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Fabrication and characterization of novel biodegradable Zn-Mn-Cu alloys

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ABSTRACT

Zn-Mn-Cu alloys with micro-alloying of Mn and Cu in Zn are developed as potential biodegradable metals. Although the as-cast alloys are very brittle, their ductilities are significantly improved through hot rolling. Among the as-cast and the as-hot-rolled alloys, as-hot-rolled Zn-0.35Mn-0.41 Cu alloy has the best comprehensive property. It has yield strength of 198.4 ± 6.7 MPa, tensile strength of 292.4 ± 3.4 MPa, elongation of 29.6 ± 3.8% and corrosion rate of 0.050-0.062 mm a^{-1}. A new ternary phase is characterized and determined to be $MnCuZn_{18}$, which is embedded in $MnZn_{13}$, resulting in a coarse cellular/dendritic $MnZn_{13}$-$MnCuZn_{18}$ compound structure in Zn-0.75 Mn-0.40Cu alloy. Such a coarse compound structure is detrimental for wrought alloy properties, which guides future design of Zn-Mn-Cu based alloys. The preliminary research indicates that Zn-Mn-Cu alloy system is a promising candidate for potential cardiovascular stent applications.

1. Introduction

Biodegradable metals (BMs) have drawn increasing attention in recent years, among which Mg-based and Fe-based alloys have been most studied [1–3]. Zn is an essential element for human beings, which plays an important role in functions of enzymes and proteins [4–6]. The melting point (T_m) and chemical reactivity of Zn (T_m = 420 °C) are much lower than those of Mg (T_m = 650 °C), which contributes to easier preparation and processing of Zn and its alloys. Thus, Zn and its alloys are believed to be the next rising stars in BMs, owing to their moderate in vitro degradation rate and acceptable cytocompatibility [2,7–11].

Mechanical and corrosion properties of various biodegradable Zn alloys are drawn in Fig. 1, the data of which come from Refs. [12–26]. Fig. 1(a) and (b) shows reported yield strengths, tensile strengths and elongations of pure Zn and various biodegradable Zn alloys. Alloying and hot deformation are two effective approaches to improve mechanical properties of pure Zn. As-cast pure Zn and its alloys are extremely brittle with a very limited elongation usually lower than 3%, showing little engineering significance. However, after hot rolling or hot extrusion, their mechanical properties can be considerably improved, which is the reason why mechanical properties of a certain material in Fig. 1(a) and (b) can vary in a wide range. General design constraints and criteria of mechanical and corrosion properties for a bioabsorbable metal stent are reported to be yield strength >200 MPa, tensile strength >300 MPa, elongation to failure > 15%-18% and corrosion rate < 20 μm a^{-1} [8]. Referring to current literatures [12–26], the only alloy over the benchmark of mechanical properties, as shown in Fig. 1(a) and (b), is an as-extruded Zn-1.2 Mg reported in Ref. [19]. However, as can be seen from Fig. 1(c) and (d), the corrosion rates of such an alloy fail to meet the benchmark, which are reported to be about 190 μm a^{-1} and 90–110 μm a^{-1} evaluated by electrochemical test and immersion test, respectively [19]. Therefore, investigation of new alloy systems and further improvement of the current alloy systems are valuable and challengeable.

In this study, novel biodegradable Zn-(0.4-0.8Mn)-0.4Cu alloys will be designed and fabricated. Alloy elements of Mn and Cu are selected since they both are essential trace elements in the human body. Cu not only can accelerate the process of revascularization through promoting the proliferation of vascular endothelial cells [27], but also can improve antibacterial properties of materials, especially against Escherichia coli and Staphylococcus aureus, and thus may reduce the risk of infection during surgical implant surgery [28,29]. Effects of alloy compositions on mechanical properties, microstructure, and corrosion behavior will be investigated systematically.

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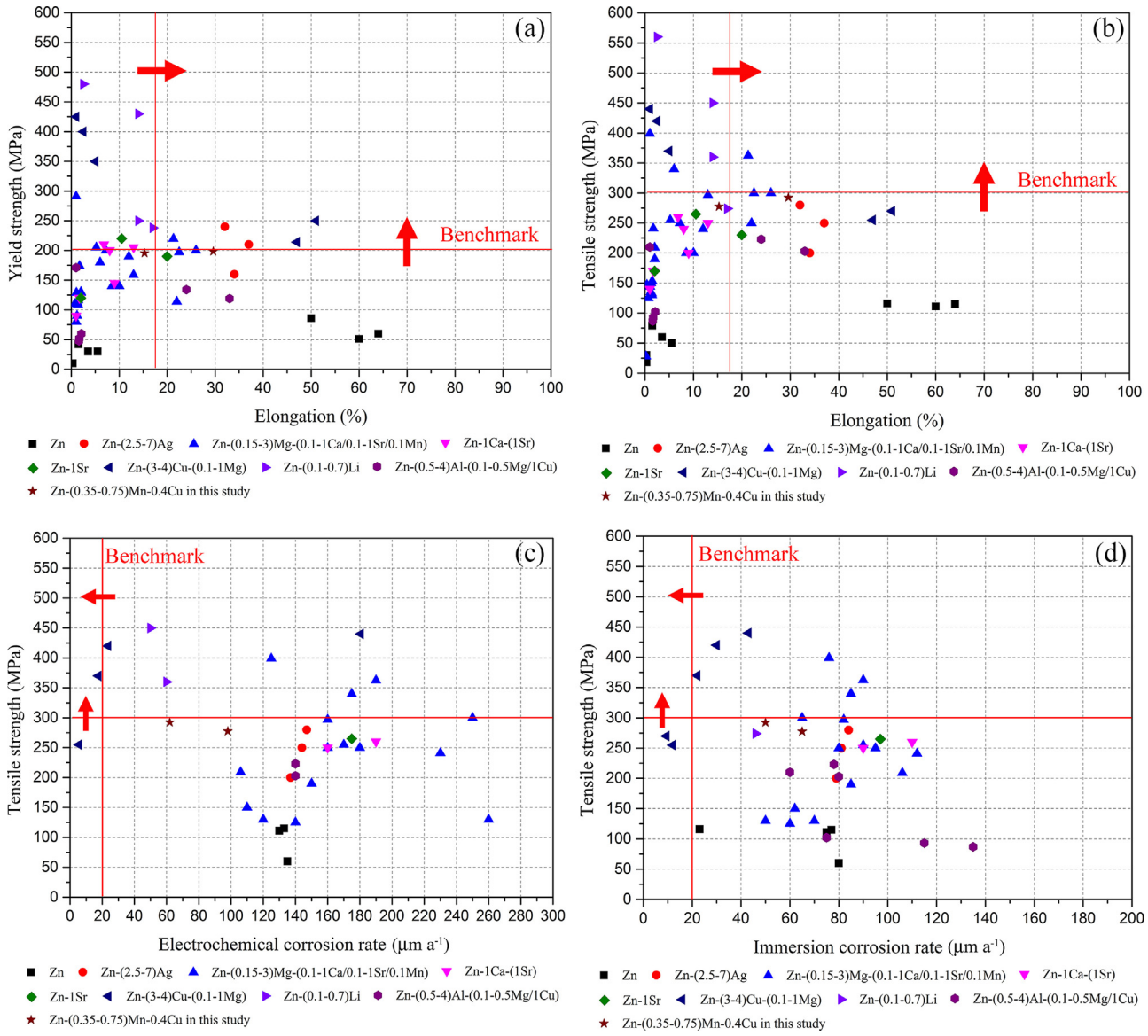

Fig. 1. Data of mechanical and corrosion properties of biodegradable Zn and its alloys collected from references [12–26]: (a) elongation and yield strength; (b) elongation and tensile strength; (c) electrochemical corrosion rate and tensile strength; (d) immersion corrosion rate and tensile strength.

2. Materials and methods

2.1. Alloy preparation

High purity Zn (99.99 wt%), Mn (99.90 wt%) and Cu (99.90 wt%) metals were received from General Research Institute for Nonferrous Metals, Beijing, China. Afterwards, composition is in weight percentage as default. The raw metals were weighted and mixed according to nominal compositions of Zn-0.8Mn-0.4Cu and Zn-0.4Mn-0.4Cu alloys. Then, the mixed metals of each alloy were melted and casted one by one. The mixed metals were put in a ZG-0.01 vacuum induction melting furnace with the protection of argon atmosphere. The melt was kept at 760 °C for 5 min, and then poured into a cylinder-shaped graphite mould for natural cooling in air. Compositions of samples of the as-cast alloys were measured through chemical analysis, which are confirmed to be Zn-0.75Mn-0.40Cu and Zn-0.35Mn-0.41Cu, close to their nominal compositions.

The as-cast alloys were homogenized first at 280 °C for 1 h and then at 380 °C for 2 h, after which they were cooled in air. The two-step homogenization avoids possible melting of phases with low melting points due to possible composition segregation usually presented in as-cast alloys. Samples of 30 mm × 20 mm × 70 mm were cut from the homogenized alloys, which were reheated at 320 °C for 1 h and then hot rolled to the size of 5 mm × 20 mm × 420 mm through 5 passes. The rolling was performed on a four-high mill with work roll diameter of 170 mm. The rolling speed was 0.3 m s^{-1}. The average and the accumulated reductions of thickness are 30.0% and 83.3%, respectively.

2.2. Electrochemical test

Samples for electrochemical tests were ground, mechanically polished, washed and dried. Electrochemical tests were conducted in a simulated body fluid (SBF) at 37 °C, of which the pH value was 7.40. Order, amounts, weighting containers, purities and formula weights of reagents for preparing 1000 ml of the SBF can be found in Ref. [30], as listed in Table 1.

The tests were performed in a standard three-electrode set-up: the sample (a square-shaped thin plate with 1 cm^2 in area and 1 mm in thickness) as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as