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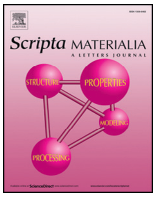

Revealing cryogenic mechanical behavior and mechanisms in a microstructurally-stable, immiscible nanocrystalline alloy

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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 superplastic 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 (7.25×10^4 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