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Evolution of microstructure and grain boundary character distribution of a tin bronze annealed at different temperatures

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ABSTRACT

Specimens cut from a rolled tin bronze sheet were annealed at 400–800 °C for 1 h and evolution of their microstructures was then characterized in details by electron channeling contrast imaging and electron backscatter diffraction techniques. Particularly, statistics on special boundaries (SBs) with $\Sigma \leq 29$ and network connectivity of random high angle boundaries (HABs) in the annealed specimens were examined to probe optimization potentials of grain boundary character distribution (GBCD) for this material. Results show that the deformed microstructure in the as-received material begins to be recrystallized when the annealing temperature increase to 500 °C and average grain sizes surge with further increasing temperatures. As a result of the recrystallization, a large number of annealing twins (with $\Sigma 3$ misorientation) are produced, leading to remarkably increased fractions of SBs (f_{SBs}). Thanks to preexisting dense low angle boundaries, the majority of SBs in the 500 °C specimen with only partial recrystallization are $\Sigma 3_{ic}$ (incoherent) boundaries, which effectively disrupt connectivity of random HABs network. Although the f_{SBs} can be further increased (up to 72.5%) in specimens with full recrystallization (at higher temperatures), the $\Sigma 3_{ic}$ boundaries would be replaced to some extent by $\Sigma 3_c$ (coherent) boundaries which do not contribute directly to optimizing the GBCD. This work should be able to provide clear suggestions on applying the concept of grain boundary engineering to tin bronze alloys.

1. Introduction

For polycrystalline materials, grain boundary has long been recognized as one of the most significant microstructural features that could be widely related to various physical and chemical properties for engineering application. In the early 1980s, Watanabe [1] proposed the concept of "grain boundary design and control" and demonstrated that improved resistance to intergranular fracture was attainable by increasing the proportion of "special" boundaries (SBs) in brass. The SBs were generally referred to as coincidence site lattice (CSL) boundaries with $\Sigma \leq 29$, where the Σ represents the reciprocal density of coinciding sites. The concept was soon adopted by many researchers and became more commonly known as "grain boundary engineering" (GBE) [2]. Moreover, in addition to achieving absolutely high fractions of special boundaries, recent studies demonstrated that their topological characteristic (network connectivity) was a more direct predictor for resistance to intergranular degradation [3].

Compared with random high angle boundaries (HABs, $\Sigma > 29$), low Σ-CSL boundaries are called SBs because all of them are believed to possess intrinsically special properties like low boundary energies [2]. Nevertheless, in practice, most successes of GBE applications in property improvement could be attributed to $\Sigma 3^n$ ($1 \leq n \leq 3$) boundaries. The $\Sigma 3$ class includes both coherent and incoherent annealing twins, plus other boundaries having a $\Sigma 3$ misorientation (60°/<111>). Therefore, the GBE is mainly applicable to low or medium stacking fault energy (SFE) face centered cubic (fcc) materials in which annealing twins could readily form after thermomechanical processing [4–5]. In this respect, to date, significant achievements have been reported for engineering materials such as Ni-base alloys [6–8], Pb-base alloys [9–10], austenitic stainless steels [11–13] and Cu-Zn (brass) alloys [14–15]. Improved properties for them include, but are not limited to, strength, ductility, creep, weldability, stress corrosion cracking and intergranular damage resistance [2].

Tin bronze (Cu-Sn-based alloy) is an important class of alloys which can be used for pump impellers and valves thank to their moderate wear- and corrosion-resistance [16]. Major constituents in most tin bronzes are usually α phases (Sn solid-solutioned in Cu), also with an fcc structure and relatively low SFE. One may thus expect enhanced properties for tin bronzes by means of optimizing microstructures through the GBE treatments. Unfortunately, our literature survey indicates that very few efforts have been attempted in this respect. In this work, therefore, a tin bronze with essentially complete α phase was

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selected and heat treated at various temperatures, followed by detailed microstructural characterization by electron channeling contrast (ECC) imaging and electron backscatter diffraction (EBSD) techniques. Particular attentions were paid to annealing twins and related grain boundary character distribution, aiming at preliminarily probe possible potentials of the GBE for this type of materials.

2. Experimental

The as-received material was a cold-worked tin bronze plate with its chemical composition listed in Table 1. As Sn was the predominant alloying element (~6 wt%), melting point of the bronze was roughly estimated to be about 850 °C according to the Cu-Sn binary phase diagram [17]. Specimens with dimensions of 20, 9 and 3 mm along rolling, transverse and normal directions (denoted as RD, TD and ND, respectively) were cut from the as-received plate. The specimens were then annealed at temperatures from 400 °C to 800 °C for 1 h, followed by quenching into water. Accordingly, those specimens would be named after their annealing temperatures in the following.

Microstructures of the RD-ND plane of the specimens as-cut and heat-treated were characterized by ECC imaging and EBSD techniques in a Zeiss Sigma HD field emission gun scanning electron microscope (SEM). The ECC images have been manifested to be capable of well charactering grain morphologies and various structural defects [18–20]. They should also be adequate to reveal microstructural features like annealing twins in the annealed tin bronze. On the other hand, quantitative crystallographic orientations of grains and their boundaries were able to be acquired with high reliability by the EBSD. More specifically, the EBSD-based orientation imaging microscopy allows fractions of different types of grain boundaries and their network connectivity to be measured conveniently [21]. The EBSD system employed in this work was composed of an Oxford Instruments NordlysMax^2 detector, with AZtec 3.1 and HKL Channel 5 software used for data acquisition and postprocessing, respectively. Step sizes used for the EBSD scanning varied from 0.25 to 2 μm, depending on grain sizes in different specimens. Fractions of various grain boundaries were measured on the basis of the length fraction by dividing pixel numbers of a particular boundary by those of all grain boundaries. The Brandon criterion [22] i.e., $\Delta\theta_{\max} = 15°\Sigma^{-0.5}$, was adopted for the critical deviation in determining special grain boundaries. Prior to ECC and EBSD examinations, all specimens were mechanically ground using SiC paper (3000# at the final step) and then electro-polished in a mixed solution of 70 vol% phosphoric acid and 30 vol% distilled water at 9 V and −20 °C for 90 s.

3. Results and discussion

Fig. 1 presents direct microstructural observation (ECC images) for the as-received specimen and those annealed at various temperatures. It is found that the as-received specimen can only be imaged with largely blurred contrasts, as shown in Fig. 1a, suggesting presence of plenty of structural defects like dislocations. Similar ECC images have also been noticed for other deformed metals [23]. In addition, dense thin twins are also observed inside several grains in Fig. 1a, most of which could be classified as deformation twins according to their morphologies [24]. A further observation at a higher magnification for the deformed microstructure of the as-received specimen is presented in Fig. 2a. Clearly, contrast non-uniformity induced by dislocation slip and grain subdivision caused by deformation twinning (down to a few tens of nanometers in width) can be confirmed. Nevertheless, rather clear boundaries (still straight) of prior grains, as revealed in Fig. 2a, suggest only a small amount of deformation (with precise value unknown).

Table 1
Chemical composition of the tin bronze (in wt% ± ~50 ppm).

Sn	Ni	Zn	Fe	As	Pb	Al	Mn	Cu
5.98	1.05	0.75	0.18	0.04	0.03	<0.01	<0.01	Bal.

For the 400 °C specimen, compared with the as-received specimen, Fig. 1b reveals essentially unchanged microstructures. After increasing the annealing temperature to 500 °C, occurrence of partial recrystallization can be noticed in Fig. 1c, as suggested by those grains with uniform contrasts. Concomitantly, annealing twins with typical morphologies [25] are frequently found inside the recrystallized grains. Widths of the annealing twins are generally a few micrometers. Besides, Fig. 1c also shows a number of unrecrystallized areas, as indicated by arrows. A magnified observation for both recrystallized and unrecrystallized structures (the black box in Fig. 1c) is exhibited in Fig. 2b, from which a scenario of recrystallization nuclei growing into deformed regions is seen. Behind the migrating boundaries, annealing twins are found to be formed immediately (Fig. 2b). For other specimens annealed at higher temperatures (600–800 °C), full recrystallization is confirmed from Fig. 1d–f, with annealing twins extensively presented inside recrystallized grains as well. Noticeably, with rising temperatures, an increasing trend in grain size can be found. In the ECC images of all specimens, there are also a number of black dots with their sizes and distributions essentially independent on the annealing temperatures. Composition measurements for them always reveal Ni and Fe, suggesting that they correspond to some stable second phase particles.

Quantitative measurements for grain sizes in all specimens are further made based on EBSD data and displayed in Fig. 3. Note that the grain size is represented by a circle-equivalent diameter of an area enclosed by high angle boundaries (HABs, $\theta > 15°$), with the 60°/<111> misorientation (annealing twin) disregarded. One can see that the average grain sizes for the as-received and the 400 °C specimens are very close (about 5.0 μm), consistent with the microstructural observation in Fig. 1a and b. For the 500 °C specimen, though considerable recrystallization has occurred (Fig. 1c), the grain size measurement still reveals an essentially unchanged average value, compared with that of the as-received specimen. It is easy to conceive growth for recrystallized grains through HABs migration at the expense of deformed structures (Fig. 2b). In the meanwhile, new recrystallization nuclei (usually submicron in size) and surrounded HABs could be continuously produced by subgrain coalescence in the unrecrystallized regions. The combination of both processes is believed to account for the stability of the average grain size in the 500 °C specimen. For the fully recrystallized specimens, i.e. those annealed at temperatures of 600–800 °C, the EBSD-based grain measurements reveal larger average sizes, in agreement with ECC images in Fig. 1d–f. Moreover, the annealing temperature is found to have exerted a very significant effect on the recrystallized grain size, which surges to 39 μm from 7.8 μm after increasing the temperature to 800 °C from 600 °C.

Fig. 4 is an EBSD inverse pole figure (IPF) map revealing reconstructed grain morphologies in various specimens. Their grain orientations are indicated by colors according to the standard triangle (the inset in Fig. 4b), while HABs and low angle boundaries (LABs, $2° < \theta < 15°$) are represented by black and white lines, respectively. In most grains of the as-received specimen (Fig. 4a), presence of dense LABs confirms the occurrence of substantial dislocation slip, as suggested by the ECC image in Fig. 1a. Also, a number of twin-like lamellae can be seen, which should correspond to either prior annealing twins (preexisting before deformation) or deformation twins. Since the latter could be ultra-thin (nanoscale as revealed in Fig. 2a), some of them may have been omitted due to the compromised step size selected for the EBSD scanning (0.5 μm in Fig. 4a). In regard to crystallographic orientations, Fig. 4a also reveals that <111> of most grains (colored in blue) are aligned parallel to the TD (<111>∥TD texture). For the 400 °C specimen, Fig. 4b shows a highly similar microstructure in all aspects to that of the as-received specimen, again confirming a minimal effect of annealing at such low temperatures. A markedly decreased density of LABs could be