Full length article

In-situ tracking the structural and chemical evolution of nanostructured CuCr alloys

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ABSTRACT

We report the thermal stability of supersaturated CuCr nanocrystallines alloys at the atomic resolution using modern spherical aberration-corrected transmission electron microscopy (TEM) via performing *in-situ* structural and spectroscopy experiments. It is found that CuCr nanocrystallines are not only subjected to a structural change but also undergo a chemical evolution upon annealing. Chemical destabilization of supersaturated CuCr nanocrystallines occurs at a quite low temperature. Heating triggers a rapid separation of Cu and Cr grains at the forced intermixing zone, accompanied by an obvious decrease of average interface width whereas the grain growth is not significant. Elemental profiles and images recorded in *real time* reveal that the local compositions vary with heating, which in turn permits to derive the concentration of excess vacancy generated by deformation and observe its evolution with temperature, further to analyze the dynamic behavior in nanocrystalline materials. Electronic structure changes at the interface forced intermixing zone are revealed by the fine structure analysis. The study uncovers the interplay between the thermal stability and chemical decomposition process of bulk nanostructured materials in *real-time*.

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Nanocrystalline (NC) materials which are of interest for both fundamental studies and engineering applications are recognized as substantially out of equilibrium. As a consequence they often rapidly coarsen at moderate temperature [1,2]. This coarsening tendency impedes the use of these materials at ambient and especially elevated temperatures [3,4]. The microstructure instability of NC materials is an important concern since it influences the resulting mechanical properties significantly. Especially, the large energy associated with the high volume fractions of GBs in NC materials represents a driving force for grain growth. Therefore, nano-grains in NC materials tend to coarsen. To address this important issue in NC materials, experimentally and theoretically attempts to find effective solutions to prevent coarsening have been made. Solute additions to NC metals can effectively retard the coarsening process but can't eliminate the tendency to coarsen [5]. Theoretically, thermodynamic-based approaches have been invoked to discuss the stability of NC materials, which to some extent are successful for some alloy systems [6–13]. More recently, by considering different parameters such as composition,

temperature, interaction parameters, enthalpies of segregation and mixing, formation of amorphous layers and two-phase nano-composites, Murdoch and Schuh [7] proposed a nanostructure stability map with regions of stability, meta-stability and instability in binary alloys. It seems very attractive to estimate the possibility of high temperature stability from thermodynamic parameters by using the regular solution approximation.

Substantial experimental studies of the thermal stability NC materials at high temperature have been carried out on metals and nanocomposites using a wide range of techniques, i.e. transmission electron microscopy (TEM), Electron-Energy-Loss Spectroscopy (EELS), atom probe tomography (APT), XRD and micro-hardness [14,15]. However, the experimental results seem divergent. The stability of NC materials differs from case to case when processed by different approaches. The thermal stability of NC materials related to different type of severe plastic deformation (SPD) is strongly influenced by the defects and stored energy generated from extreme deformation [16,17]. Among these, the studies by *in-situ* TEM are very promising to reveal the structural changes of NC materials in *real-time*. Grain growth and phase transformations can be directly visualized [18–20]. The recent experimental observation of grain growth in some NC materials during deformation

[21,22] also attracted new and increasing attention. The stability aspects of bulk nanostructured materials were reviewed [23,24], more recently by Andrievski [25], who summarized the advances on this topic.

Although numerous achievements have been accomplished, the stability of NC materials, particularly in severely plastically deformed (SPD) materials, is still in its infancy and requires further high -spatial resolution/atom-scale insights. To date, all the studies on the stability of NC materials hardly dealt with a high-spatial resolution or atomic-scale *in-situ* observation, and by tracking the chemistry and structural evolution simultaneously. Such investigations are definitely essential to demonstrate how the bulk NC materials evolve with temperature chemically and structurally, and to understand the mechanism of thermal stability at a high spatial resolution.

Unfortunately, it is experimentally quite challenging to study the chemical and structural variations of NC materials simultaneously because the grain size in NC materials is usually quite small. New opportunities enabled by modern spherical aberration (C_S)-corrected TEM with a sufficiently small probe and atomic-resolution to address this issue have appeared. The possibilities offered by modern instruments brought new inputs and fundamental understanding on deformation induced phenomena [26–30]. It is anticipated that new insights into the stability of NC materials will be gained with the advent of spherical aberration (C_S)-corrected TEM.

Here, CuCr nanostructured alloy was utilized for *in-situ* monitoring the structural evolution and chemical composition changes simultaneously. The motivation is based on two considerations. From practical application point of view, CuCr alloys are used in numerous aspects, i.e. railway contact wires [30] and electrodes for spot welding [31], and exhibit many extraordinary properties [32]. From scientific point of view, CuCr is a model system for studying the microstructure-properties relationship and thermal stability of nanostructured materials [33–38]. Especially, CuCr exhibits a positive Gibbs free energy change ΔG_c for forming a solid solution alloy in the equilibrium state and is therefore nearly immiscible in the solid state, but can form supersaturated solid solution after severely deformation [33–38]. Experimentally, CuCr is well suited for *in-situ* tracking chemical composition (distinct Cr-$L_{2,3}$ and Cu-$L_{2,3}$ absorption edges, facilitate quantifying the composition with high spatial resolution by EELS at elevated temperature) and structural variation (exhibiting a distinct intensity in Z (atomic number) contrast scanning TEM (STEM) imaging, the intensity is ~ Z^2).

1. Experimental section

1.1. Materials

A coarse-grained Cu-Cr composite material (43 wt % Cr, 57 wt % Cu, and corresponding to 48 at % Cr and 52 at% Cu, respectively) was deformed by high pressure torsion (HPT) at room temperature. The initial microstructure of the composite consists of a Cu matrix with Cr particles (volume fraction of about 50%, mean diameter of about 50 μm) produced by PLANSEE (Reutte, Austria), similar to those in Ref. [38]. Disks with a diameter of ~8 mm and a thickness (t) of ~0.8 mm were HPT deformed for different numbers of turns n under a constant pressure of 6.25 GPa with a rotation speed of 0.2 rotations/minute. And compressed air cooling was applied during the whole HPT process. HPT disks which were deformed for 25 turns (equal strains = 400) were used for *in-situ* annealing in TEM at 212 °C and 414 °C after preparing TEM specimens from the edge of the disk, where the highest strain has occurred.

2. Methods

TEM specimens were prepared by wedge Tripod polishing, and followed by final ion milling with 5–10 min. A TEM/STEM JEOL2100F operated at 200 kV and equipped with an image-side C_S-corrector and an image filter (Tridiem) was used. The alignment of the C_S-corrector was performed using the CEOS software based on the aberration measurements deduced from Zemlin tableaus. Eventually, the aberrations are sufficiently small. All HRTEM images shown here were recorded on a 2 k × 4 k pixel CCD camera at a magnification of 1.5 M × using an acquisition time of 1.0 s and a negative C_S, under which all atoms are imaged as bright dots with different bright contrasts depending on their atomic numbers.

STEM images shown in this paper were recorded using an annular STEM detector, with the detector inner angle/outer angle were set to around 54 mrad/144 mrad. Under these conditions, the STEM high-angle annular dark field (HAADF) image is nearly Z-contrast image.

The local composition variations with temperature were carefully measured by EELS using an Å-size electron probe. STEM-EELS spectrum-images were acquired using a dispersion of 0.2 eV/channel, a collection semi-angle of 10 mrad, and a convergence semi-angle of 7.5 mrad. The probe size under optimum conditions can reach 0.2 nm (or even smaller). Numerous EELS spectrum images were acquired during *in-situ* annealing. Drift compensation was applied when the spectrum images were acquired. The acquisition time for each spectrum is 0.5 s, and the total acquisition time is 15 s for one line-scan with a step interval of ~0.5 nm. For EELS spectrum images, the following process was performed. Firstly, multivariate statistical analysis (MSA) was applied to the raw data of all spectrum-images. Secondly, the background for each spectrum was removed using a power law function, and Hartree-Slater models were used to fit the L_2 and L_3 edges. The cross-sections were then subtracted within the signal window of 569.4–577.4eV for Cr-L_3 and of 578–586 eV Cr-L_2, respectively. To quantify the atomic ratio of Cr/Cu, the windows for background subtraction were set to 80 eV and 130 eV, and signal windows were set to 120 eV and 130eV for Cr and Cu respectively. All the spectra were analyzed under the same conditions, i.e. the same signal and background subtraction windows, in order to compare the change of Cr/Cu atomic ratio.

The initial microstructure was analyzed by TEM 30 days after HPT processing. *In-situ* heating in a TEM was carried out at three different temperatures, room temperature (25 °C), 212 °C for ~ 60 min (holding time), and 414 °C for ~ 60 min (holding time) using a Gatan heating holder. *Ex-situ* heating experiments were perfomed at the same temperature as for *in-situ*. In order to track the chemical composition evolution in *real time*, more than 30 interfaces and GBs were picked for extensive EELS spectrum image analysis. Some interfaces/GBs (about 20 interfaces) were then repeatedly measured at different annealing temperatures under an identical acquisition condition so that the compositional changes together with the structural evolution of the nanostructured materials were tracked with annealing temperature and time.

For determining the grain sizes, about 30 Cu particles with a distinguishable boundary were statistically measured. As the grain shapes are rather random and irregular, Cu grain sizes were then determined based on the STEM images using *Image J* software by measuring grain area changes. The grain areas were then converted into the average grain size $\overline{D}$, (the diameter of a spherical grain, see the details in supplementary materials, Fig. 2S). As the grain sizes are quite different over a large area, the error bar is a bit large, i.e. about 12 nm. The average grain size reflects the grain changes with the annealing. However, it should be noted that the Cu average