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ARTICLE

Effect of High-Pressure Torsion on Microstructure and Secondary Phase Distribution of Mg-3Zn-1Ca-0.5Sr Alloy

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Abstract: Degradable metals, represented by magnesium and magnesium alloys, have attracted significant attention as fracture internal fixation and bone defect repairing materials due to their good biocompatibility, suitable elastic modulus and degradable properties. The Mg-3Zn-1Ca-0.5Sr (wt%) alloy is considered a competitor in the biomaterial field thanks to its unique composition of essential nutrients and excellent mechanical properties. However, the presence of coarse second-phase particles in the alloy accelerates its degradation rate and causes excessive gas formation during implantation, which restricts the alloy's potential for clinical device applications. In order to further optimize the properties of the alloy, extrusion combined with high-pressure torsion (HPT) was adopted for deformation processing. The results show that by optimizing the material processing means, the grain can be refined and broken, and the second-phase distribution can be improved, thus improving the microstructure, mechanical properties, and corrosion resistance of the alloy. After 15 cycles of HPT processing, the grains of the alloy are significantly refined to the nanometer scale, reaching approximately 98 nm. Additionally, the second-phase distribution is greatly improved, transforming the original streamlined structure into a more dispersed distribution. This change in microstructure leads to a significant strengthening effect on the alloy, with a noticeable increase in hardness from 60.3 HV in the as-extruded state to 98.5 HV.

Key words: high-pressure torsion; biomaterials; microstructure; Mg-Zn-Ca-Sr; ultra-fine grain

1 Introdution

Biodegradable metals have become a popular research focus in the biomedical field due to their unique advantages in clinical applications[1]. These materials exhibit significant potential in medical uses, such as orthopedics and cardiovascular devices, offering patients new treatment methods. The biodegradable metals gradually degrade within the body after completing their intended function, thereby avoiding the problem of long-term retention. Therefore, research and development of such materials have important practical significance[2].

In recent years, the Mg-Zn-Ca-Sr alloy system has gained considerable attention[3–6]. The Mg-3wt% Zn-1wt% Ca-0.5wt% Sr alloy (ZXJ310) is considered a strong competitor in biodegradable metals due to its special composition of essential nutrients and good mechanical performance. The addition of elements Zn, Ca and Sr enhances the alloy's overall performance, making it more suitable for medical applications[7–8].

Researchers have explored various processing techniques to further optimize this alloy's performance[9–13]. High-pressure torsion (HPT), a severe plastic deformation method, can refine grain structure, thereby enhancing the material's strength and hardness. HPT can also modify the distribution of secondary phases, further improving the material's performance.

Based on the above background, the effect of HPT on the microstructure and phase distribution of the ZXJ310 alloy was investigated. Furthermore, the findings of this study may also provide valuable insights for optimizing other similar biodegradable alloys.

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2 Experiment

The as-cast ZXJ310 alloys were homogenized at 380 °C for 6 h. Extrusion processing with in-line quenching was performed using a direct extrusion machine at an extrusion ratio of 23. Specific extrusion parameters can be found in previous research[14]. The HPT samples (Φ10 mm×1.00 mm) were prepared from the extruded alloy. HPT was conducted at room temperature using an HPT-4 type device (TRANSMST, Austria) under an applied pressure of 7.85 GPa, a rotational speed of 1 r/min, and 15 torsion cycles. The schematic diagram of the processing procedure is shown in Fig.1.

After HPT, the microstructures of the cross-section, radial section and specific regions (0.5*R* and edge; *R* refers to radius) of the samples were observed by optical microscope (Zeiss Axiovert 2000 MAT). Hardness testing was conducted using a WILSON VH1150 Vickers hardness tester under a load of 5 kg with a 15 s dwell time. Prior to the testing, the samples were only polished with sandpaper. For the transmission electron microscope (TEM) analysis, the HPT-processed samples were directly polished to the ones with thickness of 80−100 μm, followed by punching into Φ3 mm circular discs vis a hole puncher. The discs were further polished to the ones with thickness of 50 μm. Subsequently, the samples were thinned using dual-beam ion milling equipped with an energy-dispersive X-ray spectroscope (EDS) system. The observation was conducted using a Tecnai G2 F20-TWIN TEM. The grain size and size distribution of the HPT alloys were measured and calculated by the Nano-Measure software.

3 Results and Discussion

Fig. 2a and 2b show the transverse and longitudinal metallographic structures of the extruded ZXJ310 alloy, respectively. The alloy consists of dynamically recrystallized equiaxed grains. The grain size of the extruded ZXJ310 alloy is determined to be 6.4 μm using the line intercept method. Fig. 2c and 2d are SEM images of the transverse and longitudinal cross-sections of the extruded ZXJ310 alloy, respectively, more clearly displaying the secondary phase distribution differences between transverse and longitudinal microstructures of the alloy. The distributions of the secondary phase in the transverse and longitudinal cross-sections of the alloy are different. In the transverse cross-section, the secondary phase is uniformly distributed between the grains, while in the longitudinal cross-section, the secondary phase exhibits a streamline-like distribution.

Fig. 2e and 2f represent the metallographic microstructures of the transverse and longitudinal observations of the

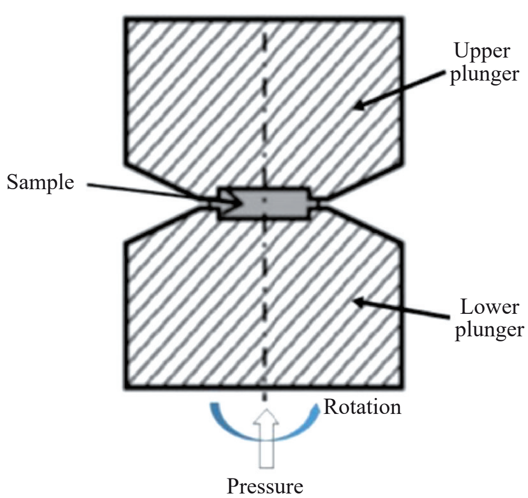

Fig.1 Schematic diagram of HPT processing

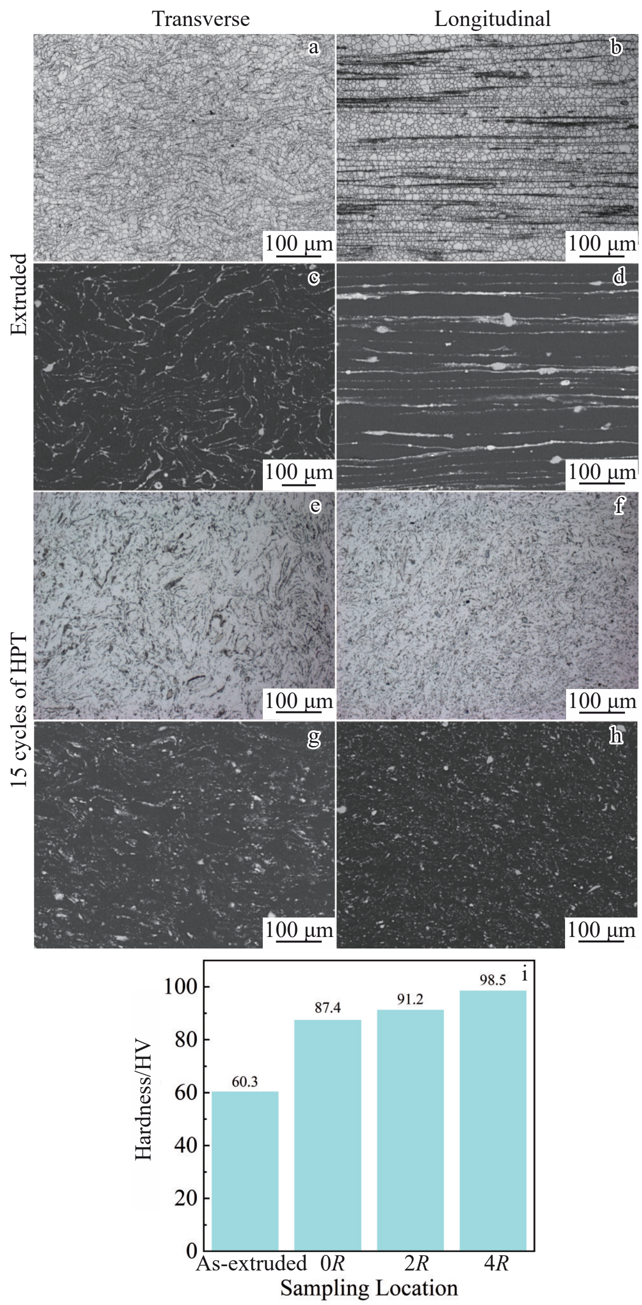

Fig.2 Transverse and longitudinal cross-sections (a–h) and hardness (i) of ZXJ310 alloys in different states: (a – d) extruded and (e–h) 15 cycles of HPT

HPT-treated ZXJ310 alloy, respectively. It can be observed that the presence of grain boundaries is almost negligible in the HPT alloy, because after 15 cycles of HPT, the grain size has refined to 98 nm, which exceeds the resolution limit of the metallographic microscope.

Fig. 2g and 2h show the transverse and longitudinal SEM images of the alloy after 15 cycles of HPT. The transverse structure of the alloy is not much different from that in the extrusion state, but the longitudinal structure has changed significantly, that is, the secondary phase distribution has changed from the original streamline-like distribution to uniformly diffused distribution.

Fig. 2i illustrates the hardness of the extruded and HPT-treated ZXJ310 alloys. After 15 cycles of HPT, the hardness of the alloy is significantly increased compared with that in the extruded state, from 60.3 HV to 98.5 HV, indicating grain refinement in the alloy. Additionally, the hardness of the HPT-treated ZXJ310 alloy increases from the center to the edge, which is consistent with the observed fracture of the secondary phase at the edge and reflects the smallest grain size at the edge.

Fig. 3a and 3b present the TEM image and selected area electron diffraction (SAED) pattern of the HPT-treated ZXJ310 alloy. The evident polycrystalline diffraction rings indicate grain refinement to the nanometer scale. As shown in Fig. 3c, the grain size of HPT-treated alloys is mostly distributed between 100 and 120 nm, and the average grain size is refined to 98.3 nm. Fig. 3d shows XRD results of the ZXJ310 alloy in extruded state and after 15 cycles of HPT, demonstrating that the alloy is still composed of α-Mg, $Ca_2Mg_6Zn_3$ and $Mg_{17}Sr_2$ phases, without any diffraction peak of the new phase. Fig. 3e shows the morphology of the alloy after 15 cycles of HPT, where the secondary phase in the alloy shows a pronounced segregation under severe shear deformation.

Fig. 3f – 3i demonstrate the EDS mappings of the alloy,

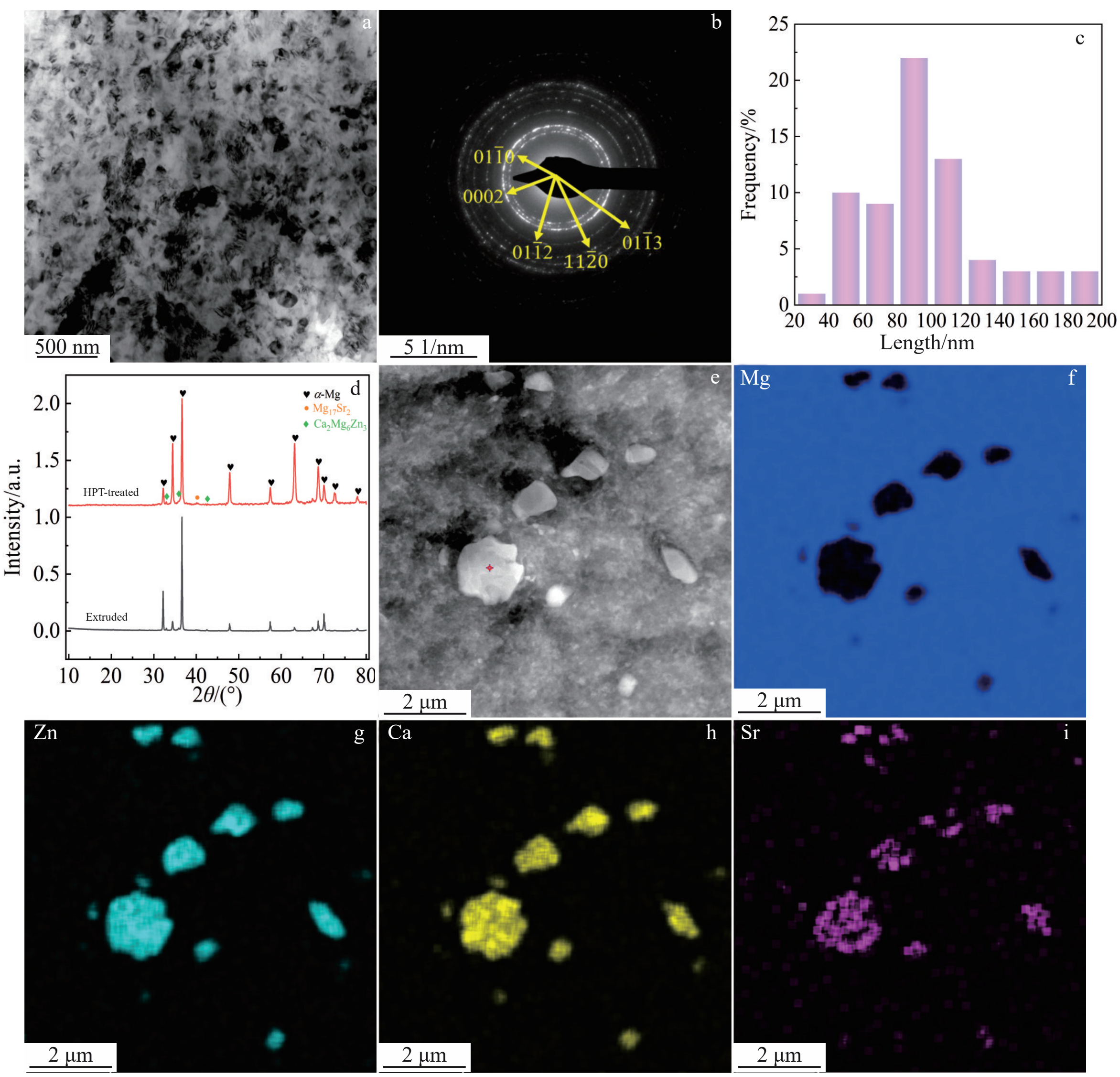

Fig.3 TEM image (a) and corresponding SAED pattern (b) of HPT-treated ZXJ310 alloy; grain size distribution (c); XRD patterns (d); morphology of the alloy after 15 cycles of HPT (e) and corresponding EDS mappings of elements Mg (f), Zn (g), Ca (h), and Sr (i)

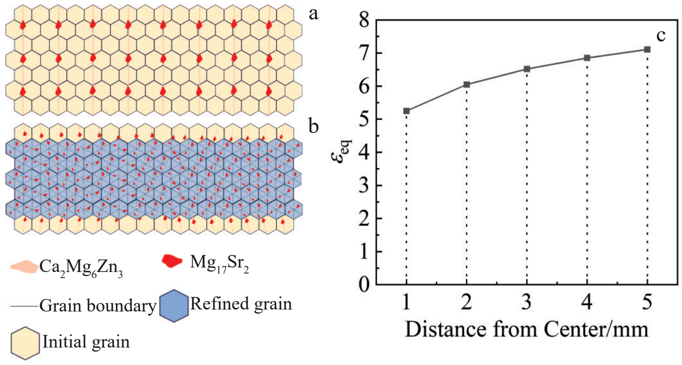

Fig.4 Refinement mechanism and equivalent deformation of ZXJ310 alloy in different states: (a) extruded and (b) after 15 cycles of HPT; (c) equivalent strains at different positions of specimen after 15 cycles of HPT process

revealing the presence of larger Mg-Zn-Ca ternary phase which is dominant and finer Mg-Sr binary phase. Combining the previous work, it can be known that the composition of these two phases is $Ca_2Mg_6Zn_3$ and $Mg_{17}Sr_2$, respectively. Importantly, combined XRD and TEM results show that no dynamic precipitation occurs in ZXJ310 during the HPT process, nor is any stress-induced phase transformation obserevd in the second-phase of the alloy.

Fig. 4 illustrates the schematic diagram of grain and secondary phase evolution and equivalent shear strain at different positions in the longitudinal cross-section of the ZXJ310 alloy. The degree of grain refinement can be reflected by Eq. (1) and Eq. (2)[15]:

$$\gamma = \frac{2\pi Nr}{h} \tag{1}$$

where γ represents the shear strain, N is the number of rotations, r is the distance to the center, and h is the thickness of the sample.

$$\varepsilon_{eq} = \frac{2}{\sqrt{3}} \ln\left[1 + \left(\frac{\gamma^2}{4}\right) + \frac{\gamma}{2}\right] \tag{2}$$

where ε_{eq} is the equivalent strain. According to Eq. (1) and Eq. (2), the shear strain and equivalent strain at $2R$ are 19.625 and 3.44, respectively; while at $4R$, the shear strain and equivalent strain are 39.3 and 4.24, respectively. Therefore, under higher equivalent strain, the grain at the edge of the alloy is more thoroughly fragmented, so the size is smaller. In addition, according to the above equations, the strain in the center of the alloy should be 0. However, based on our microstructure observation, central region has undergone notable changes, particularly through the formation of a streak-like structure. This is because, in the HPT process, the surrounding grains deform the grains in the center.

4 Conclusions

1) The extruded ZXJ310 was subjected to HPT for 15 cycles, resulting in significant grain refinement with an average grain size of 98.3 nm. At the same time, the distribution of the secondary phase in the alloy changes from an initial streamlined morphology to a uniformly dispersed distribution. The grain refinement and dispersion of the secondary phase in the alloy promote the uniform corrosion of the alloy.

2) After 15 cycles of HPT, the hardness of the alloy is significantly improved, rising from 60.3 HV in the extruded state to 98.5 HV. The most obvious refinement and strengthening effects are observed at the edge of the alloy.

3) This study demonstrates the potential application of HPT in improving microstructure and second-phase distributions in metallic materials. The technique provides a new processing method to adjust and to optimize the microstructure of metal alloys. Considering the biodegradable properties of the ZXJ310, optimizing its microstructure and hardness is expected to expand its potential applications in the biomedical field, such as manufacturing biomedical instruments or implants.

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高压扭转对Mg-3Zn-1Ca-0.5Sr合金组织和第二相分布的影响

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摘　要：近年来，以镁及镁合金为代表的可降解金属，因具有良好的生物相容性、适宜的弹性模量及可降解的特性，逐渐成为了骨折内固定及骨缺损修复材料的研究热点。生物可降解骨植入用Mg-3Zn-1Ca-0.5Sr（wt%）合金，因其具有全营养元素组成的特点及良好的力学性能，是非常具有应用潜力的医用金属材料。但由于该合金中存在粗大的第二相，合金的降解速率过快，植入时存在产气严重的现象，限制了其临床推广和应用。为了进一步优化该合金的性能，采用挤压复合高压扭转对其进行变形加工。结果表明，通过优化材料加工手段，可以细化和破碎晶粒并改善第二相分布，从而改善合金的组织，进而提升合金的力学和耐腐蚀性能。经过15周次高压扭转处理，合金晶粒细化到纳米级别，达到98 nm左右，流线组织消失，第二相破碎后呈弥散分布。显微组织的这种变化导致合金的组织均匀性提高，同时显著强化合金，硬度从挤压态的60.3 HV增加到98.5 HV。

关键词：高压扭转；生物材料；显微组织；Mg-Zn-Ca-Sr；超细晶

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