Exceptional fracture toughness of CrCoNi-based medium- and high-entropy alloys at 20 kelvin

Dong Liu, Qin Yu, Saurabh Kabra, Ming Jiang, Paul Forna-Kreutzer, Ruopeng Zhang, Madelyn Payne, Flynn Walsh, Mark Asta, Andrew M. Minor, Easo P. George, Robert O. Ritchie

CrCoNi-based medium- and high-entropy alloys display outstanding damage tolerance, especially at cryogenic temperatures. In this study, we examined the fracture toughness values of the equiatomic CrCoNi and CrMnFeCoNi alloys at 20 kelvin (K). We found exceptionally high crack-initiation fracture toughnesses of 262 and 459 megapascal-meters⁰·⁵ (MPa·m⁰·⁵) for CrMnFeCoNi and CrCoNi, respectively; CrCoNi displayed a crack-growth toughness exceeding 540 MPa·m⁰·⁵ after 2.25 millimeters of stable cracking. Crack-tip deformation structures at 20 K are quite distinct from those at higher temperatures. They involve nucleation and restricted growth of stacking faults, fine nanotwins, and transformed epsilon martensite, with coherent interfaces that can promote both arrest and transmission of dislocations to generate strength and ductility. We believe that these alloys develop fracture resistance through a progressive synergy of deformation mechanisms, dislocation glide, stacking-fault formation, nanotwinning, and phase transformation, which act in concert to prolong strain hardening that simultaneously elevates strength and ductility, leading to exceptional toughness.

Results

Given their exceptional damage tolerance, we investigated the mechanical properties of CrCoNi and CrMnFeCoNi alloys at even lower temperatures (~20 K) by performing uniaxial tensile tests and nonlinear elastic J-based fracture toughness tests in a liquid helium environment (using the testing setup shown in figs. S1 to S3). Impact tests on the CrCoNi alloy have reported high Charpy V-notch energies of close to 400 J at 77 K, which were (quasistatic compression) up to extremely high rates of 6 × 10⁸ s⁻¹ (dynamic shear) (17).

There have been several derivatives of the CrMnFeCoNi alloy (12–14), most notably the single-phase equiatomic CrCoNi medium-entropy alloy (MEA), which displays even better properties. At 77 K, this MEA was found to have a K_Ic of 273 MPa·m⁰·⁵ and a K_ss exceeding 400 MPa·m⁰·⁵ (15). Although strength and toughness are often mutually exclusive properties (16), the CrCoNi alloy exhibits exceptionally high damage tolerance, with fracture toughness values among the largest ever reported. Such CrCoNi-based multiple principal element alloys are clearly strong candidate materials for potential applications in extreme environments, such as at very high strain rates and cryogenic temperatures.

Fig. 1. J-R curves and fracture toughness values for the CrCoNi and CrMnFeCoNi alloys as a function of temperature. J-R curves showing the variation in the J-integral as a function of crack extension Δa for (A) the CrMnFeCoNi HEA and (B) the CrCoNi MEA, between room temperature (RT, ~293 K) and 20 K. Corresponding K-based fracture toughness values back-calculated from the R-curves are shown in (C) for CrMnFeCoNi and (D) for CrCoNi, where K_Ic represents the crack-initiation toughness and K_ss the crack-growth toughness, defined at the ASTM E1820 maximum limit of valid crack extension where Δa = 2.25 mm. Note how the toughness of both alloys at 20 K is higher than at other temperatures. The toughness values for the CrCoNi alloy are believed to be among the highest toughnesses ever reported.

Liu et al., Science 378, 978–983 (2022) 2 December 2022
reduced by ~10% at 4.2 K (18). However, it remains unclear how samples that contain a sharp crack would perform at temperatures below 77 K, where anomalies in the temperature dependence of strength and ductility have been reported (19–22). Furthermore, full resistance-curve measurements that define both the crack-initiation and crack-growth fracture toughness have not been performed on medium- or high-entropy alloys at low temperatures approaching that of liquid helium. In addition to measurements of the crack-initiation and crack-growth toughnesses (and their corresponding stress intensity–based values), we performed in situ neutron diffraction measurements and extensive postfracture electron backscatter diffraction (EBSD) analysis, fractography, and particularly transmission electron microscopy to examine in detail the salient plastic deformation mechanisms and defect behavior that represent the fundamental basis of their exceptional fracture resistance, which we find progressively increases with decreasing temperature, unlike for most metallic materials.

As described in more detail in the supplementary materials, the CrCoNi and CrMnFeCoNi alloys that we investigated were arc melted, drop cast, and homogenized at 1200°C before being cold worked at room temperature and recrystallized at 800°C to give a single-phase equiaxed grain structure with an average grain size of ~21 μm in CrMnFeCoNi and ~8 μm in CrCoNi. Their uniaxial tensile stress-strain curves and crack-resistance curves (R-curves), experimentally measured at 20 K, are shown in fig. 54 and Fig. 1, A and B, respectively. For comparison, Fig. 1, A and B, also shows R-curves taken at ambient (293 K), dry ice (198 K), and liquid nitrogen (77 K) temperatures. We back-calculated the corresponding stress intensity–based fracture toughness values from the J-values as a function of temperature (20 to 293 K) and plotted $K_J$ (Fig. 1, C and D), which we determined according to ASTM Standard E1820 (17), and $K_{IC}$ defined at the maximum limit of valid crack extension (17), where $\Delta a = 2.25$ mm (near the plateau of the R-curve).

Both alloys show markedly rising R-curves that progressively increase with decreasing temperature, especially CrCoNi. Exceedingly high fracture toughness values are exhibited at 20 K; the $K_{IC}$ and $K_R$ values for the CrMnFeCoNi alloy are, respectively, 262 and 383 MPa·m$^{\frac{1}{2}}$, whereas the corresponding values for CrCoNi are 469 and 544 MPa·m$^{\frac{1}{2}}$. The latter value represents one of the highest toughnesses on record. Fracture surfaces at 20 K showed no sign of brittle fracture features and exhibited 100% ductile failure by microvoid coalescence, in agreement with earlier work at higher temperatures of 77 to 293 K (10, 15), with dimple sizes in the range of several micrometers (Fig. 2, C and D).

**Fig. 2. Microstructure and fractography of the CrCoNi-based alloys.** EBSD scans show the equiaxed single-phase microstructures in (A) CrMnFeCoNi and (B) CrCoNi alloys. The sample direction associated with the IPF coloring is the direction normal to the EBSD scan plane. Fracture in both alloys occurs by microvoid coalescence. Examples of such ductile fractures in CrCoNi are shown at (C) 293 K and (D) 20 K.

**Discussion**

Despite their exceptionally high fracture toughness, these alloys do not have complex microstructures, as they are simple single-phase solid solutions (Fig. 2, A and B). Thus, an important question that immediately arises is the origin of this exceptional fracture resistance and why it should be so progressively enhanced at cryogenic temperatures.

To address this, we look to the cooperative defect behavior responsible for plastic deformation in these alloys (23–25), using mainly the CrCoNi alloy to illustrate the prototypical behavior at 20 K versus room temperature. We used postfracture EBSD analysis and high-resolution transmission electron microscopy (HRTEM) of the heavily deformed regions within the plastic zone, directly adjacent to the crack tip where local strains can readily be on the order of 60 to 100%. Although the microstructure starts off as a rather simple single-phase solid solution, deformation at 20 K transforms the structure into a rich and complex mixture of phases and defect structures.

To investigate the microscopic deformation mechanisms, the compact-tension samples used in the fracture toughness tests were first cut through the midthickness to obtain sections of the fracture path that were predominantly under plane-strain conditions. These were first mechanically and then electrolytically polished for examination with EBSD. EBSD image quality (IQ) and inverse pole figure (IPF) maps (Fig. 3) for the CrCoNi alloy tested at 20 K indicate extensive deformation-induced twinning in the highly deformed grains (under high stress triaxiality) within the plastic zone in the vicinity of the crack tip. Similar deformation mechanisms have been reported for CrCoNi-based alloys at these low temperatures in uniaxial tensile tests where the degree of triaxiality is far lower (18–22, 25). We then made sections from these regions into TEM foils using a focused ion beam (FIB) lift-out method, finishing with a 5-kV Ga+ polish, for HRTEM and four-dimensional scanning transmission electron microscopy (4D-STEM). The CrCoNi samples that were deformed and fractured at both room temperature and at 20 K show a strong propensity for planar deformation features (Fig. 4). We conducted HRTEM imaging to identify the nature of these features. At room temperature, they include both nanotwins and bands of stacking faults, but no well-defined sequence (exceeding three layers) of any hexagonal close-packed (hcp) phases (Fig. 4, A and B). We did identify, however, a
considerable number of dislocations in the area between the planar features (shown in detail in fig. S5). In contrast, for samples tested at 20 K, the dominant planar features are deformation bands full of stacking faults (Fig. 4D), with the frequent appearance of “laths” of the hcp phase with a thickness of a few nanometers (Fig. 4H). The latter are notably absent in specimens deformed at room temperature. Additionally, CrCoNi demonstrates a decreased tendency for nanotwinning at 20 K, as well as a smaller size of nanotwins compared with those formed at room temperature.

We conducted successive 4D-STEM experiments to identify the size and distribution of these microstructural features in both CrCoNi (Fig. 4) and CrMnFeCoNi (Fig. S6). Both virtual dark-field images and selected-area diffraction patterns were reconstructed to extract the spatially resolved structural information of the planar features in the CrCoNi samples tested at 293 and 20 K. The planar features generated at room temperature are primarily well-defined nanotwins or stacking faults, with the former having sizes in the range of several nanometers (Fig. 4C). In contrast, the planar deformation features identified at 20 K contain a combination of diffuse yet finer nanotwins, stacking faults, and a well-defined hcp phase (Fig. 4, F and I). We believe that this change in deformation modes at 20 K, promoted by low stacking-fault energies, is primarily responsible for the groundbreaking fracture toughness.

Stacking-fault energies for CrMnFeCoNi (26) and CrCoNi (27) have been experimentally determined as ~30 and 14 mJ·m⁻², respectively, at room temperature, which are expected to progressively decrease at lower temperatures. Indeed, measurements in CrFeCoNiMo₀.2 report the stacking-fault energy to decrease from 28 mJ·m⁻² at 293 K to 11 mJ·m⁻² at 15 K (28). However, microscopy-based measurements obtained from balancing forces on finitely disassociated dislocations in concentrated alloys have drawn criticism for neglecting local variations in the Peierls potential due to chemical fluctuations (29) and their associated lattice distortion (30), as well as grain-size dependence (31). Nevertheless, the trend of reduced stacking-fault energies at lower temperatures in these alloys is inarguable and consistent with theoretical predictions of the increasing energetic stability of the hcp phase relative to the fcc phase with decreasing temperature. In the CrMnFeCoNi samples tested at 20 K, 4D-STEM characterization (fig. S6) revealed the presence of nanotwins similar to those seen in CrCoNi but no evidence of hcp phase formation. This likely explains the former’s lower strength (fig. S4) and fracture toughness (Fig. 1, C and D).

Although low stacking-fault energies and the associated phenomena of planar slip, stacking faults, nanotwinning, and hcp phase formation have been individually observed in simpler fcc alloys, the full sequence described above, coupled with strong solid-solution strengthening and prolonged strain hardening, generally has not. Consider, for example, dilute Cu-Al alloys (containing up to 10 atomic % Al) in which the stacking-fault energy can be significantly decreased by the addition of Al (to values even lower than those of CrCoNi and CrMnFeCoNi). Nevertheless, the Cu-Al binaries remain significantly weaker at ~10 K [one-fifth to one-tenth the critical resolved shear stress of CrMnFeCoNi (26)]. Similarly, one can contemplate elements that increase solid-solution strengthening (e.g., as a result of large atomic size misfits) but have little to no effect on the stacking-fault energy, and so on for each of the mechanisms discussed above. Because a given element in an alloy will at most influence one or two of the desired mechanisms, multiple alloying elements will likely be needed to simultaneously or sequentially activate all relevant mechanisms. In the long run, this ability to control individual mechanisms, precisely when needed, may well prove to be the single biggest advantage of multiple principal element alloys such as those investigated here (32).

The low deformation temperature limits dislocation motion and twin growth by suppressing thermally activated processes. But the increased flow stress increases the formation of twins and hcp phases at 20 K, as compared with room temperature, at which no hcp formation was detected. As twinning in these alloys has been shown to be stress-controlled (33, 34), an fcc→hcp transformation (which involves a similar change in stacking sequence) would be expected to be favored as the flow stress increases with decreasing temperature. A diffuse network of the resulting planar deformation features—nanotwin and phase interfaces—acts to further decrease the mean free path for dislocation motion. Combined with suppressed dynamic recovery at these low temperatures, a synergy of deformation mechanisms—dislocation glide, stacking fault formation, deformation nanotwinning, and deformation-induced phase transformation—is created at increasing strain levels, which presents a highly efficient process for developing and, most importantly, prolonging strain hardening to restrict the localization of deformation in the crack-tip region. In simple terms, the strain hardening naturally increases strength but at the same time delays the onset of necking, which promotes ductility. Micro-mechanical models for the prediction of the fracture toughness of materials experiencing ductile fracture (35, 36) are based on a critical strain being exceeded over a characteristic microstructural dimension ahead of a crack tip; these models give the $J_{cl}$ toughness to be directly proportional to the product of the flow strength, strain to failure, and this characteristic dimension (which is related to some multiple of the particle spacing involved in the microvoid coalescence fracture). Accordingly, the corresponding elevations in strength and ductility resulting from the strain hardening, created by the prolonged sequence of multiple deformation mechanisms, act in concert to enhance the toughness. The extent of strain hardening increases as temperature decreases owing to several related factors: (i) the lower
stacking-fault energy, which hinders cross-slip by increasing the spacing between Shockley partials; (ii) the promotion of nanotwinning (also related to lower stacking-fault energy); and (iii) the onset of the deformation-induced transformation to the hcp phase (but only to a limited degree, as too much hcp could embrittle the material).

The role of the fcc→hcp transformation is particularly interesting. The in situ transformation to the hexagonal phase has now been reported in numerous papers (37–39). It enables further strain hardening at higher strains, but the resulting epsilon martensite is not necessarily beneficial for toughness, as hcp phases are generally not as ductile as fcc phases, which in sufficiently large amounts would likely cause a ductile-brittle transition at 20 K. Indeed, some researchers have reported a decrease in ductility at 4.2 to 20 K, as compared with 77 K, in alloys similar to ours, which they attribute to epsilon martensite formation (20, 40).

Intriguingly, 0 K ab initio calculations suggest that, for a given degree of (dis)order, hcp CrCoNi has a lower Gibbs energy than the fcc equivalent; this relationship inverts at higher temperatures owing to the activation of phonon modes (41) and likely spin fluctuations as well (42). This picture is consistent with the observation of somewhat larger hcp lamellae at 20 K, but it must be asked why, in contrast to similarly metastable Co (43) or CoNi alloys (44), low-temperature deformation still only minimally induces the martensitic hcp phase, which has been reported in quantities ranging from 0 to a maximum of a few vol % (18, 25, 45). This observation is also consistent with our in situ neutron diffraction data (fig. S7), where the maximum stacking-fault probability caused by deformation was estimated to be \(6.3 \times 10^{-5}\). As noted, the theoretical metastability of CrCoNi is of similar magnitude as that of elemental Co (43), which demonstrates a clear allotropic phase transition via a martensitic mechanism that is enhanced by mechanical deformation (43). Even in more stable fcc CoNi alloys, which far less readily transform spontaneously to hcp, low-temperature deformation has been found to promote sizable hcp regions (44). One particularly enticing explanation for the observed behavior is the presence of quenched-in chemical short-range order stabilizing the fcc matrix relative to the formation of less-ordered hcp regions (46). This scenario would also address the apparent restriction of existing hcp regions to thin laths within extended planar defect structures (37), where local order would be disrupted by the occurrence of earlier slip. Recent simulations (47) offer specific insight on the mechanisms by which hcp and twin nuclei freely expand in random, but not in short-range ordered, samples at room temperature. Although the material used in this study was not prepared in a manner intended to promote local ordering (48), recent measurements such as those of Oh et al. (49) have suggested that elusive atomic-scale chemical ordering could be present in even water-quenched samples. In this case, the physics of deformation would be similar to that discussed by Yu et al. (47), with a greater driving force for hcp formation at lower temperatures. Whatever the reason, because the hcp laths are relatively thin, they can provide a disproportionately large number of barriers to dislocation motion (and, in turn, work hardening), even when the overall volume fraction is small, as in the case of nanotwins (33), which contribute little to axial strain (tensile ductility) but significantly to strain hardening. For example, a single hcp lath with finite thickness introduces two new barriers within a grain, thereby splitting the grain into two or three segments (depending on lath thickness). For the sake of simplicity, if the hcp lath is assumed to be very thin and its boundaries are assumed to have the same strength as grain boundaries, the effective grain size is halved when one lath is introduced in each grain, quartered when three laths are introduced per grain, and so on. This would induce substantial strengthening by a dynamic Hall-Petch–type mechanism in
the strain-hardening regime because the phase transformation occurs dynamically during straining. As is the case with nanotwins in a polycrystalline HEA (39), the main role of the hcp phase is to enhance strain hardening, which leads indirectly to increased ductility by postponing necking instability, rather than directly contributing to the tensile strain. Despite the hcp phase being brittle, this nevertheless serves to enhance the toughness, but with the key constraint that its volume fraction must be small.

The results we present here on the CrCoNi-based MEAs and HEAs show that a monotonic improvement in fracture toughness is possible down to very low temperatures (20 K). This is rarely the case, especially in bcc and hcp alloys that undergo a ductile-brittle transition as the temperature decreases. Even many fcc alloys show a significant drop in toughness below a critical temperature. For example, the Charpy toughness of 304L stainless steel starts dropping around 223 K and by 77 K is ~35 to 67% lower, depending on the heat treatment; 316L stainless steel shows a similar drop in toughness (50). Many Al alloys, whose Charpy toughness values are not high to begin with, exhibit a noticeable toughness drop below ~200 K (57). The same can be said about Cu-Be alloys, certain bronzes, and hardenable stainless steels. Thus, as cryogenic structural materials, equiatomic, single-phase fcc CrCoNi-based medium- and high-entropy alloys, in particular the CrCoNi alloy, appear to be unique. They possess some of the most impressive mechanical properties of any metallic alloy reported to date. Indeed, their crack-initiation and crack-growth fracture toughness values at 20 K are among the highest ever recorded (Fig. 5), a fact that we ascribe to their effective strain-hardening capacity generated by their synergy of deformation mechanisms created under increasing strains, including dislocation slip, stacking-fault formation, deformation nanotwinning, and limited hcp epiion martensite formation.

A broader impact of this work is that the sequence of mechanisms outlined here can, in principle, be put to work in other alloy systems, from around room temperature all the way down to 20 K, depending on the temperature regime of interest for a given application. At the low end of temperatures (~20 K), potential applications include the long-distance transportation of liquid hydrogen. With increased emphasis on climate change and the need for clean energy, hydrogen might partially replace fossil fuels, especially if the former can be produced by electrolysis of water using renewable energy. Load-bearing materials that need to operate in the frigid temperatures of distant planets can also make use of the insights gained here. At somewhat higher temperatures (~110 to 115 K), transportation of liquified natural gas across oceans becomes an important potential application because pipelines cannot easily reach everywhere; the present findings can guide the design of damage-tolerant materials for such applications.

Conclusions

The main takeaway here is the realization that multiple strain-hardening mechanisms need to be activated, in exactly the right sequence, for simultaneous increases in strength, ductility, and toughness. This basic insight applies across the entire range of cryogenic temperatures, and HEAs and MEAs are uniquely qualified to make practical use of this because they possess the multiple compositional “dials” needed to tune each individual mechanism separately without adversely affecting the others (32)—this can be extremely difficult (if not impossible) in conventional alloys comprising just one or two principal elements.
ACKNOWLEDGMENTS

We thank M. J. Paul for support in analyzing the tensile stress-strain data. Funding: The research was primarily supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, through the Damage-Tolerance in Structural Materials program (KC13) at the Lawrence Berkeley National Laboratory (LBNL) under contract DE-AC02-CH11231, and the Multiscale Mechanical Properties and Alloy Design program (ERKCM06) at the Oak Ridge National Laboratory. The authors acknowledge the use of the ENGIN-X, ISIS Facility, at the Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, UK, for the mechanical testing in liquid helium environment, and the microscopy facilities in the National Center for Electron Microscopy, in the Molecular Foundry at LBNL, which is supported by the Office of Science, Office of Basic Energy Sciences of the US Department of Energy under contract DE-AC02-05CH11231. D.L., M.J., and P.F.-K. acknowledge support from the UK Engineering and Physical Sciences Research Council (EP/N004493/2, EP/T000368/1). B.G. acknowledges support from the ARC Future Fellowship (project FT190100484) and the UNSW Scientia Fellowship schemes. Author contributions: R.O.R., B.G., and M.A. (TEM), the latter under the supervision of A.M.M. Simulation was performed by Q.Y., M.J. and D.L (EBSD), and R.Z and M.P. (TEM), the latter under the supervision of R.O.R. The neutron diffraction data were analyzed by M.J. under the supervision of D.L. S.K. performed the uniaxial tests, with guidance from E.P.G. and B.G. The structural characterization was performed by Q.Y., M.J. and D.L. (EBSD), and R.Z and M.P. (TEM), the latter under the supervision of A.M.M. Simulation studies were conducted by F.W. under the supervision of M.A. R.O.R. drafted the manuscript, with all authors contributing. R.O.R. supervised the project. Competing interests: The authors declare no competing interests, financial or otherwise.

SUPPLEMENTARY MATERIALS

science.org/doi/10.1126/science.abp8070
Materials and Methods
Figs. S1 to S7
References (52–63)

Submitted 27 February 2022; accepted 7 October 2022
10.1126/science.abp8070