

Microstructure, mechanical and corrosion properties of ultrafine-grained Mg-2%Sr alloy

O.B. Kulyasova^{1,2}, R.K. Islamgaliev¹, E V Parfenov³, Y.F. Zheng⁴, R.Z. Valiev^{1,2}

¹ Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, 12 Karl Marx Street, Ufa, 450008, Russia

² Saint Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russia

³ Department of Theoretical Basis of Electrical Engineering, Ufa State Aviation Technical University, 12 Karl Marx Street, Ufa, 450008, Russia

⁴ College of Engineering, Peking University, 5 Yi-He-Yuan Road, Hai-Dian District, Beijing, China.

E-mail: elokbox@mail.ru

Abstract. Thermal stability of microstructure of the magnesium alloy Mg-2%Sr processed by high pressure torsion has been studied using scanning and transmission electron microscopy. It was shown that formation of bimodal structure after additional annealing at a temperature of 200°C leads to demonstration of enhanced ultimate tensile strength (245 MPa) with a ductility of 1.5%. In addition a uniform distribution of eutectic phase in bimodal structure led to a slowing down of the corrosion rate to 2% for 31 days (compared to the initial state of 78% for the same period).

1. Introduction

Many scientists are engaged in improving the biological properties of materials for the manufacture of medical implants [1-3]. Among the various materials, great attention is paid to metal implants. Magnesium and magnesium alloys have a great potential among other metals, because they are light and bioresorbable, and can be used as a material for the manufacture of screws, pins and plates should, if they have a high level of mechanical properties and a low rate of corrosion. Pure magnesium does not meet such requirements in the first place due to its low strength. Thus, for the effective use of magnesium as a biomaterial, it is necessary to increase its strength characteristics by alloying with other elements. However, the choice of alloying elements is not so wide, because these elements must also be biocompatible and not cause allergic reactions [4]. In the present work, Sr was chosen as the alloying element, since it is a natural element for the bone [5]. It was found out that the Sr content of 2wt% is optimal in the ratio of strength and ductility characteristics, but the cast Mg-2%Sr alloy still does not have sufficient mechanical properties to make medical products from it [5]. It is known that deformed magnesium alloys have a higher level of mechanical properties compared to cast alloys [7-9]. Recently, methods of controlling the structure have been actively developed by grain refinement and creating a uniform distribution of excess phases, based on the use of severe plastic deformation [10]. With the help of such methods, and in particular of high pressure torsion (HPT), deep structural changes occur, including significant grain refinement and partial dissolution of the excess phase



components. In the present work we investigated the effect of high pressure torsion and additional thermal treatment on the structural-phase, mechanical and corrosion changes of magnesium alloy Mg-2wt%Sr.

2. Experimental

As the initial material, we used samples of an Mg-2wt%Sr alloy subjected to solid solution treatment at 430°C for 24 h and subsequent quenching.

To obtain a nanostructured state in a magnesium alloy Mg-2% Sr, disks with a diameter of 20 mm and a thickness of 1 mm were subjected to HPT at a pressure of 6 GPa at room temperature. For the development of the structure, 10 revolutions were performed with a strain rate of 1 rpm.

The macrostructure was studied with an Olympus GX51 optical microscope. The microstructure was examined with a JEM-6390 scanning electron microscope (SEM) and a transmission electron microscope (TEM) JEM-2100 with accelerating voltages of 10 kV and 200 kV, respectively. The discs with a diameter of 3 mm for TEM foils were cut out after grinding to 0.1 mm. Then they were subjected to twin-jet electropolishing on Tenupole-5. Electrolyte for electropolishing consisted of HCl acid - 10% and methanol - 90%. The average grain size was determined by the intercept method and was calculated from more than 250 grains measurement.

The microhardness of samples HV was measured by the Vickers method using a Micromet-5101 device with a load of 1 N and a dwell time of 10 s. Each sample was measured along a diameter more than 20 times to provide reliable results.

Tensile tests were performed on an Instron 5982 testing machine at room temperature and initial strain rate of 10^{-3} s^{-1} using specimens with a gage dimension of $0.6 \times 1 \times 4.5 \text{ mm}^3$. A set of 3 samples was tested for each condition.

The corrosion tests were carried out according to ASTM G1-03-E. This study presents the mass loss results of magnesium alloy in a 0,9% NaCl at temperature 37 °C.

3. Results and discussion

The structure of the Mg-2%Sr alloy after homogenization is a solid solution (α -Mg), with the eutectic (α -Mg + $\text{Mg}_{17}\text{Sr}_2$) located along the grain boundaries (Fig. 1). The average grain size was $252 \pm 42 \text{ }\mu\text{m}$. The volume fraction of the eutectic was $17 \pm 1\%$.

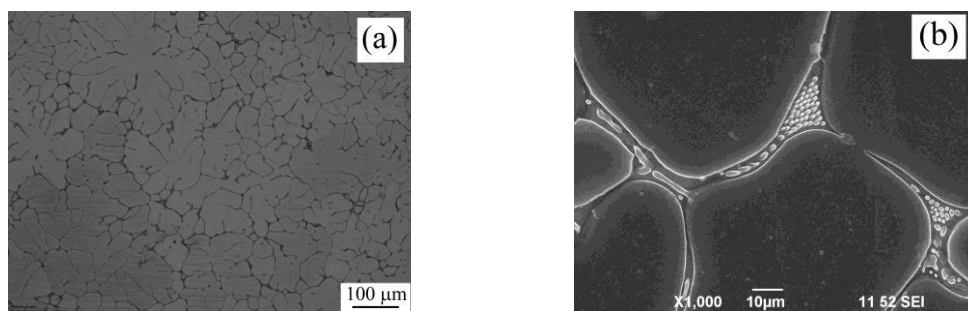


Figure 1. Microstructure of the Mg-2%Sr alloy in the initial samples

As a result of high pressure torsion, an ultrafine-grained structure with an average grain size of $432 \pm 52 \text{ nm}$ was formed in the alloy (Fig. 2). Investigations of microstructure of the HPT samples revealed a high density of dislocations in both the overall microstructure (Fig. 2a) and individual grains (Fig. 2b). However, small recrystallized grains with a size of about $200 \pm 24 \text{ nm}$, free from dislocations (Fig. 2c) were also found out. A significant difference in the structure of the eutectic (Fig. 2c) was found in comparison with the initial state. SEM images showed the eutectic phase is noticeably partitioned, and its volume fraction decreased to $11 \pm 1\%$, which indicates its partial dissolution at plastic deformation.

In the microstructure of the samples subjected to the HPT and additional annealing at a temperature of 150 °C, a small increase in the average grain size to 530 ± 37 nm was observed due to migration of grain boundaries (Fig. 3a). Inside grains a high density of dislocations was observed (Fig. 3a), and no changes in the volume fraction of the eutectic phase was detected (Fig. 3b).

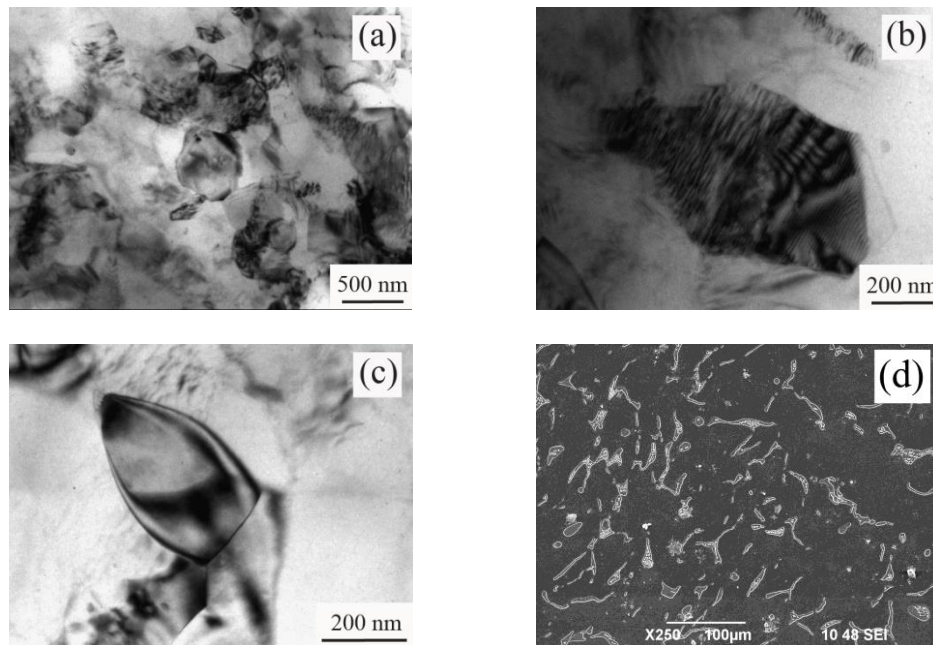


Figure 2. Microstructure of the Mg-2%Sr alloy after HPT: (a-c) TEM, (d) SEM

Studies of microstructure after HPT and additional annealing at a temperature of 200 °C revealed a strong decrease in the dislocation density (Fig. 4a). In the structure, fine grains were found with a size on the order of 0.8 ± 0.2 μm (Fig. 4a) and large ones with a size of 4 ± 1 μm (Fig. 4b). According to [11] the creation of such a bimodal structure should lead to both the high strength due to small grains and improved ductility at the expense of dislocation sliding in large ones. Changes in the volume fraction of eutectic component in this sample were not observed.

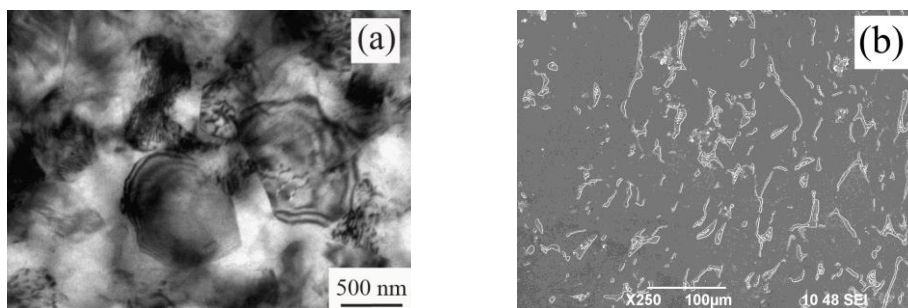


Figure 3. Microstructure of the Mg-2%Sr alloy after HPT and additional annealing at 150°C:(a) TEM, (b) SEM

Further development of recrystallization with the formation of a bimodal structure has been observed after additional annealing of the HPT samples at the temperatures of 250 (Fig. 5a) and 300°C (Fig. 6b). The eutectic with increasing temperature of additional annealing is transformed into single elongated conglomerates (Fig. 5b and 6b).

The microhardness of the initial samples was 42 ± 3 HV and increased after HPT up to 65 ± 5 HV, which is 1.5 times higher due to strong grain refinement. The study of thermal stability of the HPT samples by the microhardness measurements made it possible to establish that the samples are stable only up to temperature of 150°C (Fig. 7a). Thus, after additional annealing at 150°C , the microhardness remained practically unchanged, and after 200°C a significant decrease to 53 ± 4 HV was found out. Further, a monotonic decrease in microhardness was observed.

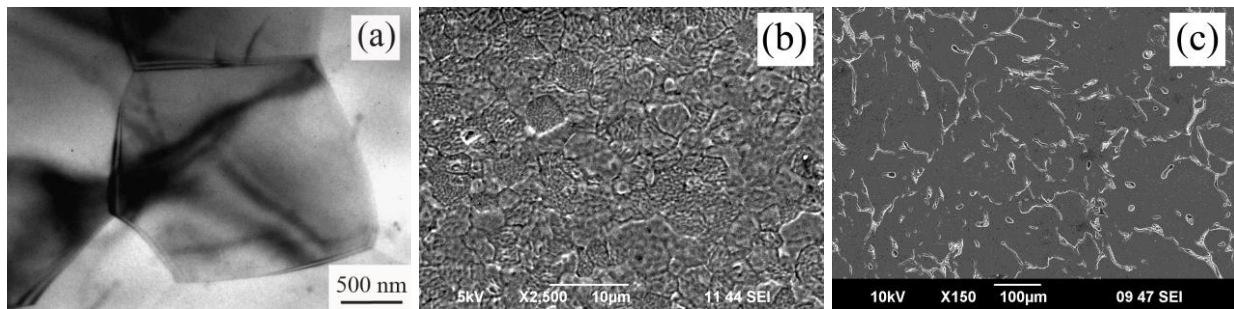


Figure 4. Microstructure of the Mg-2%Sr alloy after HPT and additional annealing at 200°C : (a) TEM, (b,c) SEM

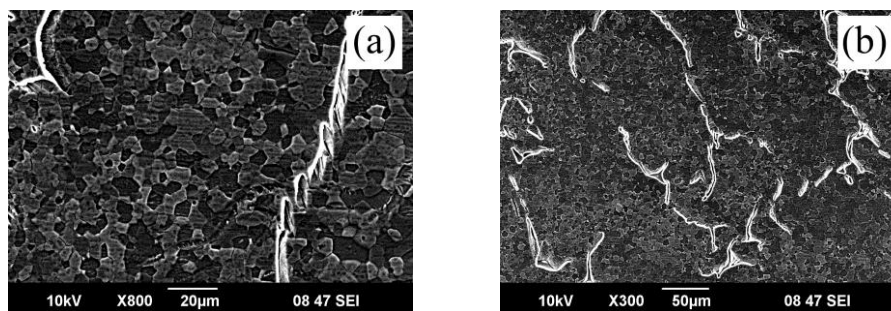


Figure 5. Microstructure of the Mg-2%Sr alloy after HPT and additional annealing at 250°C : (a, b) SEM

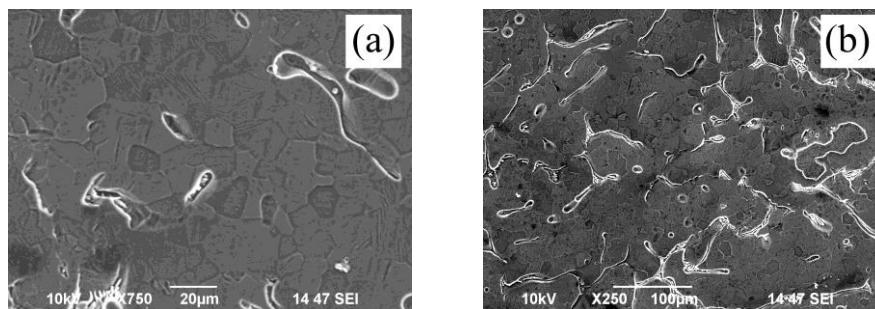


Figure 6. Microstructure of the Mg-2%Sr alloy after HPT and additional annealing at 300°C : (a, b) SEM

Figure 7b shows the results of tensile tests for the Mg-2%Sr alloy after various treatments. The initial samples after solid solution treatment do not have attractive mechanical properties compared to other magnesium alloys that have recently been developed for medical applications [8,9]. After the HPT and additional annealing at a temperature of 150°C , the samples have high microhardness, which implies the enhanced ultimate tensile strength. However, because of high internal stresses these samples showed brittle failure, not even reaching the yield stress. After additional annealing at the temperatures of 200, 250 and 300°C , the samples showed the enhanced strength and simultaneously residual ductility due to formation of a bimodal structure.

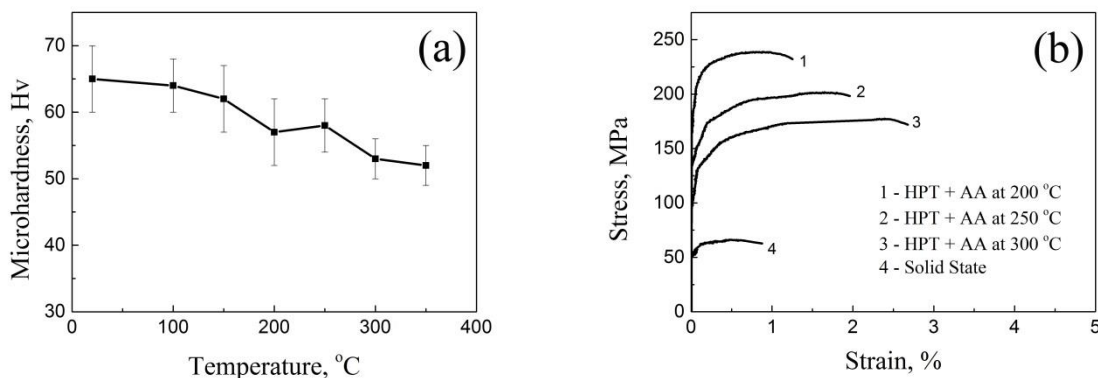


Figure 7. (a) – Microhardness dependence on the annealing temperature for the HPT samples of the Mg-2Sr alloy; (b) – results of tensile tests for the Mg-2Sr alloy at $T=20^{\circ}\text{C}$ and a strain rate of 10^{-3} s^{-1}

Studies of the corrosion resistance (Fig. 8a) of the Mg-2Sr alloy were carried out using samples subjected to HPT and additional annealing at 200°C in comparison with samples after solid solution treatment. It was found that the rate of the mass loss after solid solution treatment is higher than after the HPT and additional annealing. In particular the sample after solid solution treatment lost 72% of the initial mass after tests for 31 days, and the sample subjected to HPT and additional annealing was only 2%. Appearance of samples before the studies (0 days) and after exposure to saline (for days 15 and 27) are shown in Figure 8b. A decrease in the corrosion rate with grain refinement is typical for magnesium alloys [12-14]. In this study, an extra reason of less corrosion rate in ultrafine grained sample can be destroying at the HPT processing of a continuous grid of eutectics playing the role of a cathode at corrosion tests. So, the combination of enhanced strength and corrosion resistance observed in ultrafine grained Mg-2%Sr alloy can be attractive for next investigations of functional properties of the alloy to improve the design of implants in medicine.

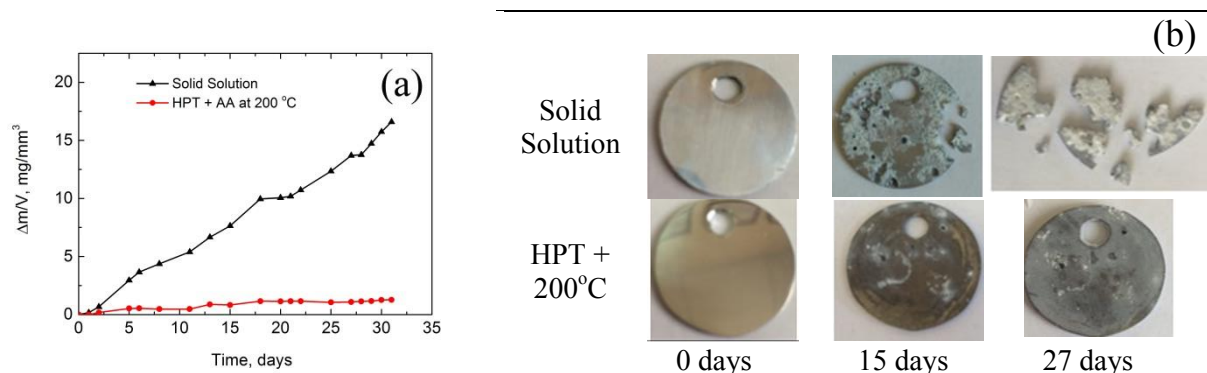


Figure 8. (a) The mass loss dependence on the exposure to saline of the Mg-2%Sr alloy; (b) appearance of the samples before (0 days) and after corrosion tests (15 and 27 days)

4. Conclusion

It was demonstrated that a combination of high pressure torsion and additional annealing at a temperature of 200°C leads to the formation of a bimodal structure providing the enhanced ultimate tensile strength of 245 MPa and residual ductility of 1.5%. In addition the grain

refinement and destroying of a continuous grid of eutectics at the HPT processing allowed reducing the corrosion rate from 78 to 2% in 0.9% NaCl for 31 days. The significant increase in both the strength and corrosion resistance of ultrafine grained Mg-2%Sr alloy can be attractive for next investigations of functional properties of the alloy to improve the design of implants in medicine. Наши будущие исследования будут нацелены на выявление условий деформационно-термической обработки сплава которые обеспечат упрочнение не только за счет повышения плотности границ, но и за счет твердорастворного/дисперсионного упрочнения.

Acknowledgments

This work was supported by Russian Foundation of Basic Research (Project No. 16-53-53039 in cooperation with NSFC, China) and by the Ministry of Education and Science of the Russian Federation through a platform grant in the field of basic research (No. 16.7268.2017) and St. Petersburg grant 6.37.204.2016.

References

- [1] Staiger M P, Pietak A M, Huadmai J and Dias G 2006 *Biomaterials* **27** 1728
- [2] Li L, Zhang M, Li Y, Zhao J, Qin L and Lai Y 2017 *Regenerative Biomaterials* **129**
- [3] Zheng Y Magnesium Alloys as Degradable Biomaterials 2016
- [4] Pogorielov M, Husak E, Solodivnik A and Zhdanov S 2017 *Interv Med Appl Sci.* **9** (1) 27
- [5] Bornapour M, Muja N, Shum-Tim D et al. 2013 *Acta Biomaterialia* **9** 5319
- [6] Guo X N, Xie X N, Li N, Zheng Y F, Qin L 2012 *Acta Biomaterialia* **8** 2360
- [7] Mingler B, Kulyasova O B et al. 2007 *Journal of Materials Science* **42** (5) 1477
- [8] Kulyasova O B, Islamgaliev R K, Zhao Y and Valiev R Z 2015 *Adv. Eng. Mat.* **17** (12)
- [9] Dobatkin S V, Lukyanova E A et al. 2017 *IOP Conf.Ser.: Mater. Sci. Eng.* **194** 012004
- [10] Valiev R Z, Islamgaliev R K and Alexandrov I V 2000 *Progress Materials Science* **45** (2) 103
- [11] Ma E 2006 *JOM* **58** (4) 49
- [12] Argadea G R, Panigrahi S K, Mishra R S 2012 *Corrosion Science* **58** 145
- [13] Liu Y, Liu D, You C, Chen M 2015 *Frontiers of Materials Science* **9** (3) 247
- [14] Saha P, Roy M, Datta M K, Lee B, Kumta P N 2015 *Mater Sci Eng C, Mater Biol Appl* **57** 294