



Synthesis of dual phase bronze alloys from elemental nanoparticle constituents

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Abstract

Dual phase ($\alpha + \beta$) copper–tin alloys were synthesized from elemental nanoparticle precursors following consolidation, annealing and quenching steps. The precursors were derived from the sequential reduction of tin and copper salts in ethanolic solution. The dual phase microstructure exhibits a duplex character with a mixture of Cu-rich and Sn-rich ($\alpha + \beta$) regions.

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1. Introduction

Nanoscale bronze alloys are of potential interest for a number of applications ranging from composite materials design to solid-oxide fuel cell technology to shape memory effects [1–7]. Examples of nanoscale alloy synthesis, such as nanoscale AuSn compounds synthesized by vapor deposition methods, have been reported in the literature [8,9]. To date, synthesis of nanoscale alloys has often involved specialized equipment, such as UHV chambers and high energy radiation sources [10,11]. Recently, Wolfenstein and co-workers synthesized the η phase of copper–tin (45at.%Sn) for a rechargeable battery application by a co-reduction of divalent Cu and Sn salts using aqueous borohydride [12]. Their bottom-up approach utilizes well known routes of nanoparticle synthesis (For example, see the work of Brust and co-workers [13]). It occurred to us that heterogeneous mixtures of un-reacted, nanoscale elemental constituents could, when heated, yield a variety of bronze alloys while possibly limiting grain growth. In this report, the diffusional reaction of heterogeneous mixtures of

nanoscale elemental constituents is demonstrated to be effective in yielding dual phase microstructures with grain structures below the micron level.

2. Experimental methods

Anhydrous Sn(II) (98% pure) and Cu(II) (97% pure) chlorides were obtained from Aldrich. Sodium borohydride was obtained from Acros (98% pure). Absolute ethanol (Aaper) was purged with dry nitrogen, degassed, and stored over Linde type 4A molecular sieves prior to use. All manipulations were conducted under a nitrogen atmosphere. In a typical synthesis of the nanoparticles, 5 ml of a 31.5 mM Sn(II) solution was added via syringe to a solution of excess borohydride (ca. 20 ml, 0.2 M) with stirring. The solution became slightly yellow upon initial addition, then turned grey and opaque over the 20 s during which the stannous solution was added. At this point, 5 ml of 154 mM Cu(II) solution was added by syringe (ca. 20 s), forming an agglomerated black precipitate. The product was ultrasonically mixed for 30 min using a Branson Model 1250 ultrasonic cleaner to facilitate dispersion of the colloids and then centrifuged. The supernatant was discarded, and the product was washed with degassed ultrapure H₂O (Millipore) to remove NaCl. The insoluble material was

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then ultrasonically mixed in the ultrapure water for 15 min, centrifuged, and the supernatant was again decanted. The aqueous washing was repeated, and then the product was re-dispersed in absolute ethanol and dried under streaming N_2 . The dried material was cold-worked by passing it once through a rolling mill to consolidate the heterogeneous mixture of nanoparticles. The initially black nanoscale powder was transformed into a copper-colored disk after this single pass. The sample was then placed in a sealed tantalum foil envelope and ramped up to 700 °C over 20 min, then held at 700 °C for 2 min. It was then quenched rapidly into an ice-water bath. After this treatment, the material exhibited a yellowish color typical of a bronze. The solid was further characterized by X-ray diffraction (XRD) using a Scintag PADV X-ray powder diffractometer; scanning electron microscopy (SEM) using a JEOL JSM6100 scanning electron microscope; and by transmission electron microscopy (TEM) using a Philips CM200 Ultra-twin and a JEOL 200CX-II transmission electron microscopes. TEM sample preparation for powdered material consisted of dispersing the powder to be analyzed in methanol, and placing a drop on an amorphous carbon grid, followed by vacuum drying. The annealed material was prepared by thinning in an ion mill.

3. Results and discussion

Powder XRD patterns, SEM images and TEM examination were used to determine the phase identity and compositions in the samples during various stages of the synthesis. Fig. 1 is the XRD pattern of the precipitated, dried nanoparticles prior to cold-working and heating. Both elemental tin and copper peaks are resolved with no evidence of a crystalline oxide. Using the Scherrer equation [14], the particle sizes for tin and copper were estimated to be 90–120 nm and 10–30 nm,

respectively, over a range of samples. The TEM image of the same material in Fig. 2a confirms the size estimate and reveals that the elemental nanoparticles are arranged into aggregates with sizes of the order of hundreds of nm. Different areas of the sample that were analyzed by electron diffraction, which indicated that the larger, darker features in Fig. 2a are tin, and the smaller aggregates are copper. Evidently there was an effective mixing of the component aggregates.

The effectiveness of the consolidation is illustrated in Fig. 2b that is a backscattered electron image of the cold-worked material prior to annealing. Following consolidation by cold rolling, the mixed aggregate array exhibited some larger scale agglomeration and yielded a few elongated micron size Sn regions as well as the finer as-synthesized Sn aggregates that were fairly well dispersed within the Cu matrix. For the cold-worked and annealed (700 °C for 2 min) material, Fig. 3 shows an XRD powder pattern consistent with FCC and BCC crystal structures, which were identified as the α and β phases [15]. Using a Nelson–Riley function to analyze the peak positions [14], it was determined that the lattice parameters for the α and β phases are 0.3696 and 0.2982 nm respectively. It is noteworthy that the lattice parameter values correspond to an α phase composition of about 8at.%Sn and a β phase composition of about 14at.%Sn respectively [16]. Moreover, the α and β phase compositions are close to the values expected for the tie line end points in the ($\alpha + \beta$) two-phase field at 700 °C [16]. This also indicates that complete reaction of the elemental components has occurred to yield an overall alloy composition in the two-phase ($\alpha + \beta$) region.

Fig. 2c, a backscattered electron image of the annealed material, reveals the two-phase microstructure. A closer inspection of the microstructural morphology that is evidenced in Fig. 2c demonstrates that the apparent Cu-rich and Sn-rich regions that are indicated by the back-scattered imaging do not represent the actual two-phase microstructure. Instead, higher resolu-

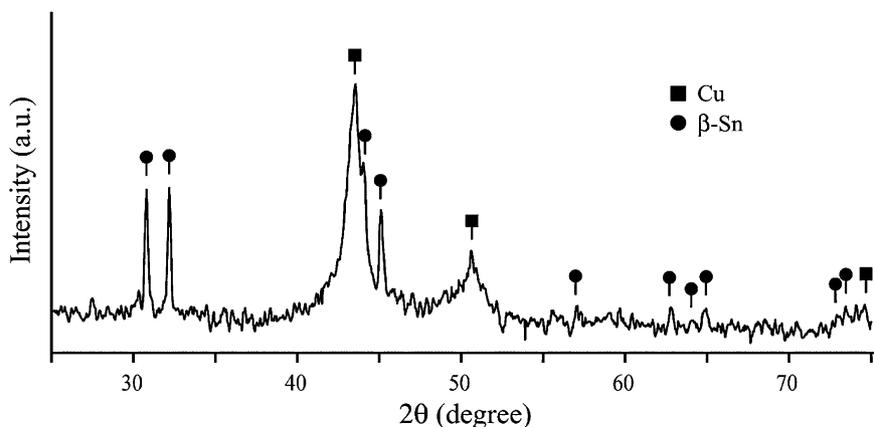


Fig. 1. XRD pattern of the precipitated, dried nanoparticles.

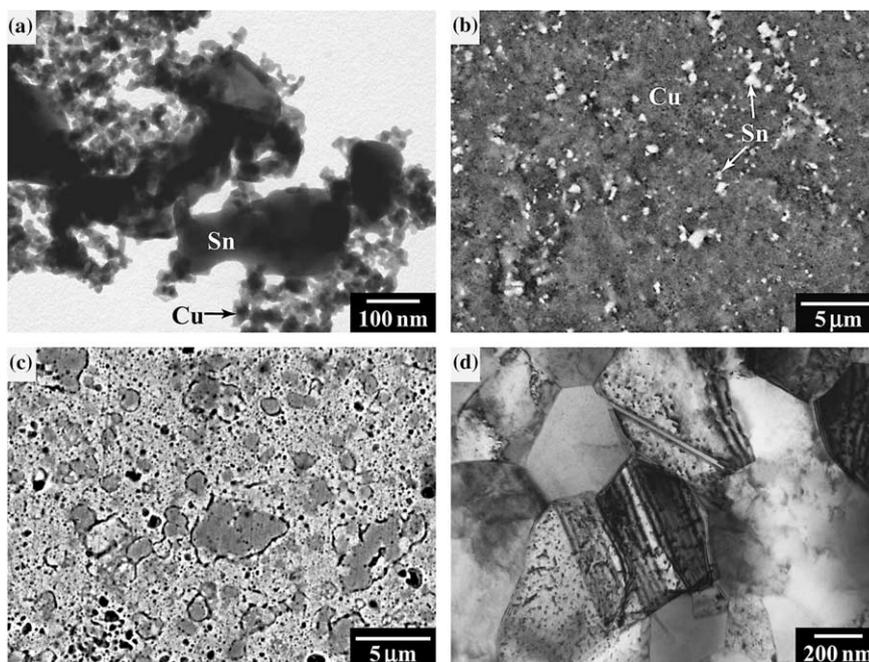


Fig. 2. (a) Bright field image of the precipitated, dried product, (b) backscattered electron image of as-rolled material, (c) backscattered electron image of the annealed material, and (d) bright field image of the annealed material.

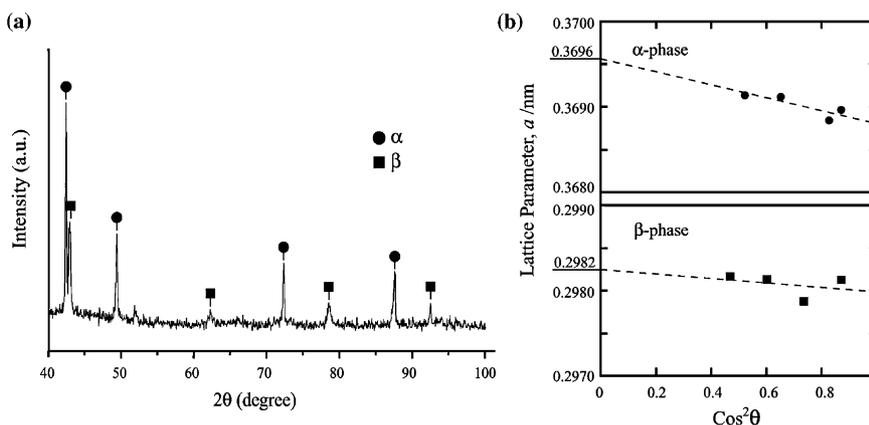


Fig. 3. (a) XRD pattern of the annealed material, and (b) a refinement in the lattice parameter measurements for the α and β phases.

tion TEM reveals that each region in Fig. 2c is actually a two-phase mixture of the α and β phases; a representative TEM micrograph is shown in Fig. 2d. In other words, there is a duplex morphology of two-phase regions consisting of a Cu-rich ($\alpha + \beta$) region and a Sn-rich ($\alpha + \beta$) region. Moreover, the size scale of the duplex morphology is comparable to that for the Sn-rich and Cu-rich regions in the consolidated, un-reacted sample (Fig. 2a). It is also evident from the relatively sharp diffraction peaks in Fig. 3 and the equilibrated two-phase morphology in Fig. 2d that on a local scale the reacted sample has the appearance of a well annealed microstructure structure with a well dispersed two-phase array. There is no clear indication of transformation of the β phase. Since the β phase for a Cu-14at.%Sn composition in bulk samples has been

reported to form martensite products upon quenching to room temperature [16], the stabilization of the β phase in the present work is an intriguing result. Further, the α phase grains also reveal annealing twins that is again characteristic of an equilibrated microstructure. However, on the larger scale of the image area in Fig. 2c, the microstructure is represented by a mixture of two-phase regions with different compositions and different phase fractions.

One key factor underlying the evolution of the hierarchical structure in Fig. 2c is the kinetics of the alloy synthesis reaction. During the reaction between the pure components several intermediate phase products form and dissolve until the end stage is reached for the ($\alpha + \beta$) mixture. A detailed analysis of each of the phase reactions that is encountered during the heating cycle used

for alloy synthesis is beyond the scope of the present discussion, but some estimates of the reaction kinetics can offer useful insight. First, with respect to the various intermediate phases in the Cu–Sn system, Onishi and Fujibuchi [17] have reported layer growth and self-diffusion rates that reveal that intermediate phase formation (and dissolution) occurs over distances of about 10 μm after 2 min at about 450 °C so that this process is not likely to be rate limiting for the thermal cycle used in the current work. For the alloy phase products, the diffusivity for Sn in a Cu–7at.%Sn α phase alloy indicates a diffusion range of about 5 μm in 2 min at 700 °C [18]. Similar diffusion measurements do not appear to be available for β phase compositions, but since it is well known that diffusion in BCC structures tends to be more rapid than that in close packed structures [19], the diffusion distance is likely to be at least 5 μm in the β phase. Thus, the conservative estimates of the extent of diffusion during alloy phase synthesis are consistent with the well-equilibrated microstructure observed in Fig. 2d. At the same time the extent of diffusion would suggest that the microstructural morphology in Fig. 2c should reflect a relatively homogeneous composition rather than the heterogeneous pattern that is evident. Of course, within each two-phase region the phase compositions are equilibrated to the tie line values. Since the equilibration means that the component chemical potentials are equal in the α and β phases, there will be no net diffusion flux of solute. Within each phase diffusion can take place by random walk. Further, within the nanoscale microstructure some coarsening is also expected due to the Gibbs Thomson effect. However, within each of the two-phase regions (i.e. the Cu-rich and the Sn-rich regions) the minor phase is enveloped within grains of the major phase so that coarsening of the minor phase grains requires transport over distances beyond the near neighbor intergrain exchange. Within a nanoscale microstructure it is expected that interphase boundary diffusion would allow for the required transport and coarsening would be rapid. Because the extent of volume diffusion during the anneal at 700 °C extends beyond the size scale of the individual two-phase regions, the observed microstructures suggest that there is also a kinetic restriction to overall equilibration between the separate two-phase regions to yield the overall average composition. The overall equilibration of the average composition also will involve a coarsening of the two-phase grain structure. There have been a number of studies that offer useful insight into the diffusion behavior in two-phase diffusion couples, but two-phase grain growth is not considered to be rate limiting [20]. The two-phase microstructures in the current work appear to exhibit equilibrated interface arrangements, but the grains do not show significant coarsening. Thus, the duplex two-phase microstructure appears to be more robust to modification than expected on simple diffusion grounds.

4. Summary

Two-phase ($\alpha + \beta$) bronze alloys with sub-micron grains can be obtained through a relatively simple synthetic diffusional reaction scheme. The product microstructure has a novel duplex morphology of dual phase regions consisting of a Cu-rich ($\alpha + \beta$) region and a Sn-rich ($\alpha + \beta$) region. The size scale of the duplex morphology is comparable to that for the Sn-rich and Cu-rich regions in the consolidated, un-reacted sample. There appears to be a kinetic restriction to overall equilibration between the separate two-phase regions to yield the overall average composition and the associated phase volume fractions.

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