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# Revealing cryogenic mechanical behavior and mechanisms in a microstructurally-stable, immiscible nanocrystalline alloy

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ABSTRACT

Here, the Cottrell–Stokes ratio in a microstructurally-stable Cu-3Ta (at.%) nanocrystalline alloy is examined from the standpoint of changes in deformation mechanisms. Toward this, uniaxial compression experiments were performed in the temperature range of 113 K – 273 K. The Cottrell-Stokes ratio at the lowest temperature tested was ~1.3, and the material exhibited a very low strain-rate sensitivity at cryogenic-temperatures. Transmission electron microscopy (TEM) characterization showed negligible average grain size coarsening and a transition in the deformation mechanism toward athermal activation processes such as twinning with the reduction in the testing temperature.

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Bulk nanocrystalline (NC) metals (average grain-size < 100 nm) were originally produced nearly 3-decades ago by Gleiter and co-workers [1]. Since then, an explosion of interest in this research topic has occurred, and as a result, exciting properties such as unique super-plastic behavior, pressure dependent deformation, limited/poor tensile ductility, and low-temperature creep responses have been observed [2–5]. Theorizing and proving the underpinning mechanisms governing these macroscopic behaviors has greatly expanded the initial field of study, see [6–9]. Despite the rapid expansion of such findings, there still exist a few specific fundamental topics within the area of mechanics that remain relatively unexplored including shock/ballistic evaluation, fatigue, radiation-damage effects, and cryogenic response. While some of these specific topics have begun to be reported on, much of the current literature data lacks consistent trends due to numerous conflicting factors [2]. The most important factors being the instability of the microstructure during evaluation, and the difficulty in generating fully consolidated, bulk NC materials (i.e. free from processing artifacts while maintaining an average grain size < 100 nm) to perform such studies on.

One relatively unexplored area of research for the NC community is the evaluation of mechanical properties under varying temperature conditions, such as cryogenic-temperatures. Sparse studies have been tried to explore the cryogenic properties in the past, which were mainly focused on pure elemental materials. For instance, the first real findings were published by Wang et al. on pure metals with ultrafine grains for Cu, Ni, Fe, Ti, and Co [10–12]. Their results showed a substantially increase in the yield strength for all of these ultra-fined grain metals tested at 77 K compared to 298 K (Cu saw an increase of ~100 MPa, Ni by 400 MPa, Fe by over 400 MPa, Ti by ~300 MPa, and Co by over 700 MPa) [10–12]. The increase of several hundred MPa in the yield strength of ultrafine grained Cu, Ni, Ti, and Co was rather surprising considering the yield strengths of coarse-grained FCC and HCP metals have an extremely low temperature dependence, while the yield strength of coarse-grained BCC metals is known to be temperature sensitive. More recent work [13,14] has been performed on two FCC alloys of Ni-20%Fe and Pd-10Au (at.%), where a substantial increases in their yield strength with decreasing temperature has been observed. Zhang et al. [15,16] also evaluated the mechanical response of NC-Cu via micro hardness indentation at room and cryogenic-temperatures and found rapid grain-growth due to deformation. This stress driven grain-growth manifested itself as a large volume fraction of grains being larger than 400 nm in Cu tested at 77 K.

With the report of these initial instabilities, extensive experimental and simulation work was conducted on a multitude of NC materials to determine the effect stress played on their grain size while undergoing deformation. A summary of these results will quickly be discussed here. Brandstetter et al. [17] performed compression test on NC-Cu and noted grain-growth but to a lesser extent than Zhang et al. [15] did using indentation. In the same study, Ni was also investigated with limited grain-growth due to the presence of impurity atoms, but two computational studies investigated NC-Ni noted stress-assisted grain-growth during deformation [18,19]. Multiple studies reported stress-driven grain-growth in thin-films composed of NC-Al tested in tension and under indentation [20,21]. Sharon et al. [22] reported an increase of over 50% in the initial grain size of NC-Pt after undergoing deformation. Finally, Fan et al. [23] reported substantial grain-growth in both NC-Ni-

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Fe and NC-Co-P alloys that underwent tension testing, while Rupert et al. [24] reported similar results in a NC-Ni-W alloy that underwent wear testing as well. Thus, the consistent trend in the current literature for NC metals, whether pure systems or alloys, is substantial increases in yield strength coincident with extensive grain-growth. This microstructural instability has been manifested as a result of undergoing practically all forms of deformation whether at room or cryogenic-temperatures in compression, indentation, tension, wear, fatigue [25], creep [26], or dynamic loading [27] conditions.

Another parameter to interpret the mechanical deformation at the cryogenic-temperature is the Cottrell–Stokes ratio, which is a ratio of yield strength at cold temperatures to the yield strength at room temperature [28]. In a recent effort, Cheng et al. [29] performed cryogenic-temperature studies on NC-Cu with an average grain size of 54 nm and observed a Cottrell–Stokes ratio of ~2. On the other hand, a Cottrell–Stokes ratio of about 1.2 to 1.3 for coarse-grained pure Cu has been reported, see [30]. Similarly, in the case of NC-Ni and NC-Co, a strong cryogenic-temperature dependence has been observed with a ratio of 1.5 and 1.8, respectively [31]. While all of these works indicate an increase in the yield strength of NC materials, i.e., a strong cryogenic-temperature dependence, there remains the issue of truly determining the mechanism at play leading to the increased strength at the cryogenic-temperatures. The instability of the microstructure during the cryogenic testing further complicates the efforts to determine the deformation mechanism at these temperatures in NC materials. This leaves us with a fundamental question to be answered: does the same mechanical behavior (a strong cryogenic-temperature dependence) pertain to a thermo-mechanically stable NC material? If not, then does the deformation behavior remains the same as coarse-grained materials (i.e., independent of grain size)?

Recently, Darling and colleagues have shown the immiscible NC-Cu-Ta alloy system is not only thermally stable [32] but also thermo-mechanically stable [3,5,33–38]. Therefore, this work looks to investigate the mechanisms at play in a stable NC alloy by mechanically testing stabilized NC-Cu-3Ta (at.%) over a range of cryogenic-temperatures from 273 to 113 K. The NC-Cu-3Ta represents an optimized Ta concentration; consequently, this work will focus on this alloy composition. The tested specimens will then have their microstructures characterized via transmission electron microscopy (TEM) to elucidate which deformation mechanisms are operating at different temperatures and address the microstructural stability. Therefore, this alloy provides a unique opportunity, for the NC community, to expand its knowledge base into one of the remaining and relatively unexplored areas of NC metals research.

The process for producing bulk NC-Cu-3Ta samples has been previously reported [37]. Samples for the testing were cut to a 3 mm diameter and 3 mm in height using an electric discharge machine. The compression tests were conducted on an Instron load frame with a 50 kN load cell. The load frame was equipped with a cooling rig that allowed for liquid Nitrogen to be utilized for cooling the sample to as low to 113 K. The samples were allowed to equilibrate at the desired temperature by holding for 30 min prior to testing. All tests were conducted at rate of 0.001 in/min at the various temperatures. With regard to TEM sample preparation, the tested specimens were then sectioned in such a manner that the TEM samples came from the center of each test specimen, see [37].

Fig. 1 shows as-received microstructure characterization for NC-Cu-3Ta along with the mechanical characterization over a range of temperatures from 113 to 273 K at a strain-rate of 0.001 in/min. Bright field (BF-) STEM images of the alloy, Fig. 1A show NC grains with dispersions of Ta based nanoclusters (pointed by red arrows). The Ta based nanoclusters are widely distributed within Cu grains as well as along the Cu grain boundaries. Grain-size distribution, Fig. 1B, generated from multiple TEM micrographs indicates an average grain size of 99 nm for NC-Cu-3Ta. Compression true stress–true strain data for the alloy is plotted in Fig. 1C. The plot clearly illustrates an increase of about 250 MPa in the yield stress and about 300 MPa in the flow stress by decreasing the testing temperature from 273 to 113 K in the case of NC-Cu-3Ta. The increase in the yield stress at 113 K observed here is ~25% of the yield stress at 273 K. Interestingly, this increase in flow stress was not at the sacrifice of continued deformation under compressive load with the decreasing temperature. None of the samples showed any radial cracking and could be tested out to 80% compression without failure. Nevertheless, the maximum stress measured at 77 K for NC-Cu tested at any strain-rate was approximately 700 MPa. The flow stress of 1300 MPa measured for NC-Cu-3Ta at 113 K which is more comparable to Ti tested at 77 K. Now, the real question that stands is what is the effect the increasing stress has with decreasing temperature on the microstructure? To realize the effect of increasing stress on the microstructure, first the Zener–Hollomon (Z) parameter was characterized for the NC-Cu-Ta system, which takes into consideration the temperature and strain-rate effects.

The Zener–Hollomon parameter (Z) was calculated as:

$$Z = \dot{\varepsilon}\ \exp\left(\frac{Q}{RT}\right) \tag{1}$$

where $\dot{\varepsilon}$ is the strain-rate, Q is the activation energy ($7.25 \times 10^4$ J/mol, [39]), R is the gas constant, and T is the absolute test temperature. Fig. 2 compares the normalized yield stress for NC-Cu-3Ta with that of coarse-grained Cu as a function of Zener–Hollomon parameter. Note that the data represents constant strain-rate data over a range of temperatures from (113 to 1073 K). The plot shows two distinct slopes for high-temperature versus cryogenic-temperatures, which intersect at a distinct transition value of $\ln \frac{Z}{Z_o} = 21$. This indicates a potential change in the deformation mechanism that is operative over the respective temperature range. The two lines corresponding to flow stress have been delineated into slip dominated and athermal, based on the intersection point, where the slope of the high-temperature regime is ~ an order of magnitude larger than the athermal regime.

This is consistent with expectations, namely the flow stress for slip in NC-Cu-3Ta and coarse-grained Cu is more temperature dependent than that for the athermal regime. The normalized yield stress, which is the Cottrell–Stokes ratio, for both NC-Cu-Ta system and the coarse-grained Cu is in the similar range of ~1.3. This ratio of 1.3 for NC-Cu-Ta and CG-Cu is significantly lower than what has been reported for NC-Cu which is around ~2 [29]. Thus, it can be inferred that the deformation mechanisms for this stable NC-alloy are certainly not similar as compared to an un-stabilized NC-metals, where a higher Cottrell–Stokes ratio (1.5–2) is indicative of some other mechanism/mechanisms than those occurring in coarse-grained materials. For instance, extensive grain-growth, grain boundary sliding, and rotation is observed as a result of deforming un-stabilized NC-metals. While in coarse-grained materials, twinning and textural evolution (not stress driven grain-growth) are the more prevalent deformation mechanisms; and hence the effects of sliding and rotation on strain-rate sensitivity are less significant. Because of this fundamental difference in operative deformation mechanisms, coarse-grained materials have lower strain-rate sensitivity ($m$) values than NC-metals.

For comparison, we plot the yield stress as a function of the Zener–Hollomon parameter for NC-Cu-3Ta, Appendix Fig. A1(A). Traditionally, the flow stress for a material at a given strain-rate and temperature is given by:

$$\dot{\varepsilon} = A_1 \sigma^n\ \exp\left(\frac{-Q}{RT}\right) \tag{2}$$

where $A_1$ is a constant, and $n$ is the stress exponent. Substituting for the strain-rate, $\dot{\varepsilon}$, in Eq. (1) results in a simplified equation relating the Zener–Hollomon parameter to the flow stress and $m$ parameter as, $\sigma = A_2 Z^m$, where $A_2 = \left(\frac{1}{A_1}\right)^m$ and $m = \frac{1}{n}$. For a given strain-rate, the flow stress can be plotted as a function of the Zener–Hollomon

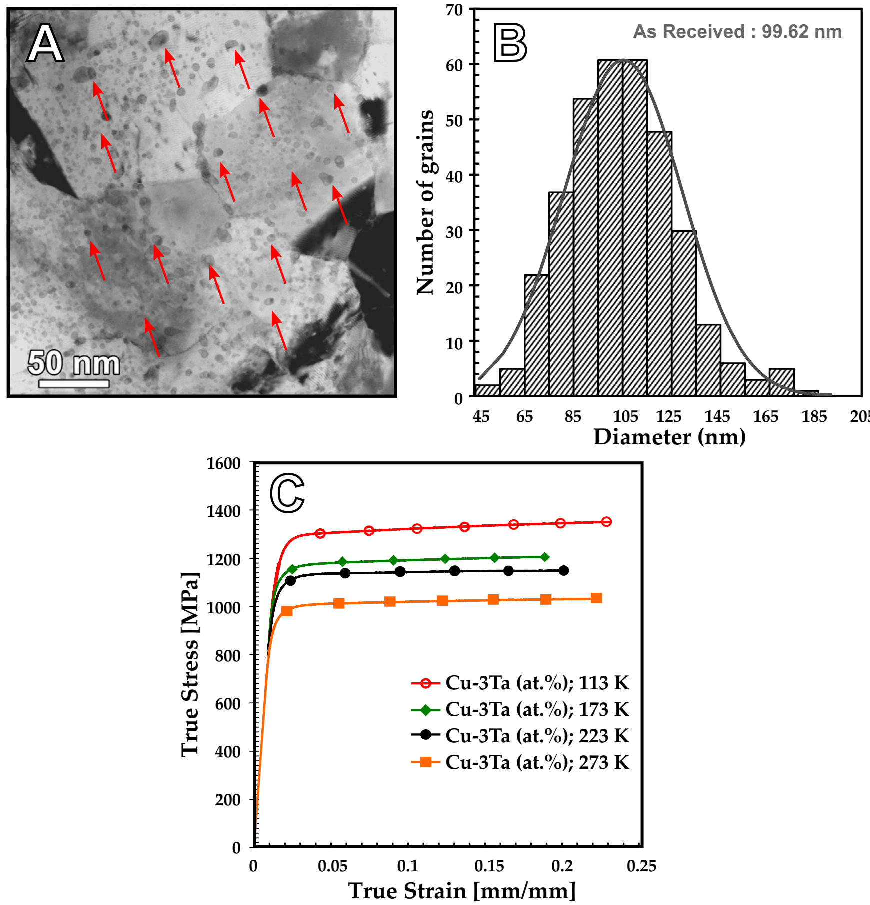


**Fig. 1.** (A) STEM Bright field (BF) image of as-received Cu-3Ta (at.%) showing the grain structure and small Ta based clusters as indicated by red arrows. (B) The number distribution of grain size for Cu-3Ta in the as-received condition. (C) Compression true stress-strain response at different cryogenic temperatures for Cu-3Ta showing near elastically perfectly plastic behavior with no apparent strain hardening. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

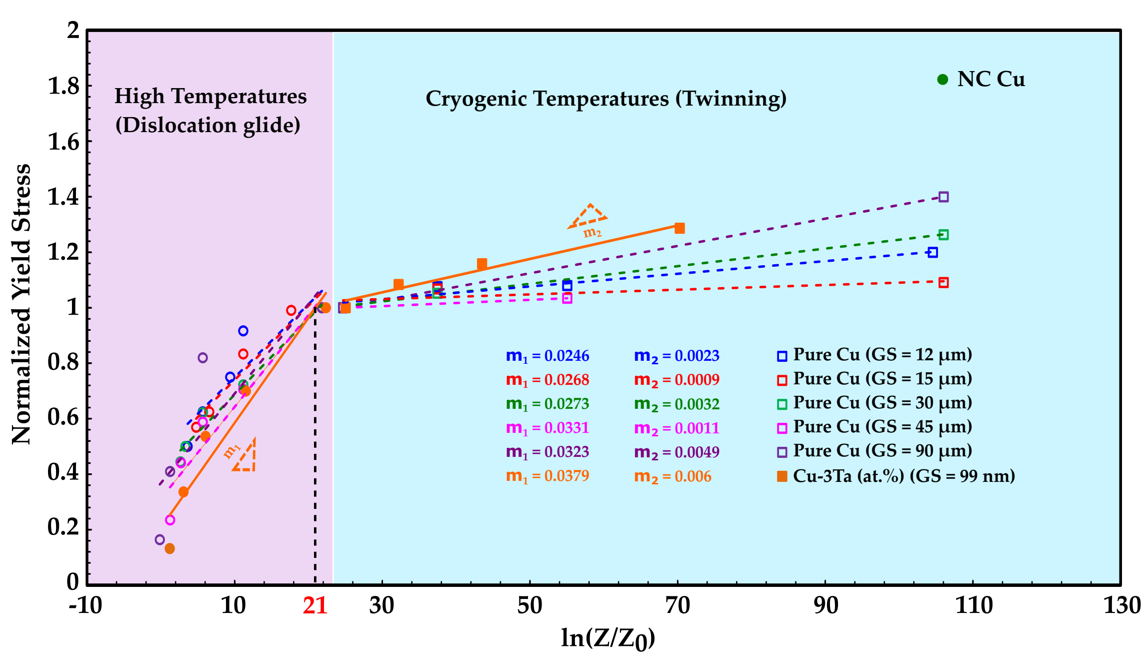


**Fig. 2.** Normalized yield stress for Cu-3Ta (at.%) plotted as a function of Zener-Hollomon parameter at various cryogenic and high temperatures and compared with that of pure Cu. (Points indicated by circular markers are for room temperature and above tests, while those indicated by square markers are for room temperature and below tests; data for NC Cu was obtained from ref. [12]).

parameter and testing temperatures (see Appendix Fig. A1(B)). The flow stress (yield stress in this case) for NC-Cu-3Ta plotted as a function of the Zener–Hollomon parameter can be fitted with a power law of type: $\sigma = 814.41Z^{0.0057}$. In the case of NC-Cu-3Ta, we see a very low value of $m = 0.0057$, which indicates that the NC-Cu-3Ta alloy exhibits a very low $m$ at cryogenic-temperatures. This in turn can be related to the athermal deformation processes operative in the microstructure, such as twinning. To clearly understand the role of athermal deformation processes, post-deformed TEM characterization was performed and is explained in the following section.

The BF-STEM images of the NC-Cu-3Ta specimens tested at 273 and 113 K are shown in Fig. 3. From these images, it is clearly noted by decreasing the testing temperature for NC-Cu-3Ta while maintaining the same strain-rate, substantially more deformation twins are formed in the specimen tested at 113 K compared to specimen tested at 273 K. This increase can be quantified as the specimen tested at 273 K having twins present in approximately 5% of the grains observed, whereas the specimen tested at 113 K have twins present in approximately 20% of the grains observed. This increase in twin density can be directly responsible for the rise in flow stress from 1000 to 1300 MPa without sacrificing any enduring deformation under a compressive load within the material. In NC-Cu-3Ta alloy, there is an active competition between dislocation motion and twinning to decide which will be the more operative deformation mechanism [40]. Thus, reducing the temperature from 273 to 113 K results in an abrupt change to twinning and increased fraction of grains containing twins. Additionally, the twinning spacing is

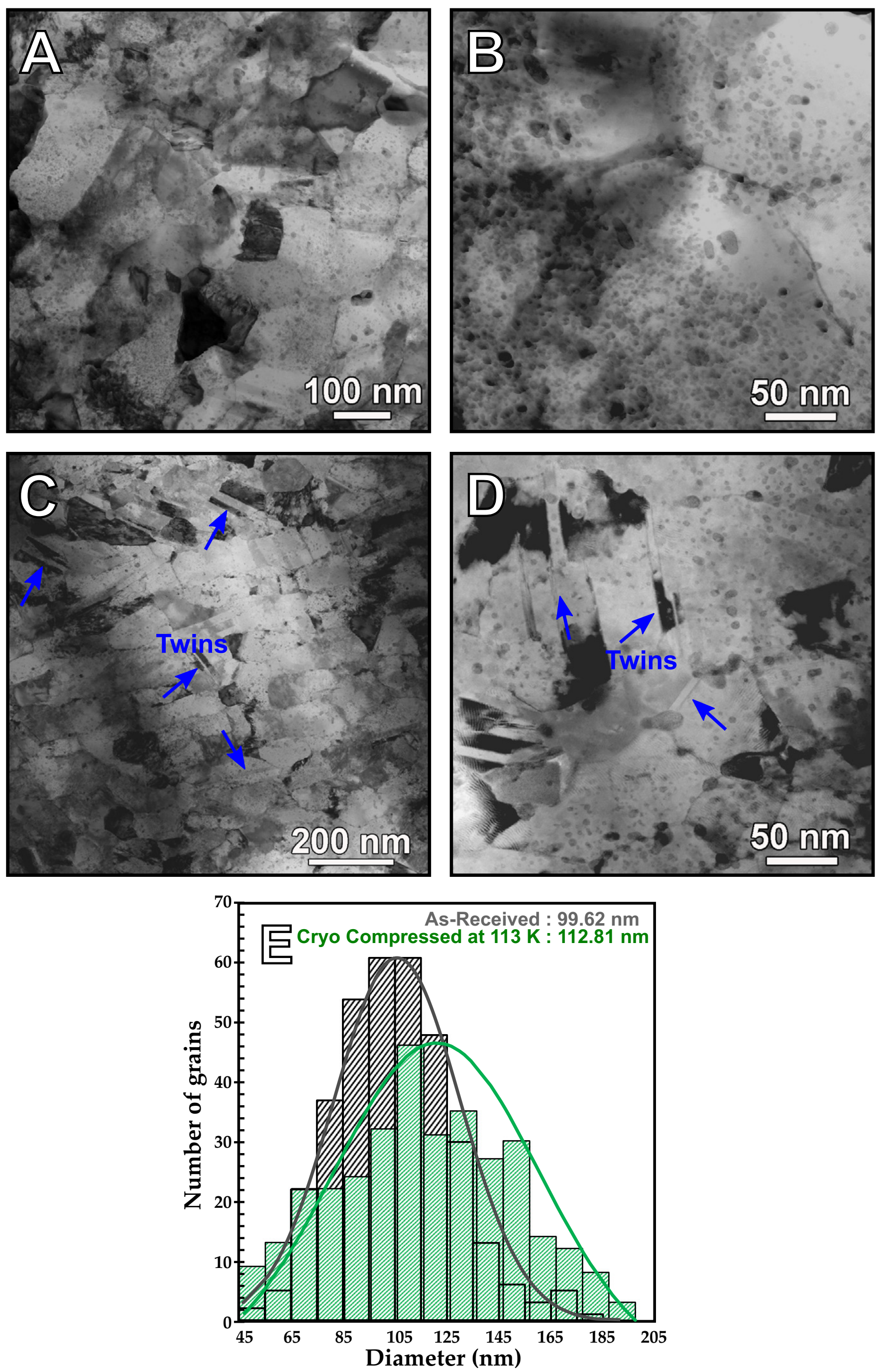


**Fig. 3.** Lower and higher magnification STEM Bright field (BF) images of cryogenically compressed (A)–(B) Cu-3Ta (at.%) at 273 K, and (C)–(D) Cu-3Ta at 113 K samples. (E) Grain size distribution of as-received and sample tested at 113 K. Lowering test temperature resulted in the shift of deformation mechanism to a more athermal processes such as twinning.

relatively constant between the two temperatures, 38 and 41 nm respectively, for 273 and 113 K. The small twin spacing speaks to the role the Ta particles play in limiting the twin growth within an individual grain (see [40]). Thus, to accommodate the additional strain at the lower temperature, the nucleation rate for twinning increases rather than the twins growing and increasing their spacing as would generally be expected. This is consistent with prior results by the authors on dynamic testing of similar Cu-Ta alloys, where the increased strain-rate (~$10^4$ $s^{-1}$), i.e., higher Z led to increased twin density and absence of dislocation glide [5]. This speaks to the higher-strain-rate increasing the stress in the material in much the same manner as the cryogenic testing reported here.

These results seem to, at least, hint at the possibility of NC-Cu-3Ta continuing to increase in strength with decreasing temperature down to liquid helium temperature without experiencing drastic reduction in strain to failure. Considering the aforementioned discussion, the parallels between cryogenic testing and extremely high-strain-rates, this might not be so unexpected. As recent results within this alloy family have shown anomalous mechanical behavior where by the materials resist brittle failure even under extremely high-strain-rate conditions [5]. The other critical observation of this material compared to the aforementioned studies on elemental NC materials is the stability of the average grain size wherein, the average grain size of NC-Cu-3Ta changes from 99 nm in the as-received state to 112 nm in the as-deformed state.

In summary, mechanical behavior of a NC-Cu-3Ta was evaluated at cryogenic-temperatures. Zener-Hollomon analysis combined with TEM studies showed that, at cryogenic-temperatures, the deformation of NC-Cu-3Ta was governed by more athermal activation processes such as twinning. Moreover, NC-Cu-3Ta alloy showed remarkable microstructure stability under the application of mechanical stress at cryogenic-temperatures leading to a lower strain-rate sensitivity and comparable to that of coarse-grained Cu. Thus, NC-Cu-3Ta demonstrates promising properties for cold-temperature applications suggesting it as a possible replacement for its coarse-grained counterparts.

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## Appendix A

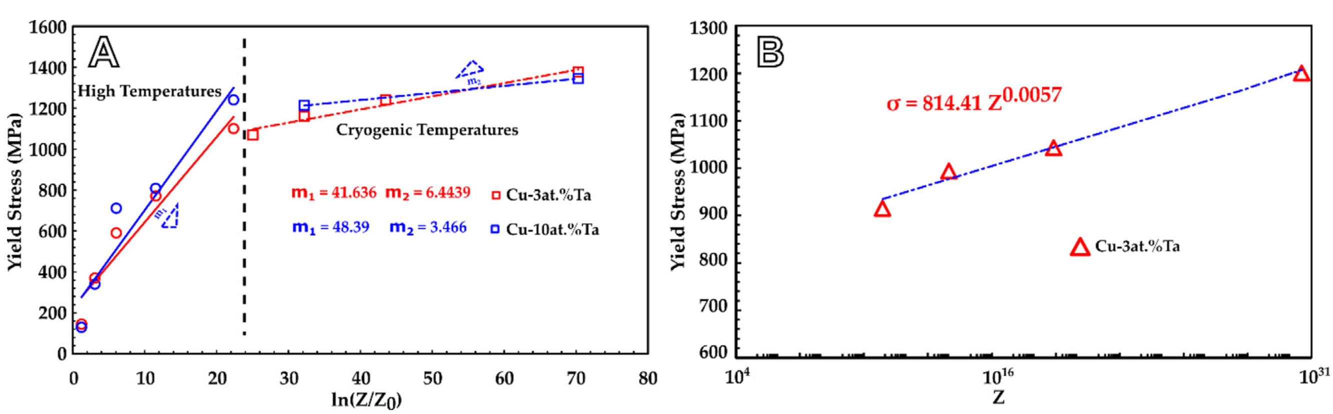


**Fig. A1.** (A) Yield stress for Cu-3Ta and Cu-10Ta plotted as a function of Zener-Hollomon parameter at various cryogenic and high-temperatures (Points indicated by circular markers are for room temperature and above tests, while those indicated by square makers are for room temperature and below tests). (B) Yield stress for Cu–3Ta plotted as a function of Zener–Hollomon parameter at different cryogenic-temperature and a strain rate of $10^{-3}$ $s^{-1}$.

## Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scriptamat.2018.09.035.

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