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# Quantifying the grain boundary segregation strengthening induced by post-ECAP aging in an Al-5Cu alloy

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ABSTRACT

Hardening on annealing (HOA) has been frequently observed in nanostructured metals and alloys. For nanostructured materials obtained by severe plastic deformation (SPD), HOA has been attributed to the reduction of dislocation sources within grains and grain boundary relaxation during annealing. In the present work, it is shown that when a bimodal grain structured (a mixture of micron-sized and ultrafine grains) Al-5Cu alloy prepared by equal channel angular pressing (ECAP) was subjected to post-ECAP natural and artificial aging treatments, the alloy shows a completely different precipitation behavior with an accelerated precipitation kinetics. No coherent θ'' or semi-coherent θ' precipitates form in the bulk of grains, while a large fraction of stable incoherent θ precipitates form along high angle boundaries. After artificial aging at low temperatures for a short time, a significant improvement of both ultimate tensile strength and uniform elongation was achieved without sacrificing the yield strength. A systematic microstructure characterization by EBSD, TEM and APT has been carried out to investigate the evolution of grain size, dislocation density and solid solution level of Cu as well as the precipitation of Al-Cu precipitates during natural and artificial aging treatments. A quantitative evaluation of different supposed strengthening mechanisms revealed that the segregation of Cu elements at grain boundaries plays a more important role than grain boundary relaxation and the dislocation source-limited strengthening to compensate the yield strength reduction caused by the decrease in dislocation density and solute content of Cu in solid solution.



## 1. Introduction

Severe plastic deformation (SPD) techniques, for instance, equal channel angular pressing (ECAP) [1–5], high pressure torsion (HPT) [6–8] and accumulative roll bonding (ARB) [9–11] have been widely applied to produce nanostructured metals and alloys. Here, nanostructured materials refer to materials comprising ultrafine grains (< 1 μm) and/or nano-sized grains (< 100 nm) [9]. The strength of nanostructured Al alloys prepared by SPD is superior to their coarse grained counterparts, which is mainly attributed to grain boundary (GB) strengthening and dislocation strengthening. In sharp contrast to the softening of coarse grained as-deformed materials subjected to annealing, an increase in yield strength accompanied by a reduction of ductility could be achieved in nanostructured metals by a short time annealing at low temperatures without recrystallization or significant grain growth, which is the so-called “hardening on annealing (HOA)” phenomenon [12]. Such a phenomenon has been found both in commercial purity (99.2 wt%) Al [10,12] and high purity (99.99 wt%) Al produced by ARB [11,13]. The HOA effect of the severely deformed metals was attributed to the reduction of the number of dislocation sources caused by the sinking of dislocations at closely spaced high angle boundaries (HABs).

Similar HOA effect has also been observed earlier in nanostructured commercial purity Ti [14], Al-1.5 wt% Mg [15] and $Ni_3Al$ [16] alloys processed by HPT, which was attributed to defect ordering at or near GBs [14–16]. Actually, defect ordering at or near GBs is in accordance with GB relaxation. GBs in UFG materials

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processed by SPD are often called "non-equilibrium" GBs, which are characterized by excess GB energy, presence of long range elastic stresses, higher diffusivity and enhanced free volumes [17–19]. The GB relaxation of non-equilibrium GBs has been proved by high resolution TEM studies [14–16,20], scanning force microscopy (SFM) studies [18], diffusion studies [21–23], dilatometry measurements [24] and differential scanning calorimetry (DSC) measurements [25,26], etc. Horita et al. [20] revealed that GBs are with a zigzag, highly stepped configuration in UFG copper. By using DSC, Detor and Schuh [25] found that the heat release scales directly with the GB area, indicating that such an exothermic peak is associated with a GB relaxation process. Divinski et al. [21] observed that GB relaxation induces a drastic change of the GB diffusion parameters at a temperature of ~400 K. Valiev et al. [15,16] suggested that the GB transparency can influence the strength of materials and non-equilibrium boundaries are more transparent, where the GB transparency is defined as a critical value of the applied stress for allowing slip to propagate through a given GB. During annealing, the relaxation of non-equilibrium boundaries happens, where the stored energy in the form of disorder or excess GB defects is released [25,27] and emission of dislocations from such relaxed GBs becomes difficult [28,29].

In fact, the HOA phenomenon is observed not only in the metals and alloys processed by SPD, but also in alloys deformed by traditional cold rolling. For example, after annealing at 225 °C for 10 min, the AA3103 alloy strip rolled to a strain of ~4.2 showed an increase in ultimate tensile strength (UTS) [30]. It was also found that the magnitude of the gained strength by HOA increased with deformation strains. The exact mechanism causing HOA was not identified, but it was suggested that atom clustering of solute elements may have played a role [30].

The HOA phenomenon has also been observed and extensively studied in dislocation-free nanocrystalline metals and alloys. For example, Ni [31], Ni-W [25,32] and Ni-Mo [26] alloys prepared by the electrodeposition method. Different from the nanostructured materials produced by SPD, the HOA phenomenon in electrodeposited dislocation-free nanocrystalline materials has been attributed to GB stabilization through GB relaxation [25,26] and/or GB segregation of alloying elements [26], which leads to the deformation mechanism change from GB-mediated processes [33–36] to generation of extended partial dislocations from GBs [26,37]. Nowadays, GB segregation has been applied as an effective strategy to stabilize the grain structure of nanocrystalline materials by lowering the GB energy [38–42].

In the present work, the aim has been to further explore the strengthening mechanisms of the HOA phenomenon in SPD processed alloys, and thus post-ECAP aging treatments at low temperatures have been conducted on a bimodal structured Al-5 wt% Cu alloy [43] produced by ECAP at room temperature (RT). Systematic investigations on the evolution of grain size, dislocation density, solid solution level of Cu and precipitation of Al-Cu precipitates during post-ECAP aging have been done. It is shown that GB segregation has a strong strengthening effect to the SPD processed alloys in addition to the GB relaxation and dislocation source-limited strengthening.

## 2. Experimental

The binary Al-5 wt% Cu alloy used in this study was prepared by melting the commercial purity Al and Cu. Prior to ECAP, solution heat treatment was conducted on the Al-5Cu bars with dimensions of 100 mm × 19.5 mm × 19.5 mm, using a salt bath furnace at 500 °C for 3 h and then at 540 °C for 24 h followed by water quenching. Then, these bars were processed by ECAP through a 90° die at RT. Route A was employed, which means that samples were pressed without rotation between each pass, leading to an imposed equivalent strain of ~1.0 per pass [1]. To lower the friction during pressing, samples were coated with a thin layer of graphite lubricant. The ECAP samples were processed up to four passes, which were labelled as 4P. The as-deformed (4P) samples were stored at RT for half an hour, and then artificially aged in an oil bath at 120 °C, 150 °C and 185 °C for different times.

Samples for microstructural characterization, hardness and tensile test measurements were cut from uniformly deformed regions of the ECAP processed bars, as shown in Fig. 1. Microstructure and composition analyses were carried out by means of electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), scanning precession electron diffraction (SPED) and atom probe tomography (APT). EBSD analyses were conducted on the longitudinal (ND-ED) cross section of the samples. The EBSD samples were prepared by mechanical grinding and then the sample surfaces were electro-polished through the Struers Lectropol-5 electropolisher, using a solution of 80% ethanol ($CH_3CH_2OH$) and 20% perchloric acid ($HClO_4$) at 20V, −30 °C for 17 s. Prior to the EBSD examination, the sample surfaces were ion-milled (Hitachi IM-3000 Flat Milling System) at 3.5 V for 45 min. EBSD was conducted in a Hitachi SU-6600 field emission gun-scanning electron microscope (FEG-SEM) equipped with a Nordif EBSD detector and the TSL OIM software. The operating parameters: voltage 20 kV, working distance 25 mm, sample tilt angle 70°, step size 0.05 μm. Thin foils for TEM were prepared by twin-jet electro-polishing (Struers TenuPol-5 electropolisher) using a solution of 33% nitric acid in methanol at −30 °C.

TEM imaging was carried out using the JEOL 2100 TEM at 200 kV. STEM, STEM-EDS and SPED mapping were performed using the JEOL 2100F at 200 kV, equipped with the NanoMegas ASTAR system. STEM was operated in the analytical mode with a 1.0 nm probe size. EDS analysis was carried out in the STEM mode. TEM-SPED is operated in the nano-beam diffraction mode, with condenser aperture: 10 μm, nominal probe size: 1.0 nm, and alpha setting: 4. The step sizes used in the present study have been indicated in the figure captions. Needle-shaped samples for atom probe tomography (APT) were prepared by a standard two-stage electro-polishing technique [44]. APT was performed in a CAMECA LEAP 4000 HR type local electrode atom probe at a temperature of 50 K with a pulse fraction of 15%, a pulse rate of 200 kHz and a detector efficiency of 36%. Reconstruction and quantitative analysis of the APT data were performed using the IVAS™ 3.6.12 software.

Electrical conductivity (EC) was measured at RT using a Foerster Sigmatest 2.069 portable instrument. The measurements were performed by contacting the probe on a clean and planar sample surface, which was prepared by grinding with SiC papers down to 1200 Mesh. Mechanical properties were characterized by both hardness and tensile tests. Vickers hardness measurements were performed using a DVK-1S Vickers hardness testing machine under

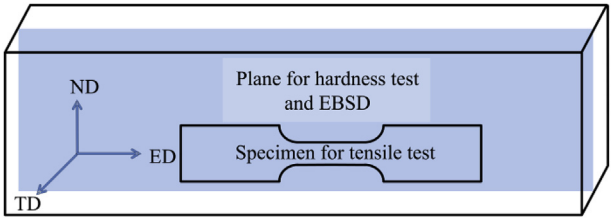


**Fig. 1.** Sketch of the sample for ECAP. ND, TD and ED are abbreviations of the normal, transverse and extrusion directions, respectively. The regions for EBSD observations, hardness and tensile tests are also indicated.