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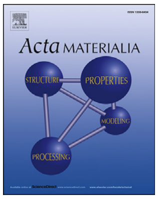

Full length article

Femtosecond laser rejuvenation of nanocrystalline metals

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ABSTRACT

Nanocrystalline metals are distinct from traditional engineering materials due to their high concentration of grain boundaries and corresponding structural disorder at grain boundaries. The effect of local disorder in nanocrystalline materials manifests in ways reminiscent of fully amorphous materials, such as mesoscale shear localization and pressure-dependent yielding, owing to the high concentration of grain boundaries and their predominance in governing plasticity. Relaxation processes in nanocrystalline materials that facilitate reconfigurations of grain boundaries and lower their energy, such as low temperature annealing, have been shown to enhance mechanical strength. However, processes that raise the energy of a nanocrystalline metal have not been observed, limiting the tunability of properties and the prospect for suppressing shear localization. Here, we use femtosecond laser processing as a unique non-equilibrium process that can generate complex stress states due to ultrafast electronic excitation and subsequent relaxation events. Experiments on nanocrystalline Al-O and Cu-Zr alloys indicate that sub-ablation femtosecond laser pulses cause up to an 87% reduction in hardness with no change in grain size, which can be ascribed to grain boundary-mediated processes. Parallels between our results and rejuvenation processes in glassy systems will be discussed in the context of controlling metastable structural configurations through novel processing routes.

1. Introduction

Nanocrystalline (NC) metals have attracted widespread interest due to their desirable mechanical properties, primarily their high strength [1–5] and wear resistance [6]. The mechanical behavior and deformation physics of metals with grain sizes finer than 50 nm are drastically different from their coarse-grained counterparts, due to their inability to facilitate traditional dislocation activity, as well as a high concentration of grain boundary (GB) regions that participate strongly in plastic deformation [4,5,7]. Many of the numerous deformation mechanisms operative in NC metals, for instance, GB sliding [8,9] and dislocation-GB processes (nucleation, propagation, absorption) [10,11], hinge on the local atomic configuration of GB regions. GBs can exhibit a large diversity of both equilibrium and non-equilibrium structures, which can drastically affect the local properties [2,12–14]. The effects of metastable GB configurations on GB energy can be large, and their role in mechanical deformation is expected to be concomitantly so [13–15]. Additionally, imperfections at GBs such as steps, kinks, and ledges can alter their deformation behavior – acting as stress concentrations, mediating the nucleation and propagation of partial dislocations [10]. Other unique deformation behavior of NC metals, such as stress-assisted grain growth, can be explained by the evolution of GB structures during plastic deformation [16,17]. These results collectively underscore the notion that the local atomic structure at GBs plays a crucial role during the deformation of NC metals.

Processing routes utilized to synthesize NC metals, including “top-down” approaches of grain refinement such as high pressure torsion [18] and ECAP [19], as well as “bottom-up” methods such as inert gas condensation [20], electrodeposition [21], and sputter deposition [22], are far-from-equilibrium processes that can produce non-equilibrium, high-energy GB structures [23]. Experimental observations and atomistic simulations of low temperature annealing [3,24,25] and mechanical cycling with amplitudes well below the global yield stress [25] of NC metals show that GB relaxation can dramatically increase the yield strength of these materials without influencing grain size. This behavior has not only

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been ascribed to GB solute segregation in binary or multicomponent alloys [3,26], but has also been shown to be caused by configurational relaxation in GB regions for both alloy and nominally pure systems [25]. Segregation of solute to GBs serves to decrease the GB energy in systems with a high enthalpy of segregation [3,26] and configurational relaxation of non-equilibrium GB structures also reduces the energy of these systems [25], increasing the activation barrier to initiate plasticity. This sensitivity to local chemistry and structure, coupled with molecular dynamics simulations indicating a multiplicity of metastable GB states for a macroscopically fixed GB [14,15], suggests that far-from-equilibrium processing routes like those used to produce NC metals may enable the formation of metastable GB structures underpinning their thermomechanical response. Chemical and structural effects may also occur in concert, wherein solute segregation to GBs has been shown to drive structural transformations at the GB [27].

Sensitivity to thermomechanical history and abundant structural disorder in interface dominated materials like NC metals, suggested by a multiplicity of metastable configurations of GBs, is reminiscent of fully amorphous materials, such as metallic glasses (MGs), which are often described as the limit of grain refinement [28]. Several researchers have noted similarities between the mechanical behavior of these materials [29–32], such as pressure dependent yielding [29] and strong shear localization [32]. Others have shown kinetic similarities between GB regions in coarse grained materials and MGs [33]. Due to the predominance for GB-mediated plasticity in NC metals, applying the understanding of MG deformation to GBs in NC metals may enable enhanced control over the mechanical behavior of NC metals.

Despite the numerous similarities between these two materials, commonalities in the history and processing dependence between NC metals and MGs have received little attention. MGs show a strong history dependence, where a more relaxed – i.e. a lower energy atomic configuration – glass has a higher yield strength and propensity for shear localization [34]; whereas a more rejuvenated – i.e. higher in energy, more liquid-like – glass has increased ductility [35]. Processing routes used to modify the energy of a MG to exploit tunable properties have been studied extensively, notably to facilitate homogeneous plasticity at room temperature [35–38]. Relaxation processing routes are similar to those for NC metals – low temperature annealing [34] and cyclic mechanical loading [39] both produce increases in yield stress and modulus of a MG. Conversely, rejuvenation processes include severe plastic deformation [40], and cryogenic cycling [41], which induce local dilatational strains, decreasing the yield strength and modulus, but increasing the ductility of the MG. Rejuvenation of an MG can be correlated to increases in free volume, stored enthalpy, and fictive temperature, but can be defined as an increase in energy of the system [35–38,40–42].

Rejuvenation processing has enabled greater functionality of MGs by enhancing their ductility, allowing for stable plastic deformation at room temperature. NC metals exhibit similar mechanical instabilities that limit their use, thus the potential of rejuvenation processing routes to enhance their properties is tantalizing. To date, no single processing route, or combination thereof, has been identified that can bi-directionally tailor the state of GBs, despite these strategies being recently employed for MGs. These processing routes categorically occur quickly and at low temperature, in order to suppress any competing structural relaxation [42]. A previously unexplored processing technique that possesses these characteristics is pulsed ultrafast laser processing. Unlike longer pulse laser-material interaction, which have been used as heat sources for processing of both NC metals and MGs [43–45], femtosecond (fs) pulse laser-material interactions are fundamentally distinct, due to the different timescales underlying electronic excitation (fs) and phonon-electron relaxation (ps) [46]. This difference in timescales facilitates a largely athermal, mechanical ablation process, which is useful in mitigating damaged zones during machining [47]. High fluence fs-laser processing has been used extensively for micromachining, enabling serial sectioning and micromechanical sample preparation, as well as other applications where material removal with minimal residual damage is required [48,49]. Many experimental observations and computer simulations have studied the ablation behavior of materials exposed to high fluence fs-laser irradiation [47,50–56]. Recent work has indicated that grain size affects fs-laser ablation, because fs-laser-material interactions at GB regions are fundamentally different than in bulk crystalline regions due to spatially heterogeneous electron-phonon coupling behavior [55]. While the bulk of the investigation into fs-laser-matter interactions have been focused on high fluence ablation behavior, hybrid two-temperature model/molecular-dynamics simulations have indicated that at energies below the ablation threshold, significant tensile and compressive stresses can be induced by the laser [55,56]. The resulting combination of high stresses, short timescales, largely athermal processing, and potential confinement to GB regions suggests that the fs-laser processing may have the characteristics necessary for rejuvenation of GBs, analogous to processing developed by the MG community.

We hypothesize that the stresses generated by the fs-laser at energies below the ablation threshold may be used to modify the mechanical behavior of NC metals via short-range atomic rearrangements at GBs. This is motivated by thermal and mechanical cycling experiments that have shown dramatic shifts in mechanical properties with negligible microstructural evolution. In this work, we report on measurements demonstrating the influence of sub-ablation threshold fs-laser pulses on location-specific properties of NC Al-O and Cu-Zr, materials selected to explore a range of different GB chemical and structural states. Our results suggest that sub-ablation fs-laser pulses cause a dramatic and recoverable reduction in hardness accompanied by negligible changes in grain size, reminiscent of rejuvenation processes in MGs.

2. Materials and methods

NC Al-O samples were synthesized by magnetron co-sputtering of 99.999% pure Al and 99.995% pure α-Al_2O_3 in an Explorer 14 Sputtering system (Denton Vacuum) on Si (100) wafers and Cu transmission electron microscopy (TEM) grids with C support films at DC powers of 200–300 W for the Al target and RF powers of 0–150 W for the α-Al_2O_3. These deposition parameters resulted in compositions of Al-0.82 ± 0.10 at.%O and Al-4.79 ± 0.48 at.%O. From here on, the samples will be referred to as Al-0.8 at.%O and Al-4.8 at.%O. Additional details of the NC Al-O sample preparation are located in Ref. [22]. Compositional information, film thickness, grain size and initial hardness information are shown in Table 1. Bright field (BF) TEM images of both as-deposited NC Al samples are shown in Fig. 1 (a, b).

NC Cu-3at.%Zr samples were prepared using mechanical ball milling in a SPEX SamplePrep 8000 M Mixer/Mill to produce powders with μm-sized particle diameters and nm-sized grains. Powders were milled for 10 h using a hardened steel vial and milling media, and stearic acid in the amount of 2 wt% was added as a process control agent. Annealing treatments were performed at 950 °C in vacuum for 1 h to promote Zr diffusion to GBs and allow for the formation of amorphous intergranular films (AIFs). Samples were then either rapidly quenched in water or slowly cooled in air from the annealed state. TEM specimens of both quenched and slowly cooled samples were made using an FEI Quanta 3D FEG