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Mechanical and corrosion properties of newly developed biodegradable Zn-based alloys for bone fixation

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ABSTRACT

In the present work Zn–Mg alloys containing up to 3 wt.% Mg were studied as potential biodegradable materials for medical use. The structure, mechanical properties and corrosion behavior of these alloys were investigated and compared with those of pure Mg, AZ91HP and casting Zn–Al–Cu alloys. The structures were examined by light and scanning electron microscopy (SEM), and tensile and hardness testing were used to characterize the mechanical properties of the alloys. The corrosion behavior of the materials in simulated body fluid with pH values of 5, 7 and 10 was determined by immersion tests, potentiodynamic measurements and by monitoring the pH value evolution during corrosion. The surfaces of the corroded alloys were investigated by SEM, energy-dispersive spectrometry and X-ray photoelectron spectroscopy. It was found that a maximum strength and elongation of 150 MPa and 2%, respectively, were achieved at Mg contents of approximately 1 wt.%. These mechanical properties are discussed in relation to the structural features of the alloys. The corrosion rates of the Zn–Mg alloys were determined to be significantly lower than those of Mg and AZ91HP alloys. The former alloys corroded at rates of the order of tens of microns per year, whereas the corrosion rates of the latter were of the order of hundreds of microns per year. Possible zinc doses and toxicity were estimated from the corrosion behavior of the zinc alloys. It was found that these doses are negligible compared with the tolerable biological daily limit of zinc.

1. Introduction

Biodegradable materials are capable of progressively degrading in the human body to produce non-toxic compounds that can be readily excreted. Biodegradable polymeric materials have been known and used for a long time as, for example, fibers for the reparation of damaged tissue or for winding biodegradable stents. However, for load-bearing applications, such as screws, plates or other fixations of fractured bones, polymeric materials are not suitable due to their low mechanical strength [1].

Among biodegradable metallic materials magnesium has attracted the greatest interest, and its properties related to bio-applications have been studied since the beginning of the 20th century [2]. The reason for this is that magnesium is non-toxic to the human body and excessive amounts of it can be readily excreted by the kidneys. Magnesium is also very important for biological functions of the human body. The main disadvantage of most magnesium alloys is that they corrode too rapidly in physiological environments. The corrosion of magnesium produces hydrogen pockets near the implant, which retard the healing process. In addition, the local increase in alkalinity close to the magnesium implant also has adverse effects on healing [2–6]. Therefore, great effort has been exerted during the last 20 years to find magnesium-based alloys that corrode at acceptably low rates and whose corrosion products, like hydrogen and alkaline materials, can be absorbed by the surrounding tissue without negative effects on the healing process.

The magnesium alloys initially considered for bio-applications were based on alloying systems originally developed for engineering applications. Among them AZ, LAE and WE type alloys have been widely studied, but only the WE43 alloy has been used to prepare a biodegradable implant, in this case a vascular stent, used in the human body [7–9]. Besides engineering alloys, some new alloying systems have been developed to provide good corrosion resistance and biocompatibility. Among them Mg–Zn, Mg–Zn–Mn–Ca, Mg–Zn–Y, Mg–Gd, Mg–Zn–Si and other systems have recently been studied [10–15]. In these systems zinc is often the major constituent. Zinc, as a more noble metal than magnesium, is well known to positively affect the corrosion resistance and strength of Mg. From a biological point of view zinc is very important for biological functions in the human body because it is involved in various aspects of cellular metabolism. Zinc is important to the proper function of numerous enzymes and it supports immune

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functions, protein and DNA synthesis and wound healing. It also supports normal growth and a proper sense of taste and smell [10,16]. The recommended dietary allowance (RDA) and recommended upper limit for zinc are 15 and 40 mg day^{-1}, respectively [17]. The consumption of zinc in amounts higher than these values is generally considered relatively non-toxic, and amounts approaching 100 mg day^{-1} can be tolerated for some time [17].

In the Mg–Zn binary phase diagram [18] there is a deep eutectic point at about 51 wt.% Zn. The existence of a deep eutectic point is the basic factor supporting the high glass-forming ability (GFA) of alloying systems. Indeed, amorphous ternary Mg–Zn–Ca alloys whose compositions are close to the eutectic point have already been prepared [19,20]. It was shown recently that amorphous Mg–Zn-based alloys containing about 50 wt.% Zn are promising candidates for biodegradable implants because they show excellent strength, high corrosion resistance, low hydrogen evolution rate and good biocompatibility within animal tissues [19,21]. However, the preparation of bulk amorphous Mg–Zn-based alloys is difficult because it requires rapid cooling rates.

The fact that zinc is a biologically tolerable element, even when its content in Mg-based alloys approaches 50 wt.% [21], indicates that Zn-based alloys may also be promising candidates for biodegradable implants. The advantage of Zn-based alloys over Mg–Zn metallic glasses lies in their much easier preparation. Zinc alloys can be prepared by classical routes such as gravity or die casting, hot rolling or hot extrusion. Another advantage is the lower melting point, lower chemical reactivity and better machinability of zinc, compared with magnesium. Therefore, melting of zinc alloys can be performed in air. To our knowledge there are only a few sources in the scientific literature that mention zinc alloys within the context of biodegradable materials [22]. Detailed studies on their mechanical and corrosion performance in simulated biological environments are lacking. For this reason, in our study we focused our attention on the mechanical and corrosion behavior of Zn-based alloys. Commercial die casting zinc alloys commonly contain aluminum and copper as the main alloying elements. These elements improve the castability and strength of zinc. However, as mentioned before, aluminum is not very suitable for biological applications. Therefore, we have selected a new alloying system, Zn–Mg, in our research because magnesium is assumed to improve the strength and biocompatibility of zinc. The bone healing process may also be improved by the addition of magnesium due to the positive effect of magnesium on bone growth [16]. The Zn–Mg equilibrium phase diagram is shown in Fig. 1. One can see that the solid solubility of magnesium in zinc is low

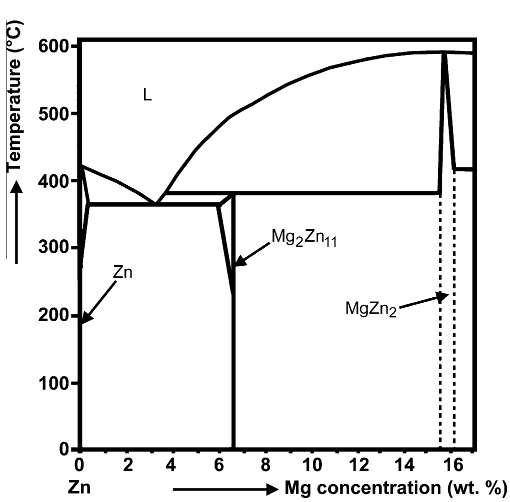

Fig. 1. Zn-rich region of the Zn–Mg equilibrium phase diagram [18].

and that the Mg_2Zn_{11} intermetallic phase forms in the structure even at small amounts of magnesium. There is a eutectic point in the diagram corresponding to about 3 wt.% Mg. Alloys with higher magnesium concentrations would thus contain primary intermetallic phases that would cause brittleness of such alloys. For this reason, we used magnesium concentrations ranging from 1 to 3 wt.% in the investigated binary Zn–Mg alloys. Pure zinc and commercial ZnAl4Cu1 (in wt.%) alloys were also investigated for comparison. In the latter alloy the addition of aluminum and copper led to mechanical strengthening. In contrast to the zinc alloys mentioned above, magnesium alloys are well documented with respect to their corrosion behavior in simulated body fluids [19]. Therefore, the behavior of the zinc alloys was compared with that of pure magnesium and high purity extruded MgAl9Zn1 (in wt.%, AZ91HP) alloy. These materials serve as standards to assess the mechanical and corrosion performance of new zinc alloys. All of the materials investigated, except for the AZ91HP alloy, were used in the as-cast state. The AZ91HP alloy was used in the as-extruded state, because hot extrusion is well known to refine and homogenize the structure, which results in better corrosion resistance and mechanical strength. Therefore, it is reasonable to compare the new Zn–Mg alloys with the corrosion resistant standard.

2. Experimental

In this study Zn, Mg, Zn–Mg, Zn–Al–Cu and Mg–Al–Zn alloys were investigated. The designations and chemical compositions of the alloys studied are given in Table 1.

Zn-based alloys were prepared by melting pure Zn (99.95%), Mg (99.90%), Cu (99.90%) and Al (99.50%) in a resistance furnace in air. To prevent excessive evaporation of the volatile zinc the melting temperature did not exceed 500 °C, and homogenization was insured by intense mechanical stirring with a graphite rod. After sufficient homogenization the melts were poured into a cast iron mold to prepare cylindrical ingots 20 mm in diameter and 130 mm in length. Their chemical composition was verified by X-ray fluorescence spectrometry, as shown in Table 1. Cylindrical ingots of pure magnesium and AZ91HP alloy of the same dimensions as above were prepared by melting Mg, Al and Zn in an induction furnace under an argon atmosphere and by casting the melts into a cast iron mold. The AZ91HP alloy was then hot extruded at 400 °C and an extrusion ratio of 1:11 to produce a 6 mm rod diameter.

The mechanical properties of the prepared alloys were characterized by Vickers hardness measurements using a loading of 5 kg. Tensile tests were also carried out in an Instron 5880 machine at a deformation rate of 1 mm min^{-1} to determine the ultimate tensile strength (UTS), yield strength (YS) and elongation (E) of the alloys.

The corrosion behavior was studied in an aerated simulated body fluid (SBF) containing 8 g l^{-1} NaCl, 0.4 g l^{-1} KCl, 0.14 g l^{-1} $CaCl_2$, 0.35 g l^{-1} $NaHCO_3$, 1 g l^{-1} glucose, 0.2 g l^{-1} $MgSO_4 \cdot 7H_2O$, 0.09 g l^{-1} KH_2PO_4 and 0.08 g l^{-1} $Na_2HPO_4 \cdot 12H_2O$ [23]. This chemical composition indicates that the SBF used has an almost neutral pH value, although real fluids in the human body may have pH values slightly different from 7. For example, it is known that the pH level may decrease to about 5 in the case of an inflammatory reaction [1]. It is also well known that the corrosion rates of both Zn and Mg increase with acidity [24]. For these reasons the corrosion rates were also measured in solutions with pH values of 5 and 10, which were obtained by adding small amounts of HCl and NaOH, respectively, to the SBF. Hereafter these solutions will be denoted as SBF (pH 5) and SBF (pH 10) for simplicity. Both immersion tests and electrochemical potentiodynamic measurements were performed to assess corrosion resistance. In the former coupons 6 mm in diameter and 2 mm in thickness were immersed in