An Atom Probe Study on Nb Solute Partitioning and Nanocrystalline Grain Stabilization in Mechanically Alloyed Cu-Nb

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Abstract

Nb solute behavior and its effect on grain size stabilization in Cu-Nb alloys was studied using a combination of Vickers hardness testing, x-ray diffraction measurements, transmission electron microscopy and atom probe tomography (APT). Cu-Nb alloys with concentrations in the range from 1 to 10 at. % Nb were studied after annealing at 400°C and 800°C. The grain growth resistance at both temperatures increased with an increase in Nb solute content. For instance, after annealing at 800°C ($0.74 T_m$), Cu-1Nb, Cu-5Nb and Cu-10Nb have a grain size that is ~8, ~14 and ~14 times respectively smaller than that of unalloyed Cu. This resistance is attributed to the formation of Nb-oxide-based clusters, elemental Nb segregation zones and large elemental (Nb)-based precipitates as observed by APT. The Nb-oxide-based clusters are the precursors of phase separation and form due to a reaction with oxygen, which is a contaminant from the milling process. Once the oxygen is consumed, the process continues and the grain boundaries accumulate more solute and begin to thicken into elemental Nb segregation zones. Eventually, Nb solute phase separates and forms Nb-based precipitates. After annealing at 400°C and 800°C, Cu-5Nb has a hardness which is approximately 2.5 times and 3 times respectively that of the hardness of unalloyed Cu after an equivalent anneal. This increase has been attributed to Hall-Petch strengthening and precipitation strengthening.

1 Introduction

As the grain size of a material decreases, its properties can also change in response to the smaller length scale. A classic example of this is Hall-Petch strengthening which predicts that yield strength increases proportional to the inverse square root of the grain size [1-3]. Consequently, nanocrystalline materials have received considerable attention because of their size-dependent mechanical, electrical, creep resistance and other related properties [4-12]. However, at these smaller length scales, there is substantial excess free energy in the system because of the interfacial energy associated with the high grain boundary density. At high temperatures, such a system is diffusively able to reduce this driving force by grain growth, with the subsequent loss of the desired properties associated with nanocrystalline grain size [13]. Consequently, the ability to stabilize nanocrystalline materials against such grain growth has been an area of active research.

Nanocrystalline stability can generally be achieved via kinetic stabilization or thermodynamic stabilization [13-15]. Kinetic stabilization refers to pinning the grain boundaries through some type of secondary phase or solute to impede boundary motion [16]. This type of grain size control is often lost at high temperatures when the boundaries are energetically able to overcome the pinning barrier [13]. Thermodynamic stabilization refers to reducing the driving force for grain growth by allowing a solute to segregate to the grain boundaries and thereby lowering the excess free energy of grain boundaries. This type of grain size control has been predicted to have a low dependence on temperature and therefore can result in stabilization at elevated temperatures [10, 13].

This concept of solute segregation to grain boundaries for thermodynamic nanocrystalline grain stabilization was developed about 20 years ago and has been an area of extensive studies [7, 8, 10, 14, 15, 17-27]. A classic prediction of thermodynamic stabilization is a decrease in grain size accompanied by increasing solute content [20, 24, 26]. For instance, in Fe-Zr alloys, on

increasing the Zr solute content from 0.3 at. % to 4 at. % at 700°C, the stabilized grain size decreased from ~ 40 nm to ~ 15-20 nm [24]. This solute segregates to the grain boundary and is accommodated in the grain boundary region resulting in a distinct equilibrium grain size for a given solute content at a given temperature. Eventually, the grain boundary reaches a saturation with respect to the amount of solute it can accommodate after which the solute is incorporated within the grain interior or forms precipitates [20]. Such a precipitation event is considered disadvantageous to grain size stabilization because precipitates provide only kinetic stabilization via Zener pinning. Consequently, thermodynamic stabilization and nanocrystalline grain size stability can be lost with a subsequent grain growth. For example, in the same Fe-Zr alloys discussed above, upon increasing the Zr content to 10 at. %, second phase precipitation occurred and the grain size did indeed increase [24].

On the other hand, recent studies on mechanically alloyed Cu-Ta and W-Cr have each reported a stable nanocrystalline grain structure despite the precipitation of a second phase [10, 23, 28]. In mechanical alloying, the nanocrystalline structure is achieved by ball milling constituent powders together which forces the solute atoms into solid solution [7, 10, 28]. Upon annealing, this solid solution is predicted to decompose and the resulting solute will segregate to the grain boundaries resulting in lowering the grain boundary free energy [10, 28]. In immiscible systems, such as Cu-Ta, the solute will initially segregate to the grain boundaries and subsequently form atom clusters (few 10s of atoms) at grain boundaries and in the lattice. This will be followed by second phase precipitation thereby pinning the microstructure and resulting in kinetic and thermodynamic stabilization [10]. Molecular dynamics simulations on Cu-Ta system have predicted Ta cluster formation along the grain boundary, which results in grain boundary pinning and thereby nanocrystalline grain size stabilization [25]. This nanocrystalline grain size stabilization with Ta clusters is concomitant with precipitation of larger Ta precipitates (approximately 100 nm) which have been shown to stabilize the nanocrystalline structure up to temperatures as high as $0.97 T_m$ [10]. Similarly, in mechanically alloyed W-Ti, the

excellent grain coarsening resistance was attributed to approximately 1 nm thick segregation zones of Ti-rich regions around the grain boundary regions [22]. These segregation zones were observed in the microstructure despite the equilibrium phase diagram predicting a solid solution. Since these segregation zones did not result in distinct reflections in the diffraction patterns, it was inferred that they did not possess a distinct crystal structure, unlike precipitates. All these studies demonstrate that stabilization mechanisms at the nanoscale can be complex and may differ from the dominant mechanisms in coarse-grained systems [10, 22, 23, 28].

Another potentially promising immiscible system with similar segregation properties to Cu-Ta is the Cu-Nb system. Cu-Nb system is not among any of the binary pairs in the thermodynamic stability maps predicting stability against grain growth, i.e. it is not known how the system will behave [29]. Segregation enthalpy (a solute's tendency to segregate to the grain boundaries) of both of these systems is quite similar and is in the range of 0 to -25 KJ/mol [29]. Their equilibrium phase diagrams do not show any regions of solubility indicating that precipitation of a second phase would be expected. Furthermore, Cu-Nb alloys have also received considerable attention as being one of the strongest Cu-alloy systems [30] with an excellent combination of ductility and mechanical strength coupled with high electrical flux and radiation tolerance [4, 31, 32]. Even more appealing would be Nb's cost, which is approximately 25 times less expensive than Ta.

Though no dedicated experimental/computational study to address nanocrystalline stability in Cu-Nb has been performed, there is circumstantial evidence in the literature to suggest that Cu-Nb may possess stability attributes that have previously been observed in Cu-Ta. In these prior Cu-Nb studies [4, 31, 33, 34], the Cu-Nb was mechanically alloyed resulting in nanocrystalline grain sizes with a decrease in grain size with increasing solute content or increase in milling time (which is equivalent to 'forcing' more solute into the matrix phase) [34]. At high solute contents and/or increased annealing time, transmission and scanning electron microscopy revealed the presence of Nb-rich precipitates

within the microstructure [4, 31, 33, 34]. Though some of these studies followed the microstructure evolution as a function of processing conditions (composition and temperature), none of them explicitly addressed how the solute behavior evolves or provides nanocrystalline stabilization. Rather, those former works primarily addressed optimizing the electrical and mechanical properties of Cu-Nb.

In this study, pure Cu and Cu-Nb alloys with concentrations from 1 to 10 at. % Nb were mechanically alloyed and annealed at 400°C and 800°C. The aim was to explore the solute behavior and track its influence on grain size stabilization and corresponding mechanical properties, using a combination of Vickers hardness, x-ray diffraction (XRD) measurements, transmission electron microscopy (TEM) and atom probe tomography (APT). An advantage of using APT is its high chemical and spatial sensitivity which can elucidate the nuances of the solute behavior, particularly at low solute concentrations, which cannot be captured by other microscopy techniques [9, 35]. This is especially important in light of the hypothesis that Nb solute leads to stabilization of the alloys; low solute concentrations should capture the initial stages of the stabilization mechanism.

2 Experimental Procedures

Hardened steel vials and 440C stainless steel balls were used for mechanically alloying Cu and Nb powders (~ -325 mesh, 99.95 to 98.5% purity) in a Spex 8000 shaker mill. A ball-to-powder ratio of 5:1 with a powder charge of 10g was used. Vials were sealed in an argon atmosphere glove box with less than 1ppm oxygen concentration prior to milling. Mechanical alloying was performed at liquid nitrogen temperatures for 4 hours and resulted in unagglomerated powders with a particle size range of 20-100µm. 3mm preform tablets were made by uniaxially pressing the as-milled powder in a 3mm diameter tungsten carbide die at 3.5 GPa. These 3 mm coupons were subsequently annealed for one hour at 400°C and 800°C under argon 3% H₂ gas.

For annealing, these 3 mm coupons were wrapped in Ta foil and placed in a quartz tube (open at one end) and then loaded into the tube furnace. The tube furnace was heated to the desired temperature and at the same time the quartz tube was placed under roughing vacuum and back filled with the forming gas, argon 3% H₂ (this procedure was repeated three times). For the last refill, the quartz tube was over-pressurized to approximately 1 psi and the pressure held constant. Once the tube furnace was at temperature, the quartz tube was rolled into the tube furnace and the sample temperature continuously monitored via an internal thermocouple. Once the samples reached the appropriate temperature, the time for the 1 hour anneal was started. After 1 hour at temperature, the tube furnace was pulled off the quartz tube and the sample cooled down to room temperature under the forming gas. The samples were then extracted from the quartz tube by bleeding off the overpressure and opening it to atmosphere.

The following four alloy compositions were prepared using ball-milling and compacted into 3 mm coupons: unalloyed Cu (control), Cu-1Nb, Cu-5Nb and Cu-10Nb (at. %). The nomenclature used in this paper reports the solute composition with the annealing temperature. Therefore, Cu-1Nb/400°C means the alloy Cu-1Nb was annealed at 400°C for an hour. All the composition units are in at. % throughout the manuscript, and all annealing times were 1 hour. The details are provided in Table1.

Although these materials were processed under flowing argon, oxygen, nitrogen, iron and carbon were found in the samples and these are generally present in ball milled materials as contaminants [10, 36]. Such contamination also represents some of the challenges in differentiating the effect of thermodynamic stabilization from kinetic stabilization on grain size. In this study, the amount of oxygen was found to be less than 1.5 at. % and that of nitrogen was < 0.6 at. %. Between Nb and Cu, Nb forms the more stable oxide and nitride [37, 38] and therefore is expected to react with oxygen or nitrogen preferentially. Most of the recent work in nanocrystalline stability has not explicitly addressed how the intrinsic contamination from the processing of the materials may effect stabilization. This could be due to the limited mass

sensitivity, chemical and spatial resolution of the techniques used in prior studies compared to that of APT. Regardless, it seems very probable that any non-noble nanocrystalline alloy produced by ball milling, melt spinning, electro-deposition or physical vapor deposition would be susceptible to these impurities and their effect on stabilization [39, 40]. The implications of these reactions will be discussed in section 4.1.

Vickers hardness testing was performed using a Beuhler Vicker's hardness tester under a 50 g load for 15 s. The hardness reported for each sample is an average of ten measured hardness indents. Care was taken to ensure that each indent was made in an area free of pores and that each indent had a uniform shape.

XRD of Cu-Nb alloys was performed using a Bruker D8 x-ray diffractometer with Co-K α as the radiation source and that of unalloyed Cu was performed using a PANalytical X'Pert powder system with Cu-K α as the radiation source. The scans were conducted in the range of $2\theta = 30^\circ$ - 105° and the (111), (200), (220) peaks used to calculate the average grain size with the Scherrer equation [41], as has been used in many previous studies on nanocrystalline grain stabilization [10, 42]. Full-width at half-maximum of these peaks was identified in Origin Pro software 8.1 using the multi-peak fit function. The calculated grain sizes (in nm) are listed in Table 2 (a).

To confirm that the grain size estimates from Scherrer analysis of XRD measurements were accurate, precession electron diffraction (PED) and electron backscatter diffraction (EBSD) studies were performed for a few samples where the divergence in actual grain sizes was most likely to occur. For PED, the TEM studies were performed using a 200 keV field emission FEI Tecnai TEM. The TEM specimens were prepared in a FEI Quanta 200 3D Dual BeamTM using a lift-out and thinning procedure with 0.5 nA and 0.3 nA current respectively at 30 keV beam energy. A low-keV clean-up step was performed using 5 keV beam energy at 70 pA current followed by a 15 minute final polish by argon ion milling using Gatan 691 precision ion polishing system. Automated crystal orientation mapping via PED was performed using the NanoMegas ASTAR® system, which

allows mapping with spatial resolution down to approximately 2 nm. Crystal orientation maps were collected over a 1 μm x 1 μm region using a step size of 4nm and a precession angle of 0.3°. The diffraction pattern indexing was performed using the ASTAR matching software with copper as the template. The orientation data was then exported to OIM Analysis 7 software, where it was optimized using grain dilation, neighbor confidence interval correlation and automated crystallography for TEM corrections. EBSD was performed using an EDAX EBSD platform on a Tescan Lyra SEM at an accelerating voltage of 20 KeV. The samples were prepared by polishing to a 3 μm surface finish, followed by vibratory polishing for 2 hrs using an aqueous 0.05 μm silica slurry. The calculated grain sizes (in nm) are listed in Table 2 (b).

APT was used to identify solute segregation using a Cameca local electrode atom probe (LEAP®) 3000XSi. The atom probe tips were fabricated in a FEI Quanta 200 3D Dual BeamTM using a lift-out and annular-milling sharpening procedure with 0.5 nA and 0.3 nA current respectively at 30 keV beam energy. A low energy clean-up step using 70 pA current and 5 keV beam energy was performed for 2 minutes to reduce the Ga ion implantation on the surface. APT experimental run parameters were optimized by a set of careful experiments. Laser pulsing, using a laser with $\lambda=532$ nm, was chosen because of the high fracture rate of high Nb solute samples under voltage pulsing. The laser pulse repetition rate was 200 kHz, pulse energy - 0.3 nJ/pulse, evaporation rate - 0.5 % and the base temperature - 233°C (40K) for all measurements. The atom probe data was analyzed using Image Visualization and Analysis Software (IVASTM) 3.6.6 package. The reconstruction was performed using voltage method and the mass spectrum bin size was kept constant at 0.01 Dalton. Typically, three tips were studied for each composition at each temperature.

Generally, grain boundaries in APT reconstructions have been inferred by discernible segregation and applying computational geometry techniques to the reconstructions [43, 44]. These techniques were applied to our data but failed to identify grain boundaries with density variations even when segregation was visually obvious. This difficulty is likely attributed to the small grain sizes, on the

order of 10 nm, and the presence of Nb clusters at the grain boundaries. Moreover, these procedures were developed to identify a uniformly distributed solute as is expected in most cases of interfacial segregation. In case of no visually obvious segregation, density fluctuations in the vicinity of the grain boundary regions have been used to identify these regions [45]. In this study, application of 2D chemical density maps to the reconstructions revealed an obvious density difference coinciding with the location of the segregation/solute clusters and was therefore chosen as one of the primary methods for data analysis. These chemical density maps used in conjunction with experimentally calculated grain sizes from XRD and TEM were then used to infer the presence of a grain boundary in the reconstruction.

3 Results

3.1. Grain size

Fig. 1(a) shows the XRD results of the (111) peaks of non-annealed/as-milled Cu, as-milled Cu-1Nb, as-milled Cu-5Nb and as-milled Cu-10Nb. Since Cu and Cu-Nb alloys were performed on diffractometers with different radiation sources, the results are normalized for comparison and x-axis is presented as the d spacing. The as-milled Cu peak is thinnest and as the amount of Nb was increased, the peaks shift to larger d-spacing values indicating an increase or expansion of the crystalline lattice caused by the incorporation of Nb into Cu matrix as a solid solution. Furthermore, as more Nb was added, the peaks broadened suggesting a refinement of grain size and/or an increase in the inhomogeneous microstrain. Upon annealing, the (111) peak of Cu-5Nb/400°C and Cu-5Nb/800°C shifted to higher angles, indicating that the solute was diffusing out of the lattice and the lattice was contracting, Fig. 1(b).

Figure 2 (a) shows the EBSD map of unalloyed Cu, and Figure 2 (b) and (c) show PED scans of the Cu-1Nb, and Cu-10Nb annealed at 800°C, which represent the extreme conditions. The bottom row of each image shows the respective grain size distributions. As expected, the average grain size decreased with an increase in solute content - from 566 nm $\pm$ 778 for unalloyed

Cu to $21.5 \text{ nm} \pm 20.8$ for Cu-1Nb/800°C to $19.3 \text{ nm} \pm 14.3$ for Cu-10Nb/800°C. Grain size distribution of unalloyed Cu shows a wide grain size distribution with a few grains even in the 10-20 μm size range. In *fcc* metals, such an abnormal grain growth has been related to the fraction of certain types of coincident site lattice grain boundaries [46]. Even though the average grain size of Cu-1Nb/800°C and Cu-10Nb/800°C is quite close, it is obvious from the Fig. 2(b and c) that the Cu-1Nb/800°C shows quite a few grains which are larger. This suggests that the limited amount of 1 at. % Nb solute impacts the grain growth depending on the grain boundary type, as has been experimentally observed in *nc* Fe-Cr system [47]. It is worth noting that the grain sizes of the Cu-Nb alloys obtained from EBSD and PED were in good agreement with those obtained from XRD.

A combination of EBSD, PED and XRD results was used to analyze the impact of temperature and Nb solute content on the Cu-Nb alloy grain size. For this analysis, grain sizes obtained from XRD results were used for Cu-Nb alloys and those obtained from EBSD results were used for unalloyed Cu. To accurately quantify the influence of temperature and Nb composition on the grain size relative to that of unalloyed Cu, a normalized grain size was calculated for each alloy at each temperature as it provided a quick reference to the degree of grain growth in each alloy. For instance, the grain size of unalloyed Cu and Cu-1Nb after annealing at 800°C is $\sim 566 \text{ nm}$ and $\sim 72 \text{ nm}$ respectively and the relative grain size is 7.8; i.e. the unalloyed Cu grains are 7.8X larger. Hence, the higher the normalized grain size, the smaller the alloy grain size that is stabilized at a particular solute content. For all the relative grain sizes, the unalloyed Cu was compared to the Cu-Nb for the equivalent annealing condition.

Fig. 3 plots the normalized grain size as a function of composition and shows the effect of annealing temperature. Consistent with the EBSD and PED scans of Fig. 2, the stabilized grain size decreased or the grain growth resistance increased as the amount of Nb was increased. For instance, the grain size of Cu-1Nb/400°C, Cu-5Nb/400°C and Cu-10Nb/400°C is ~ 6.5 , ~ 19.4 , and ~ 29.5 times respectively smaller than that of unalloyed Cu annealed at 400°C.

Similarly, the normalized grain size of Cu-1Nb/800°C, Cu-5Nb/800°C and Cu-10Nb/800°C is ~7.8, ~13.8 and ~14.1 times smaller than that of unalloyed Cu annealed at 800°C. Details of relative grain size are listed in Table 2(c). To highlight the stabilization, consider that 800°C is 0.74 T_m of Cu and the stabilized grain size on alloying with 5Nb and 10Nb is approximately an order of magnitude smaller than that of unalloyed Cu. Second, the normalized grain sizes that were stabilized in Cu-5Nb/800°C and Cu-10Nb/800°C – 13.8 and 14.1 respectively – are nearly equivalent. Liu *et al.* [20] have predicted that as grain boundary saturation is reached, further increases in solute would not affect the grain growth.

3.2. Vickers Hardness

To assess the degree of strengthening due to grain size refinement in these alloys, Vickers hardness testing was performed. According to the Tabor relationship, the flow stress of a material is approximately one-third of the Vickers hardness [48]. Using this rule of thumb, measured Vickers hardness has been converted into flow stress and plotted alongside calculated Hall-Petch strengthening from grain size [49] as a function of Nb composition. The Hall-Petch strengthening is calculated using – $\sigma = \sigma_0 + k_y/\sqrt{d}$ where $\sigma_0 = 25$ MPa, $k_y = 0.137$ MPa $\sqrt{m}$, and d = grain size [50].

Fig. 4 (a) and (b) show the results for Cu-Nb/400°C and Cu-Nb/800°C with the empty symbols representing the calculated Hall-Petch strengthening and the filled symbols representing the measured values. The main finding is that after annealing at 400°C, unalloyed Cu (data points on y-axis) has a strength of 0.67 GPa but Cu-5Nb has a strength of 1.62 GPa, an increase of approximately 2.5 times, consistent with the results of other studies [4, 51, 52]. At this temperature, grain size strengthening (represented by empty circles) contributes approximately 75-90% of the observed strength (represented by filled circles).

After annealing at 800°C, unalloyed Cu has a strength of 0.36 GPa whereas Cu-5Nb has a strength of 1.07 GPa, an increase of approximately 3 times. At this temperature for Cu-5Nb, grain size strengthening (represented by empty squares) contribute approximately 65% to the observed strength (represented by

filled squares). These results indicate that other strengthening mechanisms, in addition to grain size strengthening, are operative at various points in this composition and temperature space [7].

3.3. Microstructure evolution

APT was performed on all samples to understand the solute behavior as a function of composition and temperature in the Cu-Nb alloys. To orient the readers to the collective context of the results, a few highlights of the results have been listed before presenting the details associated with these results. As will be shown, the Cu-1Nb alloy at both 400°C and 800°C reacted with the impurities forming solute-oxide and -nitride clusters, where a cluster refers to a very early stage of phase separation (similar to Guinier-Preston (GP) zones). Quantitatively a cluster represents a distinct group of atoms which are enriched with solute, but the solute is still the minor constituent (< 50 at. %).

Cu-5Nb/400°C has elemental Nb segregation zones and Nb-oxide-based clusters and Cu-10Nb/400°C has these same features plus large elemental (Nb)-based precipitates. These ‘segregation zones’ refer to inhomogeneously distributed solute atoms, similar to the segregation zones observed by Chookajorn *et al.* [22] and by Clark *et al.* [53]. Upon annealing at 800°C, the Cu-5Nb and Cu-10Nb alloys also had Nb-oxide-based clusters in addition to the second-phase precipitation of Nb solute. Quantitatively, these precipitates are defined as having > 50 at. % solute atoms and represent advanced stages of phase separation.

3.3.1. 400°C

An atom map of (Cu+NbO+NbO₂) in Cu-1Nb/400°C, Fig. 5 (a) revealed the presence of numerous clusters. As discussed, the word ‘clusters’ is used to describe solute-rich regions with < 50 at. % solute atoms. The composition of these clusters, obtained from a proximity histogram [54] of 6 at. % (NbO+NbO₂) in Fig. 5 (b), showed that they contain 15.82 ± 0.13 at. % (NbO & NbO₂) and 2.57 ± 0.08 at. % Fe. The much higher oxide content confirmed that these clusters are Nb-oxide-based. These clusters also contain ~ 1 at. % (NbC + NbN), inset in

Fig. 5(b). As discussed in Section 2, the presence of oxygen, nitrogen, iron and carbon is believed to be a result of contamination from the steel vials/balls that were used in mechanical alloying and the gaseous atmosphere contained within the vials [10, 36].

Atom probe reconstructions do not provide 100% lattice rectification and therefore microstructural features, such as grain boundaries or dislocations, are not directly observed. However, their presence can be inferred based on either a segregating species/precipitates occurring along a three- or two- dimensional feature respectively, or on chemical density differences. Therefore, in addition to using 6 at. % (NbO+NbO₂) isoconcentration surfaces to delineate the spatial distribution of these Nb-oxide-based clusters, density maps of differences of (Fe+NbO+NbO₂) were also used, Fig. 5(c). Regions of high-density clusters in the analyzed volume are labeled (with an arrow) and the following observations were made: First, the clusters appeared to be grouped on 2D planes which are angled in different directions, and would be consistent with the planar orientation of a grain boundary. Linking this observation with the knowledge from previous experimental work [10] that coarser solute precipitates are found along grain boundaries, it is reasonable to infer that these high-density cluster groups are present along a grain boundary. Second, the size and number of these planar cluster groups were consistent with the number of grain boundaries that would be present in the atom probe reconstructed volume. For example, in Fig. 5(c), three regions of high-density cluster groups are present in the 60 nm X 60 nm x 90 nm atom map volume. This would be a reasonable number of grain boundaries for an average grain size of 25 nm, Table 2 (a). Third, the regions between these areas of high-density clusters are denuded of enriched clusters, Fig. 5 (c), suggesting that these are interior regions of the grains. Finally, the above inferences are consistent with expectations because at this low (1 at. %) solute content, the grain boundary has not yet reached the solute saturation point and can accommodate more solute. Thus, an appreciable amount of solute would not be expected within the grain interior [20].

Additionally, a negligible amount (approximately 0.03 at. %) of elemental Nb was observed in the time-of-flight mass spectrum in this Cu-1Nb/400°C alloy. This observation indicates that most of the elemental Nb has reacted with the impurities and formed the clusters at the grain boundaries. The formation of such Nb-oxide-based clusters was first hypothesized by Botchorva *et al.* [34] and this is the first experimental observation of such clusters. Clark *et al.* [53] have also noted the presence of analogous solute-oxide (MgO-type) clusters in Fe-10 at. % Mg and have proposed that these clusters could be a source of grain size stability.

Next, the Cu-5Nb/400°C microstructure is addressed as this alloy resulted in highest strength, 1.6 GPa. Fig. 6 shows projections of 15 nm thick atom maps of (a) Cu, Nb, and Fe and (b) maps of (Cu+Fe), (Nb+Fe) and (NbN+NbO) in Cu-5Nb/400°C. Fig. 6 (c) is a 1D profile with the cylinder showing the volume through which it is obtained. The composition profile reveals the presence of regions enriched with 24.26 ± 3.68 Nb, 36.76 ± 4.13 Fe, 19.11 ± 3.37 NbO and 5.88 ± 2.02 NbN (at. %) with a spatial periodicity of ~ 15 nm. This periodicity appears to be consistent with the grain size range estimated by XRD (8.4 nm) and PED (14 nm). The minor grain size difference between XRD, PED and APT could be attributed to the fact that grain size from Scherrer analysis (XRD) is an average of grain sizes along three orientations (the largest grain size being 11.5 nm) as well as XRD and PED being stereological analyses techniques. Regardless, the important observation is that with 5 at. % solute content, elemental Nb is observed to be enriched at grain boundaries in addition to Nb-oxide-based clusters.

To compare the details of this enriched zone to that of the low solute Cu-1Nb/400°C, 8 at. % NbO isoconcentration surface was created and its proxigram, Fig. 6 (d), shows their composition to be 16.83 ± 0.35 Nb, 17.50 ± 0.36 Fe, 42.67 ± 0.46 NbO, 3.29 ± 0.17 NbN (at. %). A few details that can be gleaned from the proxigram are that the peaks in composition of elemental Nb and Fe (labeled with an arrow), at 0.4 nm on the x-axis, are not co-located with the NbO peak. This indicates that the elemental (Nb+Fe) enrichment and Nb-oxide-based clusters

are adjacent to each other and are distinct features. Second, there is minimal (0.04 at. %) elemental oxygen within the isoconcentration surface (not shown in the image). This indicates that initially when Nb began to segregate, it reacted with oxygen. Once all oxygen was consumed, the remaining Nb was present as a solute in the vicinity and explains the adjacent peaks observed in the proxigram. The above described pathway resulted in the formation of Nb-oxide-based clusters followed by the remaining (Nb+Fe) solute present as a segregation zone in the vicinity.

Next, the effect of increasing the solute content to 10 at. % Nb is reported. Fig. 7(a), projections of atom maps of Cu, Fe, Nb, (NbO+NbN), and a 2D density map of Nb in Cu-10Nb/400°C, shows large Nb-rich precipitates and a region of elemental (Nb+Fe) and (NbO+NbN) enrichment. A 1D composition profile, Fig. 7 (b), was obtained through both the region of enrichment and Nb-rich precipitate with the cylinder marking the volume through which the composition profile was obtained.

The (Nb+Fe) segregation zone in this alloy contained 37.62 ± 2.71 Fe, 23.51 ± 2.37 Nb, and 11.20 ± 1.76 (NbO+NbN) (at. %) clearly indicating that elemental (Nb+Fe) is present in the same neighborhood as (NbO+NbN). This proximity of (NbO+NbN) to elemental (Nb+Fe) solute is very similar to the phenomenon observed in low solute Cu-5Nb/400°C and indicates that the pathway of segregation and cluster formation is similar. The Nb-rich precipitate is ~ 12 nm (full-width at half-maximum of Nb concentration) and has ~ 74.60 ± 3.22 Nb and ~ 10.89 ± 2.31 NbO (at. %) and does not have any Fe (unlike the elemental segregation zone). This absence of Fe clearly indicates that this Nb-rich precipitate is a separate entity from the (Nb+Fe) solute enrichment. Observing the details of peak location in the 1D profile, the peak in NbO composition is at 29 nm (labeled by an arrow) whereas the peak of Nb composition is at 31 nm. This seems to suggest that NbO formed first with oxygen acting as the limiting agent. After the oxygen was consumed, the remaining Nb solute in this high-solute content Cu-10Nb/400°C alloy formed a Nb-rich precipitate. The above described pathway is similar to that in Cu-

5Nb/400°C, but in this case the phase separation of Nb solute is in an advanced stage probably due to the higher amount of solute. This presence of solute rich, elemental Nb precipitates at high solute content is consistent with other studies [7, 9].

3.3.2. 800°C

Fig. 8 (a) is the atom map of (Cu+NbO+NbO₂+NbN) in Cu-1Nb/800°C and two distinct populations of Nb-oxide-based and NbN-based clusters were noted. Very little elemental Nb (0.08 at. %) was observed in this alloy. In this composite view, it was difficult to identify any spatial distribution patterns. However by viewing the Nb-oxide-based clusters separately, Fig. 8(b), their spatial distribution revealed two regions of high-density clusters in the vicinity of 3D features, marked by blue lines to guide the eye. The first set of high density clusters consist of 6 Nb-oxide-based precipitates, bottom left of Fig. 8 (b), and are located on a curved 3D region indicating that they are on a grain boundary. The second set of Nb-oxide-based clusters were observed around the middle of the reconstruction, Fig. 8(b), and then down the angled plane (marked by a blue line) which is consistent with a grain boundary. Two regions of such high-density precipitates are present in the atom map of 60 nm X 60 nm x 60 nm, which is a reasonable number of grain boundaries for a grain size of 72 nm. Last, the regions on both sides of these areas of high-density precipitates do not show any similar clusters, suggesting (as above) that these are interior regions of the grain. Their proximity histogram, Fig. 8 (c), shows that they have 15.72 ± 0.10 at. % (NbO₂+NbO) and have less than 2 at. % Fe. Observation of these similar clusters at 1 at. % solute content, regardless of the annealing temperature, strongly indicates that the formation of Nb-oxide-based clusters at grain boundaries is a common initial mechanism.

At the higher solute composition, Cu-5Nb/800°C, an advanced level of phase separation with two distinct phases are observed in Fig. 9 (a) – 1) (Nb+Fe) precipitates delineated by green-colored 20 at. % (Nb+Fe) isoconcentration surface, and 2) Nb-oxide-based precipitates delineated by purple-colored 8 at. % (NbO+NbO₂) isoconcentration surface. The Nb-oxide-based precipitates, Fig. 9

(b), contain 15.31 ± 0.55 NbO, 41.02 ± 0.74 NbO₂, 17.74 ± 0.58 Fe, 7.44 ± 0.40 Nb (at. %), and less than 3 at. % (NbN+NbC). These Nb-oxide-based precipitates are more enriched (~ 60 at. % compared to 15-20 at. %) in NbO and NbO₂ and are also larger (3.5 nm compared to 1-2 nm radius) compared to Nb-oxide-based clusters in any other alloy discussed in this study.

The three larger (Nb+Fe) precipitates, Fig. 9 (c), comprise of 31.26 ± 0.40 Nb and 65.10 ± 0.40 Fe (at. %). In the proxigram, there is a peak in NbO and NbO₂ at 1nm – 2nm, near the interface (marked with an arrow). This indicates that some of NbO and (Nb+Fe) precipitates, labeled with an arrow in Fig. 9 (a), are forming adjacent to each other from the same solute reservoir. This phenomenon is similar to the observations in other high-solute alloys, Cu-5Nb/400°C had elemental (Nb+Fe) solute adjacent to Nb-oxide-based clusters and Cu-10Nb/400°C had Nb-oxide-based clusters adjacent to Nb-rich precipitate, suggesting a common solute-content-dependent pathway. It is also interesting to note that this (Nb+Fe) precipitate is distinct from the Nb-rich precipitate in Cu-10Nb/400°C in that the latter did not have any Fe in it. The presence of these larger precipitates at this annealing temperature is consistent with previous studies on Cu-10Nb which showed the formation of ~ 60 nm Nb-based precipitates on annealing at 600°C [4, 31].

To emphasize the spatial distribution of each type of precipitate, Fig. 9 (d) and (e) show only the 8 at. % (NbO+NbO₂) and 20 at. % (Nb+Fe) isoconcentration surfaces respectively. The Nb-oxide-based precipitates are distributed on a 3D feature along the middle of the reconstruction, Fig. 9(d). Among the three (Nb+Fe) precipitates, two of the larger precipitates are also along this same 3D feature making it likely that both types of precipitates are forming on a grain boundary. Regardless of these details, this alloy shows the Nb solute to be in advanced stage of phase separation with the formation of (Nb+Fe) precipitates and the Nb-oxide-based precipitates.

3.3.3 Summary of microstructure evolution results

The several results presented above are summarized to emphasize the gist of the distinct microstructural features that formed as a function of Nb solute content and annealing temperature.

- Cu-1Nb/400°C has only Nb-oxide-based clusters and very little (0.03 at. %) elemental Nb solute;
- Cu-5Nb/400°C has elemental Nb segregation zones and Nb-oxide-based clusters;
- Cu-10Nb/400°C has (NbO & NbN)-based clusters, elemental Nb segregation zones and large elemental (Nb)-based precipitates; and
- Cu-1Nb/800°C has only Nb-oxide-based clusters whereas both Cu-5Nb/800°C and Cu-10Nb/800°C have both the Nb-oxide-based precipitates and the large (Nb+Fe) precipitates.

4 Discussion

4.1. Microstructure

The low solute content alloys (1 at. % Nb) have similar microstructural features at both 400°C and 800°C, i.e. Nb-oxide-based clusters at grain boundaries, Fig. 5 and 8. Similar microstructure indicates that the initial phase separation mechanism is the same regardless of the temperature. The only notable difference is that at 800°C, these solute clusters are larger (approximately 3.5 nm vs. 2 nm) suggesting that they are coarsened versions of the Nb-oxide-based clusters formed at 400°C. This size difference can easily be rationalized by faster kinetics at higher temperatures. As alluded to above, Nb-oxide-based clusters form as a result of Nb solute reacting with the oxygen. This oxygen is believed to be associated with intrinsic contamination from the mechanical alloying process used to fabricate these alloys. The total oxygen content in each of the samples measured using APT is listed in Table 3. These Nb-oxide-based clusters will form on the grain boundaries because of a reduced nucleation barrier [55] at the grain boundaries or the oxygen simply reacts with the Nb solute atoms that clustered within the boundaries. Once these clusters

nucleate, the grain boundaries act as a Nb solute reservoir [10, 56] and oxygen acts as the limiting agent for the formation of these Nb-oxide-based clusters. A similar formation of Nb-oxide-based precipitates whose amount is limited by the amount of oxygen has been inferred in other studies [31]. However those Nb-oxide-based precipitates were never directly observed, due to the small size and low volume fraction [10], until now. In the alloys containing low Nb solute, i.e. 1 at. % Nb, all the Nb that segregated to the boundaries appeared to react with the oxygen.

Since Cu-1Nb/400°C is the lowest solute content (1 at. % Nb) and the lowest annealing temperature studied, its microstructure also represents the earliest stages of phase separation. Such solute clusters present along the grain boundary are consistent with experimental results on Cu-Ta systems and molecular dynamics simulations [9, 25]. However, in this study the solute clusters in the grain boundaries react with oxygen and result in Nb-oxide-based clusters at the grain boundaries.

On increasing the solute content at 400°C, Cu-5Nb/400°C, elemental (Nb+Fe) segregation zones are found in the vicinity of grain boundaries in addition to the Nb-oxide-based clusters, Fig.6. This suggests the following sequence at 5 at. % Nb solute concentration – 1) Nb solute and oxygen form clusters limited by the amount of oxygen, 2) subsequently, the balance of elemental Nb atoms present segregate to form (Nb+Fe) zones. Comparing the size and the location of these elemental (Nb+Fe) segregation zones in Cu-5Nb/400°C with respect to Nb-oxide-based clusters, Fig. 6, and that of the clusters at grain boundaries in Cu-1Nb/400°C, Fig. 5, it can be deduced that Nb-oxide-based clusters at grain boundaries are likely the precursors of the phase separation. As the process continues, the grain boundaries accumulate more solute and begin to thicken, consistent with microstructure observations/predictions in other studies [8, 22, 23]. However, at the same solute content but at a higher annealing temperature, these segregation zones are not observed in Cu-5Nb/800°C; instead its microstructure is somewhat similar to Cu-10Nb/400°C and their features are discussed below.

Cu-5Nb/800°C, Fig. 9, has large (approximately 10 nm) (Nb+Fe) precipitates with a composition consistent with the Fe_2Nb phase (a stable high temperature phase) and 7 nm-sized Nb-oxide-based precipitates. Similarly, Cu-10Nb/400°C, Fig.7, has large (approximately 12 nm) size Nb-rich precipitates, smaller Nb-oxide-based clusters, and elemental (Nb+Fe) segregation at the grain boundaries. The main difference between these two different stages (Cu-5Nb/800°C vs. Cu-10Nb/400°C) is that (Nb+Fe) solute segregation zones were not found in Cu-5Nb/800°C. Therefore, the presence of these Fe_2Nb precipitates indicates that the precipitation of Fe_2Nb is energetically favorable compared to only the formation of Nb-rich segregation zones at the grain boundaries at 800°C.

4.2. Grain size stability and strength

Ideal thermodynamic segregation involves segregation of solute atoms to an interface and it is usually quantified by calculating interfacial excess which gives the number of atoms per unit area of the feature. The immiscible systems investigated in this study have solute clusters at the grain boundary or a thickening of grain boundaries with solute. These equilibrium phase diagrams are ineffective in reflecting the state of the microstructure. Another phenomenon which complicates the analysis and is a consequence of processing itself, is that the solute reacts with intrinsic contaminants [53, 57]. In this case, the dominant effect was the formation of Nb-oxide-based clusters due to Nb solute clusters reacting with the available oxygen. Regardless of the complications, Cu-Nb alloys have demonstrated substantially suppressed grain growth at high temperatures, consistent with other studies [9].

In Cu-1Nb/400°C, the grain boundary has Nb-oxide-based clusters on it. Even though the boundary is not completely covered, these clusters clearly provide grain size stability as the grain size is approximately 6 times smaller than that of the unalloyed Cu. Since no elemental Nb is present, one can conclude that a Zener-based pinning or kinetic stabilization appears to be responsible. On increasing the solute content to 5 at. %, one observes (Nb+Fe) segregation zones at the grain boundary in addition to the Nb-oxide-based clusters and a grain size of approximately 8.5 nm, which is about 20 times smaller than that of

the unalloyed copper. This higher degree of reduced grain growth concomitant with the segregation zones in the vicinity of the grain boundaries indicates that these zones are also responsible for this reduced grain growth, consistent with nanocrystalline grain stabilization observed in Cu-10Ta [10]. We believe both a kinetic and thermodynamic stabilization is occurring at this composition.

On further increasing the solute to 10 at. % (Cu-10Nb/400°C), the grain size is approximately 29 times smaller than that of the unalloyed Cu and one observes large Nb-rich precipitates and Nb-rich segregation zones at grain boundaries. Here, the solute content is large enough to result in formation of a distinct second phase – Nb-rich precipitates – and forms a duplex nanostructure. Interestingly, the precipitation of these Nb-rich precipitates does not result in a loss of nanocrystalline grain size, as had been noted in other studies[24]. However, our results are consistent with those of Cu-10at. % Ta [10]. Specifically, the (Nb+Fe)-rich segregation zone is retained even in the presence of Nb-rich precipitates, Fig. 7, in Cu-10Nb/400°C and Nb segregation is one of the factors responsible for the reduced grain growth. In both the Cu-5Nb and Cu-10Nb samples, Fig. 6 and 7, Fe was also shown to be present with Nb. However, Fe does not contribute thermodynamically to the stabilization because Fe is predicted to not lead to any reduction in grain boundary energy of Cu [58]. Therefore, at these solute concentrations and after annealing at 400°C, the nanocrystalline stabilization seems to be a combination of kinetic and thermodynamic factors.

At the 400°C annealing temperature, most of the strength in the material is due to grain size strengthening, Fig. 4, suggesting that the clusters in Cu-1Nb and the Nb-rich precipitates in Cu-10Nb do not play a dominant role in strengthening. Also, the ~20 nm Nb-rich precipitates would be too large to provide any Orowan strengthening.

After annealing at 800°C, the unalloyed Cu has a grain size of 566 nm and by adding 1 at. % Nb the grain size is reduced to 72 nm. As the amount of solute is increased from 1 at. % to 10 at. %, the grain size further decreases from 72 nm to 33 nm, Table 2. In Cu-1Nb/800°C, the grain boundary has only Nb-oxide-

based precipitates on it. Even though the boundary is not completely covered, these clusters again are sufficient to provide grain size stability as the grain size is approximately 7.6 times smaller than that of the unalloyed Cu. On increasing the solute content to 5 at. %, one observes Nb-rich segregation zones at the grain boundaries in addition to the Nb-oxide-based precipitates and a grain size of approximately 40 nm, which is about 14 times smaller than that of the unalloyed copper, Fig. 3. On further increasing the solute to 10 at. %, there is little difference in the stabilized grain size or the microstructure. At 400°C, an increase in solute content appeared to have a greater influence on the stabilized grain size than at 800°C, Fig. 3. This may be associated with the fact that at 400°C elemental Nb segregation zones are retained along with precipitates providing both kinetic and thermodynamic stabilization (Fig. 6 & 7), whereas at 800°C only precipitates (and no segregation zones) are present (Fig. 9). Regardless the grains still show remarkably retarded grain growth compared to the unalloyed Cu control.

At the 800°C anneal, the strength of the 5 and 10 at.% Nb was about 50% attributed to the grain size. The other strengthening mechanism is attributed to the secondary precipitation strengthening by the Nb-enriched second phase in the microstructure.

5 Conclusions

This work has shown that mechanically alloying Cu with Nb improves nanocrystalline stability in the annealing temperature range of 400°C–800°C. Increasing the Nb solute content resulted in reduced grain growth regardless of the annealing temperature. At the lowest solute concentration (1 at.%), nearly all the elemental Nb reacted with oxygen (and other impurities) forming nanoscale Nb-oxide-based clusters that were apparently along the grain boundaries providing kinetic stabilization. For the 5 and 10 at.% Nb, both Nb-oxide-based clusters and elemental Nb were present along the grain boundaries. Depending on the solute concentration and annealing temperature, the Nb formed either Nb-enriched segregation zones or Nb-rich secondary precipitates. These

microstructural features reduced the degree of grain growth via both kinetic and thermodynamic stabilization.

In this study, identifying the dominant stabilization mechanism was confounded by the presence of Nb-oxide-based clusters, which formed from intrinsic impurities of the mechanical alloying process itself. This existence of impurity-driven clusters providing kinetic stabilization has also recently been recognized and discussed in a couple of studies [53, 57]. Therefore, this work specifically used APT to understand nanocrystalline behavior in light of such impurities.

Scientifically, the ability to process bulk nanocrystalline materials free from impurities poses a challenge to the research community. From a practical standpoint, impurities are often present in industrial materials and their influence even in small amounts plays a significant role in defining microstructural evolution and physical properties. The understanding of the role of such impurities on stabilization will be especially important during industrial scale processing and commercialization of bulk nanocrystalline metals. Therefore, it is imperative that future studies on nanocrystalline stabilization identify and characterize these other contributors to stability to develop a comprehensive understanding of the stabilization mechanisms.

From a practical perspective, the Cu-Nb alloy provides impressive strength >1 GPa that demonstrates stability at elevated temperatures. With an optimal Nb concentration of ~5 at.% Nb, the electrical conductivity of the alloy likely enables applications as a conductor or electrical contact material for high-temperature service. The alloy, for example, could provide an alternative to hazardous beryllium-copper alloys (e.g. Cu-2.5Be, UNS C17200).

Acknowledgements

MK, BLB and GBT were supported by the Materials Science and Engineering Division of the US Department of Energy, Office of Basic Energy Sciences. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin

Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. KD recognizes the Army Research Laboratory for his support. Finally TK was supported by Army Research Office, grant W911NF1310436.

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Fig. 1 – X-ray diffraction results of non-annealed (a) as-milled Cu and Cu-Nb alloys with 1, 5 and 10 at. % Nb , and (b) non-annealed 5 at. % Nb, 5Nb/400°C and 5Nb/800°C. The broken line in Fig. 1(b) represents the 2θ position of unalloyed Cu (111) peak.

Fig. 1 – X-ray diffraction results of non-annealed (a) as-milled Cu and Cu-Nb alloys with 1, 5 and 10 at. % Nb, and (b) non-annealed 5 at. % Nb, 5Nb/400°C and 5Nb/800°C. The broken line in Fig. 1(b) represents the 2θ position of unalloyed Cu (111) peak.

Fig. 2 – Electron backscatter diffraction of (a) unalloyed Cu and precession electron diffraction of (b) Cu-1Nb, and (c) Cu-10Nb annealed at 800°C for 1 hr. The images in the bottom row are the respective grain size distributions.

Fig. 3 – Effect of annealing temperature on grain size stabilization as a function of Nb composition. Relative grain size (GS) is the grain size of unalloyed Cu divided by that of alloyed Cu. The lines are drawn only to guide the eye and not to infer a linear fit.

Fig. 4 – Strength as a function of Nb composition for the Cu-Nb alloys annealed at (a) 400°C and (b) 800°C for 1 hr. The filled symbols represents the measured values converted to strength from Vickers Hardness and empty symbols represent the calculated Hall-Petch strength due to grain size. The Hall-Petch constants used are 25MPa and 0.137 MPa $\sqrt{m}$.

Fig. 5 – (a) Atom map from APT of Cu-1Nb/400°C showing Nb-oxide-based clusters, (b) proximity histogram of 6 at. % (NbO+NbO₂) isoconcentration surface and 1 at. % (NbC + NbN) (shown in inset) to illustrate the distribution of the clusters in the atom map, (c) 2D density plots of (Fe+NbO+NbO₂) along x-axis and y-axis of the reconstruction to delineate the areas of high density.

Fig. 6 – (a) Atom maps from APT in Cu-5Nb/400°C Cu, Nb and Fe, (b) mixed maps of (Cu+Fe), (Nb+Fe) and (NbO+NbN), and (c) 1D composition profile obtained through the atom map with the cylinder showing the region through which the profile was obtained, and (d) Proximity histogram of 8 at. % (NbO+NbO₂) isoconcentration surface to illustrate the co-existence of Nb solute with that of NbO clusters.

Fig. 6 – (a) Atom maps from APT in Cu-5Nb/400°C Cu, Nb and Fe, (b) mixed maps of (Cu+Fe), (Nb+Fe) and (NbO+NbN), and (c) 1D composition profile obtained through the atom map with the cylinder showing the region through which the profile was obtained, and (d) Proximity histogram of 8 at. % (NbO+NbO₂) isoconcentration surface to illustrate the co-existence of Nb solute with that of NbO clusters.

Fig. 7 – (a) Atom maps from APT of Cu-10Nb/400°C showing Cu, Fe, Nb, (NbO+NbN) and 2D density map of Nb; (b) 1D composition profile obtained through the atom map with the cylinder showing the region through which the profile was obtained.

Fig. 8 – (a) Atom map from APT of Cu-1Nb/800°C showing only Cu, NbO₂, NbO and NbN ions, (b) 6 at. % (NbO₂ + NbO) isoconcentration surface only, and (c) proximity histogram of these clusters showing that they are Nb-oxide-based clusters.

Fig. 9 – (a) Atom map from Cu-5Nb/800°C showing Nb-oxide-based precipitates (purple) and (Nb+Fe)-based (green) large precipitates delineated by 8 at. % (NbO₂ + NbO) and 20 at. % (Nb+Fe) isoconcentration surfaces. Proximity histograms obtained from (b) 8 at. % (NbO₂ + NbO), and (c) 20 at. % (Nb+Fe) isoconcentration surfaces, (d) only 8 at. % (NbO₂ + NbO), and (e) only 20 at. % (Nb+Fe) isoconcentration surfaces shown for clarity. Only 1% Cu atoms are shown in atom maps.

Table 1 : Alloy composition (at. %) along with the annealing temperature (°C). All the alloys were annealed for one hour.

Annealing Temperature (°C)	Cu	Cu-1Nb	Cu-5Nb	Cu-10Nb
As-Milled	Cu-AM	Cu-1Nb-AM	Cu-5Nb-AM	Cu-10Nb-AM
400	Cu-400	Cu-1Nb-400°C	Cu-5Nb-400°C	Cu-10Nb-400°C
800	Cu-800	Cu-1Nb-800°C	Cu-5Nb-800°C	Cu-10Nb-800°C

Table 2 (a): Grain sizes (nm) of Cu-Nb alloys obtained from XRD data from Cu (111), (200), and (220) peaks.

Annealing Temperature (°C)	Cu	Cu-1Nb	Cu-5Nb	Cu-10Nb
As-Milled	24.0±14.2	16.6±6.8	7.1±2.6	4.7±1.8
400	43.1±13.4	25.2±16.1	8.4±2.9	5.5±2.0
800	547.0±570.0	72.2±22.1	41.1±15.3	40.0±16.1

Table 2 (b): Grain sizes (nm) of Cu obtained from EBSD and of Cu-Nb alloys obtained from PED.

	Cu	1Nb	5Nb	10Nb
400°C	163±99	17.6±13.9	14.2±7.0	NA
800°C	566±778	21.5±20.8	NA	19.3±14.3

NA-Not analyzed.

Table 2 (c): Relative grain size of Cu-Nb alloys obtained from EBSD results of Cu and XRD results of Cu-Nb alloys.

	1Nb	5Nb	10Nb
AM	1.4	3.4	5.1
400°C	6.5	19.4	29.5
800°C	7.8	13.8	14.1

Table 3: Oxygen content (at. %) measured using atom probe tomography.

	10Nb	5Nb	1Nb
AM	NA	0.92	NA
400°C	0.10	1.35	0.94
800°C	0.75	0.95	0.67

NA – Not analyzed.