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Corrosion behavior of extrusion-drawn pure Mg wire immersed in simulated body fluid

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Abstract: The corrosion behaviors of extrusion-drawn pure magnesium wire soaked in simulated body fluid (SBF) and 0.9% NaCl solution were studied. The corrosion law of the pure magnesium wire immersed in SBF was investigated by measuring the average corrosion rate and the pH values of the solution after corrosion. It is found that the corrosion mechanism of the pure magnesium wire was pitting after the observation of corrupted surface morphology by scanning electron microscopy (SEM). Moreover, the corrosion law of extrusion-drawing pure magnesium wire in 0.9% NaCl solution implied that the smaller the grain size of the wire is, the better the corrosion resistance exhibits.

Key words: pure magnesium wire; cold drawing; simulated body fluid; corrosion

1 Introduction

As an important essential trace element, magnesium participates almost all the human metabolism, ranking just after calcium, sodium and potassium [1−4]. Its density (1.74 g/cm^3) is close to that of natural bone (1.75 g/cm^3). Meanwhile, its high specific strength (pure Mg, 133 GPa/(g·cm^3)) and specific stiffness, which can meet the strength performance requirements of biological implant materials.

As a biodegradable implant material, magnesium provides both biocompatibility and sufficient mechanical properties. Mg alloys are very attractive due to their good biocompatibility and especially their degradability [5]. Researches found that magnesium alloys offer great potential as absorbable implant materials such as cardiovascular tube stent [6−9] and bone fixation materials for instance as bone screws or plates [10−15]. Within a certain time span after surgery, they degrade and are completely suitable to medical functions.

However, as it is known that the surface and subsurface properties of the implant were determined by the manufacturing process and therefore the corrosion behavior was obviously influenced by manufacturing process [16−17].

In this work, the extrusion and cold drawing process was used to improve the corrosion properties of pure magnesium. Primary researches focused on the corrosion property of extrusion-drawn pure magnesium wire in the simulated body fluid and 0.9% NaCl solution.

2 Experimental

2.1 Material preparation

As-cast pure magnesium (99.95% purity) ingot with *d*52 mm×40 mm in dimension was used as the starting material for extrusion. Firstly, the round rod was extruded into *d*16 mm rod. Then the *d*16 mm round rod was extruded into *d*5 mm rod. The extrusion temperature was 100 °C. At last these *d*5 mm rods were drawn into wires of three different types with 2.0, 1.2 and 0.9 mm in diameter at room temperature, respectively. In the drawing process, if the wire cracked, it would be annealed in the resistance furnace, without any protect gas. Several minutes later, it would be taken out from the resistance furnace and when it became cool in the air, it would be continued to draw until it reached the predetermined size. The annealing temperatures should be controlled in the range of 200−300 °C.

Four types of wires were chosen as corrosion experimental materials from the above material. The extruded *d*5 mm bar were cut into *d*2 mm×10 mm bar as specimen No.1. The specimen No.2 (*d*2 mm×10 mm),

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specimen No.3 (d1.2 mm×10 mm), specimen No.4 (d0.9 mm×10 mm) were all the cold drawing wires. They were polished with SiC papers to 1 200 grits, ultrasonically rinsed for 5 min in acetone solution and finally dried. Then these samples were weighed on the electronic balance. The microstructures of these samples were observed by optical microscope. The grain size was measured by the straight line intercept method.

2.2 Immersion test

In this work, a simulated body fluid (which contained 8.0 g NaCl, 0.4 g KCl, 0.14 g $CaCl_2$, 0.35 g $NaHCO_3$, 1.0g $C_6H_{12}O_6$, 0.1 g$MgC_{12}\cdot 6H_2O$, 0.06 g $MgSO_4\cdot 7H_2O$, 0.06 g KH_2PO_4, 0.06 g $Na_2HPO_4\cdot 12H_2O$, 1 L H_2O. Then pH value was adjusted to 7.5 by HCl and NaOH) and 0.9% NaCl solution were selected as the corrosion medium. The immersed samples would be used to do the following tests.

The first test: Four No.1 samples were immersed in Hank’s simulated body fluid. The soaking time was 12, 24, 48 and 72 h, respectively. The pH values of solution after immersion were measured by using pH meter and the specimen surface corrosion products were rinsed in the ultrasonic chromic acid then washed with distilled water and dried in air. The average corrosion rate (mm/a) of pure magnesium was measured by corrosion pit depth measuring method [18] (v_L=8.76v/ρ). Surface morphology of pure magnesium wire after corrosion was observed under the SEM.

The second test: Four samples were taken out from the specimen No.2, specimen No.3 and specimen No.4 respectively. They were immersed into 0.9% NaCl solution. The immersion time was 24, 48, 72 and 120 h, respectively. The average corrosion rates were measured. The relationship between corrosion behavior and grains size was investigated.

All experiments were performed in a thermostated container at a fixed temperature of (37±0.5) °C.

3 Results and discussion

3.1 Corrosion behavior

As the first test showed, lots of H_2 bubbles escaped from specimen surface as soon as they were put into in Hank's artificial simulated body fluid. With the extension of immersing time, conduction speed of H_2 bubbles gradually slows down. After soaking for 48 h, H_2 bubbles gradually stop to escape and some white sediments can be found and many erosion pits appear on specimen surface.

Figure 1 shows the pH value of SBF in different soaking periods. From Fig. 1, it can be seen that pH value increases with the extension of time because corrosion reaction produced $Mg(OH)_2$. But, when pH value reaches a certain degree, the sample surface forms a more stable $Mg(OH)_2$ film and the corrosion rate slows down. When the soaking time is about 48 h, pH value is almost stable. Pure magnesium exhibits the best corrosion resistance.

Figure 2 shows the average corrosion rate of pure magnesium wire in Hank’s simulation body fluid at different soaking time. At first, generally, with the extension of time, the average corrosion rate decreases gradually. But about 48 h later, the average corrosion rate decreases sharply. Indeed, recent research reported that it can generate $Mg(OH)_2$ film on the surface of pure magnesium after the long-time soaking in corrosive solution [19]. Therefore, the rising of pH value could be beneficial to form a stable $Mg(OH)_2$ film, to prevent wire material further corrosion and decrease the corrosion rate.

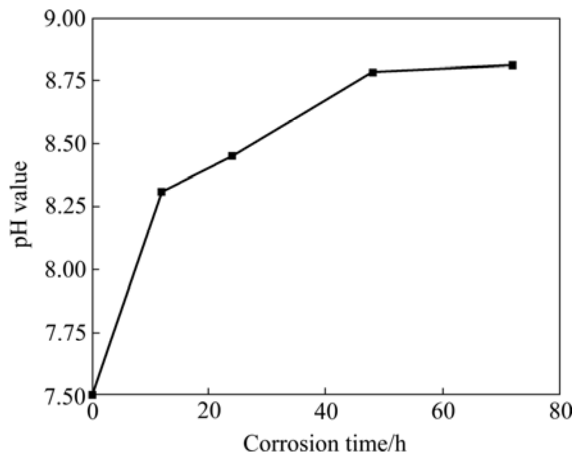

Fig. 1 pH values of SBF after different time

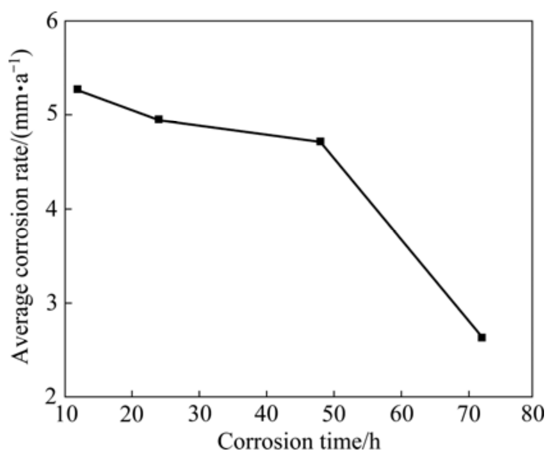

Fig. 2 Corrosion rate of pure Mg wire in SBF

3.2 Surface morphology after corrosion

Figure 3 indicates the surface morphology of pure magnesium wire after immersing for 12 h in Hank’s solution. As shown in Fig. 3(a), there are slightly small pits on the surface of samples, which explains that magnesium wire corrosion in solution began with local pitting corrosion. If the corrosion began in the local pores and developed in depth but not spread into the whole metal surface, it is holes corrosion, abbreviation pitting corrosion or pitting corrosion. It can be seen from Fig. 3(b) in the local places. That is corrosion pores to continue developing in depth and the corrosion pit becomes deeper gradually during the corrosion process.

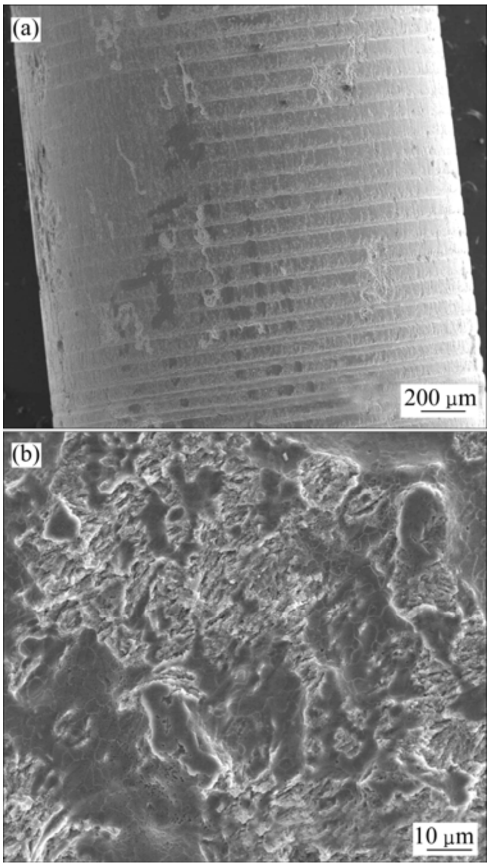

Fig. 3 Surface morphology of pure magnesium wire in Hank's simulation body fluid: (a) Low magnification; (b) High magnification

3.3 Effects of grain size on corrosion

As the second experiment stated, lots of H_2 bubbles escaped from specimen surface as soon as they were put into 0.9% NaCl solution. But bubbles escaped relatively fast from sample No.2 surface while sample No.4 relatively slow, which indicates that the grain size of pure magnesium wire affects the corrosion rate. The smaller the grain size is, the better the corrosion resistance exhibits.

In the cold drawing process, as drawing pass and deformation degree increase, the diameter of pure magnesium wire continuously decreases, and grain size is refined constantly. The microstructures of No.2, No.3 and No.4 are given in Fig. 4. The average grain size was calculated by the straight line intercept method. The average grain size of No.2, No.3 and No.4 are 14.18, 10.85 and 7.83 μm, respectively.

The average corrosion rates of different diameters of pure magnesium wires in the corrosive solution are given in Fig. 5. With the corrosion time raising, the corrosion rate decreases gradually and becomes stable.

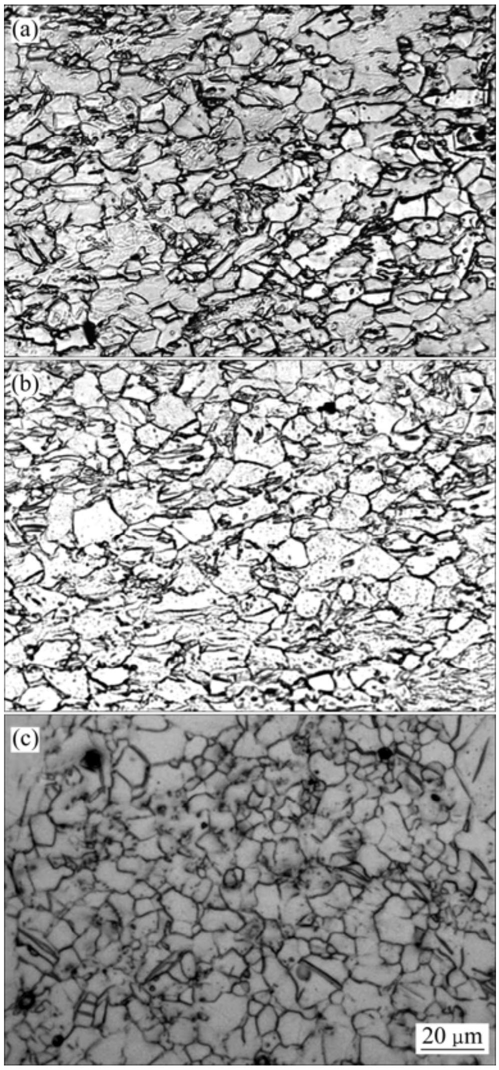

Fig. 4 Microstructures of different samples: (a) No.2; (b) No.3; (c) No.4

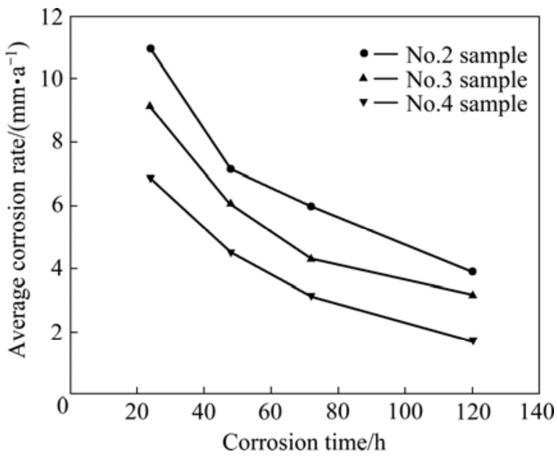

Fig. 5 Corrosion rate of pure Mg wire with different grain size in 0.9% NaCl solutions

Meanwhile, another rule can be seen from the graph, the average corrosion rate would decrease gradually with the refining of grain. The average corrosion rate of sample No.4 is the lowest, while No.2 is the highest. From Fig. 4, it can be seen that sample No.4 has the smallest grain size, while No.2 the largest.

4 Conclusions

1) After analyzing the corrosion rule and the surface morphology of the pure magnesium wires in simulated body fluid, it can be found that pure magnesium corrosion mechanism is local corrosion and the majority is the corrosive pitting corrosion. With the extension of time, the corrosion pits become deep and expand outward, and the average corrosion rate decreases gradually.

2) After the research on behaviors of different diameters of pure magnesium wires in the 0.9% NaCl solution, the results show that the smaller the grain size is, the better the corrosion resistance exhibits, which explains that grains refining may help to slow down corrosion rate.

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挤压−拉拔的纯镁丝材在人工模拟体液中的腐蚀行为

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摘 要：研究了挤压−拉拔的纯镁丝材在人工模拟体液和 0.9%NaCl 溶液中的腐蚀行为。通过测量纯镁丝材在人工模拟体液中的平均腐蚀速率和腐蚀后溶液的 pH 值来研究其腐蚀规律。通过扫描电子显微镜观察纯镁丝材腐蚀后人表面形貌，发现纯镁丝材的腐蚀机理为点腐蚀。而且，纯挤压−拉拔的纯镁丝材在 0.9%NaCl 溶液中的腐蚀行为表明，丝材的晶粒越细小丝材所表现出来的耐腐蚀性能越好。

关键词：纯镁丝材；冷拉拔；模拟体液；腐蚀

(Edited by DENG Lü-xiang)