Rare Metal Materials and Engineering
Volume
Available online at **www.rmme.ac.cn**

Cite this article as: Rare Metal Materials and Engineering,

ARTICLE

DOI: 10.12442/j.issn.1002-185X.20240272

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

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Abstract: In recent years, degradable metals, represented by magnesium and magnesium alloys, have gradually become the research focus of fracture internal fixation and bone defect repair materials due to their good biocompatibility, suitable elastic modulus and degradable properties. The Mg-3 wt%Zn-1 wt%Ca-0.5 wt%Sr alloy is considered a competitor in the biomaterial field thanks to its unique composition of essential nutrients and excellent mechanical properties. However, due to the existence of coarse second phase in the alloy, the degradation rate of the alloy is too fast, and there is a serious phenomenon of gas production during implantation, which limits the clinical promotion and application of the alloy. In order to further optimize the properties of the alloy, this study adopts extrusion composite high pressure torsion (HPT) for deformation processing. 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 of the alloy, and then improving the mechanical and corrosion resistance of the alloy. The high pressure torsion deformation process is applied to the processing of magnesium and magnesium alloys. It can improve its potential in biomedical applications. The results showed that after HPT processing, the grains at the periphery of the alloy were significantly refined to a nanometer level, reaching approximately 98 nm, the distribution of the secondary phase also improved significantly, transforming the original streamlined organization into a dispersed distribution. This change in microstructure led to a significant strengthening of 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

Biodegradable metals have become a popular research direction in today's biomedical field [1]. These materials have applications in medicine, such as orthopedics and cardiovascular devices, providing patients with new treatment methods. The biodegradable metals gradually get absorbed by the body after completing their function, avoiding the problem of long-term retention. Therefore, research and development of such materials have important practical significance [2].

The Mg-Zn-Ca-Sr alloy is one of the focuses in recent years [3-6]. The Mg-3 wt%Zn-1 wt%Ca-0.5 wt%Sr alloy (ZXJ310) is considered a strong competitor in biodegradable metals due to its special composition of essential nutrients and good me-

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Received date:
Foundation item: National Key R&D Program of China [No. 2021YFB3701004]

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chanical performance. Adding elements such as Zn, Ca, and Sr further improves its performance, making it more suitable for medical applications [7-8].

Researchers have tried various processing techniques to further optimize this alloy's performance [9-13]. High-pressure torsion (HPT), a method can achieve grain refinement, thus improving the material's strength and hardness. HPT can also affect the distribution of secondary phases, further improving the material's performance.

Based on the above background, this study aims to investigate the effect of HPT on the microstructure and phase distribution of the ZXJ310 alloy. Furthermore, the results of this study may also provide valuable references for other similar alloys.

1 Materials and Methods

The as-cast ZXJ310 alloy was subjected to homogenization treatment at 380°C for 6 hours. Extrusion processing with in-line quenching was performed using a direct extrusion machine. The extrusion ratio was 23, and specific extrusion parameters can be found in previous research [14]. The high-pressure torsion (HPT) samples were prepared from the extruded alloy. The HPT samples had a diameter of Φ10×1.00 mm. The HPT-4 type high-pressure torsion device produced by TRANSMST Company from Austria was used for processing at room temperature. The pressure was set at 7.85 GPa, the rotation speed was set at 1 rpm, and the number of torsion cycles was set at 15. The schematic diagram of the materials processing procedure is shown in Fig. 1.

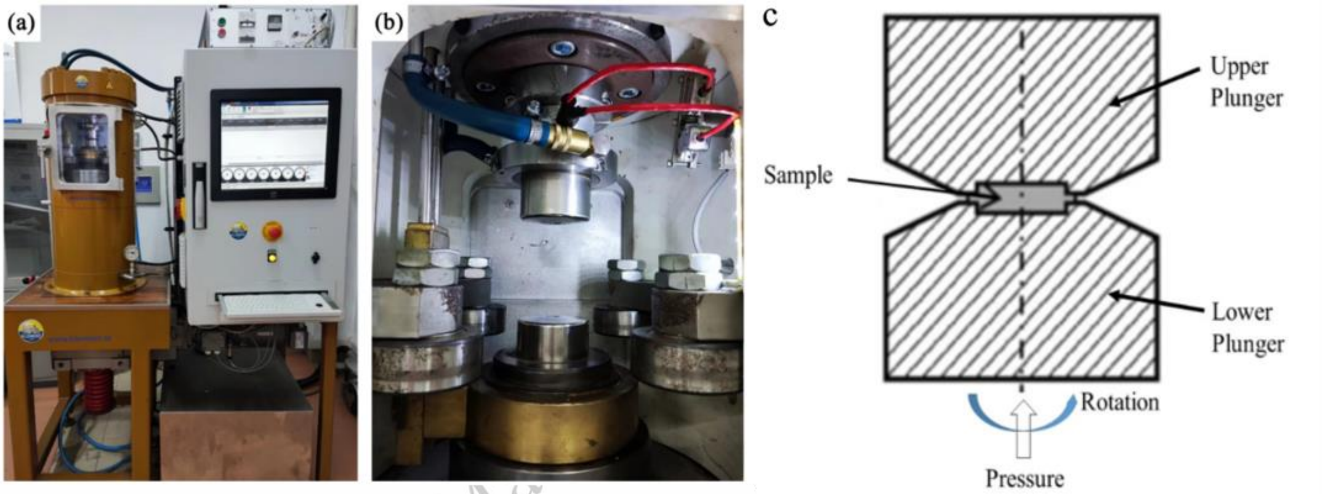

Fig. 1 Schematic diagram of HPT machine and process of magnesium alloy: (a) Equipment appearance; (b) Clamp; (c) HPT schematic diagram

After HPT, the microstructure of the cross-section and radial section of the samples, as well as the 0.5 R and edge regions, were observed under a Zeiss Axiovert 2000 MAT optical microscope. Hardness testing was conducted using a WILSON VH1150 Vickers hardness tester. The samples were only polished with sandpaper. During the testing, a load of 5 kg was applied with a 15 s dwell time. For the transmission electron microscopy (TEM) samples, the samples obtained after high-pressure torsion were directly polished until they reached a thickness of 80-100 μm. Then, circular discs with a diameter of Φ3 mm were punched out using a hole puncher. The discs were further polished to a thickness of 50 μm. Subsequently, the specimens were thinned using dual-beam ion milling with an attached energy-dispersive X-ray spectroscopy system. The observation was carried out using a Tecnai G2 F20-TWIN transmission electron microscope. The grain size and size distribution of the HPT alloys were measure and calculated by the Nano-Measure software.

2 Results and Discussion

Fig. 2(a) and Fig. 2 (b) show the transverse and longitudinal metallographic structures of the extruded ZXJ310, respectively. It can be seen that 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. 2 (c) and Fig. 2 (d) are the SEM results of the cross-sectional and longitudinal sections of the extruded ZXJ310, which show the secondary phase distribution of transverse and longitudinal microstructure differences of the alloy more clearly. The distribution of the secondary phase in the transverse and longitudinal cross-sections of the alloy is 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. 2(e) and Fig. 2(f) represent the metallographic microstructures of the transverse and longitudinal observations of the HPT ZXJ310 alloy, respectively. It can be observed that the presence of grain boundaries is almost negligible in the HPT alloy. It’s because after undergoing 15 rotations of HPT, the grain size has refined to one hundred nanometers, which exceeds the resolution limit of the metallographic microscope.

Fig. 2 (g) and Fig. 2 (h) show the transverse and longitudinal SEM results of the alloy after 15 HPT cycles, at this time, the transverse structure of the alloy is not much different from the extrusion state, but the longitudinal structure has changed significantly, that is, the secondary phase has changed from the original streamline distribution to uniform diffuse distribution.

Fig. 2(i) illustrates the hardness of the extruded ZXJ310 and the HPT-treated alloy. After 15 rotations of HPT, the hardness of the alloy has significantly increased compared to the extruded state, 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.

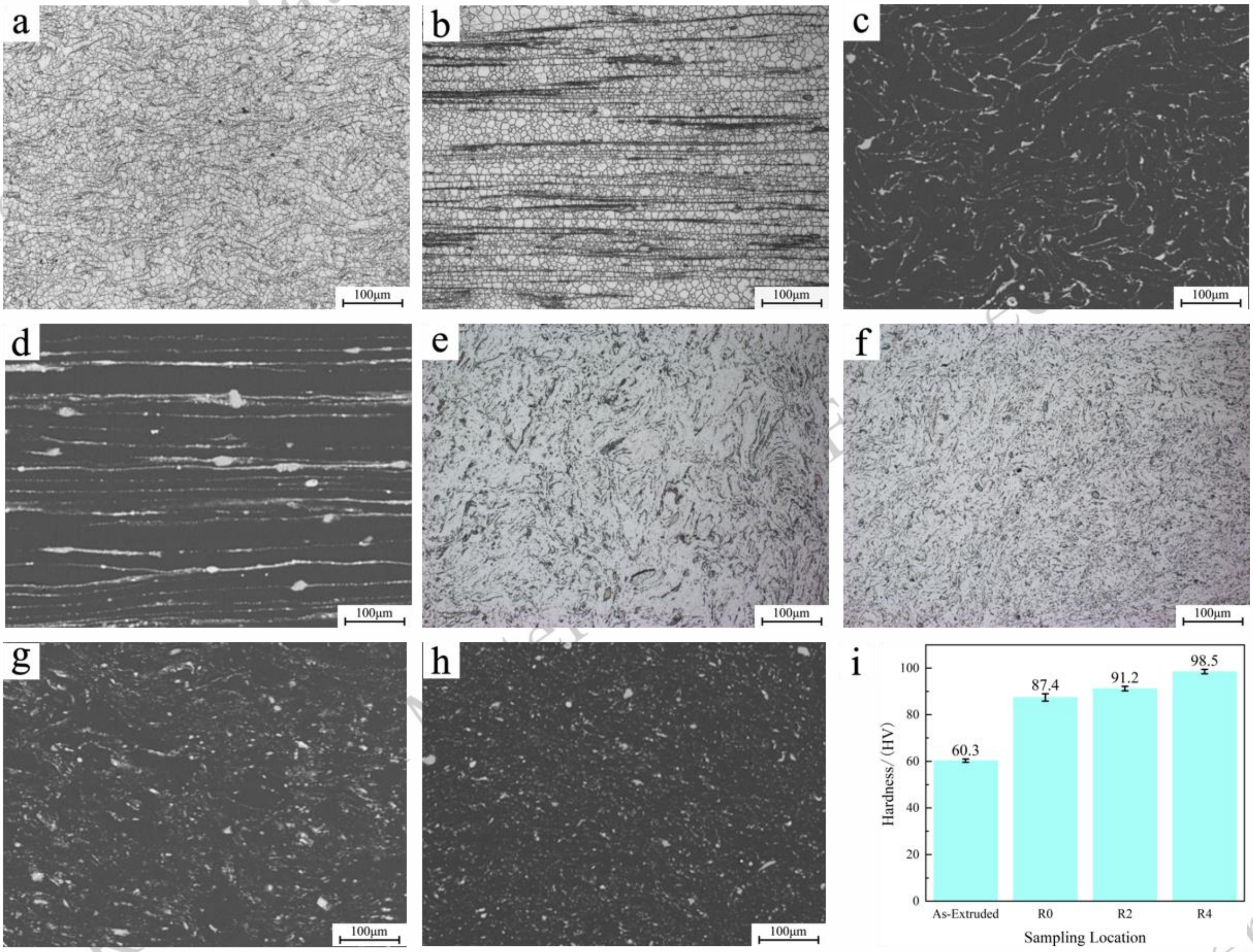

Fig.2 Microstructure and properties of ZXJ310 alloy: (a) (b) Metallographic structure of extruded ZXJ310 alloy in transverse and longitudinal directions, (c) (d) SEM results of extruded ZXJ310, (e) (f) Metallographic structure of HPT15-cycles ZXJ310 alloy, (g) (h) SEM results of metallographic structure of HPT15-cycles ZXJ310 alloy, (i) Hardness of ZXJ310 alloy in different states

Fig. 3(a) and Fig. 3(b) presents the TEM results of the HPT-treated ZXJ310 alloy, showing evident polycrystalline diffraction rings, indicating grain refinement to the nanometer level. As shown in Fig. 3(c), the grain size of HPT alloys is mostly distributed between 100 and 120 nm, and the average grain size is refined to 98.3 nm. Fig. 3(d) shows the extruded state and the XRD results of the ZXJ310 alloy after 15 HPT turns, the alloy is still composed of α-Mg, Ca2Mg6Zn3 and Mg17Sr2 phases, and there is no diffraction peak of the new phase. Fig. 3(e) shows the morphology of the alloy after 15 HPT cycles, and the second phase in the alloy shows a tendency to separate under severe shear deformation.

Fig. 3(f), Fig. 3(g), Fig. 3(h) and Fig. 3(i) demonstrate the surface scan results of the alloy, revealing the presence of the dominant Mg-Zn-Ca ternary phase with a larger size and the smaller Mg-Sr binary phase. Combined with previous work, it’s known that the compositions of these two phases are Ca2Mg6Zn3 and Mg17Sr2, respectively. It is worth noting that the combined XRD and TEM results show that there is no dynamic precipitation of ZXJ310 during the HPT process, and there is no stress-induced phase transformation in the second phase of the alloy.

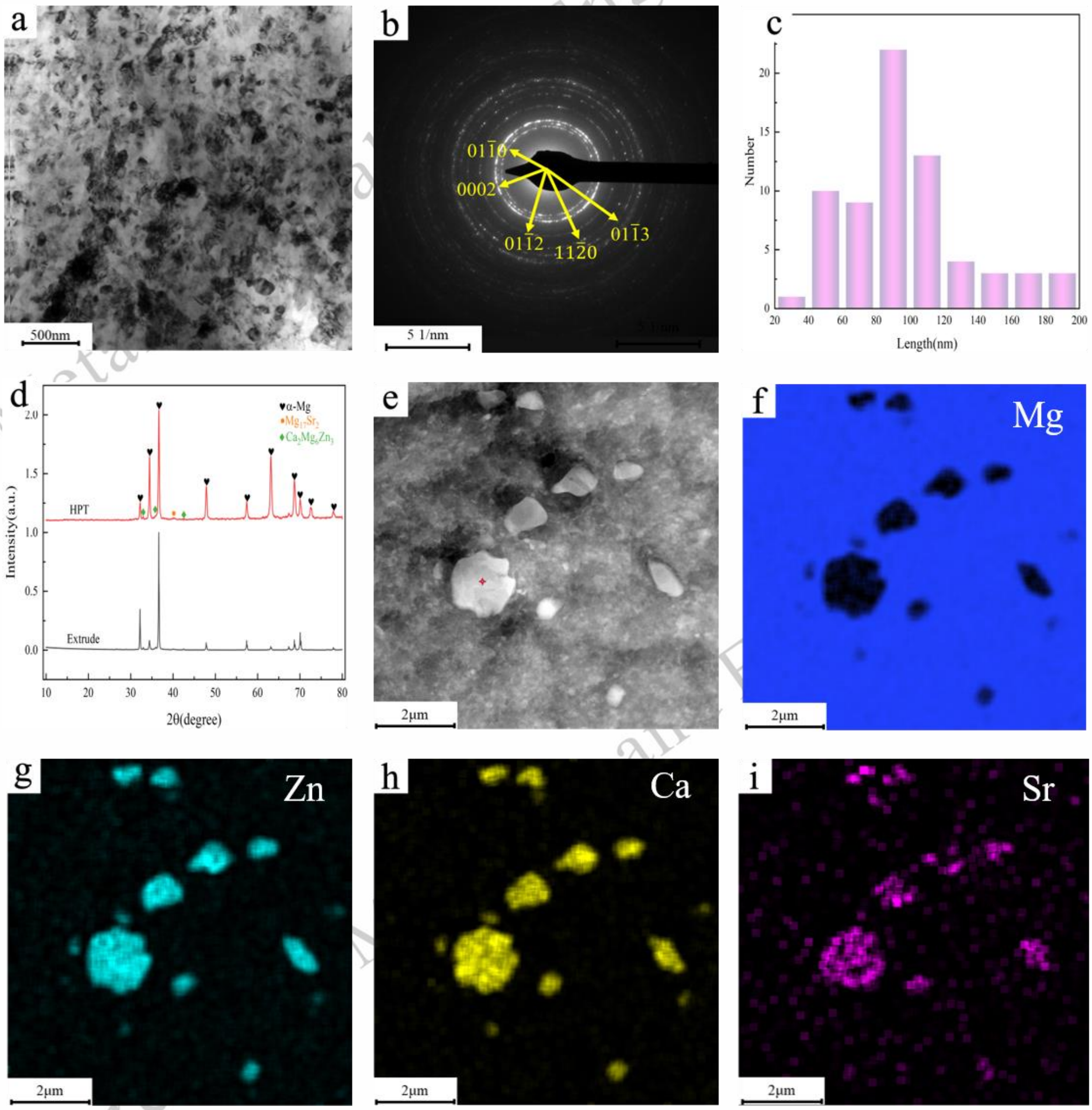

Fig. 3. TEM results of the HPT-treated ZXJ310 alloy: (a) grain structure, (b) SAED, (c) Grain size distribution,(d) XRD results, (e) morphology, (f)-(h) distribution of Mg, Zn, Ca, and Sr elements.

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 the following two equations [15]:

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

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

Equation (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. Equation (2), where εeq is the equivalent strain. According to Equations (1) and (2), the shear strain and equivalent strain at R2 are 19.625 and 3.44, respectively, while at theR4, the shear strain and equivalent strain are 39.3 and 4.24, respectively. Therefore, under higher equivalent strain, the grain size at the edge of the alloy is more thoroughly fragmented and 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, changes have occurred in the center, particularly in forming a streak-like structure. This is because, in the HPT process, the surrounding grains deform the grains in the center.

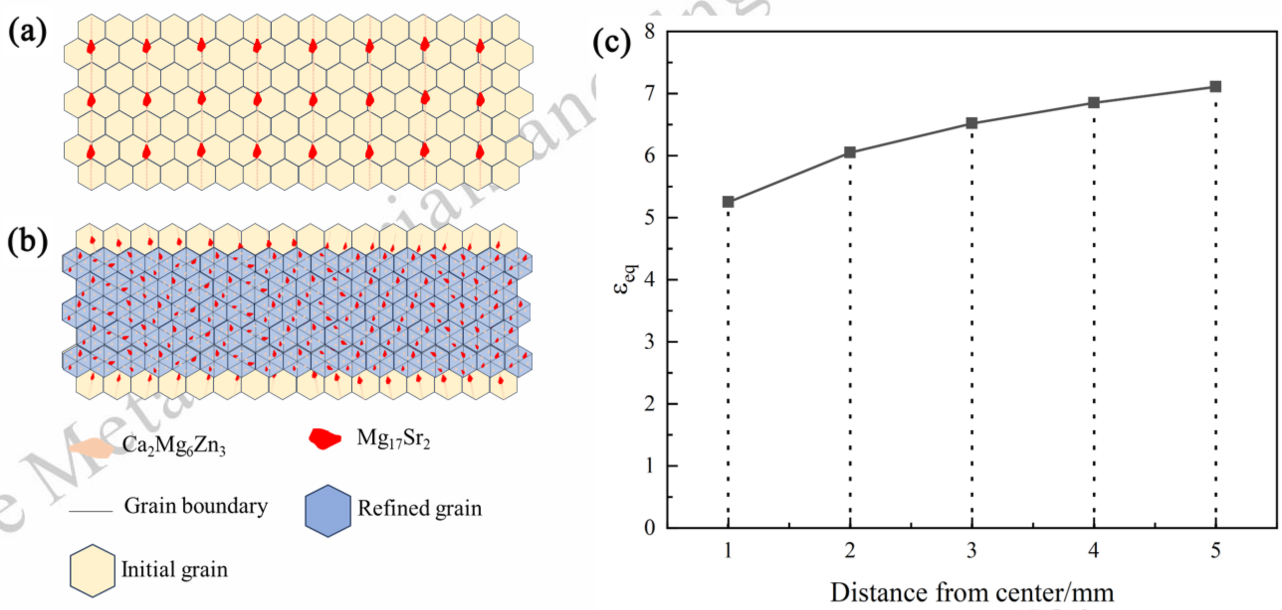

Fig.4 Refinement mechanism and equivalent deformation of ZXJ310 alloy after HPT 15 cycles: (a) As-extruded, (b) After HPT 15 cycles, (c) Equivalent strains at different positions of the specimen after 15 cycles of HPT process

3 Conclusions

In this work, the extruded ZXJ310 was subjected to 15 HPT passes, resulting in grain refining to 98.3 nm. At the same time, the distribution of the secondary phase in the alloy changed from an initial streamlined distribution to a uniform dispersed distribution. Due to the grain refinement and dispersion of the secondary phase in the alloy, this is beneficial for the uniform corrosion of the alloy. After 15 passes of HPT, the hardness of the alloy was significantly improved, increased from 60.3 HV in the extruded state to 98.5 HV， with the most obvious refinement and strengthening effects observed at the edge of the alloy. This study demonstrates the potential application of high-pressure torsion in microstructure and second-phase distribution in the field of metallic materials science and provides a new processing method to adjust and optimize the microstructure of metal alloys. Considering the biodegradable properties of the ZXJ310, optimizing its microstructure and hardness is expected to enhance its application value in the medical field, such as manufacturing biomedical instruments or implants.

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高压扭转对 Mg-3 wt%Zn-1 wt%Ca-0.5 wt%Sr 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-3 wt%Zn-1 wt%Ca-0.5 wt%Sr 合金，因其具有全营养元素组成的特点及良好力学性能，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，本研究采用挤压复合高压扭转(HPT)对其进行变形加工，通过优化材料加工手段，可以细化晶粒和破碎并改善第二相分布，从而改善合金的组织，进而提升合金的力学和耐腐蚀性能，将高压扭转变形工艺应用于镁及镁合金加工，可提高其在生物医学应用中的潜力。研究结果表明: 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，硬度从挤压态的 60.3HV 显著增加到 98.5HV。

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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