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Effect of Plastic Deformation on the Structure and Properties of the Bioresorbable Zinc Alloy Zn-0.8Li-0.1Mn

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Abstract

The study of bioresorbable alloys is a relevant and promising area. Zinc alloys, in particular, are very promising for bioresorbable applications since zinc is an inexpensive and widely available material. In this paper, studies of the effect of plastic deformation by rolling on the zinc alloy Zn-0.8Li-0.1Mn are conducted. This alloy demonstrates high mechanical properties as a result of hot rolling treatment: ultimate tensile strength and yield strength are 525 MPa and 445 MPa, respectively, and elongation is 7%. The alloy structure is examined using modern methods such as scanning electron microscopy and electron backscattering diffraction. The results of the study can be useful for further research in the field of new materials development, as well as for the practical application of zinc alloys in various industries.

Keywords: Zinc alloy; Bioresorbable alloy; Plastic deformation; Structure; Mechanical properties

1. INTRODUCTION

In the world, there is a growing interest in minimally invasive surgery and the use of biodegradable implants. They are necessary to eliminate the need for a repeated surgery for the removal of implants when they lose their functionality and become redundant [1]. Biodegradable implants must comply with a number of key requirements [2,3]. Firstly, they must be biocompatible with human tissue and have the optimum corrosion rate. Secondly, it is important for such materials to ensure sufficient mechanical strength for a period of time required to support the bone and minimize the risk of their failure before the start of the implant dissolution process.

The best studied implant materials are alloys based on iron and magnesium [4–10]. Taking into account the fact that Mg, Fe and their alloys have certain drawbacks, the scientific community continues to actively search for new approaches for these materials, related to the solution of the problems of strength and corrosion rate. A separate solution is the development of Zn-based alloys [11–15]. Being an important element in the human body, zinc plays a key role in different aspects of cell metabolism. It is necessary for the effective work of enzymes and contributes to the support of immune system, the synthesis of proteins and DNA. In addition, zinc plays an important role in normal growth and wound healing [6,16].

Lithium (0.8 wt.%) and manganese (0.1 wt.%) were chosen as the alloying elements. Li was found [17] to have a beneficial effect in the case of different neurological diseases, including brain damages, strokes, Alzheimer's, Huntington's and Parkinson's diseases, as well as spinal cord injuries and other pathologies. In its turn, Mn is necessary for the body as it assists in the metabolism of carbohydrates and glucose, participates in the synthesis and exchange of proteins, maintains the hormone balance in the body, while a lack of Mn may lead to serious diseases such as muscle pains [18]. It was found [19] that Li also increases the strength characteristics of Zn alloys through formation of intermetallic phase $LiZn_4$. However, a considerable quantity of Li reduces the material's ductility. In order to ensure the levels of ductility and strength required for the implant application, the Li content must not exceed 8 wt.% [20–23]. It is also known that deformation and heat

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treatment leads to an increase in strength characteristics and, in some cases, an increase in material ductility [24]. The rolling method is one of the most widespread highly productive methods of deformation that has been used in various production industries for over 100 years [25]. The advantages of this method are simplicity, relatively low energy expenditures, as well as the possibility to vary the processing regimes of metals and alloys.

Thus, the aim of this work is to increase the mechanical properties of the Zn-0.8Li-0.1Mn alloy by means of producing a refined structural state through the use of the highly productive method of hot rolling.

2. MATERIALS AND METHODS

The Zn-0.8%Li-0.1%Mn (wt.%) alloy samples with a diameter of 20 mm and a length of 100 mm subjected to homogenization in a Nabertherm muffle furnace at a temperature of 300 °C for 72 hours with water cooling were taken as the initial state.

The initial samples were rolled using Hankook M-Tech two-high rolling mill for section rolling in 2 stages: (1) from a diameter of 20 mm to a diameter of 15 mm at a temperature of 300 °C; (2) with the cross section changing from a circle to a square 10×10 mm^2 in size, also at a temperature of 300 °C. The strain was 1.1.

In order to reveal the structure in the longitudinal direction, the samples were immersed for 30 seconds into an etchant with the following composition: 5 ml nitric acid (HNO_3) and 95 ml ethanol. Structural analysis was performed using JEM-6390 scanning electron microscope in the mode of secondary and back-scattered electrons at an accelerating voltage of 30 kV. Electron backscatter diffraction (EBSD) maps were obtained using Thermo Scientific Q250 electron microscope manufactured by FEI at an accelerating voltage of 30 kV. The scanning step was 0.5 μm.

The microhardness of the samples was tested using an EMCO–Test DuraScan 50 hardness tester with a pyramidal diamond indenter under a load of HV 0.05 (according to Vickers) at a loading time of 10 seconds. Tensile mechanical tests were conducted on Instron 5982 test machine using small-sized samples with gauge sizes of 0.6×1×4 mm^3 at room temperature in an initial strain rate range of 10^{-4}–10^{-3} s^{-1}. The test samples were cut out from the deformed billets in the longitudinal section.

3. RESULTS AND DISCUSSION

The structure of the initial state has the $LiZn_4$ phase with a dendritic structure and the Zn + $LiZn_4$ eutectic distributed between the dendrites (Fig. 1a,b). In the intermetallic phase the secondary zinc phase Zn_{II} is also observed in the form of thin bands (needles) with a width of 0.2–1 μm (Fig. 1b,c). Fig. 1d shows the substructure of the intermetallic phase analyzed by transmission electron microscopy (TEM). Low-angle boundaries (LABs) in the form of dislocation walls are observed. The structure of the solid solution of Li in Zn, present in the eutectic, are presented in Fig. 1e,f. The sizes of the observed contrasts that apparently indicate the non-uniformity of distribution of Li in the eutectic phase body are 20–50 nm (Fig. 1f). No Mn-containing particles are detected in the structure. It was found from the Zn-Mn phase diagram that the dissolution of Mn in Zn may reach 0.8 wt.%, and therefore it can be considered that Mn is present in the solid solution of Li in Zn. EBSD studies confirm that dendrite branches of the $LiZn_4$ phase contain a significant number of LABs (Fig. 1g,h). Their fraction reaches 87%. In the eutectic mixture of phases, LABs could not be detected by EBSD due to their small sizes (20–50 nm).

Rolling leads to the formation of a banded type of structure. The average transverse size of the bands of the primary dendrites $LiZn_4$ equals 35 ± 16 μm (Fig. 2a). A developed substructure is observed in the body of the primary $LiZn_4$ bands. The pattern of LABs and high-angle boundaries (HABs) obtained by EBSD shows that the fraction of LABs remains at the same level of 86%.

Between the bands of the primary dendrites, Zn + $LiZn_4$ eutectic is observed whose structure has transformed into a granular one—the average size of the Zn and $LiZn_4$ grains being 2±1 μm. The grain structure formation in the Zn phase contained in the eutectic is also evidenced by EBSD studies, since the map of LABs and HABs demonstrates the formation of HABs (Fig. 2b,c). That being said, rolling does not lead to grain reorientation, and in the longitudinal section most grains are oriented in the prismatic planes, i.e., slip in the process of rolling evidently occurs in the basal planes.

During tensile tests the samples with a dendritic structure of the intermetallic phase exhibited brittle fracture, and consequently, the values of ultimate tensile strength and yield strength in the initial state were not determined. An increase in strength characteristics after hot rolling is indicated by a 12% increase in microhardness values which were equal to 140 ± 15 HV, while in the initial state the microhardness values were equal to 125 ± 22 HV. Fig. 3 shows the typical tensile curves of the Zn-0.8Li-0.1Mn alloy samples after rolling obtained at different initial strain rates. It was found that the rolled samples exhibit high strength and are characterized by plastic flow. The increase in strength characteristics occurred as a result of the formed work-hardened structure and the formation of a grain/subgrain structure. The appearance of tensile ductility is most probably associated with accelerated diffusion and enhanced intergranular slip at low temperatures in the Zn phase contained in the eutectic that forms around the

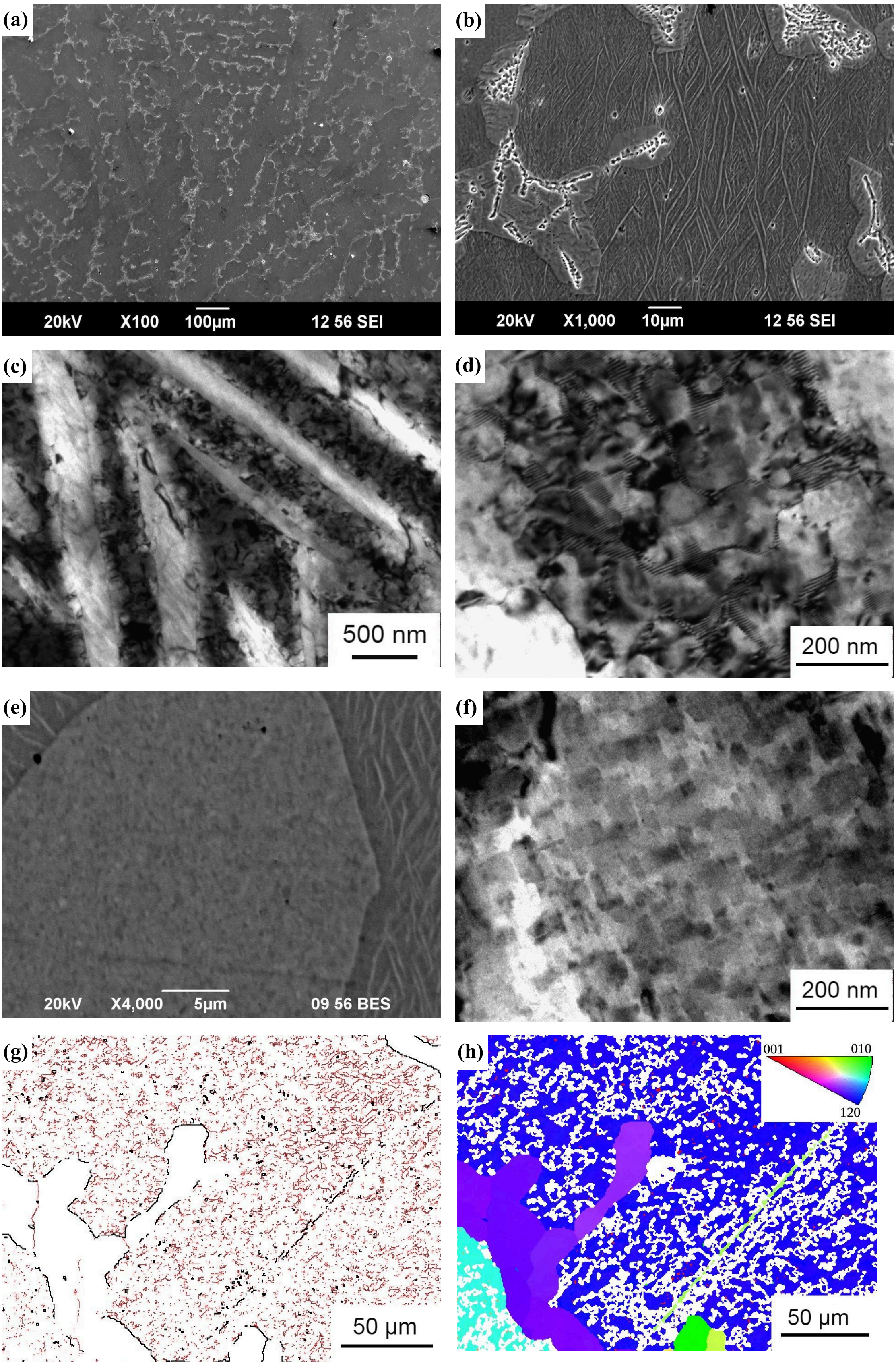

Fig. 1. Structure of the Zn-0.8Li-0.1Mn alloy in the initial state: (a,b) general view with different magnifications (scanning electron microscopy (SEM), secondary electrons mode), (c) region of the intermetallic phase $LiZn_4$ with the Zn_{II} needles (TEM, bright field), (d) view of the $LiZn_4$ intermetallic (TEM, bright field), (e) substructure of the solid solution of Li in Zn (SEM, back-scattered electrons mode), (f) substructure of the solid solution of Li in Zn (TEM, bright field), (g) the map of LABs and high-angle boundaries (EBSD), (h) grain misorientation map (EBSD).

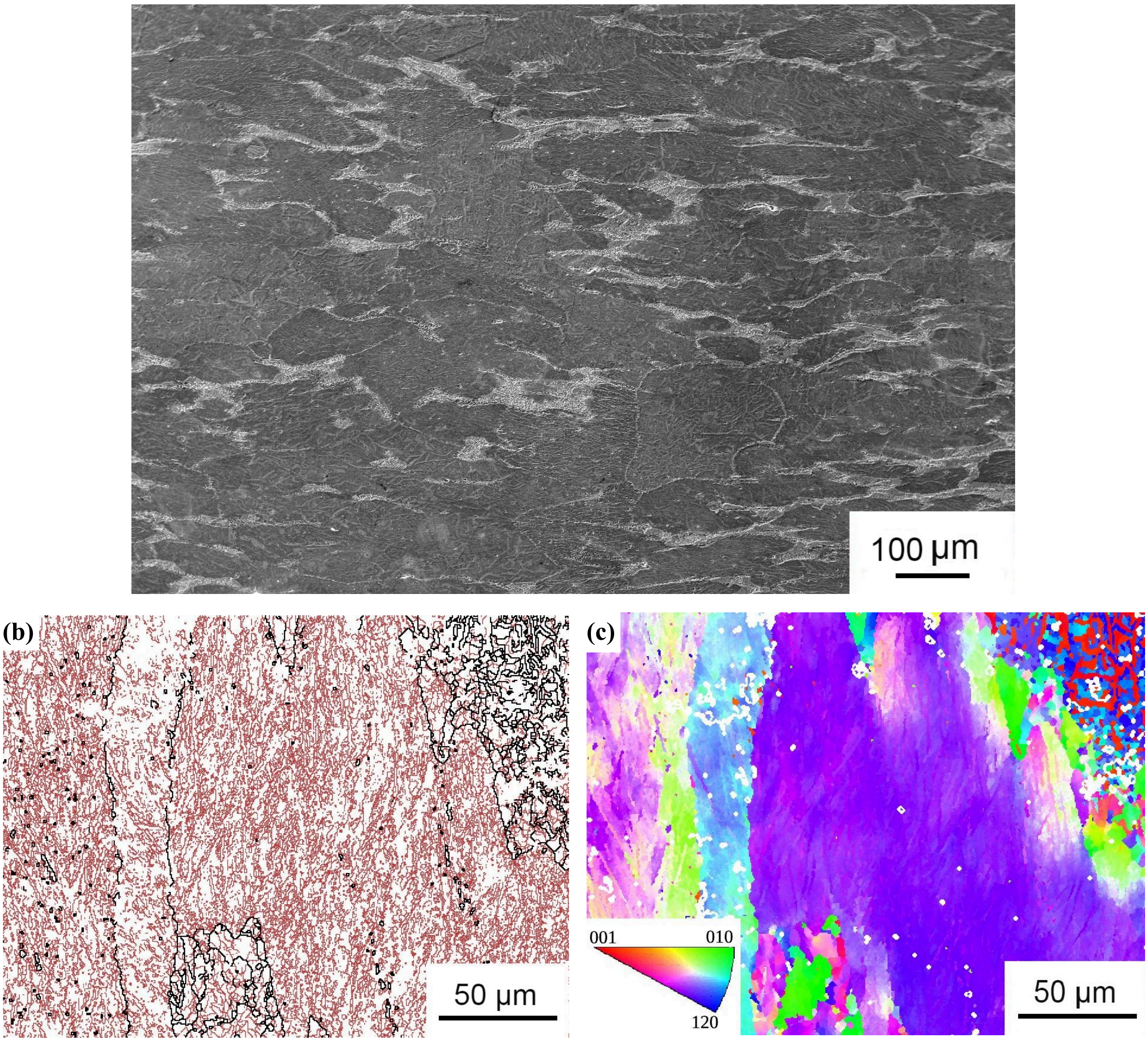

Fig. 2. Structure of the Zn-0.8Li-0.1Mn after rolling: (a) SEM, (b) map of LABs and HABs, (c) grain misorientation map.

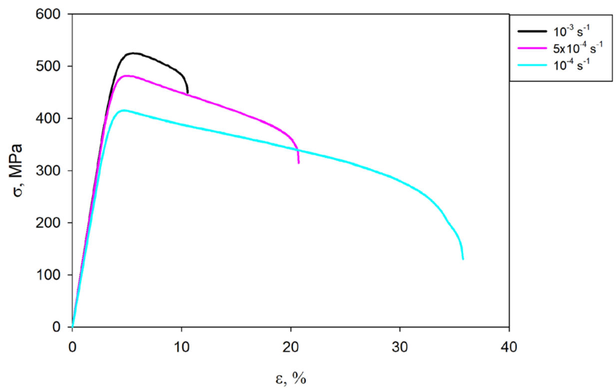

Fig. 3. Effect of the initial strain rate on the tensile curves of the Zn-0.8Li-0.1Mn alloy after rolling.

Table 1. Mechanical properties of the Zn-Li-Mn alloy in different conditions.

Condition		Mechanical properties		
		Yield strength, MPa	Ultimate tensile strength, MPa	Elongation, %
	10^{-3}	445	525	7
Rolling	$5 \cdot 10^{-4}$	400	480	18
	10^{-4}	330	415	35

intermetallic phase $LiZn_4$ in the process of rolling [26]. In addition, submicrograins in the rolled alloy may reduce the concentration of stresses by distributing them, which enables effectively avoiding crack propagation and considerably increasing the ductility of the rolled alloy [27]. It was found that a gradual decrease in the initial strain rate leads to a decrease in strength and a significant increase in ductility as a result of the more favorable conditions for diffusion processes and intergranular slip. For instance, when the initial strain rate is decreased from 10^{-3} s^{-1} to 10^{-4} s^{-1} the ductility values increase from 7% to 35% (see Table 1).

The obtained data shows that deformation processing is an efficient mean for increasing the ductility of a lowductile Zn alloys. Rolling is one of the most widespread industrial methods of deformation processing. However, there are other, more promising types of the mechanical treatment of metals and alloys by severe plastic deformation (SPD) that enable producing an ultrafine-grained structure, e.g., equal-channel angular pressing.

4. CONCLUSIONS

1. During the hot rolling of the Zn-0.8Li-0.1Mn alloy billets, a developed substructure is formed in the primary branches of the $ZnLi_4$ dendrites, and fine grains with an average size of 2 ± 1 μm are formed in the eutectic region of Zn + $LiZn_4$.

2. The formation of such type of structure enables increasing ultimate tensile strength to 525 MPa, yield strength to 445 MPa, and elongation to 7%.

3. The rolling method efficiently improves the material's strength properties, but its ductility at high rates does not make it possible to use the alloy as an implant material. Preliminary rolling increases technological plasticity, opening up new possibilities for SPD.

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Влияние пластической деформации на структуру и свойства биорезорбируемого цинкового сплава Zn-0,8Li-0,1Mn

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Аннотация. Исследование биорезорбируемых сплавов, включая цинковые сплавы, представляет собой перспективное направление, которое является актуальным в настоящее время. Исследование биорезорбируемых цинковых сплавов является перспективным направлением, так как цинк является недорогим и широкодоступным материалом. В данной работе проведены исследования влияния пластической деформации методом прокатки на цинковый сплав Zn-0,8Li-0,1Mn. Данный сплав демонстрирует высокие механические свойства в результате обработки горячей прокаткой: предел прочности и предел текучести – 525 МПа и 445 МПа, соответственно, относительное удлинение – 7%. Рассмотрена структура сплава с использованием современных методов, таких как растровая электронная микроскопия и дифракция обратного рассеяния электронов. Результаты исследования могут быть полезны для дальнейших исследований в области разработки новых материалов, а также для практического применения цинковых сплавов в различных отраслях.

Ключевые слова: цинковый сплав; биорезорбируемый сплав; пластическая деформация; структура; механические свойства