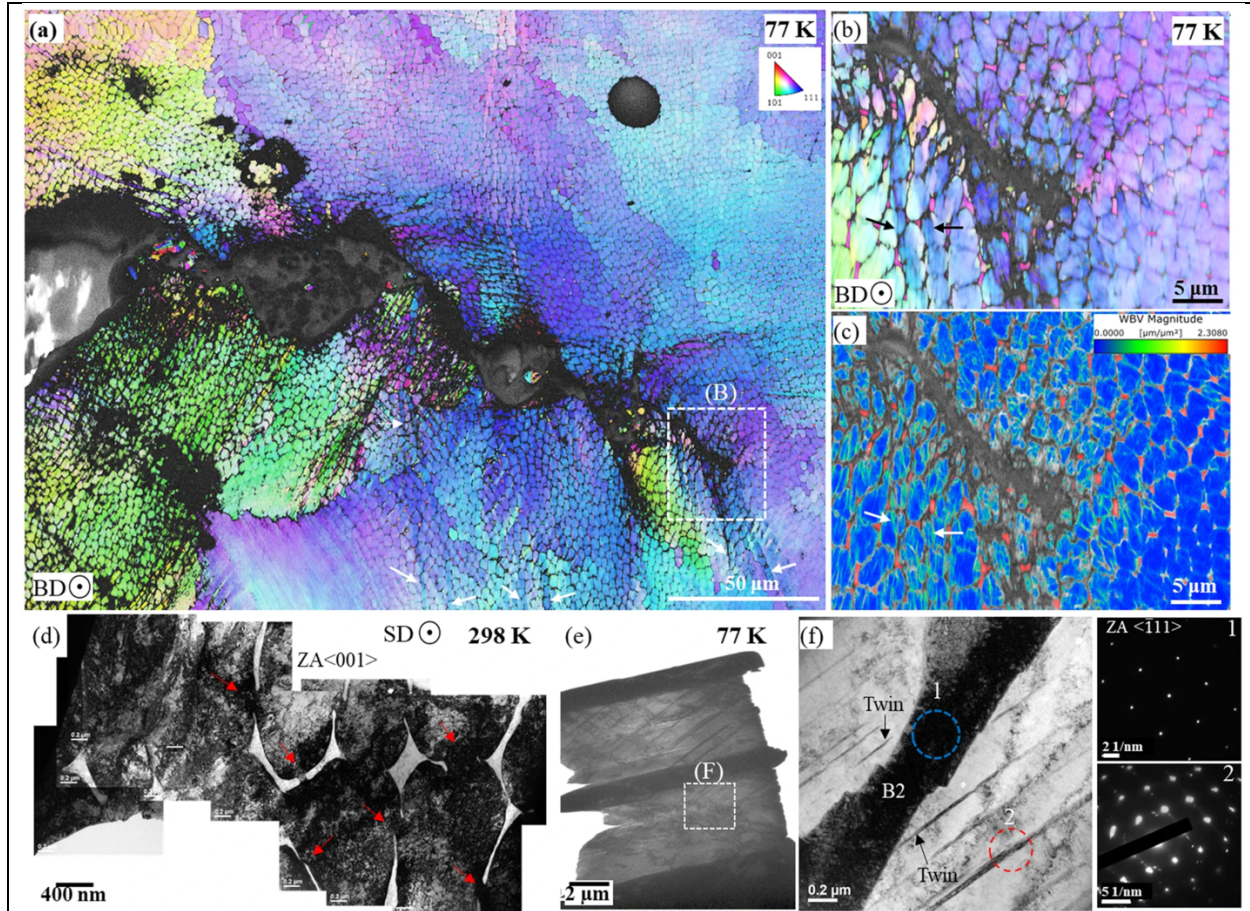


Figure 3.6: Crack-tip deformation features of the as-built microstructure. **(a)-(b)** EBSD maps of the microstructure in the vicinity of the crack-tip show bands of misorientation spreading away from the crack. A WBV map in **(c)** indicates that the deformation spreads primarily by dislocations channeling through the nanobridges connecting the *fcc* cells. **(d)** TEM near the crack-tip of the samples tested at 298 K shows that the B2 phase arrests dislocations, whereas the nanobridges allow for them to transmit between cells. At lower temperatures, (77 K), twinning is additionally activated and helps to elevate strain hardening. The B2 phase blocks twins as is illustrated in the micrograph and corresponding diffraction patterns in **(e)**.

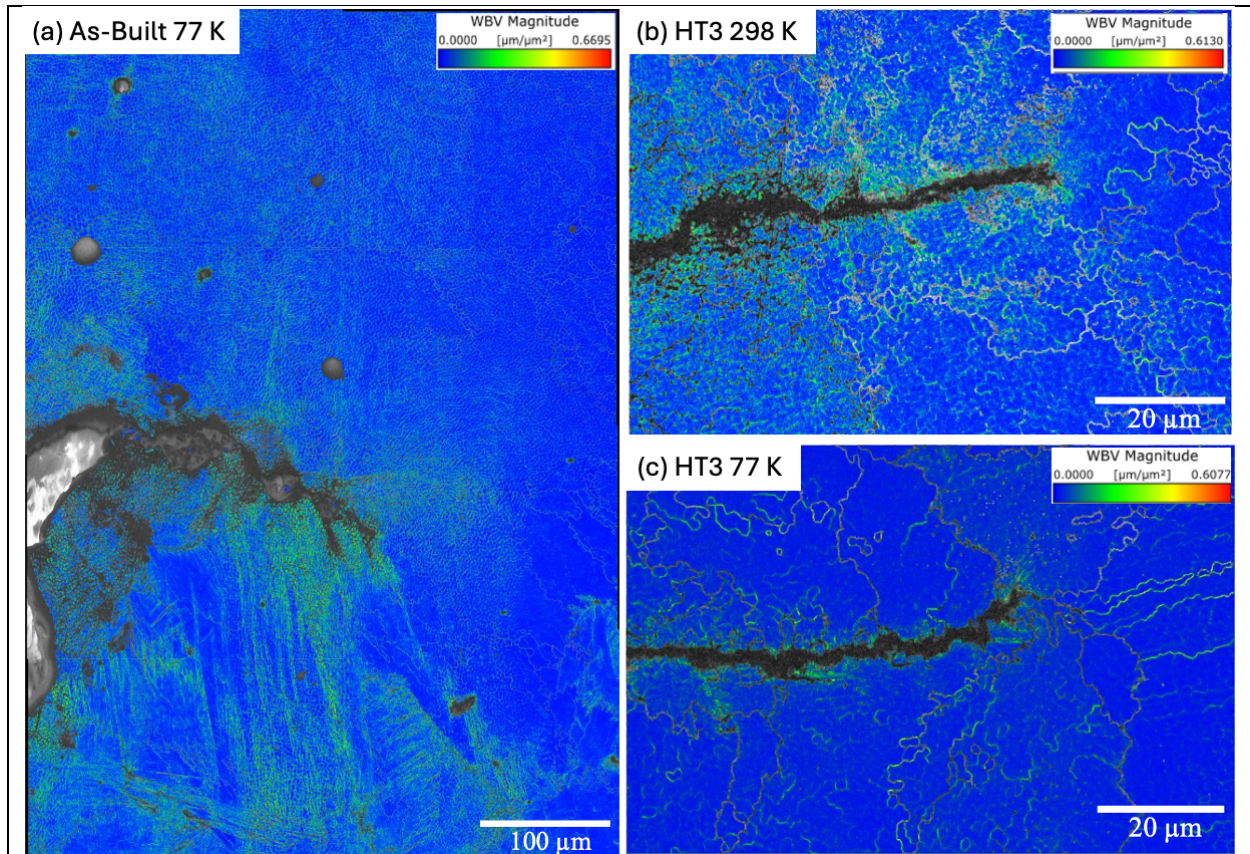


Figure 3.7: Large-scale EBSD maps of the deformation features in the as-built and HT3 microstructure. (a) A large scale WBV map shows the deformation bands spread $\sim 300 \mu\text{m}$ from the crack tip at 77 K, whereas in the material subjected to the HT3 heat treatment in the EBSD and WBV maps in (b)–(c) the deformation is restricted to $\sim 50 \mu\text{m}$ from the crack tip at 298 K and 10 μm at 77 K.

2.5 DISCUSSION

The microstructure of LPBF $\text{Al}_{0.5}\text{CrCoFeNi}$ is different than the cellular structure usually present in additively manufactured alloys. Usually, the cellular boundaries are decorated by solute atoms and intertwined dislocations. However, in LPBF $\text{Al}_{0.5}\text{CrCoFeNi}$, the cellular structure is composed of a secondary B2 phase that is interconnected by nano-bridges with high dislocation densities. Our observation of the deformation mechanisms in the preceding section illustrates that the B2 phase on the cell boundaries restricts the movement of dislocations at 298 K. This is further enhanced at 77 K by nano-twinning. The strenuous movement of dislocations and restriction to the growth of deformation nano-twins promote strain delocalization and necessitate additional energy to open the crack tip. However, this process can lead to brittle crack-propagation if the dislocations are overly restricted and cannot dissipate damage. As a result, the nano-bridge is critical, because it allows dislocations to transmit through to adjacent *fcc* cells to distribute plasticity from the crack tip (as is evidenced in Fig. 3.6(b)) [8], [45]. In combination, the nano-bridged honeycomb microstructure of the LPBF $\text{Al}_{0.5}\text{CrCoFeNi}$ provides a unique deformation mechanism resulting in a strength ($\sim 1 \text{ GPa}$) and toughness ($\sim 300 \text{ MPa}\sqrt{\text{m}}$). However, in the case of the LPBF CrCoNi with a conventional cellular structure, the combination of strength and toughness is even inferior

to their conventionally manufactured counterpart (Fig. 3.1) [10], which highlights the uniqueness of the cellular structure in LPBF Al_{0.5}CrCoFeNi.

The LPBF Al_{0.5}CrCoFeNi shows one of the best combinations of yield strength, σ_y , and fracture toughness, K_{JIC} , compared to all known structural materials as is shown in the “banana plot” in Fig. 3.8. The multiphase honeycomb microstructure is tougher and stronger than recently developed conventional single-phase high- and medium-entropy alloys and the high Mn/Ni cryogenic steels [42], [46], [47], [48, p. 304]. The honeycomb microstructure (in the as-printed condition) consists of a high dislocation density inside the cells (Fig. 3.2(d)) with the B2 phase on the cell boundaries connected by nano-bridges of dislocations (Fig. 3.6(d)) [40], [49], [50]. Both, in combination with solid solution strengthening, provide a yield strength, σ_y , ~48% higher compared to the wrought counterpart at 298 K [41]. Furthermore, during severe plastic deformation, dislocations can move through the nano-bridges connecting the B2 precipitates on the cell boundaries (Fig. 3.2(d)). Therefore, the microstructure shows a crack-initiation fracture toughness, K_{JIC} , ~306 MPa $\sqrt{m}$, by spreading the plastic damage further from the crack tip. Moreover, by activating nano-twinning at 77 K in combination with dislocation-assisted plastic deformation, the honeycomb microstructure shows a yield strength, σ_y , ~1 GPa, and fracture toughness, K_{JIC} , ~300 MPa $\sqrt{m}$. Consequently, the material’s strength and fracture toughness can be tailored to suit particular application requirements. The multiphase honeycomb microstructure produced by L-PBF, a “bottom-up” manufacturing process, highlights the possibility of alloy design for intrinsic toughening. In contrast, the uniformly distributed B2 precipitates after heat treatment completely restrict the movement of dislocation away from the crack tip (<10 μm) resulting in ~5.7 times less fracture toughness at 77 K. These two extreme results highlight the limitation of conventional “top-down” processes in simultaneously strengthening and toughening ductile materials.

2.6 SUMMARY

In summary, HEAs with the *fcc* structure can be strengthened without compromising toughness using bottom-up manufacturing techniques such as LPBF that endow the material with a hierarchical structure, similar to how structural materials are built by nature [7], [8], [42]. Indeed, the CrCoNi alloy displays the highest reported toughness on record which it derives through a synergistic sequence of mechanisms that generates 3D deformation networks that both arrest and transmit dislocations during deformation. Consequently, what begins as a simple microstructure consisting of single-phase equiaxed grains evolves to contain nanotwins, *hcp* phase, and extended stacking fault networks with increasing deformation. However, we demonstrate that analogous 3D microstructural networks can be inserted into these HEAs using additive manufacturing techniques. Consequently, pre-existing microstructures—in this case a honeycomb dual-phase microstructure—can elevate yield strength, but also effectively allow for extended strain hardening that does not localize damage at a crack-tip. In the same way that stacking faults, twins, and thin lathes of *hcp* martensite arrest dislocations but also allow for their transmission at marginally higher stresses [7], the B2 phase arrests dislocations, but the nanobridges connecting the *fcc* cells can break down with increasing deformation to allow for subsequent dislocation transmission. This mirrored deformation process does not compromise toughness despite increasing initial yield strength, unlike in traditional, single phase *fcc* HEAs.

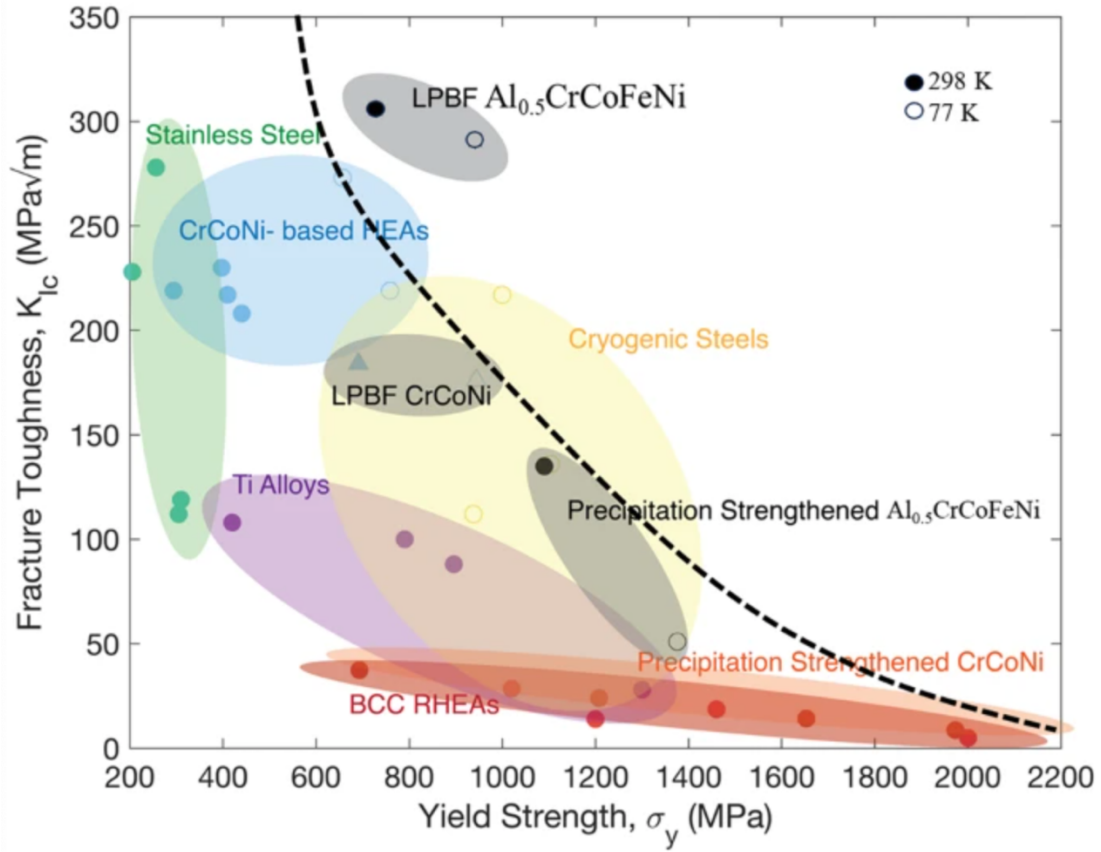


Figure 3.8: Banana plot showing the strength-toughness trade-off of *fcc* and *bcc* HEAs. The LPBF $Al_{0.5}CrCoFeNi$ alloy shows superior strength and toughness compared to other *fcc* HEAs and tradition top-down manufactured, precipitation strengthened $Al_{0.5}CrCoFeNi$.

Chapter 4

Refractory NbMoTaW

4.1 INTRODUCTION

Unlike *fcc* HEAs, dilute and concentrated refractory alloys typically have high strength but low toughness [51], [52]. One of the most popular RHEAs in the literature that exemplifies this trade-off is the model equiatomic NbMoTaW RHEA [12]. This material is a promising candidate for high-temperature structure applications because its yield strength surpasses that of Ni-based superalloys at temperatures above $\sim 1000^{\circ}\text{C}$ [12]. However, a significant caveat of the results in the literature is that all these properties have been measured in compression, a stress-state that closes any pre-existing flaws or cracks in the material that could otherwise cause a brittle failure in tension. Thus, limited information exists on this materials suitability for safety-critical applications, and incomplete conclusions have been drawn on this materials propensity for plastic deformation.

A primary reason that this material has been tested in compression is because it possesses a very high melting point that makes it difficult to process [53]. Moreover, the material has an exceptionally high ductile-to-brittle transition temperature (DBTT) which makes it difficult to process samples without cracks. For this reason, the fracture resistance of only nanocrystalline, single-crystal, and bi-crystal NbMoTaW has been investigated in the literature (no bulk-scale polycrystalline NbMoTaW has ever been tested for fracture). The nano-scale and single/bicrystal alloys show a fracture toughness, K_{Ic} , of ~ 3 , 2, and $0.2 \text{ MPa}\sqrt{\text{m}}$, respectively, abysmal compared to $K_{Ic} \sim 75\text{--}200 \text{ MPa}\sqrt{\text{m}}$ of structural materials used in safety-critical applications [5], [54], [55]. The poor fracture resistance of NbMoTaW under tension primarily originates from two factors—(i) grain boundary decohesion induced by interstitial segregation [52], [56], [57], and (ii) the alloy's failure to satisfy the condition of intrinsic cleavability (*i.e.*, in principle, it is more favorable for the crack to cleave than to emit a dislocation under applied stress) [58]. To point (i), the NbMoTaW alloy has smaller effective radii and interstitial sites than subgroup VI elements (Mo and W), which contributes to the thermodynamic driving force for interstitial segregation to grain boundaries and, ultimately, their decohesion under applied stress [59], [60]. For this reason, NbMoTaW can be embrittled with O contents as low as 100 ppm [59], which makes it challenging to process this alloy in bulk. To the latter point (ii), dislocation activity in this alloy during compression loading indicates the possibility of ductilizing the material by compositional changes, but the compositional modifications will also affect the high-temperature strength of the RHEA. Therefore, exploring alternate mechanisms of toughening NbMoTaW is essential. For example, in ceramics and dilute group VI (Cr, Mo, W) refractory alloys, where mobile dislocation activity is essentially non-existent, extrinsic toughening can improve fracture resistance through crack bridging or deflection [61]. Extrinsic toughening by crack deflection involves deviating the crack from the Mode-I direction, *i.e.*, effectively reducing the driving force for crack growth [5].

4.2 RESULTS

4.2.1 Microstructure

To investigate the tensile and fracture properties at temperatures RT to 1200 °C, nominally equiatomic NbMoTaW RHEA buttons with equiaxed and columnar microstructures were produced by arc-melting and then HIPed for four hours. Fig. 4.2(a) shows the initial microstructure of the cross-section of a NbMoTaW button after HIP at 1850 °C for four hours. Several regions can be observed: one with casting voids, a second with columnar grains, and a third with equiaxed grains. The presence of these regions in the microstructure implies that the HIP process at 1850 °C could not fully recrystallize/homogenize the microstructure or eliminate the casting voids (as incidentally can be a problem with many high-temperature RHEAs). However, a small region of equiaxed microstructure formed in the bottom half of the buttons. For details on the processing techniques that resulted in this microstructure see ref. [1]. Analysis of the grains in the equiaxed region shows a bimodal distribution of grains with an average size of $\sim 105 \pm 66 \mu\text{m}$ and smaller recrystallized grains of size $\sim 37 \pm 15 \mu\text{m}$ on the grain-boundary triple points.

While x-ray diffraction experiments indicate that the material has a single *bcc* phase, TEM investigations of the grain boundaries reveal a secondary grain-boundary phase (Fig. 4.2(b)). An energy dispersive spectroscopy (EDS) line scan across the grain-boundary phase (Fig. 4.2(c)) reveals significantly higher O content and the depletion of Mo, Ta, and W elements. The grain-boundary phase consists of Nb (~ 20 -23 at.%) and O (~ 62 -64 at.%) with a small amount of other metallic constituents, implying the formation of a metal oxide complex with Nb as the primary constituent and a structure similar to Nb_2O_5 [62], [63].

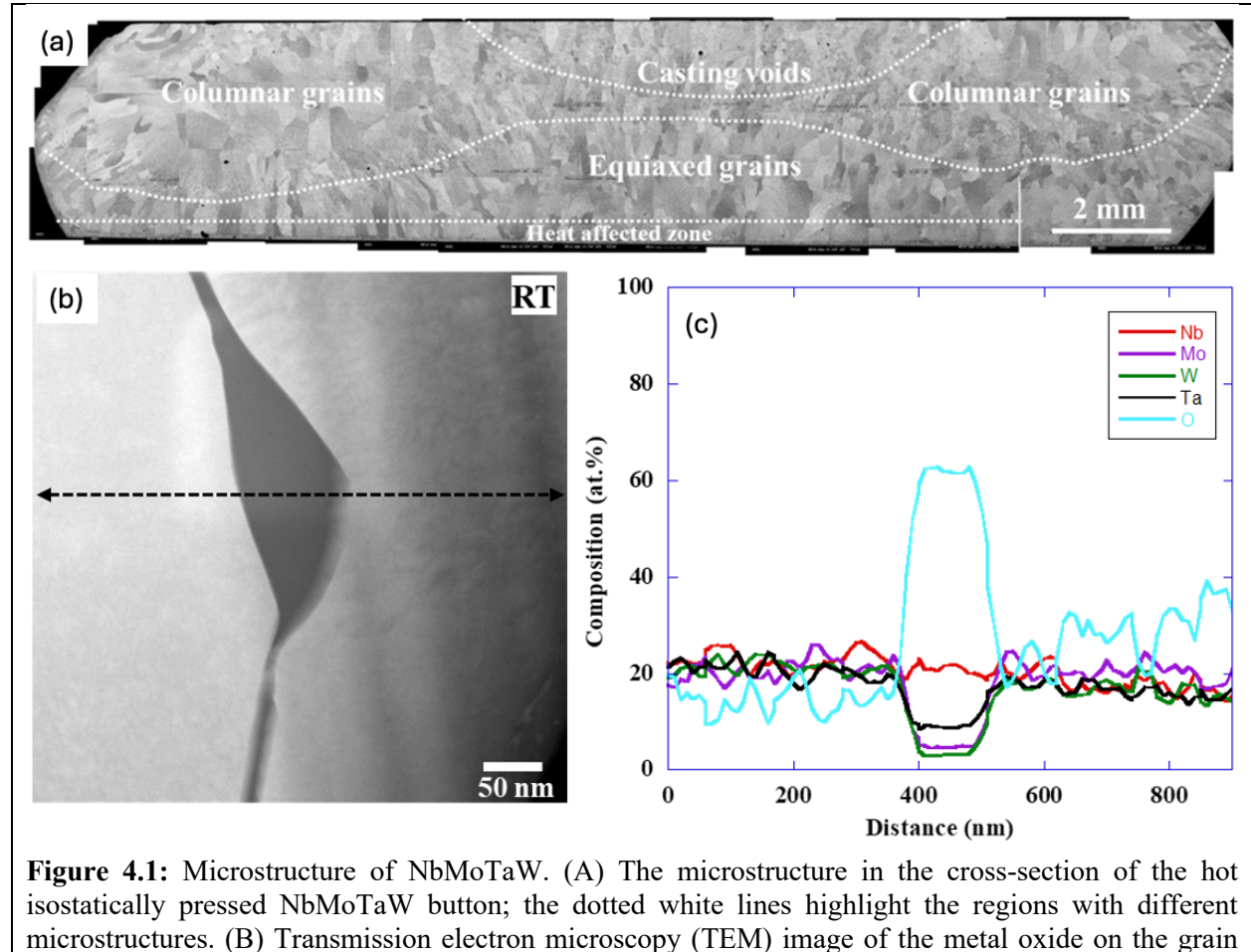


Figure 4.1: Microstructure of NbMoTaW. (A) The microstructure in the cross-section of the hot isostatically pressed NbMoTaW button; the dotted white lines highlight the regions with different microstructures. (B) Transmission electron microscopy (TEM) image of the metal oxide on the grain

boundary of NbMoTaW and (C) the result of energy dispersive spectroscopy (EDS) line scan across the metal oxide showing compositional variation of elements Nb, Mo, Ta, W, and O.

4.2.2 Mechanical Properties

The compressive true stress, σ , vs. true strain, ϵ , curves of NbMoTaW RHEA microstructure at RT, 800, and 1200 °C temperatures, are plotted in Fig. 4.2(a). The respective compressive yield strength, σ_y , and peak strength, σ_p are listed in Table 4.1. The RHEA microstructure shows an impressive average compressive yield strength, σ_y , of $\sim 1390 \pm 20$ MPa at RT and 301.5 MPa at 1200 °C. Even after a sharp decrease in compressive yield strength, σ_y , at 1200 °C, the present microstructure is stronger than most RHEAs at 1200 °C [15]. Moreover, the NbMoTaW microstructure fails after withstanding $\sim 2\%$, $\sim 9\%$, and 2% plastic deformations at RT, 800 °C, and 1200 °C, respectively.

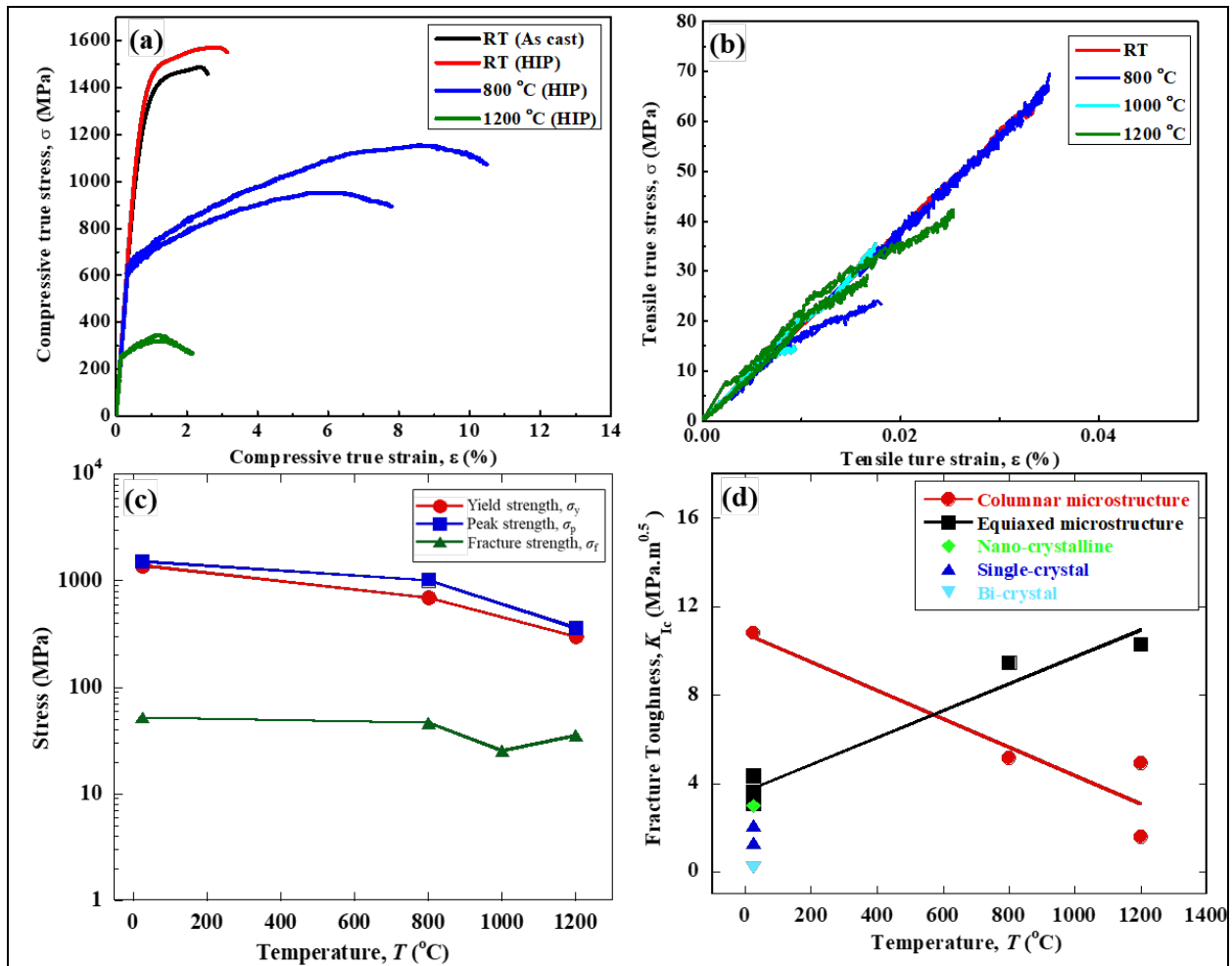


Figure 4.2: Mechanical behavior of NbMoTaW. (A) Compression true stress, σ , vs. true strain, ϵ , plots of NbMoTaW specimens at ambient temperature (RT), 800 °C, and 1200 °C. At ambient temperature, both as-cast and HIPed specimens were tested. All other stress-strain curves correspond to HIPed specimens. (B) Tensile true stress, σ , vs. true strain, ϵ , plots of NbMoTaW at RT, 800, 1000, and 1200 °C temperatures. (C) The variation in compressive yield strength, σ_y , peak strength, σ_p , and tensile

fracture strength, σ_p with temperature. (D) The fracture toughness, K_{Ic} , of columnar and equiaxed microstructure vs. temperature. The K_{Ic} fracture toughness of the nano-crystalline, single-crystal, and bi-crystal NbMoTaW are plotted for comparison [52], [57].

Temperature (°C)	Compressive yield strength, σ_y (MPa)	Compressive strength σ_p (MPa)	Tensile fracture strength, σ_f (MPa)	Fracture Toughness, K_{Ic} (MPa√m) *Conditional fracture toughness (K_Q)	
				Equiaxed grains	Columnar grains
25 (RT)	1390 ± 20	1520 ± 25	52.5 _(62.7, 42.3)	3.7 _(3.1, 3.6, 4.3)	10.8
800	694 _(691, 697)	1014.5 _(931, 1098)	46.8 _(69.5, 24)	9.5	5.1
1000			25.3 _(15, 35.5)		
1200	301.5 _(306, 297)	361.5 _(371, 352)	35.7 _(42.3, 29.2)	10.3*	3.2 _(1.6, 5)

Table 4.1: The tensile fracture strength, compressive strength, and fracture toughness of NbMoTaW at temperatures 25 °C, 800 °C, 1000 °C, and 1200 °C.

The corresponding tensile true stress, σ , vs. true strain, ε curves of the NbMoTaW alloy, however, display a markedly different trend; they are plotted in Fig. 4.2(b). Specimens at all temperatures, *i.e.*, RT to 1200 °C, fracture before yielding and the respective tensile fracture strength, σ_f , is less than 70 MPa. With increasing temperature, σ_f drops marginally (Fig. 4.2(c)). A noticeable drop of ~50% in σ_f is observed at 1000 °C, which recovers by ~30% at 1200 °C (Fig. 3c). However, the number of tests conducted for each condition is insufficient to provide a statistical trend of the tensile fracture strength, σ_f , as a function of temperature. Furthermore, the maximum tensile ductility, *i.e.*, elongation to failure, e_f , in tension is 98%, 99%, and 98% lower than the plasticity under compression at respective temperatures RT, 800 °C, and 1200 °C.

Investigations of the fracture toughness of this alloy from ambient to high temperatures (1200°C), plotted in Fig. 4.2(d) as a function of temperature, show that the toughness strongly depends on temperature and microstructure ahead of the crack tip. While the K_{Ic} of samples with the equiaxed microstructure increases with increasing temperature, samples with the columnar microstructures show an opposite trend (Fig. 4.2(d)). At RT, the K_{Ic} of the equiaxed microstructure is $\sim 3.7 \pm 0.5$ MPa√m, which is nearly three times lower than the K_{Ic} of the columnar microstructure ($K_{Ic} \sim 10.8$ MPa√m). Although the average K_{Ic} of equiaxed microstructure at RT is slightly higher than that of nanocrystalline NbMoTaW with columnar microstructure ($K_{Ic} \sim 3$ MPa√m) and single or bi-crystal NbMoTaW ($K_{Ic} \sim 2.1, 0.2$ MPa√m) [52], [57], these K_{Ic} values are also similar to those of recrystallized W-30Ta binary alloy [64]. At 800 and 1200 °C, the K_{Ic} of the equiaxed microstructures is 9.5 and 10.3 MPa√m, respectively, but the K_{Ic} of columnar microstructure is between 1.6 and 4.9 MPa√m. Although the fracture toughness of the NbMoTaW alloy remains

low, the K_{Ic} of the equiaxed microstructure above 800 °C is still slightly higher than most RHEAs investigated to date [15], [65].

4.3 DISCUSSION AND SUMMARY

To understand the origin of the trend of toughness increasing with decreasing temperature for the equiaxed microstructure, and decreasing with increasing temperature for the columnar microstructure, we investigated the fracture surfaces. At room temperature both columnar and equiaxed microstructure predominantly fail by transgranular fracture, which progressively changes to a mixture of transgranular and intergranular fracture at 800 °C and fully intergranular fracture at 1200 °C. Representative fractographs illustrating this transition are shown in Fig. 4.3. While all these failures are brittle, the intergranular failure locally forces the crack out of mode I, which provides extrinsic toughening. This is primarily driven by the lack of phase stability of the grain boundary oxide (in-situ TEM videos illustrating the phase decomposition are in ref. [1]).

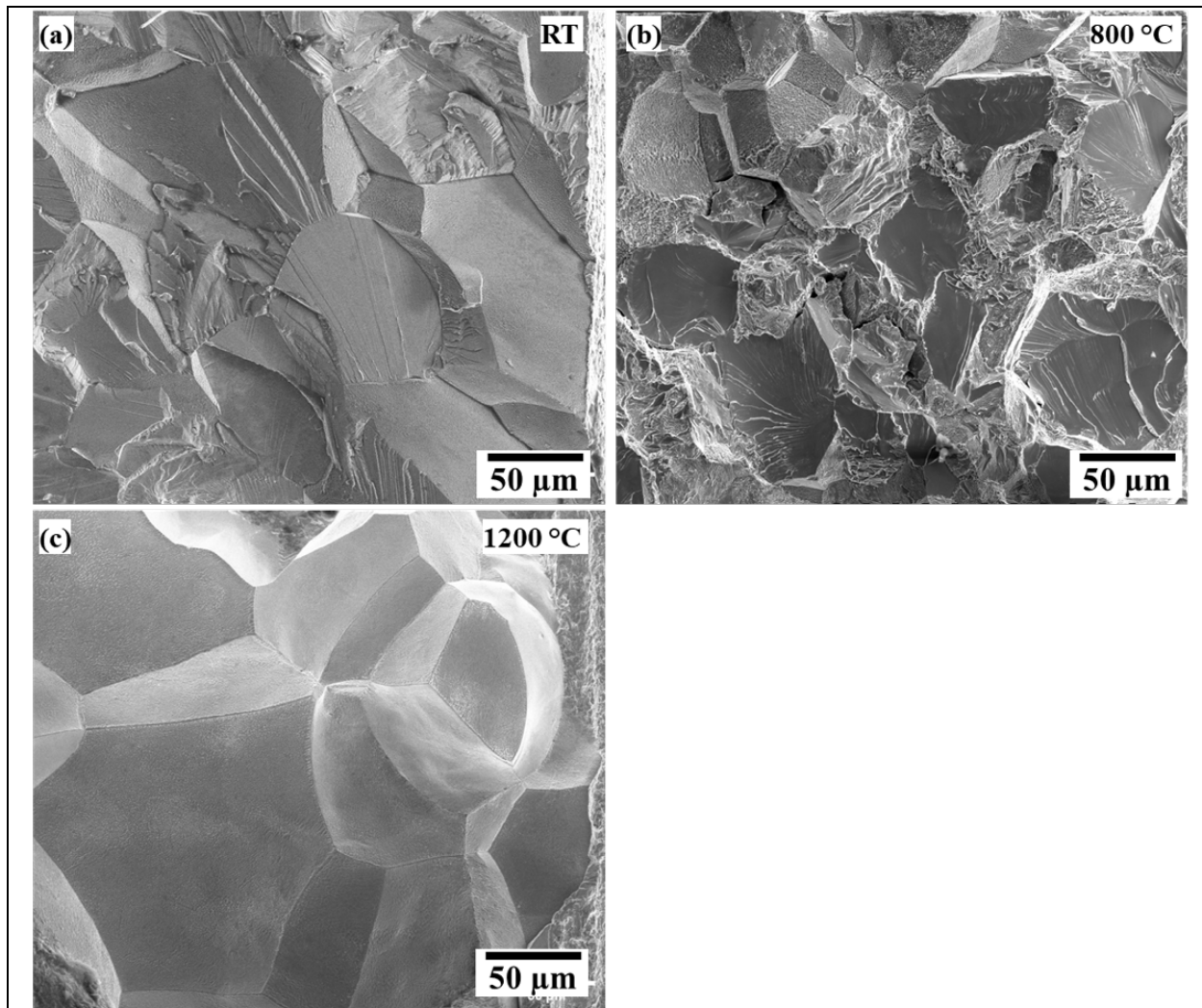


Figure 4.3: Representative SEM images of the fracture surface of fracture toughness specimens tested at (a) RT, (b) 800 °C, and (c) 1200 °C.

These results demonstrate that although the NbMoTaW alloy does have high strength even at high temperatures, it displays vanishingly small ductility and fracture toughness. This is primarily driven by the lack of intrinsic ductility in this system due to the low solubility of interstitial elements, and high Peierl's barriers for dislocation glide [16], [66]. Furthermore, these materials are very susceptible to grain boundary poisoning from interstitial elements. While this can be used to engineer grain boundaries to induce extrinsic toughening, these effects are weak. In conclusion, these materials are too brittle to be used in safety-critical applications.

Chapter 5

The role of kink bands in elevating toughness in refractory NbTaTiHf

5.1 INTRODUCTION

As demonstrated by the NbMoTaW alloy in Ch. 4, RHEAs, especially those with high-temperature strength, do not exhibit bulk plasticity in tension which results in low toughness and tensile ductility. However, a few systems, specifically those with group IV elements such as equiatomic HfNbTaTiZr alloy can display ambient temperature ductility and even high toughness. Their Achilles heel lies in their thermodynamic stability: at high temperatures multiple, brittle phases compete with the *bcc* structure and degrade high temperature ductility. Therefore, a balance must be struck between activating dislocation glide by alloying group IV elements, while keeping the *bcc* phase stable.

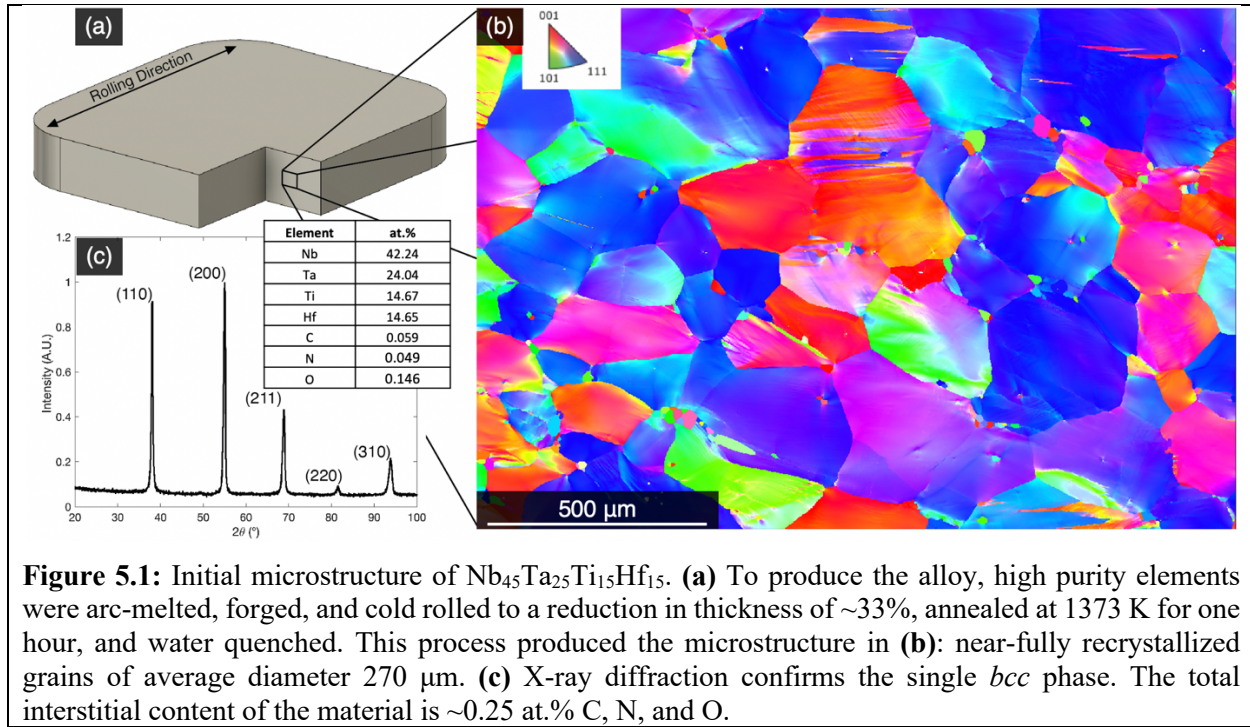
Theories for the high-temperature strength of these systems are based on the reduced mobility of edge dislocations and the pinning of screw dislocations by atomic jogs [67], [68], [69], [70]. However, there is no clear understanding of the high room-temperature toughness of 211 MPa $\sqrt{\text{m}}$ reported for the HfNbTaTiZr alloy [17]. Tensile tests of this material only add further mystery since the alloy exhibits low uniform tensile ductility ($\sim 4\%$) and a marked absence of strain hardening, which unlike the face-centered cubic (*fcc*) high-entropy alloys discussed in Ch. 2 and 3 [7], indicate that the toughness should be very low [71]. Analysis of the room temperature deformation structures reveals that, while bulk plastic flow is controlled by the lethargic motion of screw-character dislocations, local ductility can nonetheless be accommodated by collective arrays of edge dislocations, which form pairs of tilt boundaries known as kink bands [71], [72]. As first described by Orowan in zinc [73], the formation of these bands reorients crystalline slip planes along direction of high resolved shear stress, softening the material [74], [75], [76]. In polycrystalline materials, kink bands nucleate in regions of high dislocation density and propagate across grains to relax the associated stress concentration [77]. Their formation in high group IV concentration RHEAs [71], [72], as well as in pure group V *bcc* elements [78], should be detrimental to the toughness, as this mechanism in tension promotes plastic instability by suppressing uniform ductility and is thus associated with the onset of fracture. Here, we demonstrate that in a specifically engineered alloy, kink bands can induce a remarkable response as an exceptionally potent intrinsic toughening mechanism that does not necessarily inhibit high-temperature strength.

5.2 RESULTS

5.2.1 Microstructure

Specifically, we investigated the mechanical properties of a non-equiatomic Nb₄₅Ta₂₅Ti₁₅Hf₁₅ RMEA from 77 K to 1473 K by performing uniaxial tensile tests and nonlinear elastic *J*-integral based fracture toughness tests. For more information on the experimental and

computational methods see ref. [3]. The material was designed by alloying group IV elements (Ti, Hf) with group V elements (Nb, Ta) to (i) ductilize the material, (ii) generate lattice distortion to allow for high temperature strength retention, and most importantly (iii) to prioritize high temperature *bcc* thermodynamic stability lacking in Zr-containing and higher group IV concentration RHEAs [79], [80]. To make the material chemically and microstructurally homogeneous, high-purity elemental ingots were arc-melted several times and rolled at room temperature to reduce the thickness by $\sim 33\%$, then heat treated at 1373 K for one hour, and water quenched. This process produced a near-fully recrystallized, single-phase microstructure with equiaxed grains of average size 270 μm , and some smaller partially recrystallized grains of diameter $\sim 20\text{ }\mu\text{m}$ shown in Fig. 5.1(b). X-ray diffraction (XRD) (Fig. 5.1(c)) confirmed that the material forms a single *bcc* phase with the exact composition measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to be 42.24 at.% Nb, 24.04 at.% Ta, 14.67 at.% Ti, and 14.65 at.% Hf. Carbon and nitrogen interstitial elements were measured by combustion to be 0.059 and 0.0495 at.% (60 and 58 ppm), respectively; an oxygen concentration of 0.146 at.% (197 ppm) was measured by inert gas fusion (IGF). This brings the total interstitial content to ~ 0.25 at.% (315 ppm). To understand the distribution of interstitial elements, the material was investigated by atom probe tomography (APT) which revealed no segregation of interstitials throughout the matrix and grain boundaries.



3.2.2 Mechanical Properties

Uniaxial tensile tests, plotted as engineering stress vs. strain in Fig 5.2(c), were performed at five temperatures: 77 K (liquid nitrogen), 298 K (room temperature), 1073 K, 1223 K, and 1473 K. At room temperature the alloy exhibits a yield strength, σ_y , of 596 MPa, and a uniform ductility of 15.5%. As the temperature is lowered into the cryogenic regime, the strength increases to 937 MPa and the uniform ductility experiences a modest decrease from room temperature to 9%.

Conversely, as the temperature is increased through 1073 and 1223 K, the alloy's yield strength gradually decreases by, respectively, ~36% (380 MPa at 1073 K) and ~43% (340 MPa at 1223 K) compared to room temperature. At these temperatures the uniform ductility also decreases to 2.3% and 1.1%. Finally at 1473 K, a more rapid drop-off in yield strength of ~76% (140 MPa) occurs, and the uniform ductility slightly increases to 2%. Analysis of the strain-hardening behavior reveals a trend that runs counter to most materials, specifically that the strain hardening increases with increasing temperature. At 77 K, the strain-hardening exponent, n , is 0.09; as the temperature is increased to room temperature the material exhibits two stage hardening (29), with the second strain-hardening exponent increasing to $n_2 = 0.14$. At higher temperatures it generally continues to increase: 0.21 at 1073 K, 0.05 at 1223 K, and 0.33 at 1473 K.

To measure the fracture toughness, the crack-resistance curves (R -curves) were evaluated with the nonlinear-elastic energy release rate, the J -integral (kJ/m^2), as a function of the crack extension, Δa . Unlike most RHEAs, $\text{Nb}_{45}\text{Ta}_{25}\text{Ti}_{15}\text{Hf}_{15}$ exhibits stable crack growth, and markedly rising R -curve behavior at all temperatures, shown in Fig. 5.2(a)-(b). For more information on the methods used to obtain high temperature R -curves, see ref. [3]. To measure a valid, size-independent fracture toughness value, J_{Ic} , samples must satisfy the J -dominance criteria in plane strain, *i.e.*, that the uncracked ligament (b) and thickness (B) $> 10(J_Q/\sigma_f)$, where J_Q is the conditional toughness calculated by the intersection of the blunting line with the R -curve, and σ_f is the flow stress (the average of the yield and maximum tensile stresses). This condition was met for samples at 77 K, 1073 K, and 1223 K but not at room temperature or 1473 K. Instead of this, a minimum bound fracture toughness ($J_{\text{Ic,min}}$) can be calculated by rearranging the above equation: $J_{\text{Ic,min}} = B\sigma_f/10$, which combined with the conditional fracture toughness, J_Q , gives a range for the true value. Thus, at room temperature, the fracture toughness (in terms of the stress intensity) lies in the range of $253 \text{ MPa}\sqrt{\text{m}} < K_{\text{JIC}} < 323 \text{ MPa}\sqrt{\text{m}}$. When the temperature is lowered into the cryogenic regime, the crack-initiation toughness remains persistently high at $\sim 86 \text{ MPa}\sqrt{\text{m}}$, and rises to a steady-state crack-growth toughness of $K_{\text{ss}} \sim 146 \text{ MPa}\sqrt{\text{m}}$. At elevated temperatures, the material also continues to exhibit rising R -curve behavior. At 1073 K, K_{JIC} is $\sim 67 \text{ MPa}\sqrt{\text{m}}$, which rises to a steady-state value of $K_{\text{ss}} \sim 93 \text{ MPa}\sqrt{\text{m}}$. At 1223 K, the crack-initiation and steady-state fracture toughness decrease to $\sim 52 \text{ MPa}\sqrt{\text{m}}$ and $\sim 66 \text{ MPa}\sqrt{\text{m}}$, respectively. Finally, at 1473 K, the crack-initiation toughness increases again and is in the range $68 \text{ MPa}\sqrt{\text{m}} < K_{\text{JIC}} < 88 \text{ MPa}\sqrt{\text{m}}$. These values are all highly unusual and indeed remarkable for *bcc* RHEAs [1].

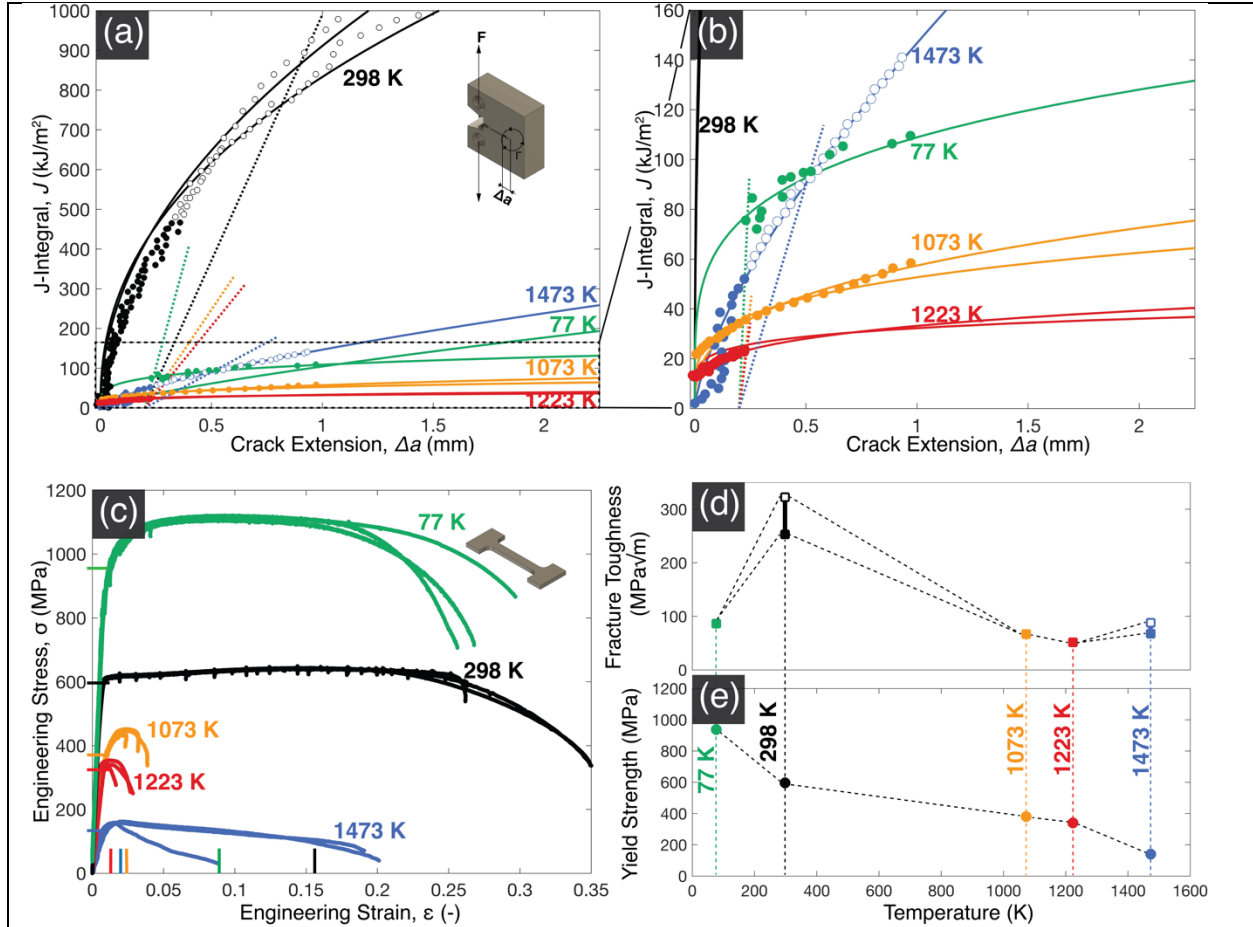


Figure 5.2: Mechanical Properties of Nb₄₅Ta₂₅Ti₁₅Hf₁₅. (a) J -Integral R -curves as a function of crack extension at 77 K, 298 K, 1073 K, 1223 K, and 1473 K, and (b) a closer view of R -curves measured at extreme temperatures. (c) Tensile engineering stress-strain curves measured from 77 K – 1473 K. Note the dynamic strain aging at 298 K corresponds to formation of Lüders bands, while the stress drops at 77 K correspond to twinning, which was accompanied by acoustic emission. (d) Fracture toughness (K_{JIC}) calculated from J_{IC} values obtained from the R -curves and (e) yield strength (σ_y) as a function of temperature. Note in (d) that the Nb₄₅Ta₂₅Ti₁₅Hf₁₅ alloy not only retains strength at high temperatures, but also exhibits extraordinary fracture toughness at all temperatures: 86 MPa $\sqrt{m}$, 253–323 MPa $\sqrt{m}$, 67 MPa $\sqrt{m}$, 52 MPa $\sqrt{m}$, and 68–88 MPa $\sqrt{m}$ at the five temperatures from 77–1473 K, respectively. The room temperature fracture toughness is the highest of any known single-phase *bcc* material, and even higher than *fcc* CrCoNi-based HEAs [8]. Note: open circles in (a), (b), and (d) denote values that are not strictly valid; the second liquid nitrogen test was excluded from (b) for a clear visualization.

5.2.3 Deformation Mechanisms

Refractory *bcc* alloys (dilute and concentrated solid solutions) typically exhibit low room temperature fracture toughness which has severely limited their safety-critical engineering applications. To put Nb₄₅Ta₂₅Ti₁₅Hf₁₅ in perspective, to reiterate section 2.2, NbMoTaW has a room temperature fracture toughness of 0.2 – 2 MPa $\sqrt{m}$, which is over two to three magnitudes lower than the minimum room temperature K_{JIC} of 253 MPa $\sqrt{m}$ obtained for Nb₄₅Ta₂₅Ti₁₅Hf₁₅ [52]. Even traditional refractory alloys based on Nb with tensile ductility do not have low temperature fracture toughness over ~40 MPa $\sqrt{m}$ [81]. Strategies to improve the fracture toughness of

refractories have historically involved alloying high concentrations of Re (an expensive and rare element) into W, which improves the fracture toughness up to 60 MPa√m, but these alloys do not exhibit rising R-curve behavior [82]. To understand the reason for this material's extraordinary resistance to fracture, especially over a very wide range of temperatures from 77 K to 1473 K, we first investigated the crack-tip deformation mechanisms across all temperatures with post-fracture electron backscatter diffraction (EBSD) analysis.

To investigate the deformation mechanisms, the compact-tension C(T) specimens used in the fracture toughness tests were cut through the mid-thickness ($\sim B/2$), perpendicular to the crack, to sample the region that experiences the highest stress triaxiality, *i.e.*, the region under complete or near-complete plane-strain conditions. Samples were first ground and then polished for examination with EBSD to understand the crystallographic changes induced by a propagating crack. EBSD band contrast (BC) and inverse pole figure (IPF) maps in Figs. 5.3(a)-(e), show the temperature-dependent evolution of deformation mechanisms. At room temperature (Fig. 5.3(b)), there are three mechanisms: conventional dislocation glide, $\{112\}<111>$ twinning (Fig. 5.3(f)) and deformation kink bands. These (rather unusual) kink bands are the prominent mechanism, as revealed by the kernel average misorientation map in fig. S4 which indicates most geometrically necessary dislocations are confined to their boundaries. Though most kink boundaries of these kink bands form low misorientations (~ 2 - 8°) with respect to the matrix of their parent grains, some are as high as 40° . In the cryogenic regime the salient mechanisms do not change, but their relative ratio does, as shown in Fig. 5.3(a). Here, dislocation motion is still present (Fig. 5.3(f)), but $\{112\}<111>$ twins become more predominant and coarser (up to $\sim 11\ \mu\text{m}$ thick). Deformation kink bands continue to form; however, there are fewer. Fracture surfaces at room temperature (Fig. 5.3(l)) show ductile microvoids with approximately 100-300 μm diameters. In the cryogenic regime, the microvoids decrease in size to $\sim 35\ \mu\text{m}$ and cleavage facets appear that are absent in the tensile tests at this temperature (see ref. [3]) due to the stress triaxiality present in pre-cracked C(T) samples.

At higher temperatures (1073 K and 1223 K (Figs. 5.3(c),(d)), the mechanisms stay nominally the same: conventional dislocation motion is still observed, kink bands form, and, remarkably for *bcc* materials at elevated temperatures, $\{112\}<111>$ twinning [83]. Another feature at these temperatures is that fracture occurs along grain boundaries. Nevertheless, microvoids are observed on the fracture surfaces (Figs. 5.3(m)-(n)), indicating significant plastic deformation can occur before the onset of crack growth. As the crack follows the intergranular path, it branches significantly. This branching leads the crack away from mode I plane until it is subsequently arrested due to a lack of a driving force, an additional extrinsic toughening mechanism [5]. Finally at 1473 K these mechanisms are supplanted by the diffusion-mediated nucleation of new, more favorably oriented grains, which significantly blunts the crack tip and prevents crack growth, as shown in Fig. 5.3(e),(h),(i). At this temperature, bands can be observed in most grains; however, their boundaries are altered by the recrystallization processes, such that they cannot be identified as kink bands by the methods discussed below.

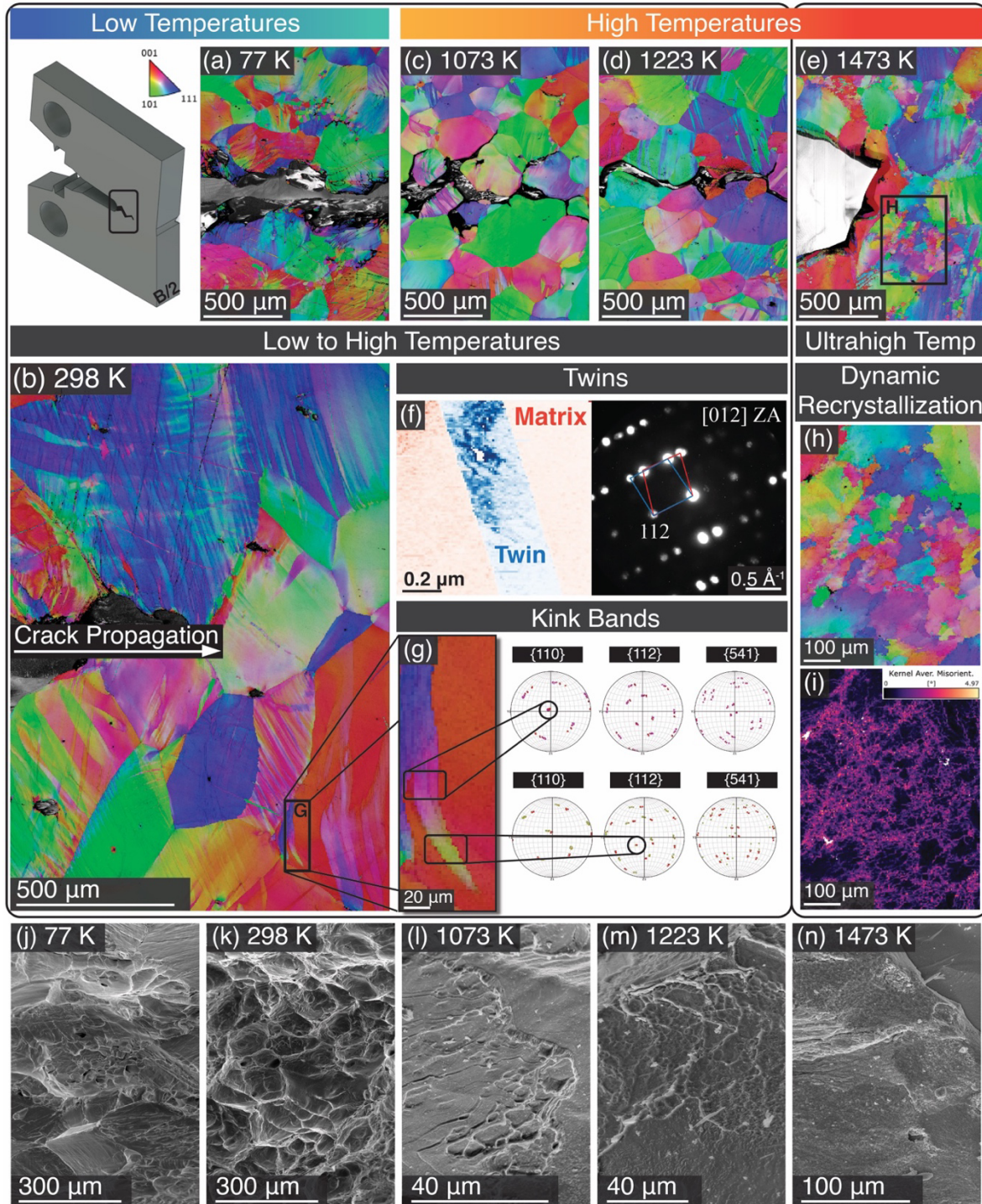
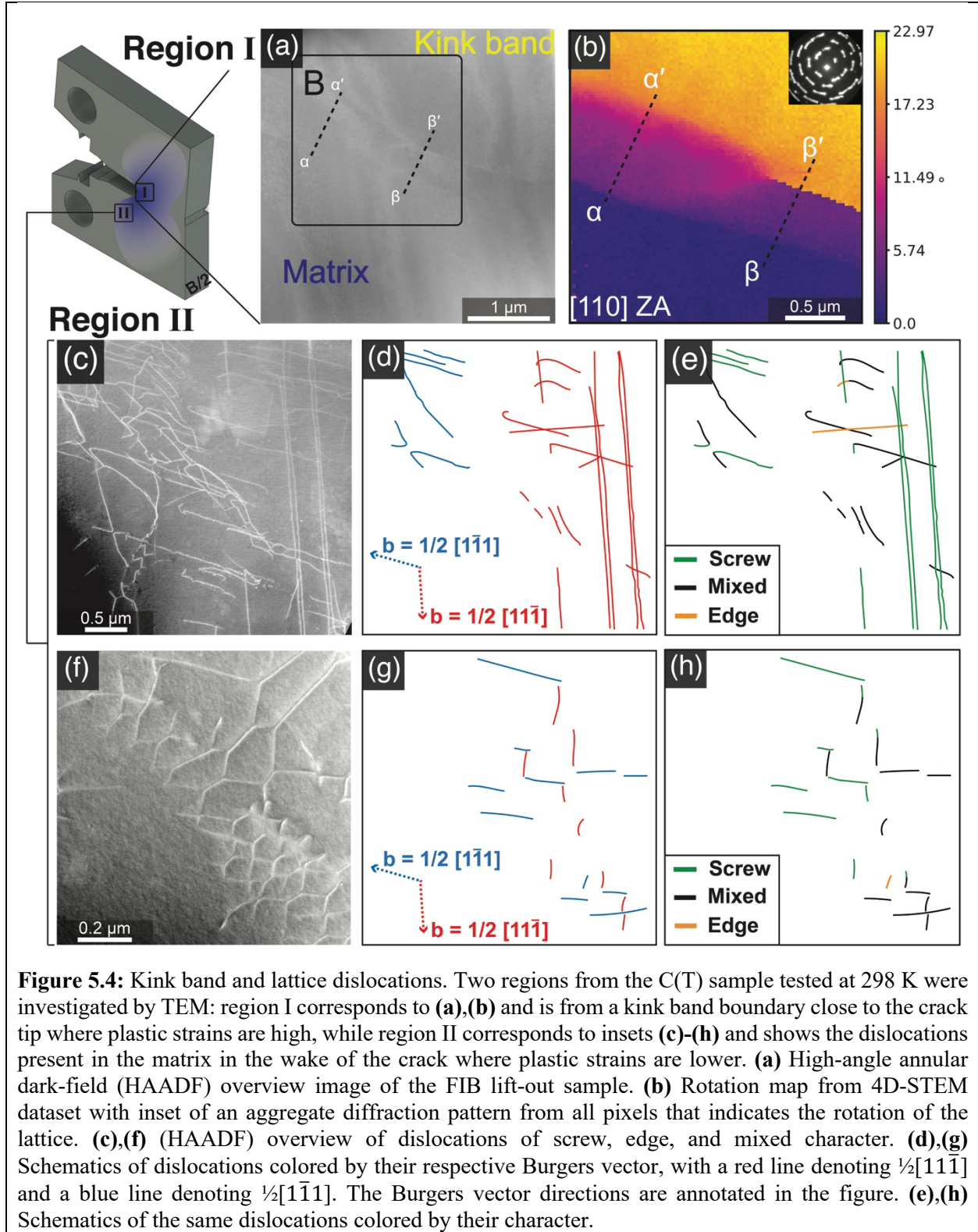


Figure 5.3: Deformation mechanisms and fracture morphology of $\text{Nb}_{45}\text{Ta}_{25}\text{Ti}_{15}\text{Hf}_{15}$ from 77–1473 K. (a)–(e) EBSD band contrast and inverse pole figure (IPF) maps of the fracture path (from left to right). Samples were taken at the mid-thickness of the C(T) samples to investigate mechanisms present in the region of highest stress triaxiality. Deformation twinning is identified by EBSD at temperatures from cryogenic (77 K) to 1223 K. (f) 4D-STEM image of a $\{112\}$ twin in the wake of the fracture path at 77 K. (g) A kink band in the plastic zone directly ahead of the crack at 298 K and associated intragranular misorientation axis analysis shows that this kink band twists internally from kinking a plane

in the $\{112\}$ family, to kinking a plane in the $\{110\}$ family. **(f)** At ultrahigh temperatures (1473 K), these mechanisms are replaced by dynamic recrystallization shown in **(h)-(i)** which destroys the original grain boundaries, inhibiting the mechanism that promotes intergranular fracture. Fracture surfaces show a mixture of cleavage and ductile microvoid coalescence at 77 K **(j)**, microvoid coalescence at 298 K **(k)**, mixed intergranular fracture and microvoid coalescence at 1073 and 1223 K **(l)-(m)**. The fracture surfaces are destroyed by oxidation at 1473 K **(n)**.

Consistent with prior reports on Group IV-rich RHEAs in tension and compression, EBSD maps in Fig. 5.3 show profuse deformation kink bands [71], [72], [84], [85], [86], [87]; however, the role played by kink bands on the overall behavior in the presence of a sharp crack is not established. To understand how kinking elevates toughness, particularly at lower temperatures where toughness of *bcc* materials suffers, we first performed an intragranular misorientation axis (IGMA) analysis to identify the crystallographic planes active in kink band formation [88]. A more detailed description of the analysis can be found in ref. [3]. Put in perspective, since a kink band is a tilt boundary formed by localization of edge-character dislocations, the type of dislocations that form them can be identified if the possible active slip systems and the kink band rotation (Taylor) axis are known [88]. This analysis (Fig. 5.3(g), ref [1]) shows that all the identified kink bands are formed predominantly by $a_0/2\langle 111 \rangle\{112\}$ edge dislocations, with the rest formed by $a_0/2\langle 111 \rangle\{110\}$ edge dislocations (more often at higher temperatures). This indicates multiple slip systems are active in kink band formation. Fig. 5.3(g) even shows that a single kink band can be a result of bending of a $\{112\}$ and a $\{110\}$ lattice plane along different lengths. The tortuous form of this kink band indicates that if kinking is no longer favored by one slip system, another slip system can activate to extend the kink band. Coupled with our observations in Fig. 3(a)-(d) that kink bands can vary in width and length (not necessarily traversing entire grains), intersect, and nucleate within each other, demonstrates that the versatility of this mechanism enables it to accommodate exceptionally high strains at a crack tip that conventional, uncoordinated dislocation glide and twinning simply cannot.

To further understand their nanoscale structure, we analyzed a small section of a $\{112\}$ kink band near the room temperature crack tip, using scanning nanobeam diffraction, also known as four-dimensional scanning transmission electron microscopy (4D-STEM). Several features were elucidated, shown in Figs. 5.4(a)-(b). First, we confirmed they are pure tilt boundaries, evidenced by the rotation of the diffraction pattern about the $[110]$ zone axis in Fig. 5.4(b), which necessitates the presence of pure $a_0/2\langle 111 \rangle\{112\}$ edge dislocations. Second, the rotation across the boundary (θ) is not always perfectly discrete as shown in Fig. 5.4(b) where the points α - α' show a gradient in orientation, in contrast to β - β' , which suggests that along certain lengths of the boundary, edge dislocations cannot perfectly space themselves without temperature-activated, non-conservative motion. Finally, the spacing between dislocations can be calculated across the boundary using the Read-Shockley equation, $d \approx b/\sin \theta$ [89], which reveals the distance between edge dislocation cores (d) is 7.4 Å apart on this boundary, which makes the individual dislocations too close to resolve with diffraction contrast TEM.



The prevalence of kink bands indicates that edge dislocation glide is highly active on the $a_0/2\langle 111 \rangle\{110\}$ and $\{112\}$ slip systems; however, kink bands do not solely account for the crack-tip plasticity. To gain a holistic picture of the deformation mechanisms, we focused on the edge of

the plastic zone in the room temperature C(T) samples to: (i) study the dislocations responsible for the uniform plastic deformation that occurs at lower strains during the first stages of crack-tip plasticity, and (ii) to distinguish the dislocations responsible for kink band formation from those responsible for the uniform plastic deformation. To identify the dislocations, we performed a $\vec{g} \cdot \vec{b}$ analysis. Dislocations with Burger's vectors $a_0/2[1\bar{1}1]$ and $a_0/2[11\bar{1}]$ shown in Figs. 5.4(c)-(h). Unlike the kink bands which are formed by $a_0/2\langle 111 \rangle\{110\}/\{112\}$ edge dislocations, the dislocations in the matrix are a mixture of long straight screw dislocations in addition to mixed and some edge. The presence of mixed and edge character dislocations (though few of the latter) suggests that their mobility is decreased in comparison to screw dislocations. While edge (and mixed) dislocations are rarely observed in elemental *bcc* metals and dilute alloys due to their very high mobility, they have been observed in RHEAs and theorized to explain the high-temperature strength of these materials [68], [90]. Taken together with the observation of kink bands closer to the crack tip, a qualitative sequence of mechanisms emerges. While the plasticity at the crack tip is initially controlled by the glide of screw and mixed dislocations, ultimately the coordinated glide of edge dislocations at higher strains results in kinking of the $\{110\}$ and $\{112\}$ planes [77]. While the screw and mixed dislocations interact with themselves, grain boundaries, and twin boundaries to promote steady strain hardening, kink bands suppress these interactions as a strain softening mechanism. These bands continually rotate the lattice to accommodate the exceptionally high strains near the crack tip, effectively distributing the damage.

Still, the observation of marked toughening in the presence of this strain softening mechanism is surprising. In the model for ductile fracture, the fracture toughness, J_{Ic} , is directly proportional to the flow stress (σ_f), strain to failure ($\tilde{\epsilon}_f$), and a characteristic dimension related to the spacing involved in microvoid coalescence ahead of a crack tip (l_o^*), i.e., $J_{Ic} \approx \sigma_f \tilde{\epsilon}_f l_o^*$ (44, 45). It is well established that the exceptionally high fracture toughness of CrCoNi-based *fcc* HEAs results from the activation of multiple strain-hardening mechanisms that prolong uniform ductility and elevate flow stress [42], [91]. Something different is happening in Nb₄₅Ta₂₅Ti₁₅Hf₁₅. Softening from kink bands negatively impacts the flow stress (at room temperature the alloy yields at 596 MPa and has an ultimate tensile strength of 640 MPa), as well as the uniform ductility. However, kink bands activate two other mechanisms that compensate for these drawbacks. First, they prolong necking which can significantly increase the fracture strain as is evident in the tensile curves shown in Fig. 5.2(c). This has been reported not only in RHEAs, but also in high-strength *bcc* Ti-alloys [92]. Second, they increase the characteristic distance between the voids ahead of the crack tip. Estimates of the characteristic spacing for void coalescence show they must be ~ 242 μm apart to account for the exceptionally high minimum J_{Ic} values (474 kJ/m²). This is a staggeringly large number considering that void coalescence occurs on the order of 1-10 μm in CrCoNi at 20 K, where this material is toughest [7]. These microvoids are readily observed on the fracture surface (Fig. 5.3(k)). Although they have a bimodal distribution due to the presence of small partially recrystallized grains, larger microvoids of an average size $\sim 140 \pm 52$ μm are apparent. Thus, when kink bands nucleate from regions of extremely high dislocation density to alleviate and distribute damage [77], they eliminate sites inside grains that lead to microvoid nucleation by providing a secondary, energetically favorable pathway for dislocations to form a low angle grain boundary, which leads to high toughness.

5.3 DISCUSSION

Understanding the conditions that promote kink band formation is critical to the design of future RHEAs that circumvent the strength-toughness trade-off. To this end, we identify two conditions in this alloy that we believe are essential for kink band formation by multiple slip systems. The first condition is an edge dislocation’s “Goldilocks mobility.” It has been postulated that kink bands occur by a depletion of slip systems required to maintain uniform plastic deformation [74], [75], [76]. This describes kinking in *hcp* materials such as in zinc and cadmium, where the basal slip system is energetically preferred [73], [76], [93], [94]; however, this argument is inapplicable for *bcc* materials with 48 slip systems, necessitating a different perspective. Kink band formation in *bcc* materials must be enabled by another factor which can be deduced to be the high edge dislocation velocities that are intrinsic to this crystal structure. High mobilities allow edge dislocations to interact on much shorter time scales at quasi-static strain rates. However, if they are too mobile, a potential high-temperature strengthening mechanism is lost [68]. Our observation of edge and mixed dislocations suggests they have relatively reduced mobilities which could contribute to high temperature strength, though this does not necessarily discount pinning of screw dislocations by atomic jogs as a high-temperature strengthening mechanism [69]. The second condition that is associated with kink band formation by multiple slip systems is an energetic isotropy of slip systems. In pure niobium, kink bands form by the $\langle 111 \rangle \{110\}$ slip systems [78], [95], [96], and alloying with group IV elements triggers a transition to additional kink band formation by the $\langle 111 \rangle \{112\}$ slip system, as seen here for $\text{Nb}_{45}\text{Ta}_{25}\text{Ti}_{15}\text{Hf}_{15}$. To understand this phenomenon, we calculated the generalized stacking fault energies (GSFEs) of the three possible slip systems — $a_0/2\langle 111 \rangle \{110\}, \{112\}, \{123\}$ — and compared them to pure Nb. The results are summarized in Table 5.1. Whereas in pure Nb, the unstable stacking-fault energy (USF) energy (the maximum on the GSFE profile) along $\{110\}$ is 15% lower than $\{112\}$ and $\{123\}$, this difference is reduced in $\text{Nb}_{45}\text{Ta}_{25}\text{Ti}_{15}\text{Hf}_{15}$ where the USF energies are equivalent in all three slip systems within the calculated statistical uncertainties. This energetic equivalence is absent in other pure refractory *bcc* metals, and binary group V-VI alloys where not only are GSFEs higher, but the $\langle 111 \rangle \{110\}$ slip system is energetically favored over $\{112\}$ and $\{123\}$ [97], [98]. This suggests that edge dislocations on the $\langle 111 \rangle \{112\}$ system can be just as easily energetically accessed, as those on $\langle 111 \rangle \{110\}$ in $\text{Nb}_{45}\text{Ta}_{25}\text{Ti}_{15}\text{Hf}_{15}$, which promotes glide and thus kink band formation by this system. It should be noted that these results do not consider the effects of short-range order. Although the low mixing energies of Nb, Ta, Ti, and Hf in this alloy suggest that it would have a low tendency to order, implying that this would have a minimal impact on GSFEs [79], the presence of short-range order can alter stacking fault energy, as is the case in the CrCoNi alloy [99]. In summary, the addition of group IV elements (in this case Ti and Hf) is essential to the formation of kink bands because these elements promote slip on $\langle 111 \rangle \{112\}$.

$$\tau = \max_x \left. \frac{\partial \gamma}{\partial x} \right|_x$$

		Nb	Nb ₄₅ Ta ₂₅ Ti ₁₅ Hf ₁₅
γ_{USF} (mJ/m ²)	{110}	665	586
	{112}	753	586
	{123}	757	602
τ_T (GPa)	{110}	9.2	8.2
	{112}	10.2	7.8
	{123}	10.8	7.7
τ_{AT} (GPa)	{110}	9.2	8.2
	{112}	12.2	9.5
	{123}	11.0	7.9

Table 5.1: Unstable stacking fault (USF) energies for Nb₄₅Ta₂₅Ti₁₅Hf₁₅, and ideal shear stresses in the twinning (τ_T) and anti-twinning direction (τ_{AT}) compared to pure Nb.

5.4 SUMMARY

In summary, this work shows that contrary to conventional understanding, complex concentrated refractory alloys can possess exceptional fracture toughness across extreme temperature ranges, even in the cryogenic regime. Although further development is needed to increase this alloy’s strength and grain boundary cohesion, its exceptional damage tolerance *opens a door* for use of these refractory alloys in safety-critical applications. To put the findings of this work in context, we compare its fracture toughness and strength to current commercial alloys in [Fig. 5.5](#), highlighting the exceptional combination of high-temperature strength and very high toughness displayed by Nb₄₅Ta₂₅Ti₁₅Hf₁₅. Understanding kink band formation from first principles is essential to discovering more damage-tolerant RHEAs with high-temperature strength. The analysis here presents a starting point with general guidelines related to dislocation mobility, activation of multiple slip systems, and formation of kink bands.

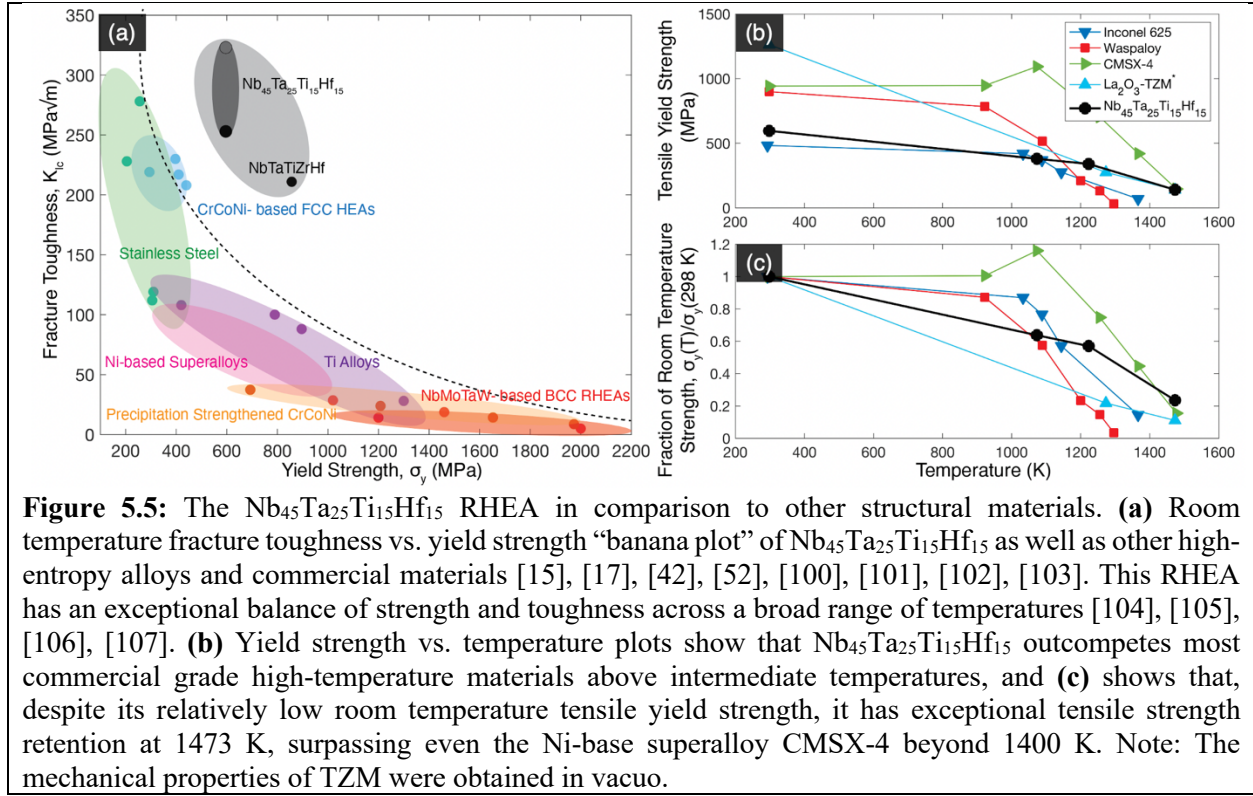


Figure 5.5: The Nb₄₅Ta₂₅Ti₁₅Hf₁₅ RHEA in comparison to other structural materials. **(a)** Room temperature fracture toughness vs. yield strength “banana plot” of Nb₄₅Ta₂₅Ti₁₅Hf₁₅ as well as other high-entropy alloys and commercial materials [15], [17], [42], [52], [100], [101], [102], [103]. This RHEA has an exceptional balance of strength and toughness across a broad range of temperatures [104], [105], [106], [107]. **(b)** Yield strength vs. temperature plots show that Nb₄₅Ta₂₅Ti₁₅Hf₁₅ outcompetes most commercial grade high-temperature materials above intermediate temperatures, and **(c)** shows that, despite its relatively low room temperature tensile yield strength, it has exceptional tensile strength retention at 1473 K, surpassing even the Ni-base superalloy CMSX-4 beyond 1400 K. Note: The mechanical properties of TZM were obtained in vacuo.

Chapter 6

Absence of a Ductile-Brittle Transition at 20 K in Refractory NbTaTiHf

6.1 INTRODUCTION

An unusual feature of the deformation of the NbTaTiHf alloy is that it does not appear to pass through a ductile-to-brittle transition temperature (DBTT) at 77 K. After all, alloys with a *bcc* crystal structure have a DBTT below which plastic deformation is restricted, leading to embrittlement [108], [109]. While this transition is typically characterized by a rise in yield stress, drop in ductility, toughness, and a transition to a brittle fracture mode, these processes do not always evolve simultaneously, making the transition difficult to universally define [110]. The general mechanical behavior, however, stems from the temperature sensitivity of screw dislocations which are significantly less mobile than their edge counterparts, and rely on the thermally activated double-kink nucleation process to glide [111], [112]. Consequently, facilitating screw dislocation glide through careful substitutional and interstitial alloying has been the governing principle to suppress the DBTT [51], [59], [113].

Similar principles have been extended to ductilize *bcc* high-entropy alloys composed from refractory elements (RHEAs), elements whose alloys, historically, can have very high DBTTs [1], [15], [16], [114]. To summarize the discussion in Ch. 4, alloying group IV into group V elements enhances screw dislocation glide by lowering unstable stacking fault energies, as demonstrated in [Table 5.1](#) [16]. This combination of elements also reduces phonon frequencies, induces high lattice distortion, and when combined with high variations in local chemical environments intrinsic to RHEAs, increases the equilibrium concentration of double-kinks on screw dislocations that eliminates the need to thermally activate them [16], [114]. Concomitantly, these effects reduce edge dislocation mobilities, providing another deformation pathway absent in dilute alloys [68], [115]. Group IV elements also decrease twinning stresses and promote a transformation to the omega (ω) phase at cryogenic temperatures [71], [79], [116], [117], [118]. Apart from the transformation, these mechanisms act in concert with kink band formation (a likely side effect of the reduced edge mobilities) to delocalize damage, which imparts exceptional high-temperature toughness, shown in the Nb₄₅Ta₂₅Ti₁₅Hf₁₅ RHEA [3].

A unique consequence in the steep drop in screw dislocation mobility with decreasing temperature is that the screw dislocation glide stresses can exceed twinning stresses that are nearly always higher, but temperature insensitive [119]. Termed the slip-twinning transition, it has only been documented in a select few *bcc* materials, such as single crystals of ultra-high purity niobium, where it tempers the steep rise in yield strength with decreasing temperature [109]. However, fracture stresses are often similar to both twinning and screw glide stresses at this transition, forcing most *bcc* materials to go through their DBTT right before or around this mechanistic transition [108], [109], [120]. As a result, the DBTT has long been associated with the increased propensity for twinning at low temperatures, a conclusion supported by observations of twins nucleating cracks at interfaces, with dislocations unable to move and distribute damage [121], [122], [123].

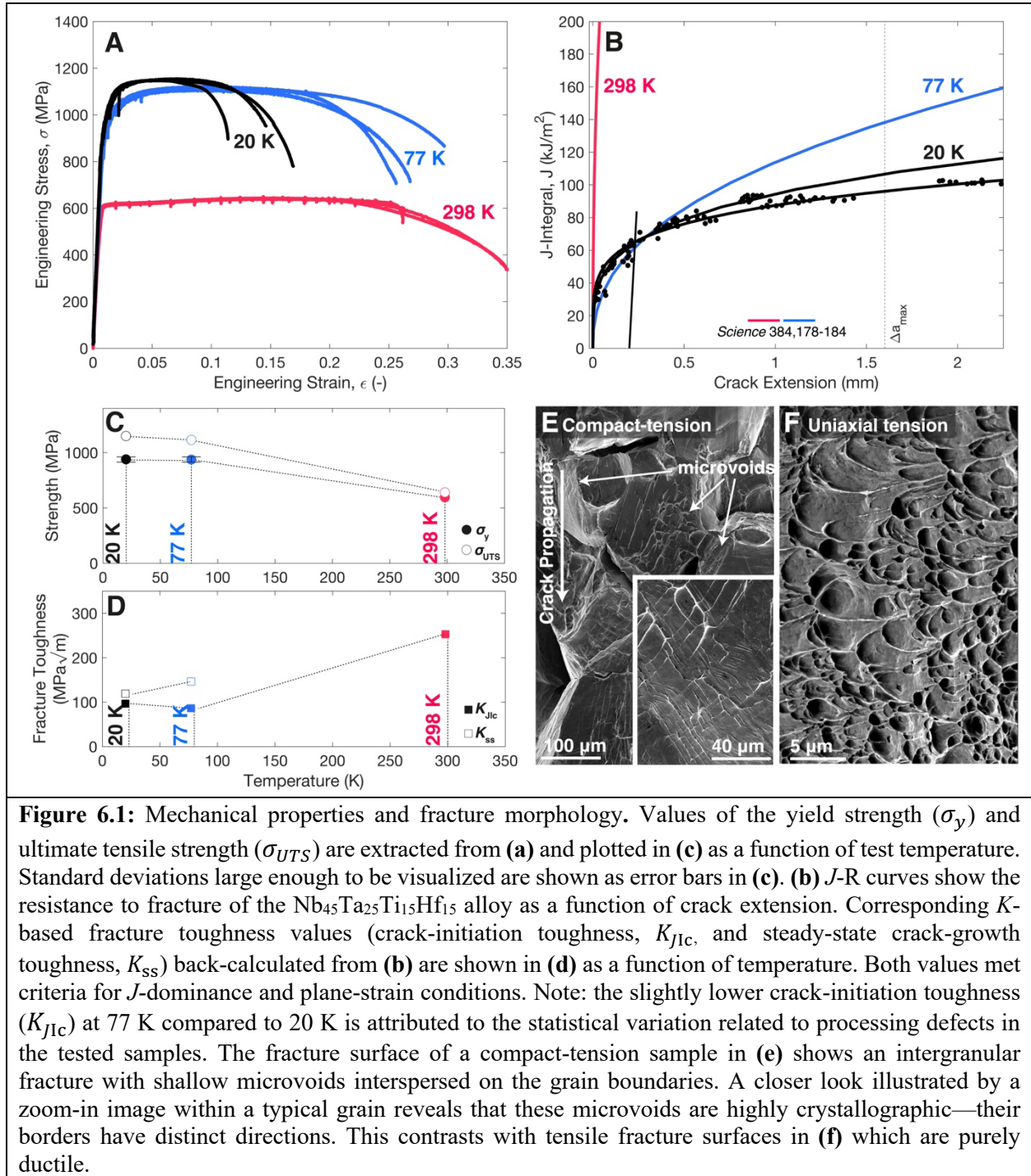
Some limited evidence that this transition occurs in $\text{Nb}_{45}\text{Ta}_{25}\text{Ti}_{15}\text{Hf}_{15}$ around 77 K has been reported, as illustrated in Fig 5.2, yet the toughness remains high at nearly $90 \text{ MPa}\sqrt{\text{m}}$ [3]. To evaluate how these mechanisms interact to affect this alloy's DBTT, we investigated its mechanical behavior in tension at 20 K, both in presence and absence of a crack to assess the role of stress-state. The alloy was processed identically as the material tested in Ch. 4. We observe that by passing through its slip-twinning transition, this alloy reverses the sequence of mechanisms occurring at higher temperatures: twins activate first, generate a plastic zone, and produce dislocation sources. Our results demonstrate that inverting the deformation mechanism sequence attributed to exceptional toughness, not just in this *bcc* alloy at higher temperatures but also in face-centered cubic (*fcc*) HEAs [7], [8], [9], [42], generates a novel temperature-insensitive plasticity pathway that also achieves high toughness, but under conditions in a crystal structure where dislocation glide is heavily restricted [124].

6.2 RESULTS

6.2.1 Mechanical Properties

The DBTT of $\text{Nb}_{45}\text{Ta}_{25}\text{Ti}_{15}\text{Hf}_{15}$ was assessed with tensile ductility and fracture resistance measurements at 20 K. Tensile stress-strain curves and crack-resistance curves (*R*-curves) measured in terms of the *J*-integral (kJ/mm^2) as a function of crack extension, Δa (mm), are shown in Figs. 6.1(a) and (b). The corresponding tensile stress-strain curves and *R*-curves at 77 and 298 K are also shown for comparison [3]. The yield strength at 20 K ($\sigma_y \approx 938.9 \pm 22.6 \text{ MPa}$) is comparable to that measured at 77 K ($\sigma_y \approx 936.6 \pm 22.4 \text{ MPa}$) (Fig. 6.1(c)). The ultimate tensile stress ($\sigma_{\text{UTS}} \approx 1149.5 \pm 3.4 \text{ MPa}$) is $\sim 35 \text{ MPa}$ higher than that measured at 77 K, while the uniform ductility and the elongation to fracture decreases by $\sim 33\%$ and $\sim 50\%$, respectively [3]. This is associated with a corresponding rise in the instantaneous strain-hardening rate immediately following yielding. A comparison to 77 and 298 K shows the strain hardening increases with decreasing temperature but is unsustainable at high strains. In the presence of a crack, the material exhibits rising *R*-curve behavior, *i.e.*, its resistance to fracture increases with increasing crack extension (Fig. 6.1(b)). The size-independent crack-initiation toughness, K_{JIC} , and crack-growth toughness, K_{ss} (defined as the toughness at maximum allowable crack extension), are calculated from the *R*-curves [43, p. 1]. The crack-initiation toughness, K_{JIC} , is $\sim 96.5 \text{ MPa}\sqrt{\text{m}}$, and the steady-state crack-growth toughness, K_{ss} , is $\sim 118 \text{ MPa}\sqrt{\text{m}}$ (Fig. 6.1(d)) at 20 K, which indicates little degradation in fracture resistance compared to 77 K.

To understand how these mechanical responses are related to fracture behavior in these two different stress-states, *i.e.*, uniaxial tension and crack-tip triaxiality, we first examined the fractured surfaces of the samples. Notably, we observe a clear distinction between the two. At 20 K under plane-strain conditions, the alloy exhibits a predominantly intergranular fracture (Fig. 6.1(e)), marking a shift from the mixed-mode (cleavage-ductile-intergranular) fracture seen at higher temperatures (Fig. 6.3(j)) [3]. Cleavage and intergranular facets look brittle fractographically, but at a toughness on the order of $100 \text{ MPa}\sqrt{\text{m}}$, this is clearly not brittle failure. A closer examination of an intergranular facet (Fig. 6.1(e), inset) reveals shallow microvoids with crystallographic ridges aligned along four discrete directions. In contrast, the uniaxial tensile specimens at 20 K fracture by microvoid nucleation and coalescence (Fig. 6.1(f)), similar to 77 and 298 K [3]. These observations underscore that stress-state plays a critical role in governing fracture mode.



6.2.2 Tensile deformation mechanisms

Our investigation began by analyzing the sequence of tensile deformation mechanisms. Tensile specimens, one interrupted shortly after yielding ($\epsilon_p = 0.004$, $\sigma_e \approx 1000 \text{ MPa}$), and a second at the uniform elongation ($\epsilon_p = 0.051$, $\sigma_e \approx 1150 \text{ MPa}$) were jet polished and examined

in a transmission electron microscope (TEM). These experiments reveal an unusual sequence; (i) twinning and a phase transformation to omega initiate yielding, preventing it from increasing with decreasing temperature, and promote subsequent strain hardening, and (ii) screw dislocations mediate plastic flow at higher strains (Fig. 6.2). Virtual dark-field reconstructions of four-dimensional scanning transmission electron microscopy (4D-STEM) scans correlated with high-resolution transmission electron microscopy (HRTEM) images of tensile specimens interrupted at 0.4% plastic strain (Figs. 6.2(a)-(c)), show conventional $\{112\}\langle 111 \rangle$ nanotwins, with a nanometer-thick interfacial layer of ω that expands in the space between the twins. In contrast, tensile samples interrupted at yielding at 77 K exhibit nanotwinning exclusively (Fig. 6.3). At lower temperatures, the energy difference between *bcc* and ω phases decreases and might even span the same statistical distribution, thereby facilitating the transformation [79]. Although it is unclear whether the crystal collapsed to ω first to aid twin nucleation second, or if the local shear stress from the twins triggered the ω transformation Fig. 6.2(c); in either case, this phase assists twin nucleation and growth [125], [126], [127].

At higher stresses, specifically at the ultimate tensile stress of 1150 MPa (which corresponds to 5.1% engineering plastic strain), bulk dislocation glide is activated. A $g \cdot b$ analysis in ref. [4] identified dislocations with various $\langle 111 \rangle$ Burgers vectors (Fig. 6.2(d),(e)). An analysis of their character in Fig. 6.2(f) shows they prefer the screw orientation, with many bowing into mixed orientations from pinning-depinning events.

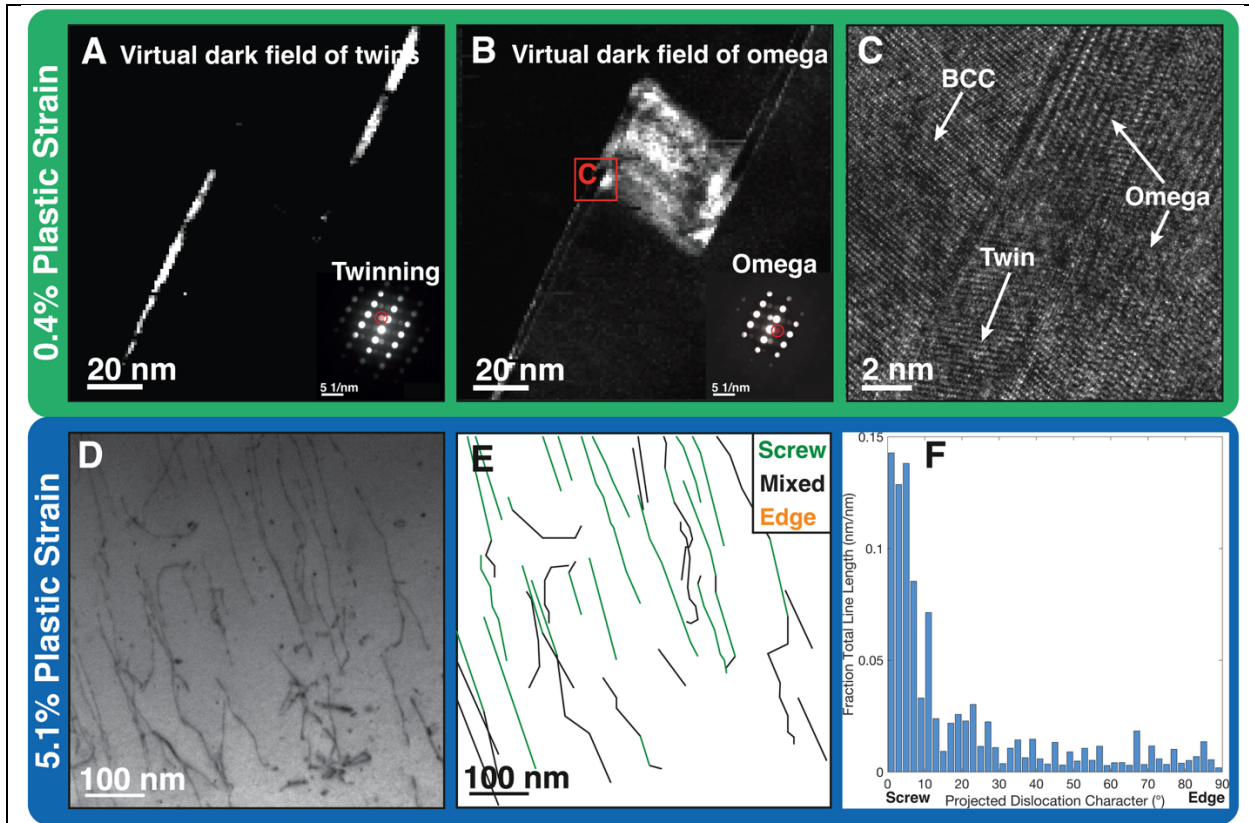


Figure 6.2: Sequence of uniaxial tensile deformation mechanisms. (a)–(c) virtual dark-field images reconstructed from 4D-STEM scans of two twins growing out of *bcc* crystal collapsed into ω phase shortly after yielding. Omega is additionally observed in (b) wetting the twin boundaries. Corresponding HRTEM scans near the head of the twin in (f) show that ω transforms back into the *bcc* phase but in the

twinning orientation. At higher stresses dislocation glide is activated, shown in a STEM image in **(d)** of dislocations in tensile samples deformed to approximately $\sim 5.1\%$ plastic strain. **(e)** A $g \cdot b$ analysis reveals that the dislocations in **(d)** predominantly have $b = [111]$. An analysis of all characterized dislocations in **(f)** shows they prefer the screw orientation. Note: the character of screw and mixed dislocations is determined under the assumption that the sample has negligible thickness. A schematic of the sequence of mechanisms is shown in **(g)** and **(h)** which also show that the difference in stress-state only allows for local dislocation glide in the presence of a crack, and global dislocation glide in tension.

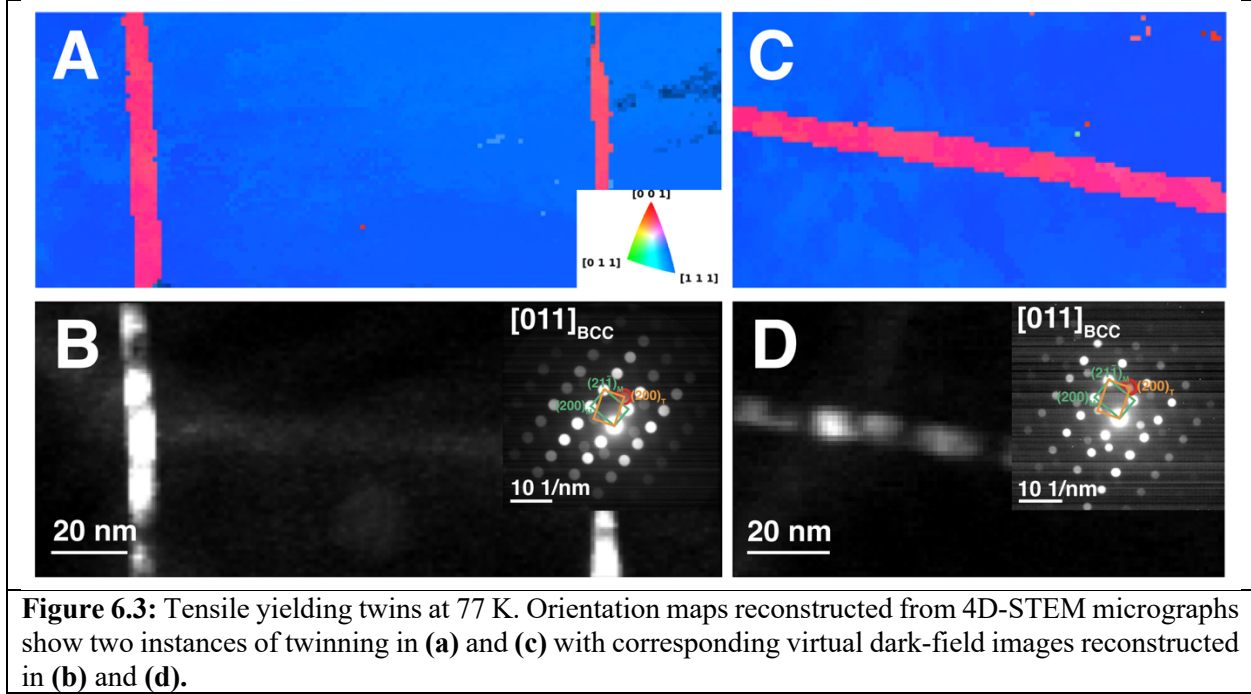


Figure 6.3: Tensile yielding twins at 77 K. Orientation maps reconstructed from 4D-STEM micrographs show two instances of twinning in **(a)** and **(c)** with corresponding virtual dark-field images reconstructed in **(b)** and **(d)**.

6.2.3 Crack tip deformation mechanisms

To understand how this inverted sequence of tensile deformation mechanisms—beginning with twinning coupled to a phase transformation and ending with screw dislocation glide—affects the fracture properties, we investigated compact-tension samples at the mid-thickness by electron backscatter diffraction (EBSD), transmission Kikuchi diffraction (TKD), and 4D-STEM. Here, it is important to note that in the vicinity of a crack there are three principal stresses; each are approximately three times higher than those in tensile specimens.[91] There also exists a marked stress gradient. This means that a sequence in tension occurs spatially at a crack, *i.e.* mechanisms active at higher stresses in tension spread from the crack tip with increasing applied stress intensity during fracture [91].

An EBSD band contrast (BC) and inverse pole figure (IPF) overview map in Fig. 6.4(a)-(b) reveals that the intergranular fracture observed in Fig. 6.1(e) is very closely associated with twinning [128], [129]. As we observed in Fig. 6.4(b) twins intersect a fracturing grain boundary with a growing microvoid. This intergranular fracture activates extrinsic toughening mechanisms such as crack deflection, branching, tortuosity, and even grain bridging [5], while with a nominally brittle failure mode, the grains close to the crack tip still undergo severe plastic deformation. In one of these highly deformed regions close to the fracture surface indicated in Fig. 6.4(a), we took focused ion beam (FIB) lift-outs for TKD where we identified in addition to twins, micro-kink

bands (kink bands with micron-scale widths) and dislocation glide (Fig. 6.4(c)). These kink bands are formed by $a_0/2\langle 111 \rangle$ dislocations with a $\{110\}$ glide plane, as we identified using an intragranular misorientation axis analysis (Fig. 6.4(d)) [85], [88]. Others, with conventional widths that can be found in ref. [4] are formed by higher order $\{112\}$ slip planes [130].

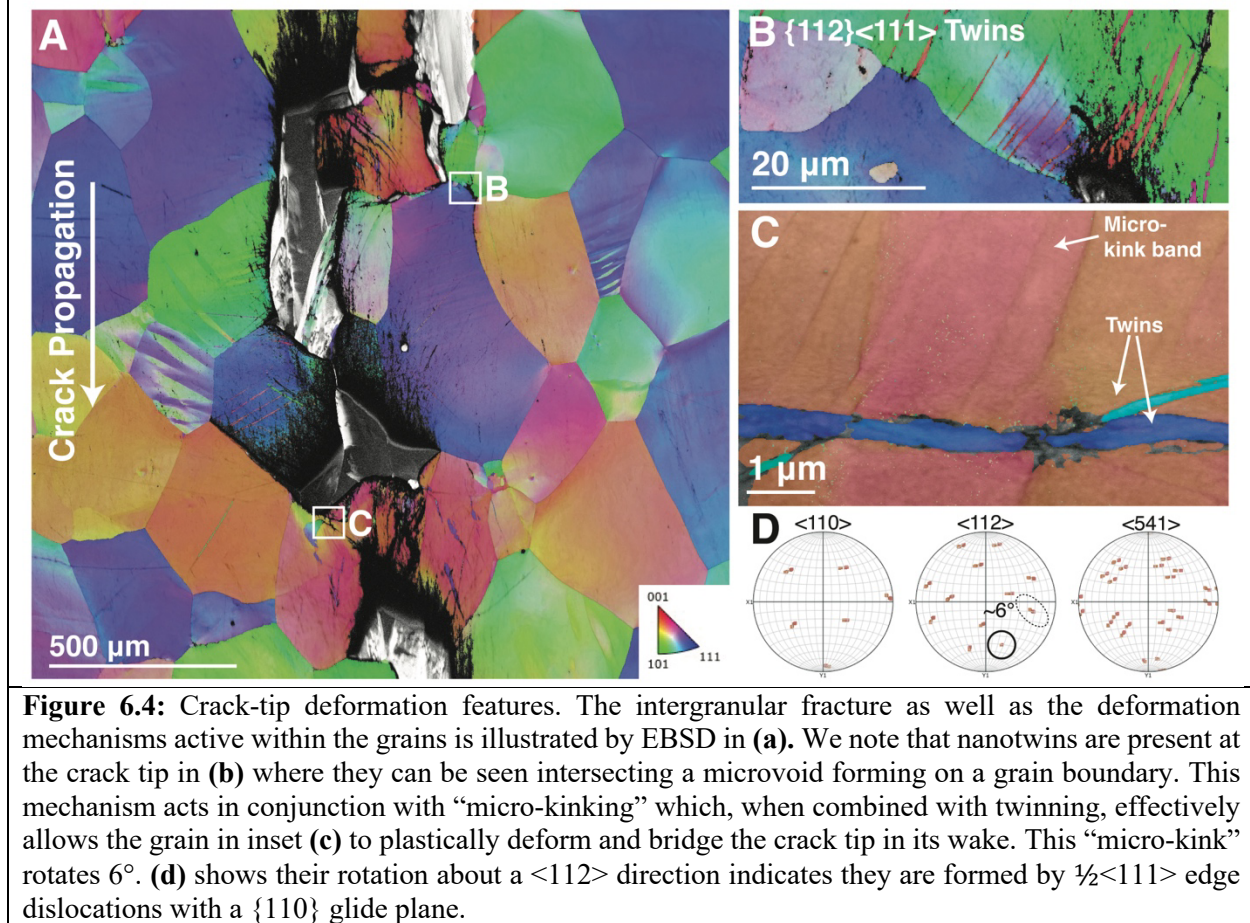


Figure 6.4: Crack-tip deformation features. The intergranular fracture as well as the deformation mechanisms active within the grains is illustrated by EBSD in (a). We note that nanotwins are present at the crack tip in (b) where they can be seen intersecting a microvoid forming on a grain boundary. This mechanism acts in conjunction with “micro-kinking” which, when combined with twinning, effectively allows the grain in inset (c) to plastically deform and bridge the crack tip in its wake. This “micro-kink” rotates 6° . (d) shows their rotation about a $\langle 112 \rangle$ direction indicates they are formed by $\frac{1}{2}\langle 111 \rangle$ edge dislocations with a $\{110\}$ glide plane.

It is not initially intuitive as to how twinning can cause intergranular fracture. After all, it is a form of plasticity. To capture the plastic events occurring both prior to and post crack extension, we performed TKD and 4D-STEM on regions near grain boundaries. FIB lift-outs were taken from a grain boundary several micrometers ahead of a crack tip (in the region captured with EBSD in Fig. 6.5(a)) and from an intergranular fracture facet shown in Fig. 6.1(e) with the distinctive crystallographic deformation markings discussed in the preceding section. Precise calculation of stress and strain using the Hutchinson–Rice–Rosengren (HRR) plastic strain field is detailed in the section 5.5. Reconstructed virtual dark-field images of 4D-STEM maps in Fig. 6.5(a)–(c) show fine nanotwins encased by omega impinging on the grain boundary. Additional instances of twins forming the crystallographic microvoids in Fig. 6.1(e) on fractured grain boundaries are documented in Fig. 6.6. Given the exceptionally high stresses at a crack tip, stress-controlled processes like twinning and the transformation can be overactivated [119], [131]. This is especially problematic since as a low symmetry hexagonal phase incapable of plastic deformation, ω can also act as a site for crack nucleation [116]. However, we only observe it wetting twin boundaries and any intergranular fracture that it could cause is delayed by

dislocations nucleated in the neighboring grain. The latter are identified by a $g \cdot b$ analysis as predominantly edges with the $\frac{1}{2}[111]$ Burgers vector (Figs. 6.5(d)-(f)), that emanate from this intersection site to delocalize damage.

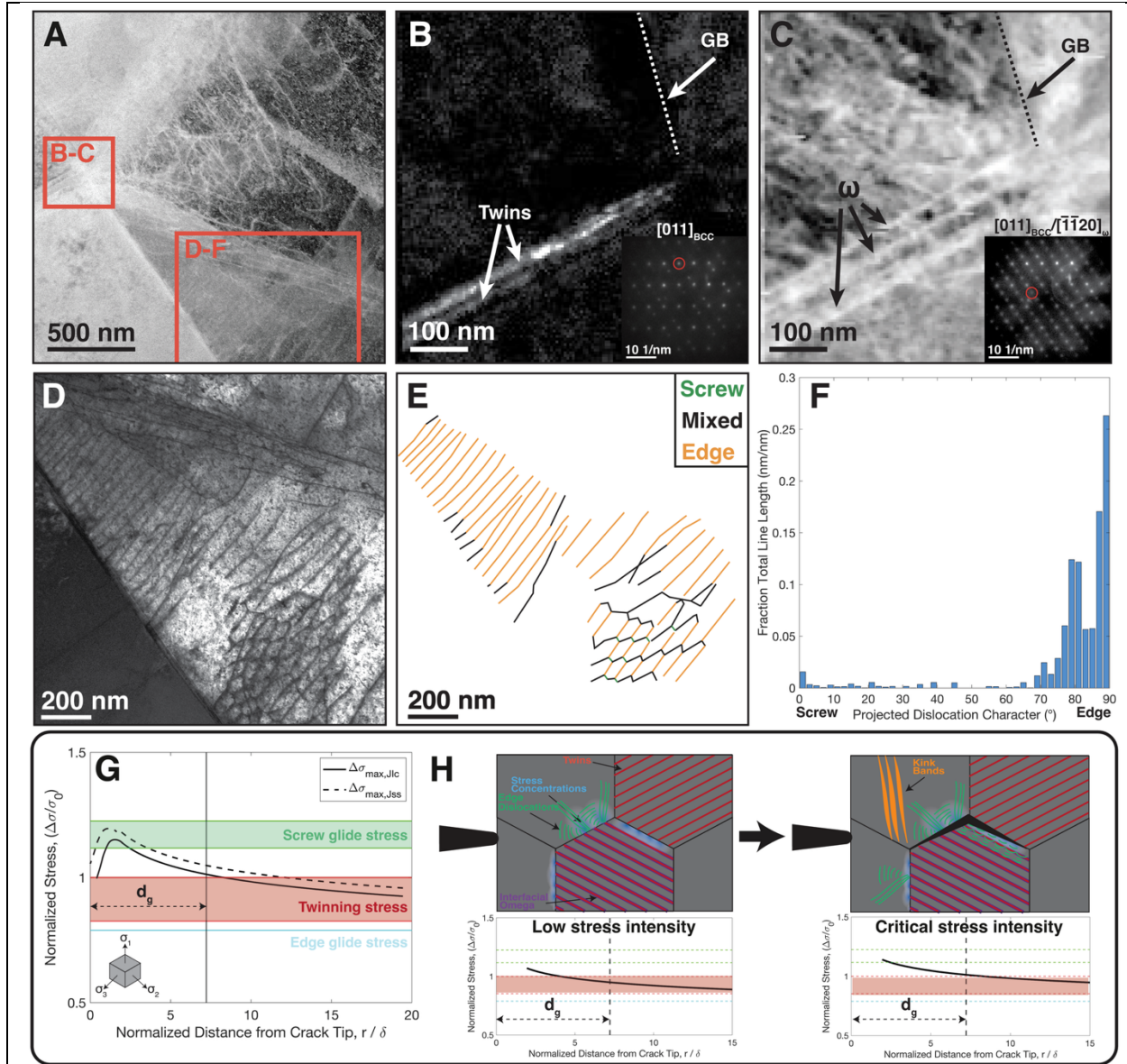


Figure 6.5: Crack-tip twinning, omega-phase, and dislocations. (a) HAADF-STEM overview micrograph of a fracturing grain boundary 30 μm ahead of the cracked-ligament. (b) Virtual dark-field 4D-STEM scans reconstructed from the circled diffraction disk indicated in (b) inset shows that the deformation at the grain boundary is produced by twinning with a phase map in (c) reconstructed from a virtual detector (highlighted in red) placed over an ω diffraction disk that shows the phase transformation occurs on twin boundaries. The stress concentration produced by twins and ω is alleviated by dislocations shown in a STEM image in (d). (e) A $g \cdot b$ analysis reveals dislocations in (D) are predominantly edge and mixed. An analysis of all characterized dislocations in (f) shows that dislocations have the preferred edge orientation. Note: the character of screw and mixed dislocations is determined under the assumption that the sample has negligible thickness. (g) These mechanisms are illustrated in a schematic that shows which part of the HRR field they create. These plots demonstrate that, unlike in tensile samples, the

constraint imposed by stress triaxiality does not allow the stresses to become high enough to activate screw dislocation glide. As a result, fracture occurs in a brittle-like process, shown in **(H)** where the stresses exceed the twinning stresses across a critical microstructural length-scale, the grain size, at the critical stress intensity.

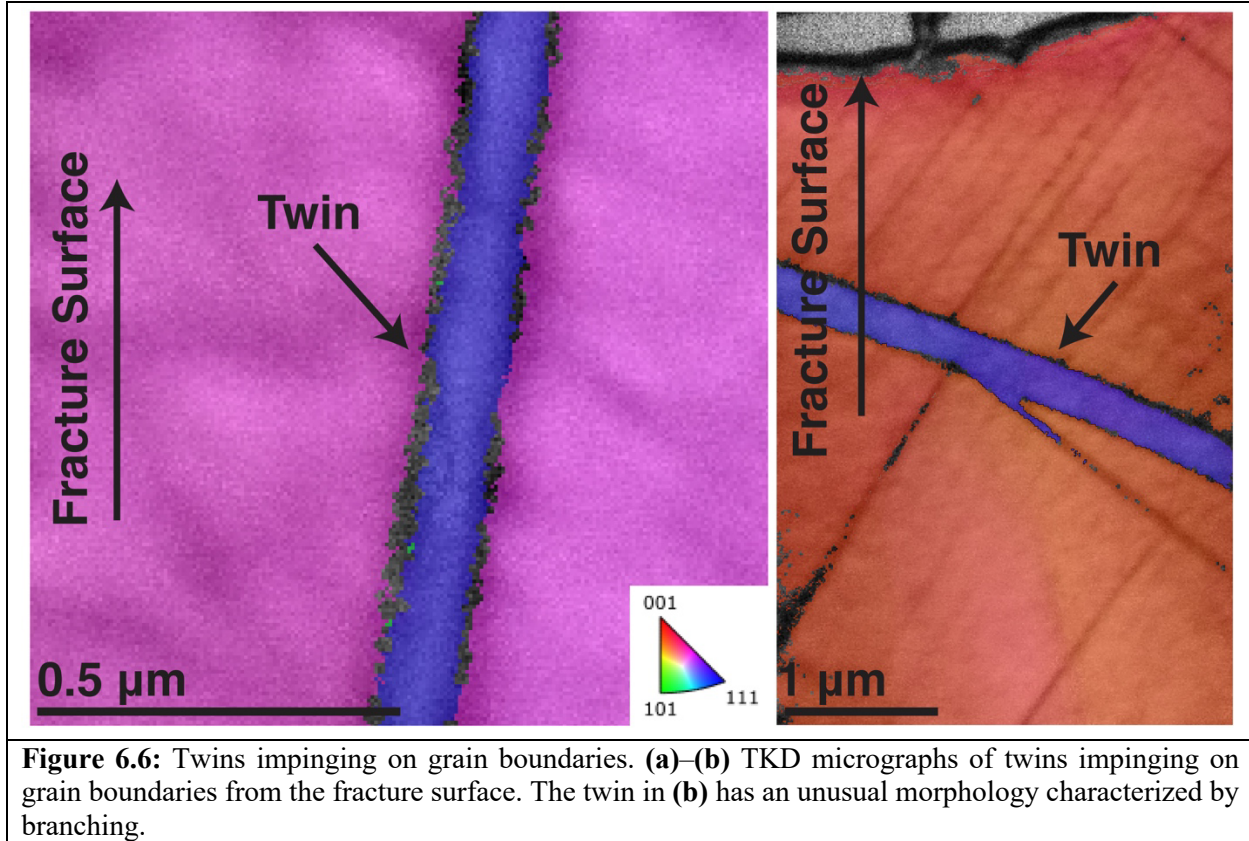


Figure 6.6: Twins impinging on grain boundaries. **(a)–(b)** TKD micrographs of twins impinging on grain boundaries from the fracture surface. The twin in **(b)** has an unusual morphology characterized by branching.

6.3 DISCUSSION

These results illustrate a complete reversal in the sequence of deformation mechanisms at lower temperatures that enables RHEAs to continue deforming plastically under conditions where dislocation glide is severely restricted [124]. The activation sequence—twinning, stress-induced ω -phase transformation, and subsequent dislocation glide—provides a novel pathway for cryogenic toughness. Specifically, activation of twinning and the omega transformation prior to dislocation glide prevents the typical rise in yield strength with decreasing temperature and promotes some strain hardening after yielding, although this hardening is not sustained over large strains once screw dislocations become mobile. This process avoids a temperature-induced, strength-mediated constriction of a crack-tip plastic zone. However, it forces dislocations to play a game of “catch-up,” where they can only glide once a twin nucleates them. These mechanisms are summarized in [Table 6.1](#). This is the exact opposite of what occurs in high-entropy alloys with the face-centered cubic structure, where the roles of these mechanisms are flipped because they activate in the reverse sequence: twinning and the phase transformation come at higher stresses to delay plastic localization from dislocation glide [7], [8], [9], [42]. The inverted sequence, however, is critical to sidestepping deformation through dislocation glide, which would otherwise cause embrittlement.

Understanding the origin of cryogenic toughness has tantalizing implications for the design of bcc alloys with low DBTTs, particularly those with superconducting properties [132], [133], [134]. To this end, we identified the conditions that allow this alloy to activate this mechanistic sequence that “threads the needle” between embrittlement caused by over activating twinning and the omega transformation or by under activating slip. This balance is achieved through the group IV elements and high chemical complexity that lower twinning migration and screw glide stresses, and conversely raise edge glide stresses [16], [79], [90], [115]. We quantified these effects using experimentally and computationally obtained values to construct a micromechanical model that accurately describes how this mechanistic sequence controls toughness (Fig 6.5(g),(h)). First, we obtained screw and edge dislocation tensile glide stresses using, respectively, the Rao-Suzuki model and the Maresca-Curtin model at 20 and 77 K with the experimental strain rate of $1 \cdot 10^{-3} \text{ s}^{-1}$ [69], [90]. Given kink widths ranging between 10–20 Burgers vectors, the theoretical strength from screws increases from a range of 1154–947 MPa at 77 K to 1384–1048 MPa at 20 K, whereas the edges remain at similar, albeit slightly lower, values: 678 MPa at 77 K and 740 MPa at 20 K [135]. We note that the screw values agree well with experimentally measured ultimate tensile stresses. Finally, we obtained the tensile twinning stresses from tensile curves, which we calculated to be in the range of 775–938 MPa (between the first twinning-induced stress drop, and the yield stress).

By mapping these stresses onto the crack-tip HRR field, plotted in Fig 6.5(g) and shown in ref. [4], we show that the constraint imposed by stress-triaxiality prevents crack-tip stresses from reaching the screw glide threshold, limiting crack-tip plasticity to twins and edge dislocations that redistribute twinning-induced damage. Our model shows that once the applied stress exceeds the twinning stress across a critical microstructural length-scale—in the case for intergranular fracture a single grain size, d_g —twinning overactivates and delaminates the grain boundary. Based on this crack-tip sequence, we demonstrate (described by the model constructed in the following section) that the toughness is simply a product of the yield stress (equivalent to the upper bound twinning stress), an integer multiple of the grain size, and a dimensionless constant that is a function of the strain hardening and tensile ductility, $\delta(N)$:

$$K_{Ic} = \delta(N)\sigma_y\sqrt{md_g}.$$

This makes the crack-initiation toughness near constant with temperature between 77 and 20 K because the crack-tip field is primarily controlled by a temperature-insensitive defect. The steady-state toughness can exceed screw glide thresholds, as it does at 77 K where they are lower, causing more pronounced rising R-curve behavior at this temperature (Fig. 6.1(b)). On the other hand, tensile specimens do not have the high constraints present at a crack tip which allows them to attain screw dislocation glide stresses, leading to a fully ductile fracture by microvoid coalescence.

While the group IV elements promote twinning and slip, they can act as a double-edged sword by promoting the transformation to omega, which is brittle in large amounts. Density Functional Theory (DFT) calculations at 0 K reveal that in NbTaTiHf alloys, increasing group IV concentrations promotes lattice instabilities from *bcc* to ω [79]. At 30 at.% Ti and Hf, the *bcc* phase in this alloy is actually very stable [79]. However, the composition of Nb₄₅Ta₂₅Ti₁₅Hf₁₅ is heterogeneous. Atom probe tomography (APT) analysis of grain boundaries in refs. [3], [4] shows that Ti and Hf enrich the boundaries in a ~ 3 nm range, raising the group IV concentration to 42 at.% in the measured region. This enrichment can produce an additional chemical driving force for stress-induced ω formation [136].

5.4 SUMMARY

To summarize, our findings demonstrate that *bcc* RHEAs containing group IV elements can retain exceptional damage tolerance, with no measurable ductile-to-brittle transition observed down to 20 K. These properties are derived from the unique mechanistic sequence which is highly unusual for *bcc* alloys that are often susceptible to high-temperature DBTTs [1]. Whereas most metallic alloys, regardless of crystal structure, generate high toughness from a mechanistic sequence that begins with dislocation glide and progresses to hardening mechanisms such as twinning and a phase transformation that delocalize dislocation induced damage [3], [7]; this sequence begins with twinning and a phase transformation with dislocations gliding to dissipate stress concentrations produced by the former two mechanisms. Consequently, crack-tip blunting is initiated by twinning, a temperature-insensitive mechanism that prevents the plastic zone from shrinking and generates edge dislocations that glide to distribute damage. Our proposed conditions and corresponding micromechanical models provide a pathway for designing future *bcc* alloys with low to non-existent DBTTs.

Stress-state	Screw Dislocations	Edge dislocations	{112}<111> Twinning	Omega Transformation	Kink Bands
Uniaxial Tension	Yes (2)	No	Yes (1)	Yes (1)	No
Crack-Tip Stress Triaxiality	No	Yes (2)	Yes (1)	Yes (1)	Yes (3)

Table 6.1. A Summary of mechanisms observed in each stress-state. Their sequential order with increasing stress is indicated in parenthesis.

6.5 METHODS

6.5.1 Crack-tip stress/strain state analysis

To quantify the stress/strain state at the crack-tip, the nonlinear elastic HRR plastic strain field was calculated as a function of the J -integral, radial distance, r , and angle, θ . To perform this calculation, the material was taken to have a power-hardening law:

$$\bar{\varepsilon}_p / \varepsilon_y = \alpha \left(\bar{\sigma} / \sigma_y \right)^N \quad (9)$$

where ε_y and σ_y are the yield strain and stress, α is a unitless constant (or order unity), and N is the strain-hardening exponent (where $1 \leq N \leq \infty$). For this alloy at 20 K, $N \approx 10$. Note that this equation is the inverse of the preceding power-hardening law. Given these material constants, the HRR field can be calculated from the following expressions:

$$\varepsilon_{ij} = \alpha \varepsilon_y \left[\frac{J}{\alpha \varepsilon_y \sigma_y I_n r} \right]^{\frac{N}{N+1}} \widetilde{\varepsilon}_{ij}(\theta, N) \quad (10)$$

where I_n is an integration constant that is a function of the strain-hardening exponent N , and $\widetilde{\varepsilon}_{ij}(\theta, N)$ is a dimensionless function of strain describing the variation of each strain component as a function of θ and N . The stress can be similarly calculated:

$$\sigma_{ij} = \sigma_y \left[\frac{J}{\alpha \varepsilon_y \sigma_y I_n r} \right]^{\frac{1}{N+1}} \widetilde{\sigma}_{ij}(\theta, N) \quad (11)$$

where similarly, $\widetilde{\sigma}_{ij}(\theta, N)$, is a dimensionless function of stress describing the variations of each stress component as a function of θ and N .

Given that the sample in Fig. 5.5 was taken 30 μm ahead of the crack-tip ($\theta = 0^\circ$) under plane-strain conditions, the strain tensor, converted to cartesian coordinates is given as:

$$\varepsilon_{ij} = \begin{bmatrix} -0.741 & 0 & 0 \\ 0 & 0.741 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot 10^{-2}$$

with the corresponding stress tensor (in MPa) as:

$$\sigma_{ij} = \begin{bmatrix} 2677.0 & 0 & 0 \\ 0 & 3876.4 & 0 \\ 0 & 0 & 3276.7 \end{bmatrix}$$

where $\sigma_{33} = \nu(\sigma_{11} + \sigma_{22})$ and $\nu \approx 1/2$ during plastic deformation. In this region, crack-tip stresses are approximately three higher and the strains are smaller than those reached in uniaxial tensile samples.

6.5.2 Micromechanical models of fracture for an inverted mechanistic sequence

We constructed a micromechanical model to predict the fracture toughness, K_{Ic} , of *bcc* alloys that undergo a sequence of mechanisms that begins with twinning. Our model assumes that dislocation glide is only activated by twinning and that the screw glide stresses are significantly higher than the twinning stresses, such that plasticity is solely controlled by twinning and subsequent edge glide. We postulate that that semi-brittle intergranular cleavage occurs when the local stress calculated by the HRR field exceeds the upper-bound twinning stress. We first consider the largest difference between the principal stress calculated from the HRR field directly in front of the crack-tip, *i.e.* when $\theta = 0$, to consider effects from constraint.

$$\Delta\sigma_{max} = \sigma_{\theta\theta} - \sigma_{rr} = \sigma_{yy} - \sigma_{xx} \quad (\theta = 0)$$

$$\Delta\sigma_{max} = \sigma_{yy} - \sigma_{xx} = \sigma_y \left[\frac{J}{\alpha \varepsilon_y \sigma_y I_n r} \right]^{\frac{1}{N+1}} \widetilde{\sigma}_{\theta\theta}(0, N) - \sigma_y \left[\frac{J}{\alpha \varepsilon_y \sigma_y I_n r} \right]^{\frac{1}{N+1}} \widetilde{\sigma}_{rr}(0, N)$$

$$\Delta\sigma_{max} = \sigma_y \left[\frac{J}{\alpha \varepsilon_y \sigma_y I_n r} \right]^{\frac{1}{N+1}} [\widetilde{\sigma}_{\theta\theta}(0, N) - \widetilde{\sigma}_{rr}(0, N)]$$

Based on our postulate, fracture occurs when $\Delta\sigma_{max}$ exceeds the twinning stress at a critical microstructural length-scale. Given that the upper bound twinning stress is the yield strength, fracture occurs when $\Delta\sigma_{max} = \sigma_y$ at $r = m d_g$, where m is an integer multiple of the grain boundary diameter, d_g .

$$\sigma_y = \sigma_y \left[\frac{J_{Ic}}{\alpha \varepsilon_y \sigma_y I_n m d_g} \right]^{\frac{1}{N+1}} [\widetilde{\sigma}_{\theta\theta}(0, N) - \widetilde{\sigma}_{rr}(0, N)]$$

Re-arranging gives:

$$J_{Ic} = \alpha \varepsilon_y \sigma_y I_n m d_g [\widetilde{\sigma}_{\theta\theta}(0, N) - \widetilde{\sigma}_{rr}(0, N)]^{-(N+1)}$$

Simplifying by substituting $\varepsilon_y = \sigma_y/E$, and converting to the critical stress intensity, *i.e.* $K_{Ic} = \sqrt{J_{Ic}E/(1 - \nu^2)}$ gives the following expression:

$$K_{Ic} = \sigma_y \sqrt{md_g \frac{\alpha I_n}{1 - \nu^2} [\widetilde{\sigma}_{\theta\theta}(0, N) - \widetilde{\sigma}_{rr}(0, N)]^{-(N+1)}}$$

to which we assign the factor:

$$\delta(N) = \sqrt{\frac{\alpha I_n}{1 - \nu^2} [\widetilde{\sigma}_{\theta\theta}(0, N) - \widetilde{\sigma}_{rr}(0, N)]^{-(N+1)}}$$

which leads to the final expression:

$$K_{Ic} = \delta(N) \sigma_y \sqrt{md_g}$$

All these values can easily be obtained from a tensile test. Approximations can be made; however, we caution that the stress intensity is sensitive to small changes in J_{Ic} values when they are low.

Chapter 6

Conclusion

This work has examined how the competing demands of strength and toughness can be reconciled in both *fcc* and *bcc* high-entropy alloys (HEAs) through control of their microstructure and activation of unconventional deformation mechanisms. In *fcc* HEAs, the challenge lies in maintaining high yield strength without sacrificing the extended strain hardening that underpins their exceptional toughness. By using additive manufacturing to process these alloys (specifically laser powder bed fusion) an engineered hierarchical microstructure composed of interwoven *fcc* and ordered *bcc* (B2) phases was introduced to the material. This approach demonstrated that “bottom-up” design can pre-embed deformation pathways into the material, elevating both strength and crack-initiation toughness by facilitating controlled dislocation glide and damage delocalization.

The second half of this work shifted focus to refractory *bcc* HEAs, which are known for their high strength but are generally limited by poor ductility and fracture resistance. Here, the alloy NbMoTaW exemplified this limitation, exhibiting extreme brittleness and minimal plasticity even at elevated temperatures. In contrast, a NbTaTiHf alloy, was shown to buck this trend. Through careful compositional design, this alloy activates deformation kink bands and twinning—mechanisms not typically associated with toughness in *bcc* metals. Remarkably, this system maintained high fracture resistance across a broad temperature range, including cryogenic conditions, and did not exhibit a traditional ductile-to-brittle transition. These results reveal that even in systems where dislocation glide is severely restricted, alternative mechanisms can enable distributed plasticity at a crack tip.

Altogether, the findings presented here underscore the importance of both intrinsic and extrinsic toughening strategies, microstructural hierarchy, and deformation pathway control in developing next-generation structural materials. By expanding the design space for toughness in both *fcc* and *bcc* HEAs, this work offers a foundation for creating damage-tolerant alloys capable of operating in extreme environments.

References

- [1] P. Kumar *et al.*, “Degradation of the mechanical properties of NbMoTaW refractory high-entropy alloy in tension,” *Acta Materialia*, vol. 279, p. 120297, Oct. 2024, doi: 10.1016/j.actamat.2024.120297.
- [2] P. Kumar *et al.*, “A strong fracture-resistant high-entropy alloy with nano-bridged honeycomb microstructure intrinsically toughened by 3D-printing,” *Nat Commun*, vol. 15, no. 1, p. 841, Jan. 2024, doi: 10.1038/s41467-024-45178-2.
- [3] D. H. Cook *et al.*, “Kink bands promote exceptional fracture resistance in a NbTaTiHf refractory medium-entropy alloy,” *Science*, vol. 384, no. 6692, pp. 178–184, Apr. 2024, doi: 10.1126/science.adn2428.
- [4] D. H. Cook *et al.*, “Divergent deformation pathways inhibit the ductile-brittle transition in a refractory medium-entropy alloy,” (*in rev.*), 2025.
- [5] R. O. Ritchie, “The conflicts between strength and toughness,” *Nature Mater*, vol. 10, no. 11, Art. no. 11, Nov. 2011, doi: 10.1038/nmat3115.
- [6] Aeso George, D. Raabe, and R. Ritchie, “High-Entropy Alloys,” *Nature Review Materials*, vol. 4, pp. 515–534, Jun. 2019.
- [7] D. Liu *et al.*, “Exceptional fracture toughness of CrCoNi-based medium- and high-entropy alloys at 20 kelvin,” *Science*, vol. 378, no. 6623, pp. 978–983, Dec. 2022, doi: 10.1126/science.abp8070.
- [8] B. Gludovatz *et al.*, “Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures,” *Nature Communications*, vol. 7, Feb. 2016.
- [9] Q. Ding *et al.*, “Real-time nanoscale observation of deformation mechanisms in CrCoNi-based medium- to high-entropy alloys at cryogenic temperatures,” *Materials Today*, vol. 25, pp. 21–27, May 2019, doi: 10.1016/j.mattod.2019.03.001.
- [10] P. Kumar *et al.*, “On the strength and fracture toughness of an additive manufactured CrCoNi medium-entropy alloy,” *Acta Materialia*, vol. 258, p. 119249, Oct. 2023, doi: 10.1016/j.actamat.2023.119249.
- [11] O. Senkov, D. Miracle, K. Chaput, and J.-P. Couzinie, “Development and exploration of refractory high entropy alloys—A review,” *Journal of Materials Research*, vol. 33, pp. 3092–3128, 2018.
- [12] O. N. Senkov, G. B. Wilks, J. M. Scott, and D. B. Miracle, “Mechanical properties of Nb₂₅Mo₂₅Ta₂₅W₂₅ and V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ refractory high entropy alloys,” *Intermetallics*, vol. 19, no. 5, pp. 698–706, May 2011, doi: 10.1016/j.intermet.2011.01.004.
- [13] O. N. Senkov, J. M. Scott, S. V. Senkova, D. B. Miracle, and C. F. Woodward, “Microstructure and room temperature properties of a high-entropy TaNbHfZrTi alloy,” *Journal of Alloys and Compounds*, vol. 509, no. 20, pp. 6043–6048, May 2011, doi: 10.1016/j.jallcom.2011.02.171.
- [14] L. H. Mills *et al.*, “Temperature-dependent tensile behavior of the HfNbTaTiZr multi-principal element alloy,” *Acta Materialia*, vol. 245, p. 118618, Feb. 2023, doi: 10.1016/j.actamat.2022.118618.
- [15] P. Kumar *et al.*, “Compressive vs. tensile yield and fracture toughness behavior of a body-centered cubic refractory high-entropy superalloy Al_{0.5}Nb_{1.25}Ta_{1.25}TiZr at temperatures from ambient to 1200°C,” *Acta Materialia*, vol. 245, p. 118620, Feb. 2023, doi: 10.1016/j.actamat.2022.118620.
- [16] P. P. O. Borges, R. O. Ritchie, and M. Asta, “Electronic descriptors for dislocation deformation behavior and intrinsic ductility in bcc high-entropy alloys,” *Science Advances*, vol. 10, no. 38, p. eadp7670, Sep. 2024, doi: 10.1126/sciadv.adp7670.
- [17] X. J. Fan, R. T. Qu, and Z. F. Zhang, “Remarkably high fracture toughness of HfNbTaTiZr refractory high-entropy alloy,” *Journal of Materials Science & Technology*, vol. 123, pp. 70–77, Oct. 2022, doi: 10.1016/j.jmst.2022.01.017.
- [18] T. Li *et al.*, “CALPHAD-aided design for superior thermal stability and mechanical behavior in a TiZrHfNb refractory high-entropy alloy,” *Acta Materialia*, vol. 246, p. 118728, Mar. 2023, doi: 10.1016/j.actamat.2023.118728.

- [19]S. Y. Chen *et al.*, “Phase transformations of HfNbTaTiZr high-entropy alloy at intermediate temperatures,” *Scripta Materialia*, vol. 158, pp. 50–56, Jan. 2019, doi: 10.1016/j.scriptamat.2018.08.032.
- [20]O. N. Senkov, J. M. Scott, S. V. Senkova, F. Meisenkothen, D. B. Miracle, and C. F. Woodward, “Microstructure and elevated temperature properties of a refractory TaNbHfZrTi alloy,” *J Mater Sci*, vol. 47, no. 9, pp. 4062–4074, May 2012, doi: 10.1007/s10853-012-6260-2.
- [21]M. E. Launey and R. O. Ritchie, “On the Fracture Toughness of Advanced Materials,” *Advanced Materials*, vol. 21, no. 20, pp. 2103–2110, 2009, doi: 10.1002/adma.200803322.
- [22]K. S. Ravichandran and A. K. Vasudevan, “Fracture Resistance of Structural Alloys,” Jan. 1996, doi: 10.31399/asm.hb.v19.a0002379.
- [23]Y. V. R. K. Prasad and P. Rama Rao, “Alloy design for fracture resistance,” *Proc. Indian Acad. Sci. (Engg. Sci.)*, vol. 3, no. 4, pp. 315–331, Dec. 1980, doi: 10.1007/BF02842917.
- [24]J. Reiser and A. Hartmaier, “Elucidating the dual role of grain boundaries as dislocation sources and obstacles and its impact on toughness and brittle-to-ductile transition,” *Sci Rep*, vol. 10, no. 1, p. 2739, Feb. 2020, doi: 10.1038/s41598-020-59405-5.
- [25]F. H. Olivares and J. Gil Sevillano, “A quantitative assessment of forest-hardening in f.c.c. metals,” *Acta Metallurgica*, vol. 35, no. 3, pp. 631–641, Mar. 1987, doi: 10.1016/0001-6160(87)90186-6.
- [26]K. Ming, X. Bi, and J. Wang, “Precipitation strengthening of ductile Cr15Fe20Co35Ni20Mo10 alloys,” *Scripta Materialia*, vol. 137, pp. 88–93, Aug. 2017, doi: 10.1016/j.scriptamat.2017.05.019.
- [27]P. Caron, Khan ,T., and P. and Veyssi re, “On precipitate shearing by superlattice stacking faults in superalloys,” *Philosophical Magazine A*, vol. 57, no. 6, pp. 859–875, Jun. 1988, doi: 10.1080/01418618808204522.
- [28]T. H. Becker, P. Kumar, and U. Ramamurty, “Fracture and fatigue in additively manufactured metals,” *Acta Materialia*, vol. 219, p. 117240, Oct. 2021, doi: 10.1016/j.actamat.2021.117240.
- [29]S. Wei, C. Hutchinson, and U. Ramamurty, “Mesostructure engineering in additive manufacturing of alloys,” *Scripta Materialia*, vol. 230, p. 115429, Jun. 2023, doi: 10.1016/j.scriptamat.2023.115429.
- [30]“Weld Metal Solidification II: Microstructure within Grains,” in *Welding Metallurgy*, John Wiley & Sons, Ltd, 2002, pp. 199–215. doi: 10.1002/0471434027.ch8.
- [31]J. Ren *et al.*, “Strong yet ductile nanolamellar high-entropy alloys by additive manufacturing,” *Nature*, vol. 608, no. 7921, Art. no. 7921, Aug. 2022, doi: 10.1038/s41586-022-04914-8.
- [32]K. G. Prashanth and J. Eckert, “Formation of metastable cellular microstructures in selective laser melted alloys,” *Journal of Alloys and Compounds*, vol. 707, pp. 27–34, Jun. 2017, doi: 10.1016/j.jallcom.2016.12.209.
- [33]D. Kong *et al.*, “About metastable cellular structure in additively manufactured austenitic stainless steels,” *Additive Manufacturing*, vol. 38, p. 101804, Feb. 2021, doi: 10.1016/j.addma.2020.101804.
- [34]“Solute trapping in rapid solidification | MRS Bulletin.” Accessed: Jun. 30, 2025. [Online]. Available: <https://link.springer.com/article/10.1557/mrs.2020.274>
- [35]Y. Zhao *et al.*, “Non-Equilibrium Solidification Behavior With Solute Trapping Associated With Powder Characteristics During Electron Beam Additive Manufacturing,” Jun. 14, 2021, *Social Science Research Network*, Rochester, NY: 3866407. doi: 10.2139/ssrn.3866407.
- [36]S.-H. Li, Y. Zhao, and U. Ramamurty, “Role of the solidification cells on the yield strength of the Al-Si-Mg alloy manufactured using laser powder bed fusion: A micropillar compression study,” *Scripta Materialia*, vol. 234, p. 115566, Sep. 2023, doi: 10.1016/j.scriptamat.2023.115566.
- [37]S.-H. Li, P. Kumar, S. Chandra, and U. Ramamurty, “Directed energy deposition of metals: processing, microstructures, and mechanical properties,” *International Materials Reviews*, vol. 68, no. 6, pp. 605–647, Aug. 2023, doi: 10.1080/09506608.2022.2097411.
- [38]S.-H. Li, Y. Zhao, P. Kumar, and U. Ramamurty, “Effect of initial dislocation density on the plastic deformation response of 316L stainless steel manufactured by directed energy deposition,” *Materials Science and Engineering: A*, vol. 851, p. 143591, Aug. 2022, doi:

- 10.1016/j.msea.2022.143591.
- [39]Z. Sun *et al.*, “Reducing hot tearing by grain boundary segregation engineering in additive manufacturing: example of an AlxCoCrFeNi high-entropy alloy,” *Acta Materialia*, vol. 204, p. 116505, Feb. 2021, doi: 10.1016/j.actamat.2020.116505.
 - [40]K. M. Bertsch, G. Meric de Bellefon, B. Kuehl, and D. J. Thoma, “Origin of dislocation structures in an additively manufactured austenitic stainless steel 316L,” *Acta Materialia*, vol. 199, pp. 19–33, Oct. 2020, doi: 10.1016/j.actamat.2020.07.063.
 - [41]R. Feng *et al.*, “Enhancing fatigue life by ductile-transformable multicomponent B2 precipitates in a high-entropy alloy,” *Nat Commun*, vol. 12, no. 1, p. 3588, Jun. 2021, doi: 10.1038/s41467-021-23689-6.
 - [42]B. Gludovatz, A. Hohenwarter, D. Catoor, E. H. Chang, E. P. George, and R. O. Ritchie, “A fracture-resistant high-entropy alloy for cryogenic applications,” *Science*, vol. 345, no. 6201, pp. 1153–1158, Sep. 2014, doi: 10.1126/science.1254581.
 - [43]*ASTM E1820: Standard Test Method for Measurement of Fracture Toughness, 2023*, West Conshohocken, PA., 2023.
 - [44]A. Haglund, M. Koehler, D. Catoor, E. P. George, and V. Keppens, “Polycrystalline elastic moduli of a high-entropy alloy at cryogenic temperatures,” *Intermetallics*, vol. 58, pp. 62–64, Mar. 2015, doi: 10.1016/j.intermet.2014.11.005.
 - [45]M. Moneghan, C. Williams, and R. Mirzaeifar, “Deformation mechanisms and defect tolerance in the microstructure of 3D-printed alloys,” *Journal of Materials Research*, vol. 35, no. 15, pp. 1984–1997, Aug. 2020, doi: 10.1557/jmr.2020.60.
 - [46]J. R. Strife and D. E. Passoja, “The effect of heat treatment on microstructure and cryogenic fracture properties in 5Ni and 9Ni steel,” *Metall Trans A*, vol. 11, no. 8, pp. 1341–1350, Aug. 1980, doi: 10.1007/BF02653488.
 - [47]D. T. Read and R. P. Reed, “Fracture and strength properties of selected austenitic stainless steels at cryogenic temperatures,” *Cryogenics*, vol. 21, no. 7, pp. 415–417, Jul. 1981, doi: 10.1016/0011-2275(81)90175-2.
 - [48]“Fracture toughness of type 304 and 316 stainless steels and their welds - W. J. Mills, 1997.” Accessed: Jun. 30, 2025. [Online]. Available: <https://journals.sagepub.com/doi/abs/10.1179/imr.1997.42.2.45>
 - [49]F. Wei *et al.*, “A comparative study of additive manufactured and wrought SS316L: Pre-existing dislocations and grain boundary characteristics,” *Materials Science and Engineering: A*, vol. 833, p. 142546, Jan. 2022, doi: 10.1016/j.msea.2021.142546.
 - [50]C. Zhang *et al.*, “Strong and ductile FeNiCoAl-based high-entropy alloys for cryogenic to elevated temperature multifunctional applications,” *Acta Materialia*, vol. 242, p. 118449, Jan. 2023, doi: 10.1016/j.actamat.2022.118449.
 - [51]B. Gludovatz, S. Wurster, A. Hoffmann, and R. Pippan, “Fracture toughness of polycrystalline tungsten alloys,” *International Journal of Refractory Metals and Hard Materials*, vol. 28, no. 6, pp. 674–678, Nov. 2010, doi: 10.1016/j.ijrmhm.2010.04.007.
 - [52]Y. Zou *et al.*, “Fracture properties of a refractory high-entropy alloy: In situ micro-cantilever and atom probe tomography studies,” *Scripta Materialia*, vol. 128, pp. 95–99, Feb. 2017, doi: 10.1016/j.scriptamat.2016.09.036.
 - [53]D. B. Miracle and O. N. Senkov, “A critical review of high entropy alloys and related concepts,” *Acta Materialia*, vol. 122, pp. 488–511, Jan. 2017.
 - [54]A. P. Mouritz, Ed., “1 - Introduction to aerospace materials,” in *Introduction to Aerospace Materials*, Woodhead Publishing, 2012, pp. 1–14. doi: 10.1533/9780857095152.1.
 - [55]W. Li, P. K. Liaw, and Y. Gao, “Fracture resistance of high entropy alloys: A review,” *Intermetallics*, vol. 99, pp. 69–83, Aug. 2018, doi: 10.1016/j.intermet.2018.05.013.
 - [56]Z. Wang *et al.*, “Solving oxygen embrittlement of refractory high-entropy alloy via grain boundary engineering,” *Materials Today*, vol. 54, pp. 83–89, Apr. 2022, doi: 10.1016/j.mattod.2022.02.006.
 - [57]Y. Xiao *et al.*, “Nanostructured NbMoTaW high entropy alloy thin films: High strength and enhanced

- fracture toughness,” *Scripta Materialia*, vol. 168, pp. 51–55, Jul. 2019, doi: 10.1016/j.scriptamat.2019.04.011.
- [58] J. R. Rice and J.-S. Wang, “Embrittlement of interfaces by solute segregation,” *Materials Science and Engineering: A*, vol. 107, pp. 23–40, Jan. 1989, doi: 10.1016/0921-5093(89)90372-9.
- [59] C. H. Belcher, B. E. MacDonald, D. Apelian, and E. J. Lavernia, “The role of interstitial constituents in refractory complex concentrated alloys,” *Progress in Materials Science*, vol. 137, p. 101140, Aug. 2023, doi: 10.1016/j.pmatsci.2023.101140.
- [60] D. Raabe *et al.*, “Grain boundary segregation engineering in metallic alloys: A pathway to the design of interfaces,” *Current Opinion in Solid State and Materials Science*, vol. 18, no. 4, pp. 253–261, Aug. 2014, doi: 10.1016/j.cossms.2014.06.002.
- [61] J. J. Cao, W. J. MoberlyChan, L. C. De Jonghe, C. J. Gilbert, and R. O. Ritchie, “In Situ Toughened Silicon Carbide with Al-B-C Additions,” *Journal of the American Ceramic Society*, vol. 79, no. 2, pp. 461–469, 1996, doi: 10.1111/j.1151-2916.1996.tb08145.x.
- [62] J. P. Guha, “Studies on Niobium Oxides and Polymorphism of Niobium Pentoxide,” *Transactions of the Indian Ceramic Society*, vol. 28, no. 4, pp. 97–101, Jan. 1969, doi: 10.1080/0371750X.1969.10855689.
- [63] A. Reisman and F. Holtzberg, “Nb₂O₅ and Ta₂O₅ Structure and Physical Properties,” in *Refractory Materials*, vol. 5, A. M. Alper, Ed., in High Temperature Oxides, vol. 5., Elsevier, 1970, pp. 217–257. doi: 10.1016/B978-0-12-053302-2.50016-7.
- [64] S. Wurster, B. Gludovatz, A. Hoffmann, and R. Pippan, “Fracture behaviour of tungsten–vanadium and tungsten–tantalum alloys and composites,” *Journal of Nuclear Materials*, vol. 413, no. 3, pp. 166–176, Jun. 2011, doi: 10.1016/j.jnucmat.2011.04.025.
- [65] K. K. Ray, U. Roy, A. Ray, M. Kumari, and A. Nath, “Underlying mechanisms for deformation and fracture behaviour of some BCC and FCC high entropy alloys,” *Theoretical and Applied Fracture Mechanics*, vol. 113, p. 102948, Jun. 2021, doi: 10.1016/j.tafmec.2021.102948.
- [66] P. P. O. Borges, R. O. Ritchie, and M. Asta, “Chemical trends favoring interstitial cluster formation in bcc high-entropy alloys from first-principles calculations,” *Acta Materialia*, vol. 294, p. 121091, Aug. 2025, doi: 10.1016/j.actamat.2025.121091.
- [67] F. Maresca and W. A. Curtin, “Mechanistic origin of high strength in refractory BCC high entropy alloys up to 1900K,” *Acta Materialia*, vol. 182, pp. 235–249, Jan. 2020, doi: 10.1016/j.actamat.2019.10.015.
- [68] F. Wang *et al.*, “Multiplicity of dislocation pathways in a refractory multiprincipal element alloy,” *Science*, vol. 370, no. 6512, pp. 95–101, Oct. 2020, doi: 10.1126/science.aba3722.
- [69] S. I. Rao, C. Woodward, B. Akdim, O. N. Senkov, and D. Miracle, “Theory of solid solution strengthening of BCC Chemically Complex Alloys,” *Acta Materialia*, vol. 209, p. 116758, May 2021, doi: 10.1016/j.actamat.2021.116758.
- [70] W. A. Curtin, S. I. Rao, and C. Woodward, “Progress and challenges in the theory and modeling of complex concentrated alloys,” *MRS Bulletin*, vol. 47, no. 2, pp. 151–157, Feb. 2022, doi: 10.1557/s43577-022-00306-5.
- [71] S. Wang, M. Wu, D. Shu, G. Zhu, D. Wang, and B. Sun, “Mechanical instability and tensile properties of TiZrHfNbTa high entropy alloy at cryogenic temperatures,” *Acta Materialia*, vol. 201, pp. 517–527, Dec. 2020, doi: 10.1016/j.actamat.2020.10.044.
- [72] H. Chen *et al.*, “Influence of Temperature and Plastic Strain on Deformation Mechanisms and Kink Band Formation in Homogenized HfNbTaTiZr,” *Crystals*, vol. 11, no. 2, Art. no. 2, Feb. 2021, doi: 10.3390/cryst11020081.
- [73] E. Orowan, “A Type of Plastic Deformation New in Metals,” *Nature*, vol. 149, no. 3788, Art. no. 3788, Jun. 1942, doi: 10.1038/149643a0.
- [74] P. E. J. Flewitt and A. G. Crocker, “The formation of deformation kinks in body centred cubic crystals,” *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics*, vol. 34, no. 5, pp. 877–891, Nov. 1976, doi: 10.1080/14786437608222057.
- [75] A. G. Crocker and J. S. Abell, “The crystallography of deformation kinking,” *The Philosophical*

- Magazine: A Journal of Theoretical Experimental and Applied Physics*, vol. 33, no. 2, pp. 305–310, Feb. 1976, doi: 10.1080/00318087608225776.
- [76] J. B. Hess and C. S. Barrett, “Structure and nature of kink bands in zinc,” *JOM*, vol. 1, no. 9, pp. 599–606, Sep. 1949, doi: 10.1007/BF03398902.
- [77] K. Li, W. Chen, G. Yu, J. Zhang, and J. Sun, “A novel deformation mechanism in Ti-V binary metastable β -Ti alloys: Deformation kinking promoted by dislocation accumulation,” *Journal of Alloys and Compounds*, vol. 875, p. 159982, Sep. 2021, doi: 10.1016/j.jallcom.2021.159982.
- [78] C. Y. Chan, C. N. Reid, and B. J. Duggan, “Kinking in niobium,” *Materials Science and Technology*, vol. 18, no. 4, pp. 449–457, Apr. 2002, doi: 10.1179/026708302225001688.
- [79] P. P. O. Borges, R. O. Ritchie, and M. Asta, “Local lattice distortions and the structural instabilities in bcc Nb-Ta-Ti-Hf high-entropy alloys: An ab initio computational study,” *Acta Materialia*, vol. 262, p. 119415, Jan. 2024, doi: 10.1016/j.actamat.2023.119415.
- [80] C. Zhang *et al.*, “Cold-workable refractory complex concentrated alloys with tunable microstructure and good room-temperature tensile behavior,” *Scripta Materialia*, vol. 188, pp. 16–20, Nov. 2020, doi: 10.1016/j.scriptamat.2020.07.006.
- [81] K. Ramachandran, Y. C. Jayakody, and D. D. Jayaseelan, “Oxidation behaviour and its effect on fracture toughness of Niobium metal,” *International Journal of Refractory Metals and Hard Materials*, vol. 110, p. 106033, Jan. 2023, doi: 10.1016/j.ijrmhm.2022.106033.
- [82] S. Wurster, B. Gludovatz, and R. Pippan, “High temperature fracture experiments on tungsten–rhenium alloys,” *International Journal of Refractory Metals and Hard Materials*, vol. 28, no. 6, pp. 692–697, Nov. 2010, doi: 10.1016/j.ijrmhm.2010.03.002.
- [83] R. Gröger, J. Holzer, and T. Kruml, “Twinning and antitwinning in body-centered cubic metals,” *Computational Materials Science*, vol. 216, p. 111874, Jan. 2023, doi: 10.1016/j.commatsci.2022.111874.
- [84] M. Wu *et al.*, “Dislocation glide and mechanical twinning in a ductile VNbTi medium entropy alloy,” *Journal of Materials Science & Technology*, vol. 110, pp. 210–215, May 2022, doi: 10.1016/j.jmst.2021.09.016.
- [85] S. Wang, M. Wu, D. Shu, and B. Sun, “Kinking in a refractory TiZrHfNb_{0.7} medium-entropy alloy,” *Materials Letters*, vol. 264, p. 127369, Apr. 2020, doi: 10.1016/j.matlet.2020.127369.
- [86] S. Zharebtsov, N. Yurchenko, D. Shaysultanov, M. Tikhonovsky, G. Salishchev, and N. Stepanov, “Microstructure and Mechanical Properties Evolution in HfNbTaTiZr Refractory High-Entropy Alloy During Cold Rolling,” *Advanced Engineering Materials*, vol. 22, no. 10, p. 2000105, 2020, doi: 10.1002/adem.202000105.
- [87] T. Cao *et al.*, “Strain rate dependent deformation behavior of BCC-structured Ti₂₉Zr₂₄Nb₂₃Hf₂₄ high entropy alloy at elevated temperatures,” *Journal of Alloys and Compounds*, vol. 891, p. 161859, Jan. 2022, doi: 10.1016/j.jallcom.2021.161859.
- [88] M. Yamasaki, K. Hagihara, S. Inoue, J. P. Hadorn, and Y. Kawamura, “Crystallographic classification of kink bands in an extruded Mg–Zn–Y alloy using intragranular misorientation axis analysis,” *Acta Materialia*, vol. 61, no. 6, pp. 2065–2076, Apr. 2013, doi: 10.1016/j.actamat.2012.12.026.
- [89] W. T. Read and W. Shockley, “Dislocation Models of Crystal Grain Boundaries,” *Phys. Rev.*, vol. 78, no. 3, pp. 275–289, May 1950, doi: 10.1103/PhysRev.78.275.
- [90] C. Lee *et al.*, “Strength can be controlled by edge dislocations in refractory high-entropy alloys,” *Nat Commun*, vol. 12, no. 1, Art. no. 1, Sep. 2021, doi: 10.1038/s41467-021-25807-w.
- [91] R. O. Ritchie and A. W. Thompson, “On macroscopic and microscopic analyses for crack initiation and crack growth toughness in ductile alloys,” *Metall Trans A*, vol. 16, no. 1, pp. 233–248, Jan. 1985, doi: 10.1007/BF02815305.
- [92] S. Sadeghpour, S. M. Abbasi, M. Morakabati, and L. P. Karjalainen, “Effect of dislocation channeling and kink band formation on enhanced tensile properties of a new beta Ti alloy,” *Journal of Alloys and Compounds*, vol. 808, p. 151741, Nov. 2019, doi: 10.1016/j.jallcom.2019.151741.
- [93] K. C. A. Blasdale and R. King, “Tensile Kinking in Single Crystals of Cadmium,” *physica status solidi (b)*, vol. 10, no. 1, pp. 175–184, 1965, doi: 10.1002/pssb.19650100117.

- [94] K. C. A. Blasdale, R. King, and K. E. Puttick, "The microstructure of tensile kinks in cadmium crystals," *physica status solidi (b)*, vol. 18, no. 2, pp. 491–503, 1966, doi: 10.1002/pssb.19660180202.
- [95] J. Nagakawa and M. Meshii, "The deformation of niobium single crystals at temperatures between 77 and 4.2 K," *Philosophical Magazine A*, vol. 44, no. 5, pp. 1165–1191, Nov. 1981, doi: 10.1080/01418618108235801.
- [96] G. Taylor and J. W. Christian, "Experiments on the deformation of niobium single crystals. I. Stress versus strain curves and slip systems in compression and tension," *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics*, vol. 15, no. 137, pp. 873–892, May 1967, doi: 10.1080/14786436708221635.
- [97] J. Qian, C. Y. Wu, J. L. Fan, and H. R. Gong, "Effect of alloying elements on stacking fault energy and ductility of tungsten," *Journal of Alloys and Compounds*, vol. 737, pp. 372–376, Mar. 2018, doi: 10.1016/j.jallcom.2017.12.042.
- [98] N. I. Medvedeva, Yu. N. Gornostyrev, and A. J. Freeman, "Electronic Origin of Solid Solution Softening in bcc Molybdenum Alloys," *Phys. Rev. Lett.*, vol. 94, no. 13, p. 136402, Apr. 2005, doi: 10.1103/PhysRevLett.94.136402.
- [99] J. Ding, Q. Yu, M. Asta, and R. O. Ritchie, "Tunable stacking fault energies by tailoring local chemical order in CrCoNi medium-entropy alloys," *Proceedings of the National Academy of Sciences*, vol. 115, no. 36, pp. 8919–8924, Sep. 2018, doi: 10.1073/pnas.1808660115.
- [100] Y. Murayama and S. Hanada, "High temperature strength, fracture toughness and oxidation resistance of Nb–Si–Al–Ti multiphase alloys," *Science and Technology of Advanced Materials*, vol. 3, no. 2, pp. 145–156, Jan. 2002, doi: 10.1016/S1468-6996(02)00005-0.
- [101] M. F. Ashby, Ed., "Appendix A - Data for Engineering Materials," in *Materials Selection in Mechanical Design (Fourth Edition)*, Oxford: Butterworth-Heinemann, 2011, pp. 495–523. doi: 10.1016/B978-1-85617-663-7.00018-7.
- [102] Y. H. Jo *et al.*, "Analysis of damage-tolerance of TRIP-assisted V10Cr10Fe45Co30Ni5 high-entropy alloy at room and cryogenic temperatures," *Journal of Alloys and Compounds*, vol. 844, p. 156090, Dec. 2020, doi: 10.1016/j.jallcom.2020.156090.
- [103] F. Chen, Y. Gu, G. Xu, Y. Cui, H. Chang, and L. Zhou, "Improved fracture toughness by microalloying of Fe in Ti-6Al-4V," *Materials & Design*, vol. 185, p. 108251, Jan. 2020, doi: 10.1016/j.matdes.2019.108251.
- [104] P. Hu *et al.*, "High temperature mechanical properties of TZM alloys under different lanthanum doping treatments," *Journal of Alloys and Compounds*, vol. 711, pp. 64–70, Jul. 2017, doi: 10.1016/j.jallcom.2017.03.346.
- [105] A. Sengupta *et al.*, "Tensile behavior of a new single-crystal nickel-based superalloy (CMSX-4) at room and elevated temperatures," *JMEP*, vol. 3, no. 1, pp. 73–81, Feb. 1994, doi: 10.1007/BF02654502.
- [106] Haynes International, "Haynes Waspaloy alloy," Haynes International, 2017. [Online]. Available: [https://haynesintl.com/docs/default-source/pdfs/new-alloy-brochures/high-temperature-alloys/brochures/waspaloy.pdf?sfvrsn=e77229d4_26#:~:text=HAYNES%C2%AE%20Waspaloy%20alloy%20\(UNS,gas%20turbine%20and%20aerospace%20components](https://haynesintl.com/docs/default-source/pdfs/new-alloy-brochures/high-temperature-alloys/brochures/waspaloy.pdf?sfvrsn=e77229d4_26#:~:text=HAYNES%C2%AE%20Waspaloy%20alloy%20(UNS,gas%20turbine%20and%20aerospace%20components).
- [107] Special Metals, "Inconel alloy 625," Special Metals Corporation, Aug. 2013. [Online]. Available: <https://www.specialmetals.com/documents/technical-bulletins/inconel/inconel-alloy-625.pdf>
- [108] S. Takeuchi, T. Hashimoto, and K. Maeda, "Plastic Deformation of bcc Metal Single Crystals at Very Low Temperatures," *Trans. JIM*, vol. 23, no. 2, pp. 60–69, 1982, doi: 10.2320/matertrans1960.23.60.
- [109] J. W. Christian, "Some surprising features of the plastic deformation of body-centered cubic metals and alloys," *Metall Trans A*, vol. 14, no. 7, pp. 1237–1256, Jul. 1983, doi: 10.1007/BF02664806.
- [110] R. O. Ritchie, J. F. Knott, and J. R. Rice, "On the relationship between critical tensile stress and fracture toughness in mild steel," *Journal of the Mechanics and Physics of Solids*, vol. 21, no. 6, pp. 395–410, Nov. 1973, doi: 10.1016/0022-5096(73)90008-2.

- [111] L. Dezerald, L. Proville, L. Ventelon, F. Willaime, and D. Rodney, “First-principles prediction of kink-pair activation enthalpy on screw dislocations in bcc transition metals: V, Nb, Ta, Mo, W, and Fe,” *Phys. Rev. B*, vol. 91, no. 9, p. 094105, Mar. 2015, doi: 10.1103/PhysRevB.91.094105.
- [112] P. A. Gordon, T. Neeraj, Y. Li, and J. Li, “Screw dislocation mobility in BCC metals: the role of the compact core on double-kink nucleation,” *Modelling Simul. Mater. Sci. Eng.*, vol. 18, no. 8, p. 085008, Nov. 2010, doi: 10.1088/0965-0393/18/8/085008.
- [113] S. Wang *et al.*, “The effects of interstitial oxygen on mechanical properties of TiZrNb medium-entropy alloy over a wide temperature range,” *Journal of Alloys and Compounds*, vol. 989, p. 174394, Jun. 2024, doi: 10.1016/j.jallcom.2024.174394.
- [114] T. Tsuru *et al.*, “Intrinsic factors responsible for brittle versus ductile nature of refractory high-entropy alloys,” *Nat Commun*, vol. 15, no. 1, p. 1706, Feb. 2024, doi: 10.1038/s41467-024-45639-8.
- [115] B. Chen, S. Li, J. Ding, X. Ding, J. Sun, and E. Ma, “Correlating dislocation mobility with local lattice distortion in refractory multi-principal element alloys,” *Scripta Materialia*, vol. 222, p. 115048, Jan. 2023, doi: 10.1016/j.scriptamat.2022.115048.
- [116] J. Ballor, T. Li, F. Prima, C. J. Boehlert, and A. Devaraj, “A review of the metastable omega phase in beta titanium alloys: the phase transformation mechanisms and its effect on mechanical properties,” *International Materials Reviews*, vol. 68, no. 1, pp. 26–45, Jan. 2023, doi: 10.1080/09506608.2022.2036401.
- [117] S. Wang *et al.*, “TiZrHfNb refractory high-entropy alloys with twinning-induced plasticity,” *Journal of Materials Science & Technology*, vol. 187, pp. 72–85, Jul. 2024, doi: 10.1016/j.jmst.2023.11.047.
- [118] S. Jha, A. Sharma, S. Dasari, S. Muskeri, R. Banerjee, and S. Mukherjee, “Orientation dependent stress-induced martensitic and omega transformations in a refractory high entropy alloy,” *Materialia*, vol. 28, p. 101741, May 2023, doi: 10.1016/j.mtla.2023.101741.
- [119] M. A. Meyers, O. Vöhringer, and V. A. Lubarda, “The onset of twinning in metals: a constitutive description,” *Acta Materialia*, vol. 49, no. 19, pp. 4025–4039, Nov. 2001, doi: 10.1016/S1359-6454(01)00300-7.
- [120] C. N. Reid, “A review of mechanical twinning in body-centred cubic metals and its relation to brittle fracture,” *Journal of the Less Common Metals*, vol. 9, no. 2, pp. 105–122, Aug. 1965, doi: 10.1016/0022-5088(65)90088-3.
- [121] A. Gilbert, G. T. Hahn, C. N. Reid, and B. A. Wilcox, “Twin-induced grain boundary cracking in b.c.c. metals,” *Acta Metallurgica*, vol. 12, no. 6, pp. 754–755, Jun. 1964, doi: 10.1016/0001-6160(64)90230-5.
- [122] M. J. Marcinkowski and H. A. Lipsitt, “The plastic deformation of chromium at low temperatures,” *Acta Metallurgica*, vol. 10, no. 2, pp. 95–111, Feb. 1962, doi: 10.1016/0001-6160(62)90055-X.
- [123] A. S. Argon and S. R. Maloof, “Fracture of tungsten single crystals at low temperatures,” *Acta Metallurgica*, vol. 14, no. 11, pp. 1463–1468, Nov. 1966, doi: 10.1016/0001-6160(66)90166-0.
- [124] *Thermally Activated Mechanisms in Crystal Plasticity*. 2003. Accessed: Apr. 04, 2025. [Online]. Available: <https://shop.elsevier.com/books/thermally-activated-mechanisms-in-crystal-plasticity/caillard/978-0-08-042703-4>
- [125] S. Q. Wu *et al.*, “{112}<111> Twinning during ω to body-centered cubic transition,” *Acta Materialia*, vol. 62, pp. 122–128, Jan. 2014, doi: 10.1016/j.actamat.2013.09.040.
- [126] B. Chen and W. Sun, “Omega transitional structure associated with {112}<111> deformation twinning in a metastable beta Ti-Nb alloy, revealed by atomic resolution high-angle annular dark-field scanning transmission electron microscopy,” *Journal of Alloys and Compounds*, vol. 766, pp. 123–130, Oct. 2018, doi: 10.1016/j.jallcom.2018.06.281.
- [127] H. Xing and J. Sun, “Mechanical twinning and omega transition by {111} {112} shear in a metastable β titanium alloy,” *Applied Physics Letters*, vol. 93, no. 3, p. 031908, Jul. 2008, doi: 10.1063/1.2959183.

- [128] B. Edmondson and N. P. Allen, “The effect of composition and structure on the tensile properties of high-purity iron single crystals, with particular reference to the question of brittle fracture,” *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 264, no. 1317, pp. 176–197, Jan. 1997, doi: 10.1098/rspa.1961.0192.
- [129] B. A. Bilby and R. and Bullough, “LXXI. The formation of twins by a moving crack,” *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, vol. 45, no. 365, pp. 631–646, Jun. 1954, doi: 10.1080/14786440608520468.
- [130] C. R. Weinberger, B. L. Boyce, and C. C. Battaile, “Slip planes in bcc transition metals,” *International Materials Reviews*, vol. 58, no. 5, pp. 296–314, Jun. 2013, doi: 10.1179/1743280412Y.0000000015.
- [131] D. Banerjee and J. C. Williams, “Perspectives on Titanium Science and Technology,” *Acta Materialia*, vol. 61, no. 3, pp. 844–879, Feb. 2013, doi: 10.1016/j.actamat.2012.10.043.
- [132] J. Guo *et al.*, “Robust zero resistance in a superconducting high-entropy alloy at pressures up to 190 GPa,” *Proceedings of the National Academy of Sciences*, vol. 114, no. 50, pp. 13144–13147, Dec. 2017, doi: 10.1073/pnas.1716981114.
- [133] R. Hidayati, J. H. Kim, S.-G. Jung, K.-S. Cho, J. H. Yun, and J.-S. Rhyee, “Enhancement of critical current density and critical magnetic field of superconducting medium entropy alloy Nb₂/5Hf₁/5Zr₁/5Ti₁/5,” *Acta Materialia*, vol. 261, p. 119420, Dec. 2023, doi: 10.1016/j.actamat.2023.119420.
- [134] F. von Rohr, M. J. Winiarski, J. Tao, T. Klimczuk, and R. J. Cava, “Effect of electron count and chemical complexity in the Ta-Nb-Hf-Zr-Ti high-entropy alloy superconductor,” *Proceedings of the National Academy of Sciences*, vol. 113, no. 46, pp. E7144–E7150, Nov. 2016, doi: 10.1073/pnas.1615926113.
- [135] W. Wang, A. A. Abu-Odeh, R. O. Ritchie, M. Asta, and S. I. Rao, “Modeling and Accurate Molecular Dynamics Simulations of Solid Solution Strengthening in Nb₄₅Ta₂₅Ti₁₅Hf₁₅,” *Acta Materialia (Under Review)*.
- [136] A. Devaraj *et al.*, “Experimental evidence of concurrent compositional and structural instabilities leading to ω precipitation in titanium–molybdenum alloys,” *Acta Materialia*, vol. 60, no. 2, pp. 596–609, Jan. 2012, doi: 10.1016/j.actamat.2011.10.008.