Materials and Design 113 (2017) 178–185

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Microstructural evolution in a nanocrystalline Cu-Ta alloy: A combined in-situ TEM and atomistic study

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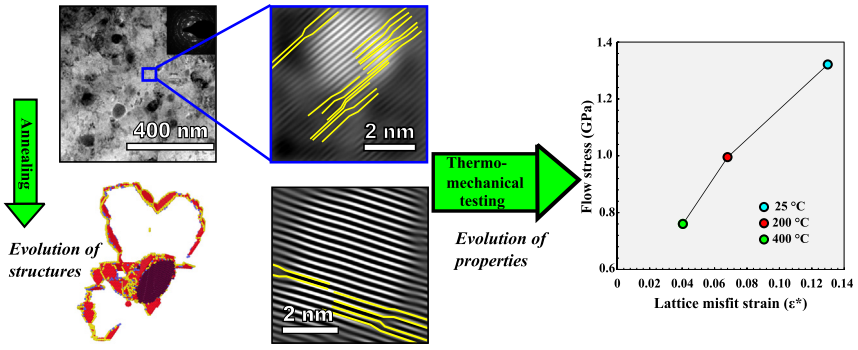
HIGHLIGHTS

- Nanocrystalline Cu-10at.%Ta shows exceptional thermal stability unlike any other NC and ultra-fine grained metals
- Local structural changes at the interface between nanoclusters and matrix influence the thermo-mechanical properties
- The evolution of such fine structures is critical for developing nanocrystalline alloys with extreme properties

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 June 2016
Received in revised form 7 August 2016
Accepted 9 October 2016
Available online 11 October 2016

Keywords:
In situ TEM
Nanocrystalline
Atomistic
Misfit strain

ABSTRACT

Under intense heating and/or deformation, pure nanocrystalline (NC) metals exhibit significant grain coarsening, thus preventing the study of length scale effects on their physical response under such conditions. Hence, in this study, we use in-situ TEM heating experiments, atomistic modeling along with elevated temperature compression tests on a thermally stabilized nanostructured Cu–10 at.% Ta alloy to assess the microstructural manifestations caused by changes in temperature. Results reveal the thermal stability attained in NC Cu-10 at.% Ta diverges from those observed for conventional coarse-grained metals and other NC metals. Macroscopically, the microstructure, such as Cu grain and Ta based cluster size resists evolving with temperature. However, local structural changes at the interface between the Ta based clusters and the Cu matrix have a profound effect on thermo-mechanical properties. The lattice misfit between the Ta clusters and the matrix tends to decrease at high temperatures, promoting better coherency. In other words, the misfit strain was found to decrease monotonically from 12.9% to 4.0% with increase in temperature, leading to a significant change in flow stress, despite which (strength) remains greater than all known NC metals. Overall, the evolution of such fine structures is critical for developing NC alloys with exceptional thermo-mechanical properties.

1. Introduction

Metals with a mean grain size *(d)* below 100 nm, i.e., nanocrystalline (NC) materials, have garnered significant interest due to their superior mechanical properties as compared to coarse-grained materials [1] A

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http://dx.doi.org/10.1016/j.matdes.2016.10.020
0264-1275/

large number of experimental and computational studies have explored how grain boundary mediated plasticity and microstructural size effects impact the mechanical behavior of NC materials [2–4]. For example, the Hall-Petch [5,6] relationship describes the experimentally-observed increase in yield strength with decreasing grain size down to grain diameters as small as 20 nm [1,2]; this behavior is generally followed by a plateau/negative slope region for grain sizes below a critical size (e.g., 8–15 nm for Cu [7]). This inverse Hall-Petch effect has been directly attributed to changes in the governing deformation mechanisms away from traditional dislocation glide and pile-up processes [8]. Fundamental changes in deformation mechanisms are also known to cause many other intriguing and unexpected physical responses of NC metals, including altered strain rate and pressure dependencies of deformation [9], superplasticity [10], and low temperature creep [11], to name a few (see [12,13]). Generally, these unique deviations in behavior are solely attributed to a continual reduction in grain size and an increase in the fraction of grain boundaries and triple junctions, which leads to the experimentally reported mechanisms of deformation twinning, grain boundary (GB) rotation/sliding and viscous flow [14–16].

Despite significant gains in knowledge related to the development and engineering of plasticity in nanomaterials, there still persists a sizeable gap in the fundamental understanding of the mechanical behavior of these materials, especially under extreme conditions such as at ultra-high temperatures. This gap is critical as the material performance at high temperatures is significantly different from the room temperature (RT) behavior. Limited studies have explored the mechanical behavior of NC materials at room or moderately low temperatures where a drastic change in the microstructure (grain growth) has been reported. For example, Farrokh and Khan investigated the uniaxial compressive behavior of NC Cu and Al (grain size 32 nm and 82 nm, respectively) prepared through mechanical alloying at a strain rate of 0.01/s (Cu) and a significant effect of temperature on the strength was observed [17]. At the homologous temperatures of 0.4 T_m and 0.56 T_m (T_m being the melting temperature), the strength was reported to be 40% and 72% of the RT strength for NC Cu and Al, respectively [17]. In case of alloy systems such as NC multiphase Al alloys (Fe, Cr and Ti minor additions), a similar trend in loss of strength with temperature was reported for samples with the grain sizes of 50 and 80 nm tested at quasistatic rates. This significant loss in strength in the NC metal/alloy systems was attributed to the loss in nanocrystallinity (grain coarsening) [18–22] which led to the dislocation-based mechanism to be a dominant deformation mechanism at elevated temperatures [23].

In general, the thermal and mechanical stability of NC microstructures has been regarded low based on other experimental observations [19,24,25]. For instance, under thermal heating experiments, the pure NC Cu exhibits rapid grain growth to the micron-scale at just 100 °C [26–28]. Further, indentation studies at liquid nitrogen temperature revealed that NC Cu undergoes rapid grain growth, where the microstructure consists of grains as large as 700 nm (with sizeable volume fraction) after 30 min of dwell time in liquid nitrogen temperatures as compared to an average grain size of 20 nm [24]. These examples illustrate that, for nominally pure NC metals, the nanoscale microstructure is an inherent barrier to experimental studies of their properties even under relatively low temperature conditions. It is expected that more intense conditions, either thermal or mechanical, will result in a more rapid grain coarsening and a sudden loss of the material's intrinsic physical and structural features. Recently, alternative methodologies have been successfully employed to impart greater stability to NC metals. These methodologies are based on thermodynamic considerations [29–33] coupled with classical kinetic mechanisms [34]. Such techniques allow for the retention of the as-processed fine grain size, especially during high temperature consolidation. Hence, it may be stated that such methodologies establish the fabrication pathway and, thus the application of NC metals with desirable properties.

Recently, quasi-static and dynamic yield strengths of >1 GPa were measured in bulk samples of a NC Cu–Ta alloys, which could not be explained by grain size strengthening alone [35]. The increase in strength was attributed to the thermal decomposition of a non-equilibrium Cu rich Cu-Ta solid solution over a range of temperatures (700–900 °C), which led to the formation of a high density of small coherent Ta-rich nanoclusters (~2 nm in diameter) [35,36]. The presence of these Ta nanoclusters within grains and along grain boundaries resulted in strength levels approximately twice as high as those predicted by Hall–Petch hardening [37]. These studies suggest that the presence of Ta-based clusters play a commanding role in defining the deformation response as compared to the NC grain size alone. Therefore, in the present study, we examined the microstructural evolution, i.e., the underlying changes in the Cu matrix grain size and the corresponding Ta nanoclusters by in-situ transmission electron microscopy (TEM) heating experiments and atomistic simulations.

This work shows that the thermal stability achieved with this NC Cu-10 at.% Ta alloy diverges from those observed for conventional coarse-grained metals as well as other NC metals. That is, macroscopically, the microstructure (Cu grain and Ta based cluster size) of NC Cu-10 at.% Ta was morphologically stable in shape and size. However, local structural changes at the interface between the Ta based clusters and the Cu matrix have a significant effect on thermo-mechanical properties. Specifically, the misfit strain was found to decrease monotonically from 12.9% to 4.0% with increase in temperature, leading to a significant change in flow stress, despite which remains greater than all known NC metals.

2. Experimental details

High-energy cryogenic mechanical alloying was used to synthesize NC powders with a composition of Cu-10 at.% Ta using very high purity (99.9%), ~325 mesh size elemental Cu and Ta powders. The ball milling was carried out in a SPEX 8000M shaker mill at cryogenic temperatures (verified to be ~− 196 °C) using liquid nitrogen with a milling time of 4 h. The milling medium was 440C stainless steel balls and a ball-to-powder ratio of 5-to-1 by weight was maintained. Cryogenic mechanical milling resulted in an un-agglomerated powder mass with a particulate size range of 20 μm to 100 μm. The as-milled powders were placed into nickel cans and sealed inside the glove box. Prior to Equal Channel Angular Extrusion (ECAE), the die assembly was heated to 350 °C. The nickel cans loaded with as-milled powders were equilibrated (for 40 min) in a box furnace purged with pure Ar cover gas at 700 °C. The equilibrated cans were then quickly removed from the furnace, dropped into the ECAE tooling, and extruded at an extrusion rate of 25.4 mm/s using 90° rotations for four passes. This process resulted in dense 12 mm diameter rod samples with a stable initial grain size distribution. To identify the impurity content in these alloys, atom probe tomography was performed on the as-milled powder as well as the NC Cu − 10 at.% Ta ECAE sample processed at 700 °C where a minimal concentration of 1.25 at.% was detected for O. Fe contamination was detected using APT and varied between 0.05 at.% and 1 at.%, indicating a relatively impurity-free alloy [9].

Quasistatic compression tests were carried out over a temperature range from 25 °C to 400 °C using an INSTRON load frame with a 50 kN load capacity and a furnace rated up to 1800 °C. The pushrods of the load frame were constructed with precision machined ZrO_2 rods to minimize heat losses. The specimens were cylinders with a 3 mm diameter and 3 mm in length, machined using an electric discharge machine from the same sample batch. Boron nitride lubricated polished WC-disks were used as platens. The system was held at the testing temperature for about 30 min to attain equilibrium and thermocouples were attached on the specimen to monitor the temperature. Specimens were loaded under strain control with a strain rate of 0.1/s.

In-situ TEM heating experiments were carried out in the aberration corrected FEI-TITAN TEM at 300 kV using an Inconel heating holder and the temperature was monitored digitally. Aberration corrected ARM-200F operating at 200 kV was also used to acquire images, especially