

Article

Mechanical and Corrosion Properties of Mg–Gd–Cu–Zr Alloy for Degradable Fracturing Ball Applications

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Abstract: Generally, excellent mechanical properties of Mg alloys are desired, but their rapid degradation properties are seldom utilized. Petroleum fracturing techniques are required to take full advantage of this rapid degradation. Therefore, we have prepared an as-extruded Mg–6.0Gd–1.2Cu–1.2Zr (wt.%) alloy and treated it with peak aging to analyze its potential as a degradable fracture ball. The results show that the as-extruded alloy mainly consists of an α -Mg matrix, second phase, and large elongated α -Mg grains (LEGs). After aging, the LEGs undergo static recrystallization, which improves the mechanical properties of the alloy, and a lamellar long period stacking ordered (LPSO) phase is observed. Under simulated underground temperature conditions (93 °C), the ultimate tensile strength and elongation of both as-extruded and as-aged alloys are over 4 MPa and 11.1%, respectively, and the ultimate compressive strength and elongation of both alloys are over 336 MPa and 16.9%, respectively. The corrosion rate of the as-extruded alloy in 3 wt.% KCl solution at 93 °C reaches 1660.8 mm/y by mass loss test, and that of the as-aged alloy increases to 1955.1 mm/y. The atomic force microscope analysis result confirms that the second phase shows the highest corrosion potential, followed by the lamellar LPSO phase and α -Mg matrix. The as-extruded and as-aged Mg–6.0Gd–1.2Cu–1.2Zr alloy with good mechanical properties and a high corrosion rate in this work shows promising potential for degradable fracturing ball applications.

Keywords: Mg–Gd–Cu–Zr alloy; aging; extrusion; mechanical properties; corrosion; atomic force microscope; degradable fracturing ball



Citation: Jiang, J.; Geng, X.; Zhang, X. Mechanical and Corrosion Properties of Mg–Gd–Cu–Zr Alloy for Degradable Fracturing Ball Applications. *Metals* **2023**, *13*, 446. <https://doi.org/10.3390/met13030446>

Academic Editor: Ulrich E. Klotz

Received: 27 December 2022

Revised: 6 February 2023

Accepted: 18 February 2023

Published: 21 February 2023



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1. Introduction

In the industrial field, hydraulic fracturing technology is mainly used in unconventional oil and gas exploitation [1,2]. The use of hydraulic fracturing technology can effectively increase oil and gas production and recoverable reserves. Therefore, the related technologies and tools of hydraulic fracturing have become the focus of oil and gas development research. The fracturing ball is the key factor that determines the success of fracturing technology [3]. In general, during the process of fracturing, the fracturing ball can temporarily block the lower layer, separate the construction oil layer from the production oil layer, and ensure the smooth development of the fracturing operation. Meanwhile, when the fracturing ends in the oil and gas production stage, the fracturing ball needs to accelerate its dissolution rate and achieve complete degradation as soon as possible [4]. Finally, due to the high working environment temperature, the fracturing ball is needed to support high-temperature operation. Most of the materials currently used for fracturing balls are stainless steel, aluminum alloy, and other non-degradable materials [5]. They should be removed at last by traditional milling or drilling, which is complex and difficult to control and also increases production costs. There are also polymer materials used to prepare fracturing tools, but they are prone to serious plastic deformation, and the degradation products of these polymer materials may have a serious impact on the environment. In addition, it is difficult to control their degradation behavior, hence seriously affecting

production safety [6,7]. The preparation of fracturing balls using degradable materials is considered to be the most effective solution. Therefore, it is urgent to develop environmentally friendly fracturing ball materials with sufficient strength and a fast degradation rate that can effectively reduce construction costs and risks, shorten the construction period, and improve construction efficiency.

Mg alloys have low density, high specific strength and stiffness, good damping, and electromagnetic shielding performance, which makes them candidate materials for many practical applications such as automobiles and aerospace [8–10]. However, the standard electrode potential of Mg alloys is low, and their corrosion resistance is poor in the chloride ion environment, which restricts their broad engineering applications [11,12]. As for degradable fracturing ball materials, controllable fast degradation and sufficient mechanical properties at high working temperatures are necessary [13]. Mg alloys have good feasibility as fracturing tools, nevertheless, compared with traditional fracturing materials, the mechanical properties of Mg alloys need to be further improved, and the degradation of Mg alloys should be significantly increased to meet the practical application requirements. Recently, researchers have focused on how to improve the mechanical properties and accelerate the degradation of Mg alloys for fracturing ball application.

Generally, alloying can effectively improve the mechanical properties of Mg alloys by solid solution strengthening, second phase strengthening, and grain refinement strengthening [14,15]. Zr and Cu are often used to strengthen Mg alloys by refining grains and promoting the recrystallization of Mg alloys [16–18]. The addition of Zr can further increase the peak aging hardness of Mg–RE alloy. In particular, the introduction of Cu, Zn, Ni, and other transition elements in rare earth (such as Gd, Y, Ho, Er, Dy, etc.) containing Mg alloys can also form long-period stacking ordered (LPSO) structures, which are beneficial to purify the alloy, refine the microstructure, and improve the mechanical properties [19,20]. In addition, extrusion and heat treatment are also effective methods to improve the strength of Mg alloys due to the combined effects of grain refinement, solution strengthening, and precipitation strengthening [21–23]. At present, only a few researchers choose extruded alloys as temporary plugging materials for fracturing [7,16,24].

It is well known that when the content of Fe, Ni, or Cu in Mg alloys exceeds the tolerance limit, the corrosion of Mg alloys will be greatly accelerated [4,7,24,25]. These elements have low solubility in Mg alloys, and as the cathode active position of galvanic corrosion, they accelerate corrosion of the substrate. Xiao et al. [17] have found that the addition of Cu in Mg–Al–Zn alloys affects the quantity, morphology, and distribution of the $\text{Al}_7\text{Mg}_8\text{Cu}_3\text{Zn}_1$ phase, and the corrosion rate is accelerated due to the intensification of micro-galvanic corrosion. Zhang et al. [7] found that the corrosion rate of Mg–3Zn–1Y alloy increased by 38 times after adding Cu. Tan et al. [14] also found that the corrosion rate Mg–2.5Cu alloy in 3 wt.% KCl solution reached 1113 mm/y. Zhang et al. [4] used the micro-galvanic effect of Fe to accelerate the corrosion, which aggravated the corrosion degree of Mg–6Al–1Zn alloy, and the mechanical properties of the alloy were more stable after annealing. In addition, the composition, distribution, quantity, and morphology of the LPSO phase have beneficial or adverse effects on the corrosion properties of Mg alloys: on the one hand, it can promote degradation of Mg alloys by the formation of a galvanic couple; on the other hand, it may restrict corrosion as a barrier [26,27]. In general, the LPSO structure exists in the Mg–RE–Zn/Ni/Cu/Co system (RE = Y, La, Ce, Pr, Sm, Nd, Dy, Ho, Er, Gd, and Tm) [28]. In addition, the solubility of gadolinium (Gd) in Mg is 23.49 wt.% at the eutectic temperature, which plays a key role in the solid solution strengthening of Mg alloys [29]. Ma et al. [16] changed the distribution of the LPSO structure in a Mg–7.2Y–2.8Ni alloy using annealing treatment and improved the degradation rate and tensile strength of the alloy (280 MPa). This can make it become one of the candidate materials for a fracturing ball. Therefore, the introduction of the LPSO phase is beneficial to regulate the degradation rate of Mg alloys, which can provide new insights for the new type of fracturing temporary plugging Mg alloys. At present, there are few works in the literature on Mg–Gd–Cu alloys with high degradation rates. In order to meet the self-degradation of the fracturing ball

and high mechanical properties in a high-temperature environment, in this work, Mg–6Gd–1.2Cu–1.2Zr alloy was prepared using gravity casting and then hot extruded, followed by aging treatment. By simulating the underground working environment, we studied whether both the as-extruded and as-aged alloys have stable mechanical properties at high temperatures and fast degradation rates and evaluated whether it has reliable performance for degradable fracturing ball applications.

2. Experimental Methods

The Mg–6.0Gd–1.2Cu–1.2Zr (wt.%) alloy was prepared with gravity casting using pure Mg (99.99%), Mg–30Gd (wt.%), Mg–30Cu (wt.%), and Mg–30Zr (wt.%) master alloys [18,30]. The ingots (Φ 60 mm $\times$ 50 mm) were hot extruded at 400 °C into rods (Φ 20 mm) with an extrusion ratio of 9:1. Before hot extrusion, the as-cast alloy was homogenized at 400 °C for 24 h. The as-extruded alloy was optimized using a reasonable aging treatment. Finally, the alloy with the highest microhardness was obtained with aging at 170 °C for 8 h.

The samples were cut along perpendicular and parallel extrusion directions, ground with SiC paper, polished with 2.5 μ m diamond paste, and then etched in a picric acid solution for microstructure observation. The microstructure was characterized using an optical microscope (OM, OLYMPLUS GX51) and a scanning electron microscope (SEM, Zeiss-Merlin Compact) coupled with an energy dispersion spectrometer (EDS, Oxford Atec X-Max 50). The SEM observation was conducted at 7.0 kV under the secondary electron mode. X-ray diffraction (XRD, Rigaku Ultima-IV) was used to analyze the phases of the alloy with a working voltage of 40 kV, scanning angle of 20°~80°, and scanning speed of 6°/min.

The tensile properties of the alloy at ambient temperature and the tensile and compressive properties at simulated underground temperature (93 °C) were evaluated using an electronic material testing machine (Zwick/Roell, Z030TH) equipped with a heating chamber. Each sample with a gauge length of 15 mm, width of 3.5 mm, and thickness of 2 mm was held for 30 min to ensure uniform heating prior to the tensile test at 93 °C. The samples with a dimension of Φ 8 mm $\times$ 12 mm were also heated to 93 °C and held for 30 min for the compression test. The tensile and compression speeds were 1 mm/min. The fracture morphologies of the specimens were observed using SEM.

Commonly, 3 wt.% KCl solution is used as a base fluid to stabilize the clay and prevent its expansion in the oil industry, which is helpful to maintain the chemical environment of the clay particles. Moreover, the fracturing ball works underground, and the ambient temperature is higher than room temperature [14]. To evaluate the corrosion rate of the alloy under simulated underground conditions, three parallel samples with a dimension of Φ 13 mm $\times$ 3.5 mm were polished and then immersed in 3 wt.% KCl solution at 93 °C for hydrogen evolution and mass loss tests.

The hydrogen was collected using a burette which was filled with KCl solution and placed on top of a funnel with a specimen in the center of the funnel. The volume of hydrogen evolution was recorded every 10 min, and then the burette was filled with KCl solution immediately again to collect hydrogen. After 60 min of immersion, the samples were placed in a boiling chromic acid solution (200 g/L) to remove the corrosion products. The corrosion rate of the alloy was calculated using the following formula [8,30]:

$$v = 95.05 \frac{v_H}{\rho A T} \quad (1)$$

$$v = 87.6 \frac{\Delta w}{\rho A T} \quad (2)$$

where v is the corrosion rate (mm/y), v_H is the amount of hydrogen evolution (mL), Δw is the mass loss (mg), ρ is the density of the alloy (g/cm³), A is the surface area of the specimen (cm²), and T is the immersion time (h).

The potentiodynamic polarization test was conducted in 3 wt.% KCl with an electrochemical workstation (Parstat 2273). A platinum rod was used as the counter electrode, the saturated calomel electrode as the reference electrode, and an alloy sample as the working

electrode. The scanning speed was 1 mV/s. An atomic force microscope (AFM, Bruker Multimode 8) was used to measure the corrosion potential of the different phases, and Nanoscope Analysis 1.7 software was used to analyze the data.

3. Results and Discussion

3.1. Microstructure and Phase

Figure 1 shows optical micrographs of the as-extruded and as-aged Mg–6.0Gd–1.2Cu–1.2Zr alloy from both perpendicular and parallel extrusion directions. It can be seen from Figure 1a,b that the microstructure of the as-extruded alloy is mainly composed of dynamic recrystallized (DRXed) equiaxed α -Mg grains, a discontinuously distributed second phase, and some long-elongated α -Mg grains (LEGs). After the aging treatment, lamellar structures appear near the black second phase that can be inferred to be LPSO according to our previous studies [30], the LEGs cannot be observed, and much finer grains are formed, indicating the occurrence of static recrystallization. Moreover, the second phase seems to be reduced and more discontinuously distributed along the matrix grain boundaries. Compared with the as-cast alloy [30], the as-extruded alloy and as-aged alloy have obvious grain refinement, which is mainly due to the recrystallization during the extrusion and aging treatment.

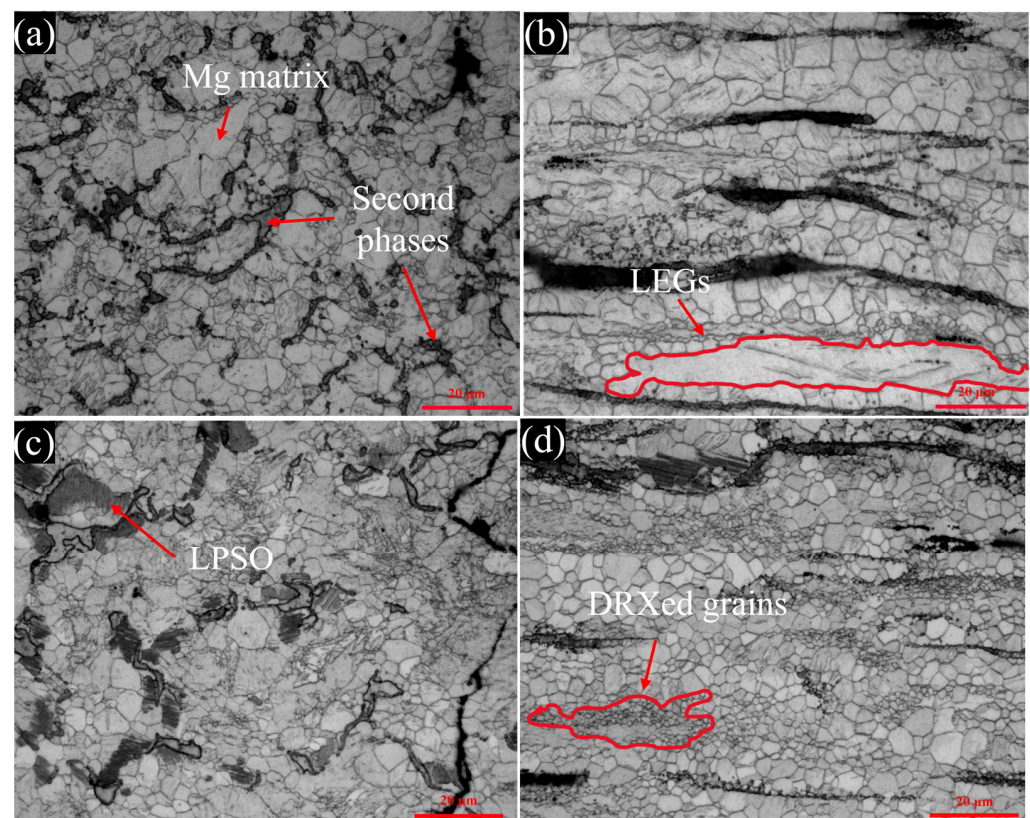


Figure 1. Optical micrographs of the alloy perpendicular (a,c) and parallel (b,d) to the extrusion direction for the (a,b) as-extruded alloy and (c,d) as-aged alloy.

SEM images with higher magnification are presented in Figure 2 to better show the second and LPSO phases. It is clear that the second phase in the as-extruded alloy distributes more dispersive as compared to that in the as-aged alloy. Importantly, LPSO structures located near the second phase are formed (marked as C1 in Figure 2c) after the aging treatment. EDS analysis was performed to compare the chemical compositions of different regions marked in Figure 2a,c, and the results are listed in Table 1. The second phase is rich in Gd and Cu in both the as-extruded and as-aged alloys, and the content

of Gd is slightly higher than that of Cu. After the aging treatment, the content of Gd and Cu slightly increases in the matrix but decreases in the second phase. The LPSO structure marked as C1 contains 15.06 wt.% Gd and 8.17 wt.% Cu, which is lower than the second phase but much higher than the α -Mg matrix. In addition, Zr distributes in all the phases.

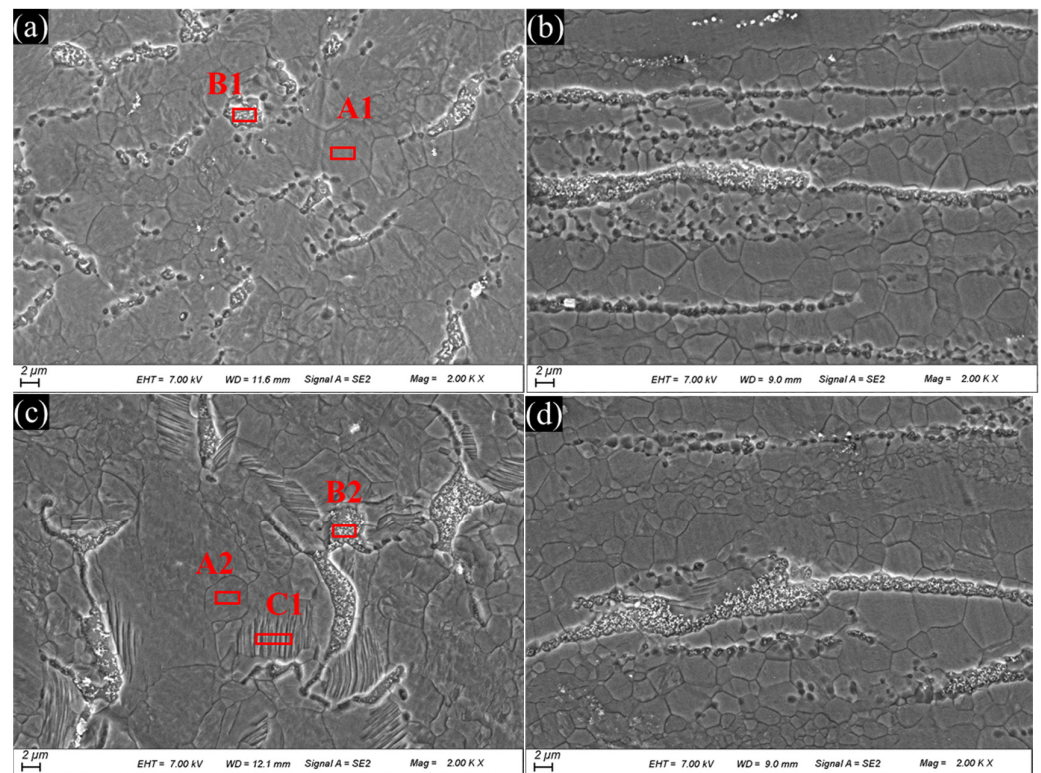


Figure 2. SEM micrographs of the alloy perpendicular (a,c) and parallel (b,d) to the extrusion direction for the (a,b) as-extruded alloy and (c,d) as-aged alloy.

Table 1. Chemical compositions (wt.%) of the marked areas in Figure 2.

Areas	Gd	Cu	Zr	Mg
A1	3.95	0.86	0.83	Balance
B1	25.88	24.65	0.18	Balance
A2	4.29	1.58	0.41	Balance
B2	24.85	22.31	0.32	Balance
C1	15.06	8.17	0.48	Balance

The XRD patterns of the as-extruded and as-aged alloys are shown in Figure 3. The $\text{Mg}_2(\text{Gd}, \text{Cu})$ phase was detected in addition to the α -Mg matrix, which is consistent with the phases under as-cast and solution-treated conditions [30]. $\text{Mg}_2(\text{Gd}, \text{Cu})$ corresponds to the second phase observed using OM and SEM. The volume fraction of the LPSO structure is low so that its diffraction peaks cannot be observed clearly.

The alloy has obvious partial dynamic recrystallization during extrusion. In general, under the action of extrusion stress, a large number of dislocations in Mg alloys encounter obstacles to reorganize and merge, forming sub-grain structures along grain boundaries. With the increase in sub-grain orientation difference, large angle grain boundaries are formed, and new recrystallized grains are formed [31]. It can be seen from Figure 1b that some LEGs did not undergo dynamic recrystallization but show coarse and elongated morphology along the extrusion direction. This may be due to a relatively low extrusion ratio or extrusion temperature, which results in insufficient deformation energy storage to trigger recrystallization in some local regions [32]. After extrusion, the dislocation density

around the LEGs is high, which belongs to the sub-structure grains. The aging treatment promotes thermodynamic recrystallization, transforming these substructural grains into new finer equiaxed grains known as static recrystallization [33]. According to the EDS results in Table 1, Gd and Cu atoms diffuse from the second phase with higher content to the α -Mg matrix, resulting in an increase in Gd and Cu in the matrix and a decrease in them in the second phase during the aging treatment. Consequently, the outer edges of some matrix grains near the second phase are rich in Gd and Cu elements and form the LPSO structure that contains moderate Gd and Cu among the α -Mg, the second phase, and the LPSO phase. Moreover, the second phase can provide the area for LPSO growth and reduce the free energy barrier required for LPSO formation [34,35]. Wu et al. [19] also found that lamellar LPSO structures were formed in the matrix of the Mg–10Gd–1Zn–0.5Zr alloy after aging treatment.

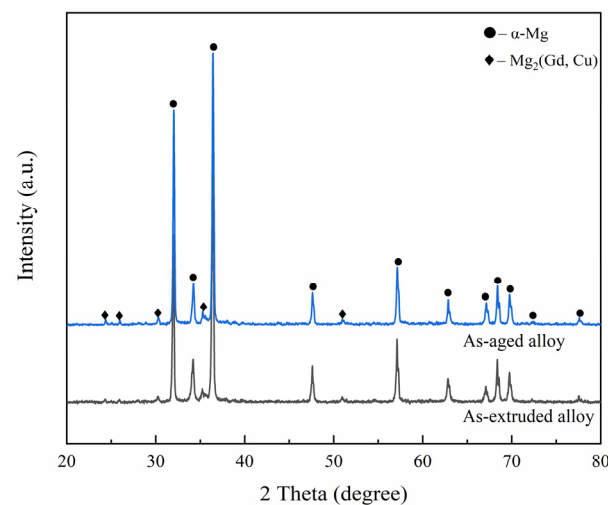


Figure 3. XRD patterns of the Mg–6.0Gd–1.2Cu–1.2Zr alloy.

3.2. Mechanical Properties

The tensile yield strength (TYS), ultimate tensile strength (UTS), compressive yield strength (CYS), ultimate compressive strength (UCS), and elongation of the as-extruded alloy and as-aged alloy under different test conditions are shown in Table 2. The TYS (231 MPa) and UTS (254 MPa) of the as-aged alloy are increased by 11.0% and 11.6%, respectively, compared to those of the as-extruded alloy at room temperature. The elongation in the as-aged alloy (10.4%) is much higher than that in the as-extruded alloy (5.6%), which shows an 85.7% increase. Under the 93 °C test condition, both TYS and UTS of both alloys decrease, the TYS (203.8 MPa) and UTS (234.3 MPa) of the as-aged alloy are still slightly higher than those of the as-extruded alloy (TYS = 191.4 MPa, UTS = 226.0 MPa), but the elongation in the as-aged alloy is slightly lower than that in the as-extruded alloy. Moreover, the TYS and UTS of both alloys are a little lower, but the elongation is higher at 93 °C than those at 25 °C. Compared with the tensile mechanical properties, the CYS of both alloys shows little difference, but the UCS and elongation increase significantly. It is clear that the UCS and elongation of the alloy decrease after the aging treatment.

After the aging treatment, the TYS increases by 11.0%, which can be explained by the following comprehensive reasons: solid solution strengthening, fine grain strengthening caused by static recrystallization, LPSO strengthening, and the decrease in the second phase which weakens the precipitation strengthening [36–40]. It is well known that Gd has a high solid solubility in Mg alloys, which can be used as an effective solute enhancer to strengthen Mg alloys [36]. Combined with the EDS results from Table 1, more Gd and Cu are dissolved into the matrix of the as-aged alloy, which can cause lattice distortion and hinder dislocation slip, thus playing a role in solid solution strengthening. Moreover, there are more fine static recrystallization grains in the as-aged alloy that can contribute to strength improvement

through grain refinement strengthening. In addition, when the LPSO structure is parallel to the extrusion direction, the short fiber reinforcement mechanism can effectively hinder the dislocation movement and even accumulate dislocations, thereby improving the TYS of Mg alloys [40]. However, after the aging treatment, the second phase shows aggregated blocks, and the amount is reduced. Therefore, the strengthening effect of second-phase precipitation is weakened. Based on the above strengthening mechanism, the TYS of the as-aged alloy at room temperature is better than that of the as-extruded alloy.

Table 2. Mechanical properties of the Mg–6.0Gd–1.2Cu–1.2Zr alloy at room temperature and 93 °C.

Tests	Alloys	T (°C)	TYS/CYS (MPa)	UTS/UCS (MPa)	Elongation (%)
Tensile	As-extruded	25	208.2 ± 2.1	228.0 ± 2.2	5.6 ± 1.3
	As-extruded	93	191.4 ± 1.5	226.0 ± 2.3	12.9 ± 1.2
	As-aged	25	231.0 ± 2.4	254.4 ± 2.2	10.4 ± 1.4
	As-aged	93	203.8 ± 2.2	234.3 ± 2.1	11.1 ± 1.1
Compression	As-extruded	93	194.3 ± 1.8	374.5 ± 13.8	19.7 ± 1.3
	As-aged	93	193.3 ± 2.9	336.1 ± 16.8	16.9 ± 0.9

At 93 °C, the TYS and UTS of both alloys decrease, and the TYS and UTS of the as-aged alloy decrease by 11.8% and 7.9%, respectively, compared with those at ambient temperature. This is because the second phase of Mg alloys will soften at high temperatures, and the dislocation movement of the alloy is more easily activated at 93 °C, resulting in a slight decrease in strength. Moreover, the decrease in UTS is also related to dislocation activation. The increase in temperature is beneficial to activate the dislocation motion, thus reducing TYS [41].

As for elongation at ambient temperature, the tensile elongation in the as-aged alloy (10.4%) is almost twice that in the as-extruded alloy (5.9%). It is well known that the elongation in Mg alloys is related to microstructure [42]. The distribution of the second phase in the as-extruded alloy is relatively uniform, but due to the presence of LEGs, they are difficult to coordinate deformation. When dislocations slip to these grain boundaries, dislocations are hindered and accumulate severely, which is prone to cause stress concentration and eventually result in fracture. Although, these LEGs transform into equiaxed fine grains due to static recrystallization during the aging process that are conducive to coordination and transmission of deformation, thus leading to much better ductility. The fracture morphologies of both alloys under ambient temperature and 93 °C are shown in Figure 4. The cleavage planes for the LEGs and secondary microcracks can be observed in Figure 4a, which play a negative role in ductility, but the fracture morphology of the as-aged alloy at ambient temperature is full of tiny dimples, indicating good ductility. At 93 °C, the tensile elongation in the as-aged alloy increases slightly (only about 7%), but that in the as-extruded alloy increases by 130%, which is mainly due to the occurrence of static recrystallization at this tested temperature since no coarse cleavage planes can be observed in Figure 4c. Furthermore, the residual stress release during the test at 93 °C may also play a positive role in the elongation improvement of the as-extruded alloy.

At 93 °C, The CYS/TYS of the as-extruded and as-aged alloys are 1.01 and 0.94, respectively, showing good tension-compression symmetry. Due to the symmetric nature of sliding, prismatic and basal sliding should behave identically under tension and compression, resulting in good tension-compression yield symmetry [43,44]. Grain refinement is also beneficial to weaken the tension and compression asymmetry of Mg alloys. Moreover, the UCS and compressive elongation in both alloys are much higher than the UTS and tensile elongation. This is largely attributed to the different tensile and compressive deformation mechanisms of Mg alloys: Tensile deformation is mainly matrix slip, hindered by dislocations and grain boundaries, but according to the Mohr–Coulomb criterion, the specimen will be cut off at an angle of 45° during compression [45], and the friction related to compressive stress will be generated inside the alloy, which will hinder the movement in

the section and make it difficult for the crack tip to expand. Compared with the tensile tests, this friction is more effective than the hindrance of dislocations and grain boundaries.

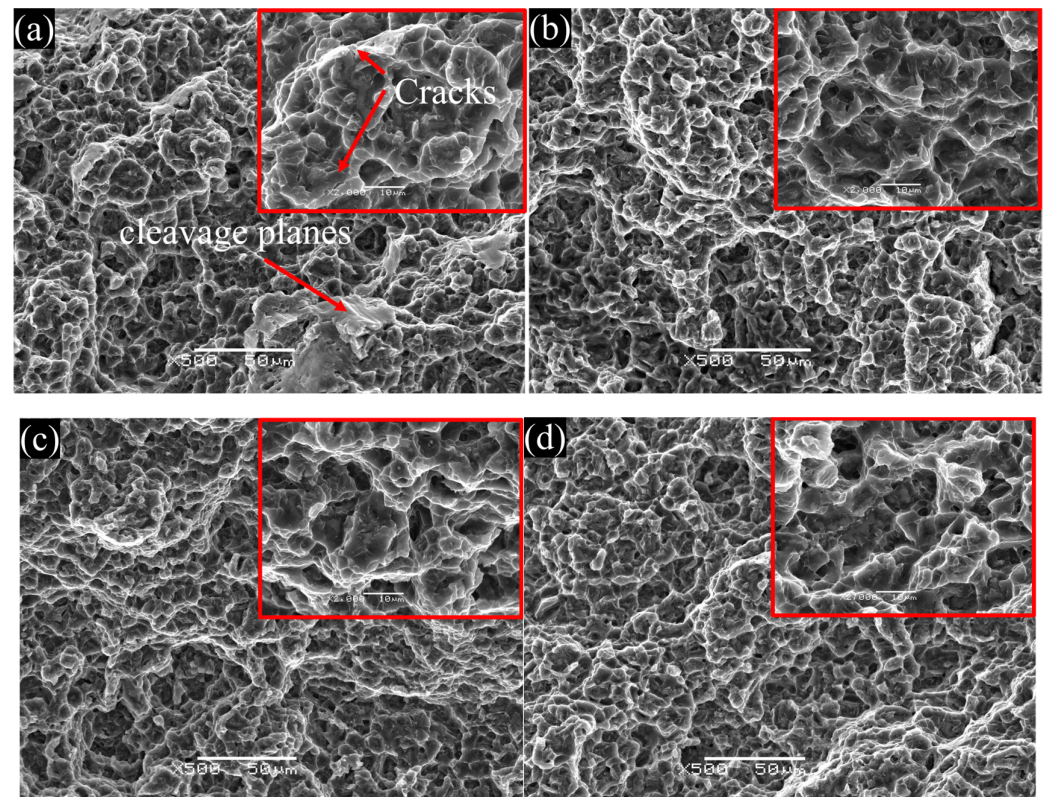


Figure 4. Tensile fracture morphologies of the as-extruded (a,c) and the as-aged (b,d) alloys at 25 °C (a,b) and 93 °C (c,d).

3.3. Corrosion Behavior

The hydrogen evolution curves of both alloys are shown in Figure 5a. It shows that the hydrogen evolution volume of the as-aged alloy is larger than that of the as-extruded alloy during the 60 min immersion test, indicating a higher corrosion rate. Three corrosion stages can be inferred from the hydrogen evolution curves: (1) in the first 10 min stage, the hydrogen evolution curves of both alloys are relatively flat and stable; (2) during the 10–40 min stage, the slope of hydrogen evolution curve of both alloys increases with prolonging immersion time, indicating an increased corrosion rate at this stage; and (3) during the 40–60 min stage, the hydrogen evolution curves present nearly linear, demonstrating a stable corrosion rate at this stage. This is probably related to the corrosion product on the surface of the alloys [45,46]. At the beginning of immersion, $\text{Mg}(\text{OH})_2$ film is formed on the surface of the samples which can protect against further corrosion to some extent. As the immersion time prolongs, the insoluble $\text{Mg}(\text{OH})_2$ film reacts with Cl^- and generates soluble MgCl_2 , and the samples undergo rapid corrosion accompanied by thick corrosion products on the surfaces. Then, the continuous penetration of the corrosion solution into the uncorroded surface and the increased corrosion products keep balance, resulting in a stable corrosion rate at the last immersion stage.

Figure 5b shows the corrosion rates of the alloys calculated based on the mass loss test and hydrogen evolution test. The mass loss corrosion rate of the as-extruded alloy (1660.8 mm/y) and the as-aged alloy (1955.1 mm/y) are a little higher than their corrosion rates calculated from hydrogen evolution (1518.6 mm/y and 1814.6 mm/y, respectively). This may be due to the fact that the corrosion reaction is still ongoing when the gas-collecting burette is replaced during the hydrogen evolution experiment, and this part of the hydrogen has not been collected. In addition, some incompletely corroded second

phase falls off after pickling, which increases the corrosion rate of the alloy using the mass loss test compared with the hydrogen evolution test.

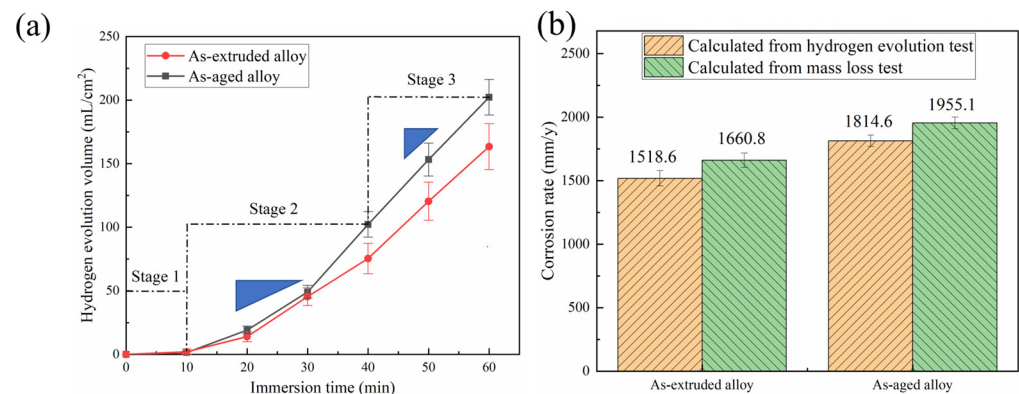


Figure 5. Hydrogen evolution curves (a) and corrosion rates (b) of the Mg-6.0Gd-1.2Cu-1.2Zr alloy immersed in 3 wt.% KCl for 60 min.

Figure 6 shows the corrosion morphologies of both alloys immersed in 3 wt.% KCl solution at 93 °C for 60 min. The corrosion products on the surfaces can be clearly observed, and there are some bright acicular corrosion products on the top layer. According to the analysis of EDS results in Figure 6b,d, the corrosion products mainly contain Mg, O, and Cl, as well as some K and Gd elements. Since EDS cannot detect the presence of H, combined with other corrosion studies, the surface of the corrosion layer mainly consisted of $\text{Mg}(\text{OH})_2$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and MgO , and the acicular corrosion products are a mixture of MgO and $\text{Mg}(\text{OH})_2$ [3,47].

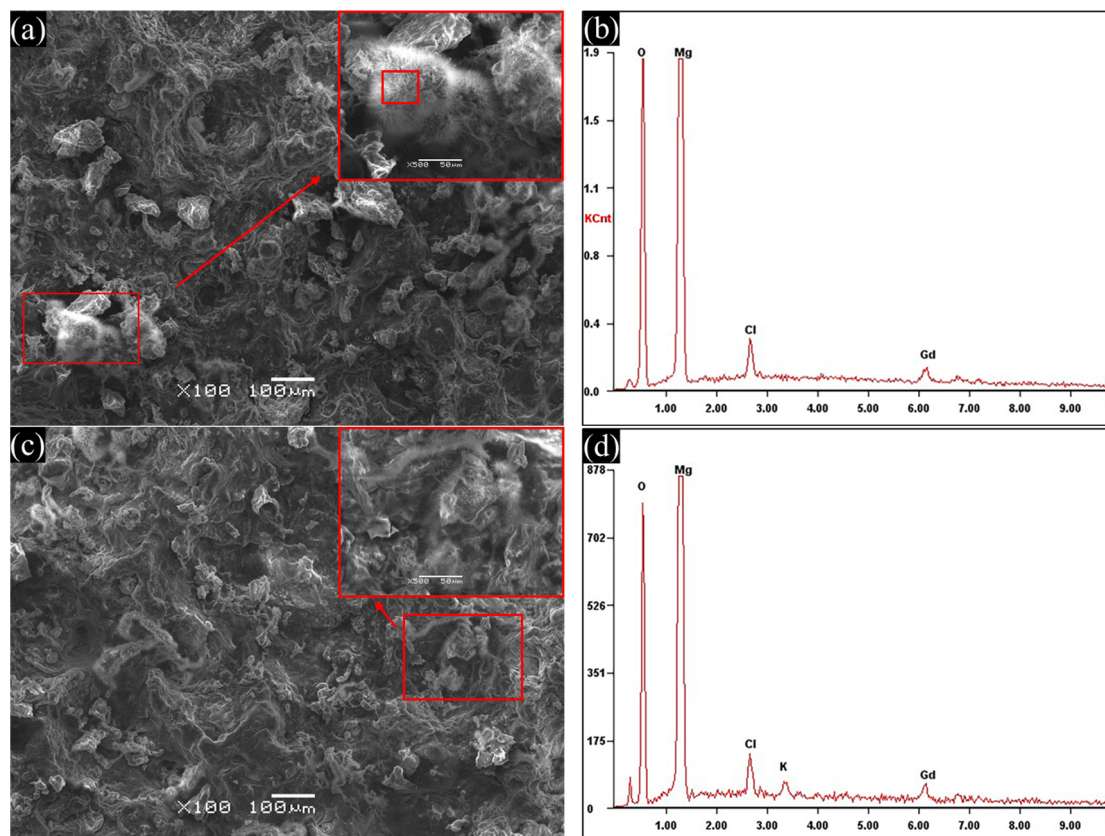


Figure 6. Surface morphologies of the as-extruded alloy (a) and the as-aged alloy (c) alloy immersed in 3 wt.% KCl for 60 min and selected area EDS spectra (b,d).

In order to further determine the corrosion behavior of both alloys, the electrochemical polarization curves are shown in Figure 7, and the corresponding fitting results are listed in Table 3. The corrosion potential of the as-aged alloy (−1.50 V) is lower than that of the as-extruded alloy (−1.45 V), which indicates a faster corrosion tendency from thermodynamics, and the corrosion current density of the as-aged alloy is higher as compared to that of the as-extruded alloy, which means a higher corrosion rate from corrosion dynamics [48]. The electrochemical results are consistent with those obtained using the hydrogen evolution and mass loss tests.

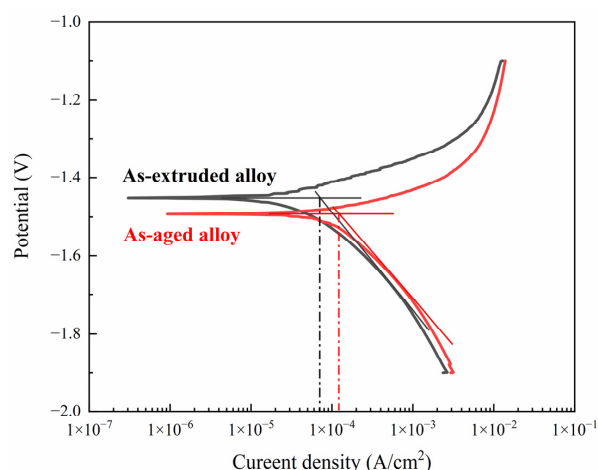


Figure 7. Polarization curves of the Mg-6.0Gd-1.2Cu-1.2Zr alloy in 3 wt.% KCl solution.

Table 3. Electrochemical parameters of the Mg-6.0Gd-1.2Cu-1.2Zr alloy obtained using Tafel extrapolation from Figure 7.

Alloy	E_{corr} (V)	I_{corr} (A/cm ²)
As-extruded	−1.45	6.3×10^{-5}
As-aged	−1.50	1.2×10^{-4}

The corrosion rates of the as-extruded and as-aged alloys in 3 wt.% KCl solution at 93 °C are 1660.8 and 1955.1 mm/y, respectively, which is desired for degradable fracturing ball applications. Generally, grain refinement can decrease the corrosion rate of Mg alloys because Mg alloys with fine grains more easily form a dense corrosion product film on a corroded surface, thereby protecting the substrate from corrosion [49]. Moreover, fine grains may also reduce the corrosion rate of Mg alloys if they have obvious passivation behavior [50]. However, in the present work, both alloys have no obvious passivation stage in Figure 7, so fine grains do not reduce the corrosion rate of the alloy. In addition, studies have shown that refined grains mean more grain boundaries. The grain boundary is a typical surface defect with high energy that has priority corrosion and can be used as a corrosion channel to accelerate the corrosion rate [51]. The as-extruded alloy obtained many fine grains by dynamic recrystallization, so they have many grain boundaries, which provides a favorable channel for corrosion propagation and accelerates the corrosion of the alloy [52]. Due to the static recrystallization during aging, the number of fine grains is obviously more than that of the as-extruded alloy, which owns more driving force for corrosion and thus leads to faster corrosion.

It is well known that the corrosion barrier and micro-galvanic effect are two different aspects of the second phase in corrosion. A uniformly distributed tiny second phase can reduce the corrosion rate, while a discontinuously distributed bulky second phase will accelerate the corrosion rate of the Mg alloy [53]. During corrosion, the second phase usually acts as a cathode and accelerates the corrosion of the anode substrate. After the aging treatment, the second phase is more aggregated, forming a “large cathode and small anode” galvanic corrosion, which accelerates the galvanic corrosion process.

The effect of the LPSO phase on the corrosion of a Mg alloy is also dual: the LPSO phase could act as a micro-cathode to accelerate corrosion if it distributes discontinuously; however, if it distributes continuously along the grain boundaries or at the outer edge of matrix grains, it could act as a bridge and restrict corrosion caused by galvanic corrosion between the matrix and eutectic phase [30]. Furthermore, it has been found that the lamellar LPSO phase can also be used as a cathode phase to provide a driving force for galvanic corrosion of the α -Mg matrix [54]. The discontinuous lamellar LPSO phase in the as-aged alloy makes it unable to protect the matrix and accelerates corrosion.

Figure 8 shows the local potential distribution between the α -Mg matrix, second phase, and LPSO phase observed in the parallel extrusion direction. The line in Figure 8a intersects different phases, the three-dimensional volt potential of the tested regions is shown in Figure 8b, and the corresponding volt potential curve of the analyzed line is shown in Figure 8c. The volt potential of the three phases shows the following order: second phase > LPSO phase > α -Mg matrix, which indicates that both the second phase and the LPSO act as cathodes in the microcell to accelerate the corrosion of the matrix.

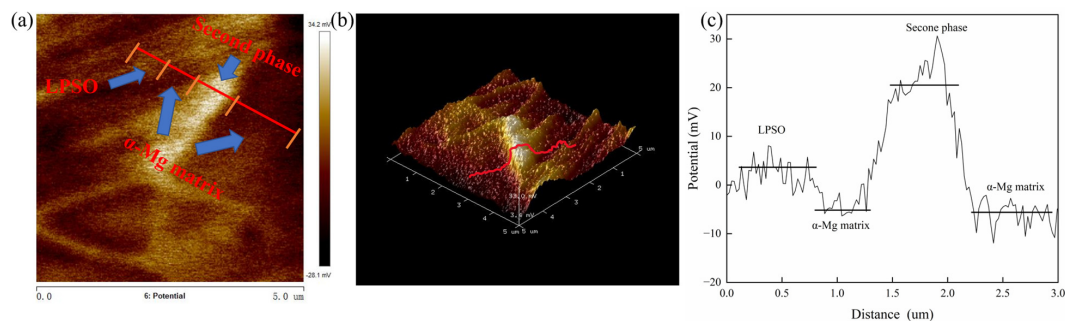


Figure 8. Volt potential distribution of as-aged alloy: (a) two-dimensional volt potential distribution, (b) three-dimensional volt potential distribution, (c) volt potential distribution of the selected line.

Figure 9 shows the comparison of the ultimate compressive strength and corrosion rate of Mg–6.0Gd–1.2Cu–1.2Zr alloy in this work and other Mg alloys [14,15,25,37,46,55–57]. It is clear that the Mg–6.0Gd–1.2Cu–1.2Zr alloy with moderate strength and a high corrosion rate exhibits excellent comprehensive properties that can be effectively applied to the field of temporary plugging. A much higher corrosion rate of the studied alloy in this work may be attributed to the addition of Cu and particular microstructures.

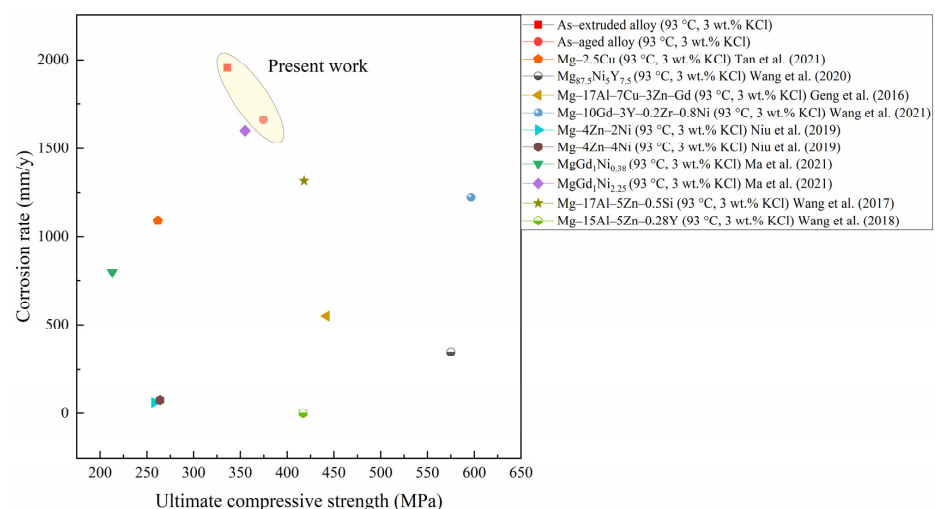


Figure 9. Comparison of the ultimate compressive strength and corrosion rate among the present Mg–Gd–Cu–Zr alloy and other Mg alloys for degradable fracturing ball applications [14,15,25,37,46,55–57].

4. Conclusions

- (1) The microstructure of the as-extruded Mg–6.0Gd–1.2Cu–1.2Zr alloy consists of an α -Mg matrix, a second phase, and un-recrystallized large, elongated grains. After the aging treatment at 170 °C for 8 h, the large, elongated grains disappear due to static recrystallization and a lamellar LPSO structure is formed because of the diffusion of the Gd and Cu atoms.
- (2) The tensile yield strength of the as-extruded Mg–6.0Gd–1.2Cu–1.2Zr alloy is slightly improved after the aging treatment due to the compromise between solution strengthening, grain refinement strengthening, LPSO strengthening, and second phase strengthening. The significant improvement in elongation after aging or testing at 93 °C is mainly attributed to static recrystallization. The ultimate compressive strength of the as-extruded and as-aged alloys at 93 °C is 374.5 MPa and 336.1 MPa, respectively, which may meet the requirements of underground temperature work.
- (3) The corrosion rate of the as-extruded and as-aged Mg–6.0Gd–1.2Cu–1.2Zr alloy in 3 wt.% KCl solution at 93 °C is 1660.8 mm/y and 1955.1 mm/y, respectively. Galvanic corrosion plays a leading role in the whole corrosion process. The aggregated second phase, the formation of the LPSO phase, and the refined grains by static recrystallization are responsible for the more rapid corrosion after the aging treatment.
- (4) The comprehensive mechanical properties and corrosion rate of the Mg–6.0Gd–1.2Cu–1.2Zr alloy under the as-extruded and as-aged conditions exceeds most reported Mg alloys, and the alloy shows promising potential for degradable fracturing ball applications.

Author Contributions: Conceptualization, J.J. and X.Z.; methodology, J.J.; validation, X.G. and J.J.; formal analysis, J.J.; investigation, J.J. and X.G.; resources, X.Z.; data curation, J.J. and X.G.; writing—original draft preparation, J.J.; writing—review and editing, X.Z.; visualization, J.J. and X.G.; supervision, X.Z.; project administration, X.Z.; funding acquisition, X.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This project was supported by the National Natural Science Foundation of China (52071175), the Key Research & Development Plan (Social Development) of Jiangsu Province (BE2020702), and the Innovative Foundation Project for Students of Nanjing Institute of Technology (TB202217002).

Data Availability Statement: The research data are available upon reasonable request to the authors.

Conflicts of Interest: The authors declare no conflict of interest.

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