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Precipitation induced room temperature superplasticity in Zn-Cu alloys

Ehsan Mostaed¹, Morteza Shaker Ardakani, Malgorzata Sikora-Jasinska, Jaroslaw W. Drelich

Department of Materials Science and Engineering, Michigan Technological University, USA

Abstract

In this study, the effect of grain size and precipitates on tensile properties of Zn-1.0Cu alloy were investigated. The alloy was cold rolled and annealed to manipulate the grain size and precipitation of CuZn₄ particles at grain boundaries. Cold rolling resulted in an almost ultrafinegrained structure alongside precipitation of nano-sized CuZn₄ particles. Strain induced precipitates triggered room temperature superplasticity through activation of Zn/CuZn₄ boundary sliding, exhibiting maximum elongation of 470% at the strain rate of $1.0 \times 10^{-4} \text{ s}^{-1}$. Short-time annealing led to significantly reduced strain rate sensitivity due to the reduction of CuZn₄ fraction, while the grain size remained nearly intact. This suggests that precipitates rather than grain size mainly influence the mechanical properties of Zn alloys.

Keywords

Zn; Biodegradable implant; Superplasticity; Precipitation softening

1. Introduction

Recently, zinc (Zn) has been added to a short list of biodegradable metallic implant candidates due to its ideal corrosion rate and acceptable biocompatibility [1]. However, its low mechanical strength has prompted a search for Zn alloys with improved mechanical properties via elemental composition and/or processing manipulation [2, 3]. Furthermore, as a structural material, Zn suffers other critical mechanical challenges that have not been addressed yet. Zn has a low recrystallization temperature, which results in strain softening during the deformation. More importantly, Zn is strongly strain rate sensitive at room temperature (RT) and thus, an implant made of zinc, which is under the cyclic loading, may collapse due to the creep-fatigue interaction [2].

¹Corresponding author: Ehsan Mostaed, emostaed@mtu.edu.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

In addition, during manufacturing processes, Zn alloys might undergo a meaningful cold metalworking, which influences the microstructure and thereby the mechanical properties of the final product. Accordingly, although cold work processing is an essential consideration for manufacturing of Zn-based structural devices, it has not been addressed by materials and biomedical communities so far.

It is reported that Zn alloys containing high-solubility biocompatible elements such as Ag and Cu are the most promising biodegradable implant candidates since their mechanical properties could be improved through tuning the fraction of second phase particles [2, 4]. In this work, Zn-1.0 wt.%Cu, as a potential alloy system for biomedical application was developed and subjected to cold working. The microstructural evolution and mechanical properties of the cold worked samples were systematically investigated. Most importantly, the effect of grain size, which is of great importance to biomedical implants, on the mechanical properties was rigorously studied.

2. Materials and methods

Zn-1.0Cu was prepared by melting Zn (99.995%) and Cu (99.9%) at 700°C in a graphite crucible. The ingots were solution heat treated at 380°C for 4 h followed by water quenching. The annealed samples with an initial thickness of 20 mm were cold rolled to 0.6 mm. The reduction ratio was 7% for each rolling pass. Selected rolled samples were annealed at 300°C for 15s to 1h soaking times. Microstructural examination was carried out on the surface parallel to the rolled face of the samples. Microstructure was recorded under optical microscopy and PHILIPS XL 40 scanning electron microscopy (SEM). X-ray diffraction was performed for phase identification using XDS- 2000 θ - θ diffractometer (Scintag Inc., Cupertino, CA) with CuK α radiation ($\lambda = 1.540562 \text{ \AA}$). Diffraction patterns were generated for 30–90°. Samples for electron backscattered diffraction (EBSD) analysis were prepared by standard mechanical polishing followed by low-angle argon ion milling. Mechanical properties were evaluated by tensile testing on the rolled sheet according to ASTM E8-04. Tensile tests were performed at room temperature, which is 43% of the alloy's melting point (T/T_m), and at strain rates ranging from $1.0 \times 10^{-4} \text{ s}^{-1}$ to $1.0 \times 10^0 \text{ s}^{-1}$.

3. Results and discussion

Fig. 1 presents the microstructure and corresponding XRD patterns of the alloy at solution treated (ST) and cold rolled (CR) conditions. As shown in Fig. 1a, ST alloy features a single-phase supersaturated solid solution with a coarse-grained structure. After applying extensive amount of cold work the microstructure was markedly refined into reasonably equiaxed grains with an average size of $1.2 \pm 0.2 \mu\text{m}$ (Fig. 1b). This is due to the low recrystallization temperature of zinc [2], which causes the occurrence of dynamic recrystallization even at RT.

Fig. 1c shows the XRD patterns of the ST and CR samples. ST sample produced only peaks corresponding to the α -Zn solid solution, confirming that there are no secondary phases (Fig. 1a). After cold rolling extra peaks corresponding to ϵ -CuZn₄ phase appeared.

Fig. 1d shows the SEM images of CR sample, taken in a back-scattered electron (BSE) mode. A large number of extremely fine precipitates with a mean value of $210 \pm 40\text{nm}$ (see the inset in Fig. 1d) formed homogeneously throughout the Zn matrix. Both XRD pattern in Fig. 1c and BSE image in Fig. 1d confirm the presence of nano-sized nearly spherical precipitates that formed during the CR process without any deliberate aging treatment. Hence, when a non-equilibrium solid solution Zn-Cu alloy is refined down to ultrafine-grained (UFG) regime, and simultaneously subjected to the plastic deformation, it experiences precipitation of secondary phases. In fact, in the UFG alloy the grain boundary density, which is considered as high speed diffusion path for elements is considerably high [5], This magnifies the diffusion of solute atoms during the cold working and thereby, induces the CuZn_4 precipitates at RT.

It should be noted that in such alloys alongside the grain refinement effect (known as Hall-Petch strengthening) the deformation induced precipitates might have an additional effect on the mechanical properties.

Fig. 2a shows RT tensile properties of CR alloy at varying strain rates. Surprisingly, unlike typical cold worked metals, Zn-1.0Cu alloy exhibits a reduced peak flow followed by a pronounced strain softening, leading to a remarkably large elongation of 370% at the strain rate of 1.0×10^{-3} . Furthermore, tensile tests at different strain rates reveal that this alloy is strongly strain rate sensitive. Typically, the flow stress decreases with decreasing the strain rate and large ductility is recorded at low strain rates [6]. However, as mentioned earlier, the strain induced CuZn_4 precipitates might have a crucial contribution to the tensile properties of the alloy. Accordingly, in order to isolate the effect of grain size, the CR alloy was annealed for up to 1h and its tensile properties were evaluated at the strain rate of 1.0×10^{-3} . As seen in Fig. 2b, interestingly, already after 15s of annealing the peak flow remarkably increased from 107MPa to 152MPa accompanied by nearly 70% drop in elongation notwithstanding the fact that both samples possessed nearly identical grain sizes (Fig. 1b vs Fig. 3a).

Continuation of the annealing to 60s caused only a slight grain growth, from $1.3 \pm 0.4\mu\text{m}$ to $1.6 \pm 0.2\mu\text{m}$, with the majority of the grains remaining unchanged (Fig. 3b). For this sample, the strain softening was suppressed and the maximum strength (178MPa) was obtained. Fig. 3c shows that the grain coarsening became more evident after 300s of annealing, which resulted in about 11% drop of tensile strength to 158 MPa. Eventually, after 3600s of annealing, grain size increased to $42\mu\text{m}$ (Fig. 3d), causing a reduced yield strength alongside a strong strain hardening rate, which is attributed to the activation of twins (Fig. 2b).

BSE images show that with the annealing advancement the fraction of the precipitates drastically decreases (Figs 3a' and 3b'). It is deduced that in the early stage of the annealing precipitates gradually dissolve in the matrix and thereafter, the grain growth occurs.

Fig. 2c summarizes the tensile properties of the Zn-1.0Cu alloy at varying strain rates. After cold rolling, with decreasing the strain rate the strain rate sensitivity exponent (m) value increases. At strain rates of $1.0 \times 10^{-4}\text{ s}^{-1}$ and $1.0 \times 10^{-3}\text{ s}^{-1}$ the m values of 0.31 and 0.26

were achieved, respectively. Such a high value of m supports the hypothesis that slip-accommodated grain boundary sliding (GBS) dominates the deformation, leading to a maximum elongation of 470% at $1.0 \times 10^{-4} \text{ s}^{-1}$. However, at higher strain rates the m value significantly decreases, suggesting that the rate-controlling deformation process was dislocation slip. It is well documented that grain refinement in metals enhances the superplastic ductility [7]. Superplasticity is a diffusion-controlled process requiring temperatures above $0.5T_m$ and grain size smaller than $10\mu\text{m}$ [8]. However, in metals with UFG structure, superplasticity could occur even at temperatures below $0.5T_m$ [7]., it might be assumed that the room temperature superplasticity (RTS) is attributed to the nearly UFG structure. However, Fig.2c shows that the measured m values for the 60s-annealed alloy (which exhibited comparable grain size to the CR alloy, but reduced number of precipitates), are significantly smaller than those for CR sample in all tested strain rates. Thus, it is believed that for CR alloy, GBS is not the rate-controlling flow mechanism and the RTS is strictly related to the presence of precipitates.

Recently, Bednarczyk et al. [9] found RTS in Zn-0.5Cu processed by ECAP and they declared that RTS was due to the significant contribution of GBS. However, our findings reveal that RTS is due to a phenomenon which we named “precipitation softening”, occurring in UFG microstructures consisting of refined and dispersed CuZn_4 precipitates, where the density of Zn/CuZn₄ interphase boundaries is considerably high. Such a microstructure could be achieved only through massive cold working. It is worth to note that in our research we also observed the mentioned phenomenon in other Zn alloy systems with different alloying concentration (to be published).

Previous studies on Zn-22Al eutectic alloy have reported that the sliding occurs preferentially on the Zn/Al interface boundaries and less sliding occurs at Zn/Zn boundaries [7]. We assume that the diffusion at Zn/CuZn₄ interphases is higher than that for Zn/Zn. Thus, the remarkably fine spherical-shaped precipitates provide extensive amount of interfaces to take part in phase boundary sliding (PBS). Indeed, RTS is mainly dominated by PBS rather than GBS. This highlights the prominent effect of precipitates over grain size on the mechanical properties of Zn alloys so that with a slight modulation in their fraction a wide range of properties could be obtained.

4. Conclusions

Zn-1.0Cu was selected as a potential alloy system for biomedical applications. Mechanical properties were evaluated with a focus on strain rate sensitivity which is detrimental for devices subjected to cyclic loading. It was found that massive cold working induced refined and well-distributed precipitates. Instead of strengthening, the strain induced precipitates drastically drop the tensile strength and promote strain rate sensitivity due to the activation of Zn/CuZn₄ boundary sliding. The sliding contribution on the Zn/CuZn₄ interphases is significantly higher than that on the Zn/Zn interface, leading to room temperature superplasticity with a maximum elongation of 470% at strain rate of $1.0 \times 10^{-4} \text{ s}^{-1}$. Short time annealing could remarkably enhance the mechanical strength and suppress the strain rate sensitivity through reduction the amount of Zn/CuZn₄ interphases.

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Research highlight:

- The effects of grain size and precipitates on the tensile properties were studied
- Cold rolling of the solid solution Zn-1Cu resulted in precipitation of CuZn₄ phase
- Strain induced precipitates promoted room temperature strain rate sensitivity
- Grain boundary sliding had a minor contribution to room temperature superplasticity
- Flow stress and room temperature superplasticity were affected by Zn/CuZn₄ boundary density

Fig. 1.
 (a) Optical micrograph of ST alloy, (b) EBSD map of CR alloy, (c) XRD spectra for ST and CR alloys and (d) BSE image of CR alloy.

Fig. 2. Tensile curves of CR at different (a) strain rates, (b) annealing times and (c) the variation of flow stress versus strain rates for CR and annealed samples.

Fig. 3.
EBSD maps (a-d) and BSE images (a', b') of Zn-1.0Cu alloy after different annealing times
(a, a') 15s, (b, b') 60s, (c) 300s and (d) 3600s.