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Elucidating microstructure of spinodal copper alloy through annealing

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ABSTRACT

Improvement in the characteristics of a polycrystalline material is done through engineering of microstructures. Spinodal decomposed copper alloy has been annealed at high temperature with systematic variation in time on multiple specimens. Extensive electron backscatter diffraction experiment was carried out to understand the grain boundary characteristics and morphologies of the alloy as a function of annealing time. The logical variation of annealing time strongly influences diffusion induced grain characteristics such as, shape, size, geometry, inclination, density, types, distribution, misorientations and the nature of subsequently induced twinning morphologies.

1. Introduction

Grain boundaries are two-dimensional defects and important origin of microstructural heterogeneity in polycrystalline materials [1]. They play crucial roles in deformation, fracture, phase transformation and other associated metallurgical phenomena in most of the polycrystalline alloys. When the degree of heterogeneity increases, metallurgical phenomena associated with these grain boundaries can take place locally [2]. Quantitative analysis of polycrystalline microstructure is a fundamental problem in material science. According to Watanabe et al. [1], grain boundary deformation and fracture control the bulk mechanical properties of polycrystals. Altering grain boundary character distribution (GBCD), as a relatively new microstructural parameter, can effectively alter material's properties. This was originally proposed by Watanabe in the early 1980s, the elegant concept, “grain boundary design and control” which has been referred to as grain boundary engineering (GBE) [3,4]. Elucidating microstructural development is recently one of the most crucial tasks in material science. The conventional concept of grain growth, derived from coarse-grained polycrystalline materials research [5], is that the process is driven by reduction of total grain boundary area in the material. GBE is manipulation of relative extent of *special* boundaries to improve materials' properties [6].

Spinodal decomposed copper alloys, such as Cu-9Ni-6Sn and Cu-15Ni-8Sn are extensively used as excellent spring materials, often employed in high performance electronics applications, connectors, bearing material in aerospace components, ground engaging machinery, tribologic parts for mechanical systems, mining equipments, oil and gas exploration components, internal combustion engines etc. [7–9]. These alloys are poised to meet current demands for superior combinations of strength, toughness, tribology, formability, fabricability, corrosion resistance and improved reliability [9]. Materials for electrical applications such as lead frame and connectors are generally required to have high strength, low elastic modulus as well as good electrical conductivity. Therefore, copper-based alloys are widely being utilized for applications due to their high electrical conductivities. The strength of these materials can be enhanced by employing various common techniques such as GBE, strain hardening, solid solution hardening, quench hardening, dispersion strengthening and precipitation hardening [10]. Spinodal decomposition in Cu-9Ni-6Sn alloys triples the yield strength (YS) of base metal and results from coherency strains produced by uniform and high-number density dispersion of Sn-rich perturbations in Cu-matrix.

Considerable experimental evidences are available in the published domains, which demonstrate that grain boundary structural transformation induced by temperature can cause significant influence on grain boundary energy, migration, sliding and segregation [1]. According to Watanabe et al. [1], diffusion controlled grain boundary phenomena depend on grain boundary character and structure at high and low temperatures. Watanabe et al. [1] in their pioneering work showed that low energy grain boundaries have higher thermal stability than high energy random boundaries, dependent upon grain boundary misorientation and temperature. Therefore, it is possible that thermal stability of grain boundary microstructure of a polycrystalline material may be controlled by managing the fraction of low energy grain boundaries with higher thermal stability, i.e., GBCD. Generally polycrystals undergo

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microstructural changes to reach a lower energy state so as to reduce total grain boundary energy [11].

Improving the physical and mechanical properties of polycrystalline alloys, and thereby increasing their performances, by adapting and controlling the microstructure has been of considerable interest to material scientists and engineers for last decades. In view of above literatures finding, the grain boundary details (i.e., rearrangements, modifications etc.) and their geometries have been quantitatively analyzed in current research by methodically varying annealing time of a spinodal decomposed Cu-9Ni-6Sn alloy at high temperature. Thus, the goal of this work is to evaluate the polycrystalline microstructure by GBE through systematic annealing treatment.

2. Experiments

2.1. Alloy

The alloy was prepared in an induction melting furnace with verified nominal chemical compositions of Cu-9%Ni-6%Sn (wt.%) under inert atmosphere. The extent of impurities (i.e., oxygen, aluminium, silicon, carbon etc.) evolved during melting were very negligible in the cast alloy. This alloy was homogenised at 800 °C for about 2 h (according to sample size) and subsequently quenched in normal room temperature water. Homogenised alloy was then subjected to cold work treatment from 16 mm diameter rod to 4 mm thick sheet (about 25% reduction approximately). The cold rolled alloy was further annealed to 800 °C for about 30–45 min (according to sample size) and subsequently water quenched. Second stage of cold rolling was performed from 4 mm thick sheet to 2 mm thick sheet (about 50% reduction approximately). After that, multiple specimens were extracted from 2 mm thick sheet and annealed individually (seven different samples) at 850 °C for different time periods (in between 15 and 3600 s) followed by water quenching. These specimens have been used for different microstructural entity measurements under Field Emission Gun-Electron Backscatter Diffraction (FEG-EBSD).

2.2. Hardness

The hardness of all orderly annealed samples with various time intervals was measured by Vickers hardness tester. The load was 30 kgf and dwell time was maintained for 15 s. For each specimen, five readings were taken to get the statistics of hardness measurement data.

2.3. Metallography

Specimens for generating microstructure were extracted from all the annealed blocks. Samples for FEG-EBSD experiments were first prepared by mechanical grinding with waterproof silicon carbide paper up to 2000 grits. Conventional metallographic technique was employed throughout for sample polishing. The plane grinding was followed by chemical-mechanical vibratory polishing with a mixture of colloidal silica (OP-S) suspension and distilled water for prolonged duration. All the conventionally (metallography) polished samples were ultrasonically cleaned followed by acetone washing. Electro polishing was performed by using electrolyte of mixture HNO_3:$CH_3OH = 1:3$ maintaining the bath at 0 °C throughout with voltage 12 V (DC) to acquire mirror surface finished samples.

2.4. Electron Backscatter Diffraction

The grain boundary microstructures of all annealed samples were quantitatively examined under FEG-SEM-EBSD instrument equipped with orientation imaging microscopy (OIM) and HKL Channel 5 software. The OIM observations were conducted at an operating voltage of 20 kV. The step size of all scans was maintained constant to 1.0 μm with a square grid. Approximately, >5000 grains were framed and scanned for all the annealed samples. In general, the pattern (FCC phase) indexing quality was very high (>90%) and consistent for all the frames scanned. All scanned frames were analyzed *off-line* by using HKL Channel 5 software. In this study, grain boundaries with $1 \leq \Sigma \leq 29$ have been defined as coincidence site lattice (CSL) boundaries [12] and Brandon's criterion, $\Delta\theta = 15/\Sigma^{0.5}$ [13] has been used to categorise the grain boundaries. In current experiments, the annealing twins in FCC phase included coherence and incoherence twins. Although the grain boundary energy is not fully predicted by Σ value ≤29, there has been much experimental evidences that CSL boundaries with exhibit a higher resistance to grain boundary degradation than random boundaries [14,15]. Strictly speaking, the grain boundary structure is determined by boundary plane orientation as well as grain boundary relative misorientation relationship (the rotation axis and misorientation angle) [16]. In current investigation, grain boundaries with $\Sigma \leq 29$ were classified as CSL boundaries with low energy, the others as random boundaries with high energy.

The grain boundary microstructural properties such as grain size, grain boundary misorientations and GBCD have been evaluated on the basis of experimental OIM data. The standard terminology for GBCD analysis used here are: low angle grain boundaries (LAGB), medium angle grain boundaries (MAGB), high angle grain boundaries (HAGB), coincidence site lattice boundaries (CSLB) and Σ3 CSL. In the present study, LAGB is defined as boundaries with ≤10° misorientation, MAGB is in the range of 10–30° and HAGB is in the range of >30° which has been taken into account according to the study of Kumar et al. [17]. Since the experimental accuracy for orientation evaluation by EBSD method commonly does not exceed 1.0°, grain boundaries below 2.0° were excluded from the consideration. All the twin related grain boundaries (i.e., Σ3, Σ9, Σ27) were also examined and quantified to elucidate microstructure.

3. Results and Discussion

3.1. Grain Size

Fig. 1 shows Euler images of the orderly annealed samples (longitudinal sections) at various time intervals. It is visually noted that with increase in annealing time, there is logical variation in grain geometries (i.e., size, shape, aspect ratio and distribution) with their respective orientations. Different colors of polycrystalline grains designate different orientations of FCC polycrystals. In the polycrystalline alloys, grain size serves as an internal microstructural scale, which correlates with yield strength (YS) via the well-known Hall-Petch equation. Grain size, shape, aspect ratio and density changes with annealing time and are attributed to diffusion induced grain growth due to orderly annealing treatment at different time intervals. From visual impressions, it can be seen that with increase in annealing time, grain size is increasing significantly. Considerable amount of annealing twins is also observed in all cases. Annealing time helps the polycrystalline grains to grow. During grain growth, average grain size must increase as a result of grain boundary migration and invasion of dominant grains to surroundings. Normally, certain grains can preferentially grow in certain direction resulting in anisotropic grain growth. It is well known that migration behaviour of grain boundaries strongly depends upon the type and structure of grain boundaries. Fig. 2 shows grain size (intercept length) distribution plot as a function of annealing time. For two samples (15 and 30 s), it is represented that there are high peaks at grain sizes of approximately 5–8 μm. For rest of the samples, the peak heights have been drastically reduced and they are found to be varied scientifically with the variation of annealing time. In these cases, the peaks are observed at grain sizes ranging 10-25 μm. For the first two samples (15 and 30 s), similar kind of grains (i.e., size, geometry and shapes) are found and for the rest of samples, grain size (i.e., peak positions) is found to be consistently increased with increasing annealing time. This may be attributed to high grain boundary mobility at higher annealing time at