

# Regulating the Microstructure, Texture, Electrochemical Behavior and Discharge Performance of Mg–Sn–Bi–Gd Alloy Anodes for Mg–Air Batteries through Extrusion Ratio Control

**Yingzhu Wang**

Harbin University of Science and Technology

**Hongze Xu**

Rongcheng College, Harbin University of Science and Technology

**Fangyu Jing**

Rongcheng College, Harbin University of Science and Technology

**Xiaofang Yuan**

Rongcheng College, Harbin University of Science and Technology

**Zehua Yan**

[yzh@hrbust.edu.cn](mailto:yzh@hrbust.edu.cn)

Harbin University of Science and Technology

**Lei Li**

Binzhou Institute of Technology

---

## Research Article

**Keywords:** Magnesium–air battery, Mg–Sn–Bi–Gd alloy, extrusion ratio, microstructure evolution, discharge stability

**Posted Date:** August 27th, 2026

**DOI:** <https://doi.org/10.21203/rs.3.rs-10646918/v1>

**License:** © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.  
[Read Full License](#)

**Additional Declarations:** No competing interests reported.

---

# Regulating the Microstructure, Texture, Electrochemical Behavior and Discharge Performance of Mg–Sn–Bi–Gd Alloy Anodes for Mg–Air Batteries through Extrusion Ratio Control

Yingzhu Wang<sup>1,2</sup>, Hongze Xu<sup>2</sup>, Fangyu Jing<sup>2</sup>, Xiaofang Yuan<sup>2</sup>, Zehua Yan<sup>\*,1,2</sup>, Lei Li<sup>3</sup>

<sup>1</sup> School of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin, 150040, China

<sup>2</sup> Rongcheng College, Harbin University of Science and Technology, Weihai, 264300, China

<sup>3</sup> Shandong Key Laboratory of Advanced Aluminum Materials and Technology, Binzhou Institute of Technology, Binzhou 256606, China

\*E-mail addresses: yzh@hrbust.edu.cn (Zehua Yan)

**Abstract :** The influence of extrusion ratio (ER16, ER25, ER64) on the microstructure, electrochemical behavior, and discharge performance of Mg–1.5Sn–1.5Bi–0.75Gd alloy anodes was systematically examined. With increasing extrusion ratio from 16 to, 25, and 64 (named ER16, ER25, ER64), the average grain size was observed to initially decrease from 9.83  $\mu\text{m}$  to 9.32  $\mu\text{m}$  and then increase to 14.41  $\mu\text{m}$ , while the recrystallized fraction rose from 45.9% to 87.1%, accompanied by the transformation of low-angle into high-angle grain boundaries. KAM analysis indicated a non-monotonic evolution of orientation difference and dislocation density, suggesting that higher extrusion ratios promote strain release and microstructural homogenization. Electrochemical tests revealed that ER64 exhibited the lowest charge transfer resistance 13.74  $\Omega\cdot\text{cm}^2$ , reduced corrosion current density, and suppressed hydrogen evolution. Under a current density of 2.5  $\text{mA}\cdot\text{cm}^{-2}$ , ER16 delivered a higher and more stable discharge voltage with the highest anode efficiency (36.2%). The discharge product layer was loose and uniform, facilitating dynamic  $\text{Mg}(\text{OH})_2$  formation and detachment, as well as continuous electrolyte penetration. In contrast, coarse and heterogeneous microstructures in ER16 promoted dense product accumulation and localized dissolution, causing voltage fluctuations. These results demonstrate that extrusion ratio regulates recrystallization, dislocation density, and slip coordination, thereby controlling hydrogen evolution kinetics and surface product layer structure, and ultimately determining the discharge stability and efficiency of magnesium–air battery anodes.

**Keywords:** Magnesium–air battery; Mg–Sn–Bi–Gd alloy; extrusion ratio; microstructure evolution; discharge stability

## 1. Introduction

The growing global demand for energy, coupled with the environmental issues associated with conventional fossil fuels, has driven intense research into high-energy-density and sustainable energy storage technologies. Among these, metal–air batteries have attracted particular attention due to their utilization of oxygen from air as the cathodic active species, enabling exceptionally high theoretical energy densities, [1-3]. Magnesium–air batteries (Mg–air batteries) stand out as one of the most promising metal–air systems, owing to magnesium’s unique physicochemical properties. Magnesium exhibits a high theoretical specific capacity ( $2205 \text{ mAh g}^{-1}$ ) [4], a low electrochemical equivalent, and a highly negative standard electrode potential ( $-2.37 \text{ V vs. SHE}$ ) [5], which collectively confer a remarkable theoretical energy density. Furthermore, magnesium is abundant in the Earth’s crust, can be extracted from seawater, and is cost-effective. Its safety during storage and transport is also notable, as the low tendency for dendrite formation mitigates the risk of short circuits[6]. These advantages make Mg–air batteries attractive for applications in marine equipment, emergency power systems for electric vehicles, and large-scale energy storage. Despite these favorable characteristics, practical applications of Mg–air batteries are constrained by several critical challenges. Magnesium exhibits high chemical reactivity in aqueous electrolytes, leading to pronounced self-corrosion accompanied by hydrogen evolution, which substantially reduces the utilization efficiency of the anode. In addition, during discharge, the formation of a  $\text{Mg(OH)}_2$ -dominated surface layer can partially passivate the anode, hindering uniform dissolution and promoting localized corrosion[7-9]. Consequently, voltage fluctuations occur, and the electrochemical efficiency is compromised. Addressing these issues requires strategies that enhance anode discharge activity while suppressing self-corrosion, ensuring a stable and uniform electrochemical process.

Alloying has emerged as an effective approach to improve the performance of Mg–air battery anodes[10-12]. Among the alloying elements explored, Sn, Bi, and rare-earth elements have attracted particular attention due to their pronounced effects on both microstructure and electrochemical behavior. Mg–Sn alloys, for instance, are recognized for their structural stability and favorable electrochemical properties [13]. Tin exhibits low solubility in magnesium and tends to form  $\text{Mg}_2\text{Sn}$  intermetallic compounds during solidification. These intermetallics possess high thermal and mechanical stability. Electrochemically, the micro-galvanic structures formed between  $\text{Mg}_2\text{Sn}$  and the  $\alpha\text{-Mg}$  matrix facilitate anodic dissolution, thereby enhancing electrochemical activity[14]. Moreover, a fine and dispersed distribution of  $\text{Mg}_2\text{Sn}$  contributes to grain refinement and improves corrosion morphology, enabling more uniform dissolution during discharge. As a result, Mg–Sn alloys often exhibit higher discharge voltages and improved anode utilization [15]. Bismuth similarly plays a unique role in magnesium-based anodes. Due to its extremely low solubility in magnesium, Bi is typically present as secondary phases such as  $\text{Mg}_3\text{Bi}_2$ . These Bi-rich phases influence surface electrochemical reactions by promoting anodic activation and reducing the stability of passive films, thereby maintaining sustained and uniform anode dissolution [16]. Additionally, Bi incorporation can partially suppress hydrogen evolution, reducing self-corrosion

and enhancing discharge efficiency[17]. Consequently, Mg–Bi alloys are recognized as effective materials for improving the stability of magnesium anodes [18]. Rare-earth elements have also been extensively studied in magnesium alloys for their ability to refine microstructure and enhance corrosion resistance[19-21]. Gadolinium (Gd), in particular, exhibits a large atomic radius and strong solid-solution strengthening capability. The addition of Gd promotes grain refinement and the formation of stable intermetallic phases, improving microstructural uniformity. Gd can also modify the composition and stability of surface corrosion product layers, resulting in enhanced electrochemical stability during discharge [22-24]. Previous studies have shown that Gd-containing magnesium alloys typically display lower corrosion rates and more stable electrochemical behavior in chloride-based electrolytes [25,26]. Although Mg–Sn, Mg–Bi, and Mg–Gd binary systems each offer certain advantages, single-alloy systems often fail to simultaneously optimize electrochemical activity, corrosion resistance, and discharge stability. Mg–Sn alloys exhibit high anodic activity but remain prone to localized corrosion; Mg–Bi alloys improve discharge stability but require further enhancement of structural stability; and Mg–Gd alloys provide corrosion resistance but relatively low anodic activity. Therefore, the synergistic incorporation of Sn, Bi, and Gd into multicomponent Mg alloys has emerged as a key strategy to achieve a balanced combination of high electrochemical activity, enhanced corrosion resistance, and improved discharge stability. Specifically, Mg–Sn–Bi–Gd alloys are expected to leverage the high electrochemical activity of Sn, the surface reaction kinetics improvement of Bi, and the grain refinement and corrosion resistance provided by Gd, offering a comprehensive enhancement in Mg–air battery anode performance. In addition to alloy composition, plastic deformation processing plays a crucial role in tailoring the microstructure of magnesium alloys, which in turn affects their electrochemical behavior[27-29]. Extrusion is particularly effective, as it can refine grains, homogenize the distribution of secondary phases, and induce dynamic recrystallization under substantial plastic deformation. Grain refinement increases the density of grain boundaries, promoting uniform electrochemical reactions and stable anodic dissolution. Fragmentation of coarse secondary-phase particles during extrusion further homogenizes their distribution, mitigating localized galvanic corrosion and enhancing discharge stability[30]. Among extrusion parameters, the extrusion ratio is a critical factor influencing microstructural evolution [31]. Despite the recognized importance of extrusion, systematic studies on the electrochemical behavior of complex multicomponent Mg alloys under varying extrusion ratios remain limited, particularly for Mg–Sn–Bi–Gd systems.

Based on this background, the development of Mg–Sn–Bi–Gd multicomponent alloys as Mg–air battery anodes is of significant scientific and practical interest [32]. The simultaneous introduction of Sn, Bi, and Gd enables multiple synergistic effects on microstructure and electrochemical performance. However, composition alone cannot fully realize the potential of multicomponent alloys; grain size, crystallographic texture, and secondary-phase distribution must also be optimized. Controlled plastic deformation, particularly extrusion, provides a means to fine-tune these microstructural features. Systematic investigation of microstructural evolution and

electrochemical behavior under different extrusion ratios is therefore essential to elucidate the intrinsic relationships between structure and anodic performance. Such studies offer critical insights for the rational design and fabrication of high-performance Mg–air battery anodes and pave the way for their practical application in energy storage and power supply systems.

## 2. Experiment

The Mg–1.5Sn–1.5Bi–0.75Gd alloy was prepared by high-temperature melting and casting under a protective gas mixture of 98 % CO<sub>2</sub> and 2 % SF<sub>6</sub>. The ingots were homogenized at 350 °C for 3 h, followed by 500 °C for 3 h to eliminate segregation. Subsequently, the homogenized ingot with a diameter of 80mm was placed in an extrusion cylinder with an inner diameter of 100mm, and then extruded horizontally at 1 mm·s<sup>-1</sup> with extrusion ratios of 16, 25, and 64 (ER16, ER25, ER64), producing Mg alloy rods (Figure 1a). The extruded rods were sectioned into anode samples and mechanically polished using SiC and metallographic papers until a scratch-free surface was obtained. Corrosion morphology was examined after etching with a solution of 2 g oxalic acid, 2 mL acetic acid, 4 mL deionized water, and 40 mL ethanol. Optical microscopy (OM, ZEISS AxioVert.A1) was used for general microstructural observation, while SEM (HITACHI SU5000) coupled with EDS analyzed secondary-phase particles. Crystal orientation was characterized by EBSD (Oxford Instruments) and processed using Channel 5 software. All observation and corroded surfaces were 10 mm × 10 mm squares, and three parallel samples were prepared for each condition. Electrochemical behavior was evaluated via immersion and electrochemical methods. Electrochemical tests were conducted on a CHI660E workstation using a conventional three-electrode setup: a saturated calomel reference electrode, a platinum counter electrode, and the Mg alloy as the working electrode, with 3.5 wt.% NaCl as the electrolyte. EIS and Tafel polarization measurements were obtained for all samples; EIS was performed at open-circuit potential over 100 kHz–0.01 Hz with a 5 mV amplitude (Figure 1b). Hydrogen evolution was measured using a setup comprising a graduated cylinder, inverted funnel, and beaker. The 10 mm × 10 mm exposed sample surface was positioned beneath the funnel to collect hydrogen. After immersion, samples were ultrasonically cleaned in 20 wt.% chromic acid for 15 min to remove corrosion products, and SEM was used to examine surface morphology (Figure 1c). Discharge performance was evaluated using a half-cell constant-current method in a metal–air battery system with a commercial carbon-based air cathode. Constant-current discharge tests were conducted at 2.5 mA·cm<sup>-2</sup>, with three repetitions under identical conditions to ensure reproducibility (Figure 1d). Discharge products were separated and cleaned in anhydrous ethanol via ultrasonic treatment for 10 min, then dried. Anode utilization and efficiency were calculated according to equations (1) and (2) [33,34].

The anode utilization of the discharged Mg alloy samples ( $\eta$ ) was calculated using the following equation:

$$\eta = \frac{M_t}{M_a} \times 100\% \quad (1)$$

Where,  $M_t$  is the theoretical mass loss of the sample, and  $M_a$  is the actual mass loss measured after discharge.

The theoretical mass loss of the discharged sample was calculated as:

$$M_t = \frac{I \times t}{F \times \sum \left( \frac{x_i \times n_i}{m_i} \right)} \quad (2)$$

Where,  $I$  is the applied current (A),  $t$  is the discharge time (s),  $F$  is the Faraday constant,  $x_i$  is the mass fraction of element  $i$ ,  $n_i$  is the valence of element  $i$ , and  $m_i$  is the atomic mass of element  $i$  ( $\text{g} \cdot \text{mol}^{-1}$ ).

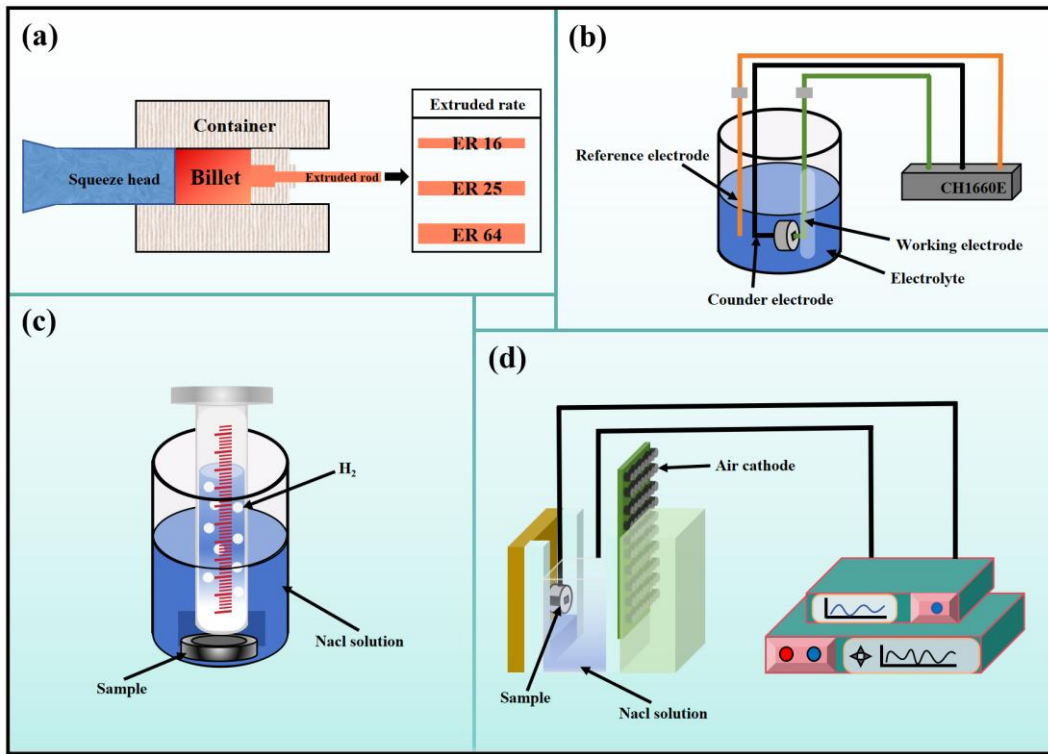


**Fig. 1** Schematic illustrations of material preparation and electrochemical testing procedures. (a) extrusion process; (b) electrochemical testing; (c) hydrogen evolution testing; (d) Mg–air battery discharge experiment.

### 3. Results and Discussion

#### 3.1 Microstructure and texture analysis

According to the XRD results shown in Figure 3, the strongest peak of Mg-1.5Sn-1.5Bi-0.75Gd magnesium alloy after homogenization treatment corresponds to the  $\alpha$  - Mg phase, and peaks corresponding to the intermetallic compounds  $\text{Mg}_3\text{Bi}_2$  and  $\text{MgBiGd}$  are also visible, but the Sn containing phase is not observed. In the XRD pattern, only  $\text{Mg}_3\text{Bi}_2$  and  $\text{MgBiGd}$  phases were

detected, and no Sn containing phase was found. The main reason is as follows: firstly, Sn has a high solid solubility in the magnesium matrix, and its maximum solid solubility can reach 9.8 wt.% percent at the homogenization temperature (500 °C) [35]. And the Sn content of this alloy is only 1.5 weight percent. Therefore, Sn is likely to completely dissolve in the magnesium matrix without reaching the critical concentration for precipitation, preferentially forming thermodynamically more stable  $\text{Mg}_3\text{Bi}_2$  and  $\text{MgBiGd}$  phases, while the formation free energy of  $\text{Mg}_2\text{Sn}$  phase is relatively low, making it difficult to compete for nucleation during alloy solidification and homogenization processes.

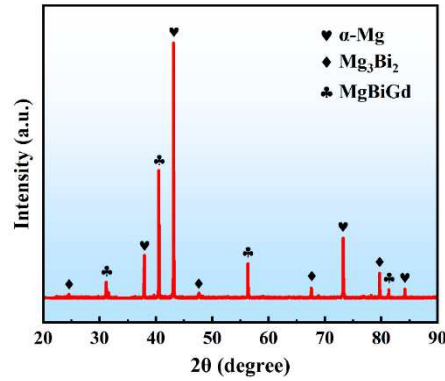


Figure 2: XRD spectrum of Mg-Sn-Bi-Gd alloy

Figure 3 presents the microstructure of the Mg–Sn–Bi–Gd alloy deformed under different extrusion ratios (16, 25, and 64) at a constant temperature. From Fig. 3(a), it can be seen that after homogenization treatment, the number of second phases at the grain boundaries of the alloy is relatively small, and there are a small amount of granular second phases inside. The average grain size exhibits a non-monotonic trend, first decreasing and then increasing, which results from the combined effects of deformation-stored energy, dynamic recrystallization (DRX), and thermal influences. When the extrusion ratio increases from 16 to 25, the material experiences a significant rise in accumulated strain, leading to a rapid increase in dislocation density and substantial accumulation of intragranular distortion energy. These factors provide a strong driving force for DRX nucleation. Simultaneously, the elevated strain enhances twinning and dislocation interactions, accelerating grain refinement and producing fine, uniform recrystallized grains. However, at a further increased extrusion ratio of 64, although the degree of plastic deformation continues to rise, the severe deformation generates substantial deformation heat that cannot dissipate efficiently, causing localized temperature elevation. The increased effective deformation temperature enhances atomic diffusion and grain boundary migration, allowing newly formed DRX grains to grow rapidly. Moreover, excessively high strain rates may shorten the DRX nucleation stage, enabling grain growth to dominate the microstructural evolution and diminishing the refinement effect. Consequently, at a moderate extrusion ratio (ER25), DRX proceeds most effectively while grain growth is suppressed, resulting in the finest grains. In contrast, at higher extrusion ratios (ER64),

thermal effects and grain growth mechanisms become more pronounced, ultimately leading to a reversed increase in average grain size.

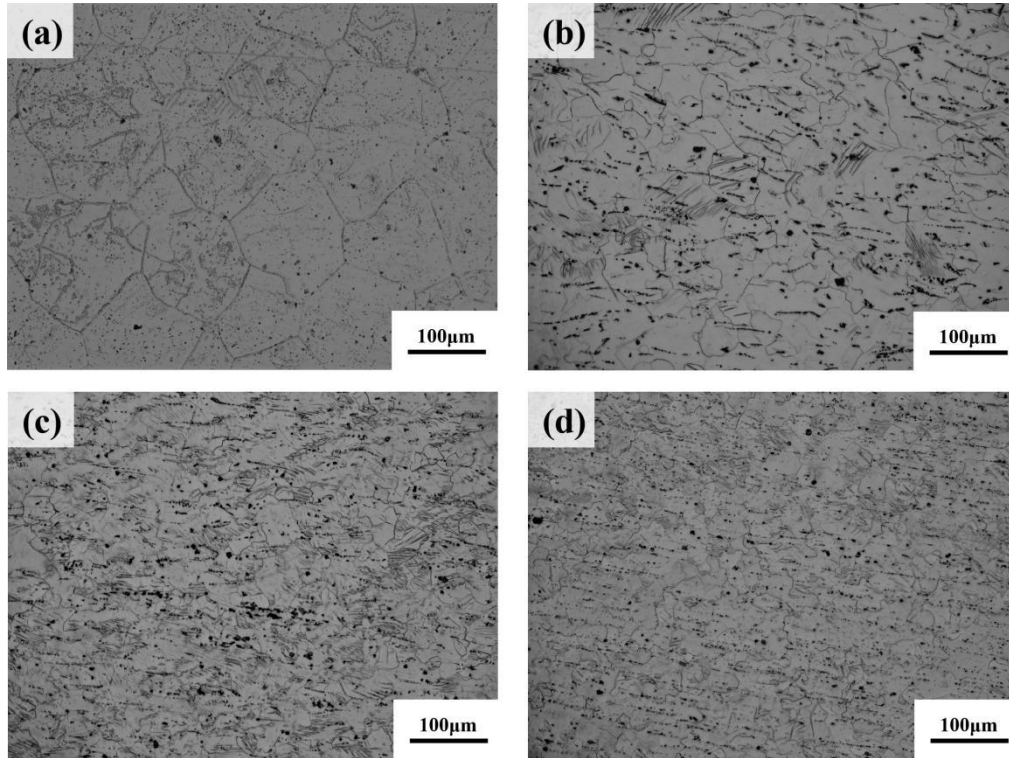


Fig. 3 OM of alloy under homogenization and different extrusion ratios (a): homogenized alloy; (b) ER 16; (c) ER25; (d) ER64

Figure 4 presents the inverse pole figures (IPF) maps and pole figures (PF) of the Mg–Sn–Bi–Gd alloy deformed under different extrusion ratios (ER16, ER25, and ER64). It is evident from Figures 4(a)–(c) that the extrusion ratio significantly affects both the grain orientation distribution and microstructural homogeneity. At ER16, the alloy exhibits an average grain size of 9.83  $\mu\text{m}$ , while the difference between the largest and smallest grains reaches 144.54  $\mu\text{m}$ , reflecting a typical bimodal microstructure characterized by the coexistence of fine equiaxed grains and coarse grains (Figure 3d). This phenomenon is primarily attributed to the limited accumulated strain at low extrusion ratios, which results in insufficient deformation-stored energy and weak DRX nucleation driving force. Consequently, DRX occurs only locally, leading to heterogeneous microstructure. Additionally, coarse-grained regions accumulate higher dislocation density, whereas fine-grained regions exhibit pronounced grain boundary strengthening, further aggravating the local deformation incompatibility. When the extrusion ratio is increased to 25, microstructural homogeneity improves markedly. The number of coarse grains decreases, the grain size distribution narrows to 56.66  $\mu\text{m}$ , and the average grain size reduces to 9.32  $\mu\text{m}$ . The higher deformation level promotes extensive dislocation multiplication and accumulation, enabling coarse grains to be refined via mechanisms such as dislocation entanglement, subgrain rotation, and grain boundary migration, eventually forming fine grains approximately one-half to one-third of the original size. Meanwhile, some pre-

existing fine grains grow modestly due to subgrain coalescence, forming recrystallized grains of  $\sim 20\text{ }\mu\text{m}$  (e.g., grains 10–12). Variations in energy absorption among different grains increase the fraction of randomly oriented grains, effectively enhancing microstructural uniformity. Correspondingly, Figure 4(e) shows that low-angle grain boundaries ( $<15^\circ$ ) account for  $\sim 51.5\%$ , indicating the formation of dense dislocation walls characteristic of subgrain structures. The presence of low-angle boundaries reflects a dislocation-dominated evolution mechanism, which can gradually transform into high-angle boundaries through rotation and coalescence, representing a key pathway for continuous dynamic recrystallization. Nevertheless, portions of the microstructure remain in a transitional state between deformed and recrystallized structures. At ER64, the microstructure exhibits new characteristics. The average grain size increases to  $14.41\text{ }\mu\text{m}$ , with a maximum-to-minimum grain size difference of  $62.56\text{ }\mu\text{m}$ . Grain orientations increasingly align along the basal plane (0001), revealing strong texture development. Under high extrusion ratios, severe plastic deformation induces substantial deformation heat, raising the effective deformation temperature, which enhances atomic diffusion and grain boundary migration [36]. During this process, low-angle boundaries gradually transform into high-angle boundaries, whose fraction increases to  $\sim 84.7\%$ , indicating nearly complete DRX. Residual deformation-stored energy is further released through grain growth and boundary consumption, resulting in partial coarsening of the grains. Orientation analysis shows that spatially separated grains (e.g., grains 13–16) adopt similar crystallographic directions, suggesting preferential orientation evolution during grain growth and ultimately forming a more uniform and stable microstructure. The increased fraction of basal plane (0001) reflects the selective evolution of crystallographic orientations during deformation. Finally, the pole figure results in Figures 4(f)–(h) further confirm the texture evolution. With increasing extrusion ratio, the maximum texture intensity rises from 10.34 to 13.60, indicating progressive alignment of grain orientations and pronounced texture strengthening. This evolution not only reflects crystallographic reorientation and the development of preferential orientations during deformation but also corroborates the dominant role of DRX coupled with grain growth under high extrusion ratios.

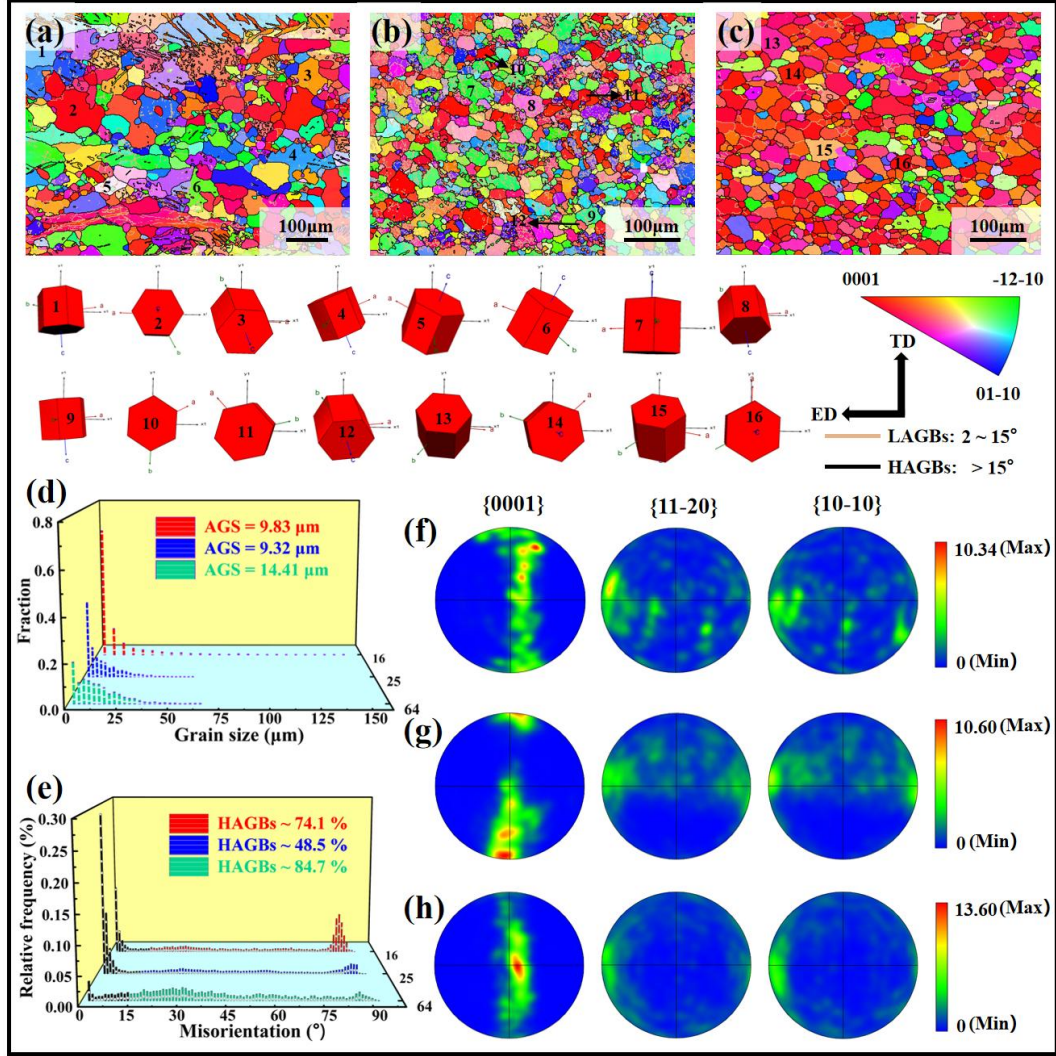


Fig. 4: IPF (a~c), PFs (f~h), grain size (d), and grain boundary angle ratio (e) of alloys under different extrusion ratios: (a) and (f) 16, (b) and (g): 25, (c) and (h) 64

The underlying mechanism for the increase in maximum texture intensity with rising extrusion ratio can be further elucidated through Figure 5. Figures 5(a)–(c) illustrate representative grain orientation features corresponding to the strongest texture intensity under different extrusion ratios. At ER16, grains are predominantly oriented along the  $(10\bar{1}0)$  and  $(11\bar{2}0)$  planes. In the triangular inverse pole figure, the orientation points are mostly distributed within the interior region, indicating a dispersed orientation and deviation from the ideal orientation. This distribution reflects insufficient orientation evolution during deformation, with a degree of local randomness and limited recrystallization, resulting in a weak, diffuse texture and relatively low maximum texture intensity. When the extrusion ratio increases to 25, the types of grain plane orientations remain similar to those at ER16, still dominated by non-basal plane orientations. However, the orientation points shift noticeably toward the edges of the inverse pole figure, and their distribution range becomes broader. The points approach the ideal crystallographic boundary positions, indicating that grain orientations are closer to ideal directions, with reduced spatial deviation and improved crystallographic

consistency. This edge-concentrated orientation pattern suggests that grains have undergone more complete reorientation and coordinated deformation during extrusion, transforming the texture from diffuse to concentrated and significantly enhancing the maximum texture intensity. At ER64, grain orientations undergo a pronounced change, becoming predominantly aligned along the basal plane (0001). Orientation points cluster tightly at the basal plane edges in the inverse pole figure, reflecting strong preferential orientation. This observation indicates that, under high extrusion ratios, grain basal planes increasingly align parallel to the extrusion direction. With increasing accumulated strain, crystallographic reorientation is more thorough, and the texture becomes highly concentrated, leading to further enhancement of the maximum texture intensity. Furthermore, previously dispersed high-intensity texture regions gradually converge into a single concentrated area, suggesting that high extrusion ratios promote large-scale dynamic recrystallization accompanied by pronounced preferential orientation growth. Figures 5(d)–(i) further analyze grain orientation differences in representative regions under varying extrusion ratios. At ER16, grains within the bimodal microstructure exhibit large misorientation angles, most exceeding  $80^\circ$ , indicating significant crystallographic heterogeneity and poor coordination during deformation. The corresponding scatter plots show clear deviation of grain orientations relative to the transverse direction, corroborating the diffuse texture characteristics. At ER25, misorientation angles are substantially reduced, forming a structure with interspersed high- and low-angle grain boundaries within individual grains. This optimized orientation difference facilitates more coordinated deformation between grains and promotes rational dislocation distribution and release, thereby guiding the texture toward a stable configuration. At ER64, misorientation angles decrease further, with most falling below  $60^\circ$ , reflecting highly consistent grain orientations and enhanced crystallographic coherence. Under these conditions, dynamic recrystallization proceeds more completely, and grains grow cooperatively through orientation selection and grain boundary migration, ultimately forming a uniform, stable, and strongly aligned texture. This analysis systematically elucidates, from the perspective of microstructural orientation evolution, the intrinsic mechanism by which the maximum texture intensity continuously increases with extrusion ratio. The combined effects of enhanced recrystallization, preferential orientation selection, and coordinated grain growth under higher deformation conditions account for the pronounced texture strengthening observed in the Mg–Sn–Bi–Gd alloy.

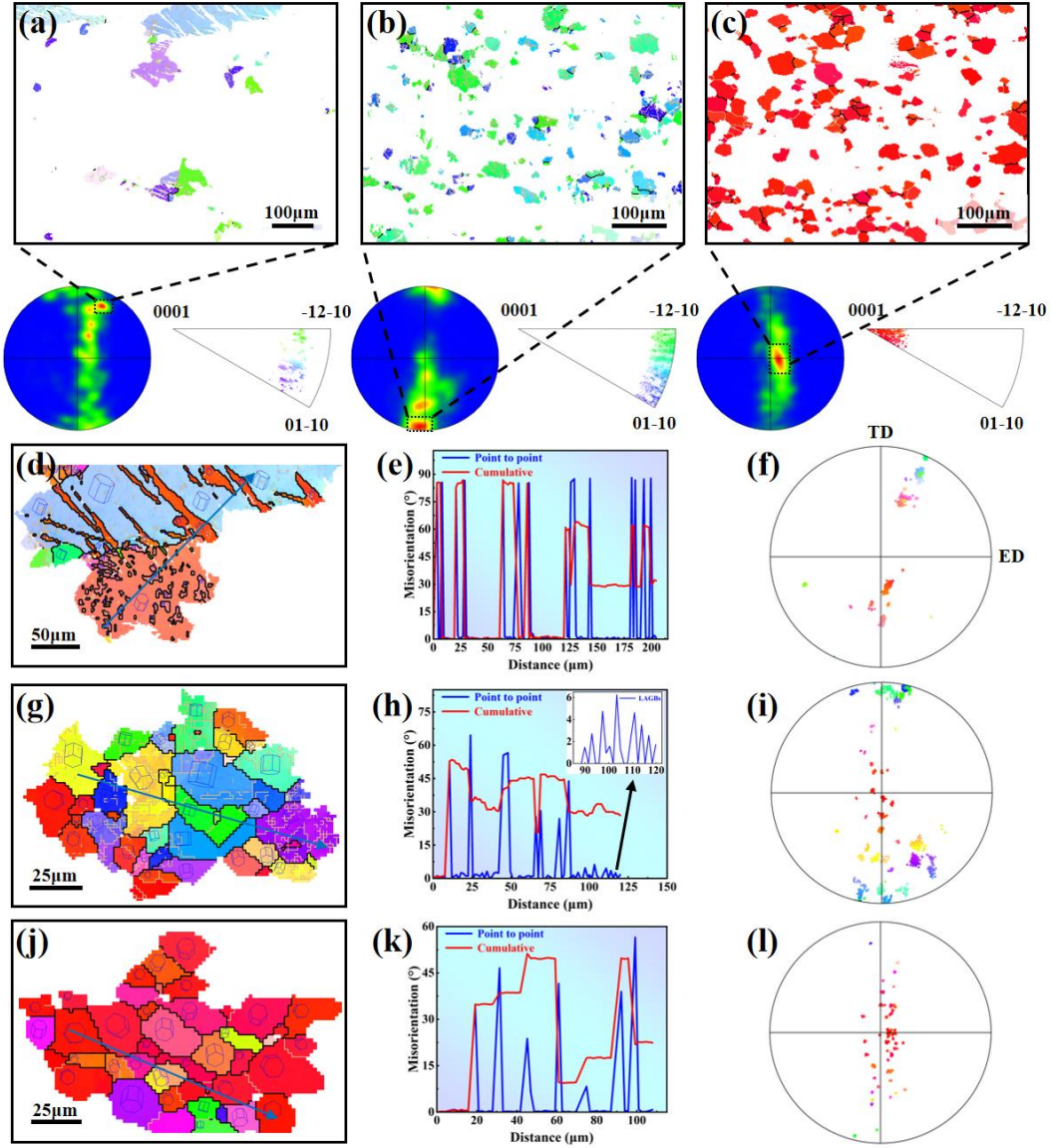


Figure 5: The strongest texture corresponding to the grains and their regional grains (a, d, e, f) in the pole figure of three extrusion ratio alloys: ER16; (b, g, h, i) ER25; (c, j, k, l): ER64;

The characterization of grain boundary misorientation and orientation randomness from IPF maps alone is insufficient to fully describe the internal deformation heterogeneity and defect distribution within the material. Therefore, kernel average misorientation (KAM) maps, as shown in Figure 6, were introduced to systematically analyze local orientation deviations and dislocation density distributions within grains under different extrusion ratios. The KAM value effectively reflects the local strain gradient and geometrically necessary dislocation (GND) density, serving as a key parameter for evaluating deformation-stored energy and microstructural uniformity. As shown in Figures 6(a)–(c), at ER16, regions with high KAM values (green areas) are primarily concentrated within coarse, elongated grains, whereas fine equiaxed grains exhibit predominantly low KAM values. This indicates that deformation is localized, with poor strain compatibility between grains and a highly heterogeneous internal strain distribution. This behavior is consistent with the limited

deformation and insufficient dynamic recrystallization (DRX) under low extrusion ratios, where coarse grains accommodate most of the plastic deformation. When the extrusion ratio increases to 25, high KAM values become widely distributed across most grains, indicating a significant increase in overall deformation. Dislocations are extensively generated, entangled, and accumulated within grains, leading to pronounced local orientation deviations. Simultaneously, the formation of numerous low-angle grain boundaries gives rise to well-developed subgrain structures, suggesting that the material is in a state of intense strain accumulation. Statistical analysis (Figures 6d–f) shows that the average KAM value increases markedly from  $0.55^\circ$  to  $1.12\%$ , reaching a maximum, which indicates the highest level of stored energy and a highly unstable microstructural state. At ER64, the distribution of high KAM values is significantly reduced, with the microstructure dominated by low KAM regions (blue areas), and only a few localized regions exhibiting high misorientation. This observation suggests that, with further deformation, DRX becomes more complete, and dislocations within grains are effectively annihilated through mechanisms such as climb, cross-slip, and mutual annihilation. Meanwhile, low-angle grain boundaries progressively transform into high-angle boundaries, facilitating crystallographic reorientation and significantly reducing the stored energy. Consequently, the average KAM value decreases to  $0.39^\circ$ , indicating a substantial reduction in strain gradients and a transition toward a more homogeneous and stable microstructure. Based on the average KAM values and the Burgers vector ( $b=3.21\times 10^{-10}$  m) [37], the corresponding dislocation densities are calculated to be  $2.14 \times 10^{15} \text{ m}^{-2}$ ,  $4.65 \times 10^{15} \text{ m}^{-2}$ , and  $1.39 \times 10^{15} \text{ m}^{-2}$  for ER16, ER25, and ER64, respectively, showing a trend consistent with the KAM evolution. The peak dislocation density at ER25 reflects the most pronounced lattice distortion and deformation accumulation, whereas the significant reduction at ER64 indicates effective defect elimination through recrystallization, leading to a more stable crystal structure. Overall, with increasing extrusion ratio, the microstructure evolves from localized strain concentration (ER16) to intensified strain accumulation (ER25), and finally to fully developed dynamic recrystallization with efficient defect release (ER64). The coupled evolution of KAM values and dislocation density reveals, at the microscale, the transition from a high-energy, heterogeneous structure to a low-energy, homogeneous one, highlighting the competitive and cooperative interplay between deformation and recrystallization processes

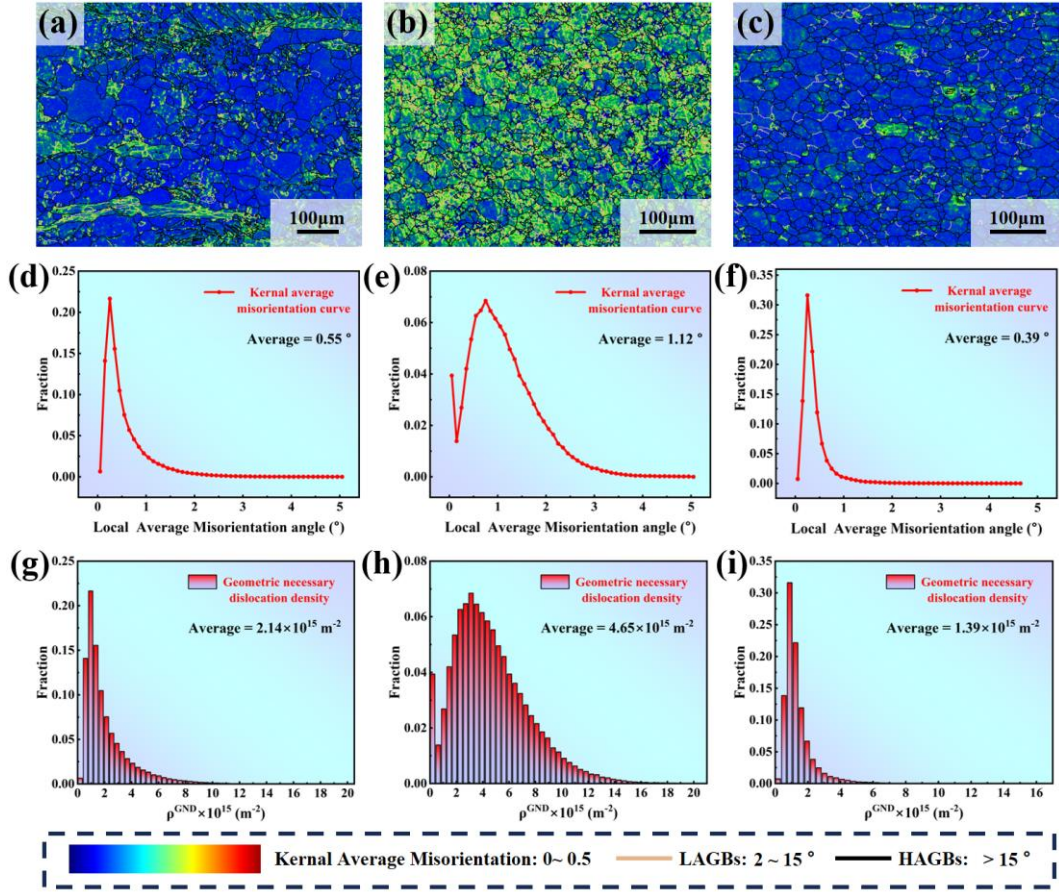


Fig. 6: KAM results of three different extrusion ratio alloys: (a, d, g) ER16; (b, e, h) ER25; (c, f, i) ER64.

To further elucidate grain formation and microstructural evolution, the recrystallization fraction maps shown in Figure 7 were analyzed to quantify the proportions of recrystallized grains, substructured (recovered) grains, and deformed grains under different extrusion ratios. The results indicate that the extrusion ratio exerts a pronounced influence on the microstructural evolution pathway and the distribution of different grain types. At ER16, recrystallized grains account for 45.9%, while recovered and deformed grains constitute 33.6% and 20.5%, respectively. Under this condition, the relatively low extrusion ratio results in limited overall deformation, and the development of dynamic recrystallization (DRX) remains incomplete. Recrystallization is primarily governed by strain-induced nucleation, preferentially occurring at high-energy regions such as original grain boundaries and twin boundaries. However, due to the heterogeneous deformation, recrystallized grains exhibit non-uniform size distribution and relatively random orientations. Meanwhile, some coarse, elongated grains retain a deformed structure with high internal dislocation density, indicating that localized regions remain in a state of strain accumulation. Consequently, the microstructure exhibits a transitional feature characterized by the coexistence of recrystallized and deformed structures. When the extrusion ratio increases to 25, a significant shift in microstructural characteristics is observed. Deformed grains dominate the microstructure, accounting for 72%, while recovered and recrystallized grains decrease to 24.4% and 3.6%, respectively. This indicates

that the material is in a stage of intense plastic deformation, during which dislocations are extensively generated, entangled, and rearranged within grains, forming pronounced recovery structures. In conjunction with the KAM and orientation analyses, the high dislocation density is mainly concentrated in the deformed grain regions, suggesting that deformation and recovery mechanisms dominate at this stage, while DRX is partially suppressed and occurs only locally in high-energy regions. This microstructural state reflects a condition of significant stored energy accumulation, providing a strong driving force for subsequent recrystallization. At ER64, the microstructure undergoes a marked transformation. The fraction of recrystallized grains increases dramatically to 87.1%, becoming the dominant feature, with recrystallized grains uniformly distributed throughout the material, indicative of typical complete DRX. In contrast, the fractions of recovered and deformed grains decrease to 8.1% and 4.8%, respectively, demonstrating that the stored deformation energy is effectively released through the recrystallization process. Combined with the previous orientation and KAM analyses, the dislocation density within grains is significantly reduced, and the microstructure evolves toward a stable and homogeneous state with enhanced crystallographic compatibility between grains. Overall, with increasing extrusion ratio, the microstructure evolves progressively from partial recrystallization (ER16), to a high-energy state dominated by deformation and recovery (ER25), and finally to a fully recrystallized structure (ER64). This evolution fundamentally reflects the dynamic balance between the accumulation and release of deformation-stored energy: at low extrusion ratios, recrystallization occurs locally via strain-induced nucleation at high-energy sites; at intermediate ratios, stored energy accumulates rapidly; while at high extrusion ratios, this energy is efficiently released through extensive DRX, leading to microstructural reconstruction and homogenization.

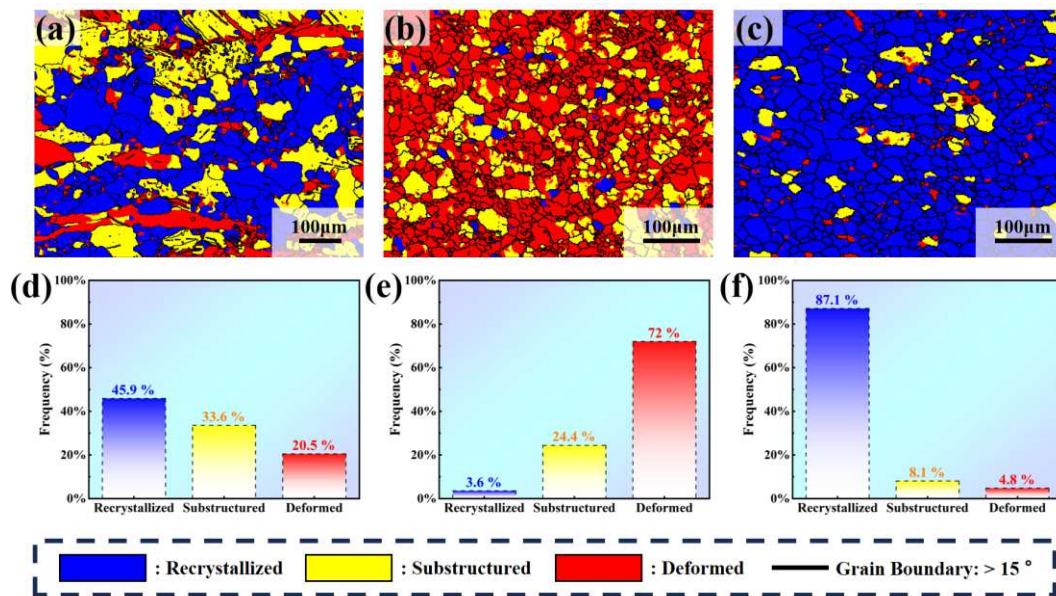


Fig. 7 Grain types and their proportions of three different extrusion ratio alloys: (a, d) ER16; (b, e) ER25; (c) (f)

ER64

Building upon the previously discussed grain growth mechanisms, it is essential to further

elucidate the plastic deformation mechanisms during extrusion and their correlation with macroscopic mechanical behavior. Schmid factor analysis provides an effective approach to identify the dominant slip systems under a given loading direction and to interpret the anisotropic deformation behavior of Mg alloys [38]. Fig. 8 presents the distribution of grains with respect to different slip systems along the  $\langle 11\text{-}20 \rangle$  loading direction under varying extrusion ratios. Specifically, basal  $\langle a \rangle$  slip (Figs. 8(a)–(d)), prismatic  $\langle a \rangle$  slip (Figs. 8(i)–(l)), and pyramidal  $\langle c+a \rangle$  slip (Figs. 8(e)–(h)) are analyzed on the (10-10) and (11-22) planes. As shown in Figs. 8(d), (h), and (l), the Schmid factor for basal slip decreases from 0.21 to 0.15 as the extrusion ratio increases from 16 to 64. This indicates that the basal planes are oriented nearly perpendicular to the extrusion direction, resulting in minimal resolved shear stress and making basal slip difficult to activate. Moreover, this constraint becomes more pronounced at higher extrusion ratios, further stabilizing the basal orientation. Consequently, under high extrusion conditions, basal slip contributes minimally to plastic deformation, and deformation is primarily accommodated by prismatic  $\langle a \rangle$  and pyramidal  $\langle c+a \rangle$  slip systems. In contrast, the Schmid factor for prismatic slip increases slightly from 0.44 to 0.46 with increasing extrusion ratio, suggesting that prismatic slip gradually becomes the dominant deformation mechanism at higher extrusion ratios. This observation is consistent with the texture evolution shown in Figure 5, where grains concentrated near the edges of the inverse pole figure correspond to orientations with higher Schmid factors, facilitating the activation of prismatic slip. As a result, a coordinated deformation mechanism is established, promoting compatibility among grains. Further insights can be obtained by correlating these results with the orientation distributions shown in Figures 5(m)–(o). When the extrusion ratio increases from 16 to 25, a certain degree of orientation randomness persists in localized regions. Grains with high Schmid factors preferentially activate prismatic slip systems, leading to increased dislocation density and the formation of numerous low-angle grain boundaries, which reflects the heterogeneous nature of plastic deformation. As the extrusion ratio increases to 64, the fraction of randomly oriented grains decreases significantly, and most grains adopt a strong basal texture. These grains are predominantly recrystallized, exhibiting high orientation consistency. Under such conditions, prismatic and pyramidal slip systems are activated more uniformly, enabling coordinated plastic deformation within grains and ensuring macroscopic deformation compatibility. This behavior is consistent with the KAM and dislocation density analyses, which revealed effective dislocation annihilation and regulated energy release at high extrusion ratios. In summary, Schmid factor analysis reveals the evolution of deformation mechanisms with increasing extrusion ratio. At low extrusion ratios (ER16), basal slip is theoretically favorable but remains limited, while prismatic slip is insufficiently activated, resulting in localized dislocation accumulation and poor strain compatibility. At intermediate extrusion ratios (ER25), basal slip remains constrained, whereas prismatic and pyramidal slip systems are increasingly activated in grains with high Schmid factors, leading to elevated dislocation density and a pronounced strain accumulation state. At high extrusion ratios (ER64), basal slip is strongly suppressed, while prismatic and pyramidal slip systems are uniformly

activated. Combined with the highly consistent grain orientations and fully developed dynamic recrystallization, dislocations are effectively released, and macroscopic plastic compatibility is significantly enhanced.

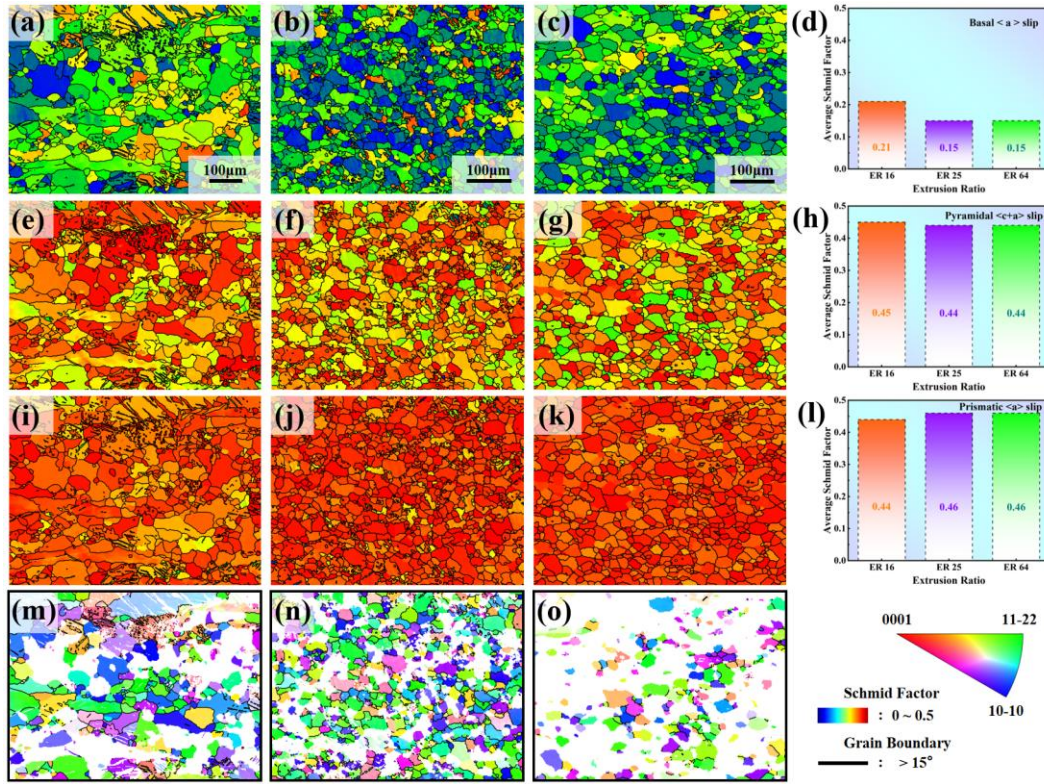


Fig. 8: Grain distribution corresponding to Schmidt factor size of alloy slip system under different extrusion ratios: (a)~(d): basal<a>slip; (e) ~(h): Cone slip<c+a>; (i) ~(l): Cylindrical<a>slip; (m) ~(o): The cylindrical<a>slip of crystal planes (10-10) and (11-22) corresponds to the grain size

### 3.2 Electrochemical behavior

Figure 9 shows the time-dependent evolution of the open-circuit potential (OCP) for Mg–Sn–Bi–Gd alloy samples with different extrusion ratios (ER16, ER25, and ER64) in 3.5 wt.% NaCl solution over 3000 s. As observed, all samples exhibit a gradual increase in OCP within the initial 500 s, indicating the initial formation of surface corrosion products and the ongoing activation process. After approximately 1000 s, the OCP tends to stabilize, suggesting that a dynamic equilibrium between the formation and dissolution of corrosion products has been established. However, distinct differences are evident among the samples at longer times. The ER25 sample shows a pronounced increase in OCP after ~2300 s, whereas ER16 and ER64 maintain relatively stable potentials during this period. Notably, the ER64 sample exhibits the highest OCP stability throughout the entire test duration. This behavior indicates that a higher extrusion ratio effectively suppresses localized potential fluctuations caused by corrosion product accumulation, thereby providing enhanced electrochemical stability under prolonged discharge conditions. The microstructural origin of the OCP evolution can be systematically interpreted by correlating with

the analyses in Figures 4–8. At ER16, the alloy exhibits a bimodal grain structure, consisting of 45.9% recrystallized grains, 33.6% recovered grains, and 20.5% deformed grains. The heterogeneous grain size distribution and random orientations, combined with limited activation of basal  $\langle a \rangle$  slip (due to low Schmid factors) and insufficient prismatic and pyramidal slip activity, result in poor intragranular plastic compatibility. Consequently, dislocations accumulate in localized high-energy regions, leading to heterogeneous surface microstructures and non-uniform corrosion behavior, which may cause fluctuations in OCP at later stages. At ER25, the microstructure is dominated by deformed grains (72%), with 24.4% recovered grains and only 3.6% recrystallized grains, indicating a state of significant strain accumulation. The increased density of low-angle grain boundaries and the activation of prismatic and pyramidal slip systems enhance deformation, but their spatial distribution remains non-uniform. Localized strain concentration regions may induce micro-galvanic heterogeneity in electrochemical reactions, resulting in noticeable instability in the OCP response. In contrast, at ER64, recrystallized grains dominate (87.1%), with a uniform grain size distribution and highly consistent crystallographic orientations. The transformation of low-angle grain boundaries into high-angle boundaries, together with the uniform activation of prismatic and pyramidal slip systems, leads to excellent intragranular deformation compatibility. Correspondingly, KAM values and dislocation densities are significantly reduced, indicating effective release of stored energy and a highly homogeneous microstructure. Under these conditions, the electrode surface exhibits uniform electrochemical potential distribution, and a dynamic balance between corrosion product formation and detachment is maintained. As a result, the OCP remains stable over prolonged testing, demonstrating superior electrochemical stability

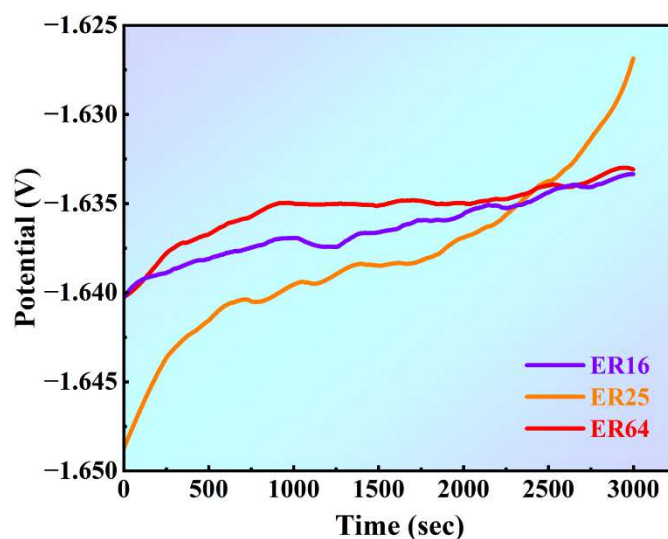


Fig. 9 Open circuit potential diagram of Mg-Sn-Bi-Gd alloy with different extrusion ratios

Figure 10 presents the cathodic and anodic polarization curves of Mg-Sn-Bi-Gd alloy samples with different extrusion ratios (ER16, ER25, and ER64). From these curves, key electrochemical parameters—including corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $J_{\text{corr}}$ ), Tafel slopes

( $\beta_a$  and  $\beta_c$ ), and polarization resistance ( $R_p$ )—were extracted, as summarized in Table 1. The cathodic branch primarily reflects the hydrogen evolution reaction (HER) kinetics [39]. As shown in Figure 10, with increasing extrusion ratio, the cathodic curves initially shift toward higher current densities and subsequently move back toward lower current densities, indicating a non-linear variation in hydrogen evolution rate. In contrast, the anodic branch is closely associated with the uniform dissolution behavior of the Mg matrix, and its morphology reflects the kinetics of anodic reactions. According to Table 1, the ER25 sample exhibits the most positive  $E_{corr}$ , suggesting enhanced thermodynamic stability and relatively superior corrosion resistance. However,  $J_{corr}$ , which represents the corrosion rate, shows a different trend. Although the ER64 sample has a slightly lower  $E_{corr}$ , it exhibits a significantly reduced  $J_{corr}$ , indicating a lower corrosion rate and more uniform surface reactions. The Tafel slopes ( $\beta_a$  and  $\beta_c$ ) describe the kinetics of anodic and cathodic reactions; lower slope values indicate faster reaction kinetics and reduced polarization resistance. Meanwhile,  $R_p$  reflects the overall charge transfer resistance at the electrode–electrolyte interface, where higher values correspond to the formation of a more stable surface film and improved corrosion resistance. By correlating the polarization behavior with the microstructural characteristics, the role of extrusion ratio in regulating electrochemical performance can be systematically understood. At a moderate extrusion ratio (ER25), the optimization of grain size, recrystallization fraction, and dislocation distribution leads to a balance between thermodynamic stability and reaction kinetics. In contrast, at a high extrusion ratio (ER16), the improved grain uniformity and coordinated slip behavior increase the charge transfer resistance, thereby enhancing corrosion resistance and stabilizing electrochemical reactions. From a mechanistic perspective, the microstructure and slip behavior under different extrusion ratios directly influence both the hydrogen evolution rate and the uniformity of anodic dissolution. At ER64, the alloy exhibits a bimodal grain structure with incomplete recrystallization, heterogeneous grain size distribution, and random orientations. High dislocation density is localized in deformed grains, and prismatic and pyramidal slip systems are activated only locally, resulting in strain concentration at the microscale. This heterogeneity accelerates localized anodic reactions, leading to a broader anodic branch and increased  $J_{corr}$ . At ER25, deformed grains dominate, accompanied by a high density of low-angle grain boundaries and elevated dislocation density. Although prismatic and pyramidal slip systems are more active, their spatial distribution remains non-uniform. The resulting localized strain accumulation enhances hydrogen evolution kinetics while concentrating anodic dissolution, which manifests as higher current densities in both cathodic and anodic branches, together with a more positive  $E_{corr}$ . At ER16, the microstructure is characterized by nearly complete dynamic recrystallization, uniform grain size, and highly consistent orientations. The transformation of low-angle grain boundaries into high-angle boundaries, along with reduced KAM values and dislocation density, indicates effective release of stored energy. Furthermore, prismatic and pyramidal slip systems are activated uniformly, leading to enhanced intragranular deformation compatibility. This microstructural homogeneity enables a balanced relationship between hydrogen evolution and

uniform anodic dissolution. Consequently, the polarization curves exhibit lower  $J_{\text{corr}}$  and more stable Tafel behavior, indicating more uniform electrochemical kinetics and a reduced corrosion rate.

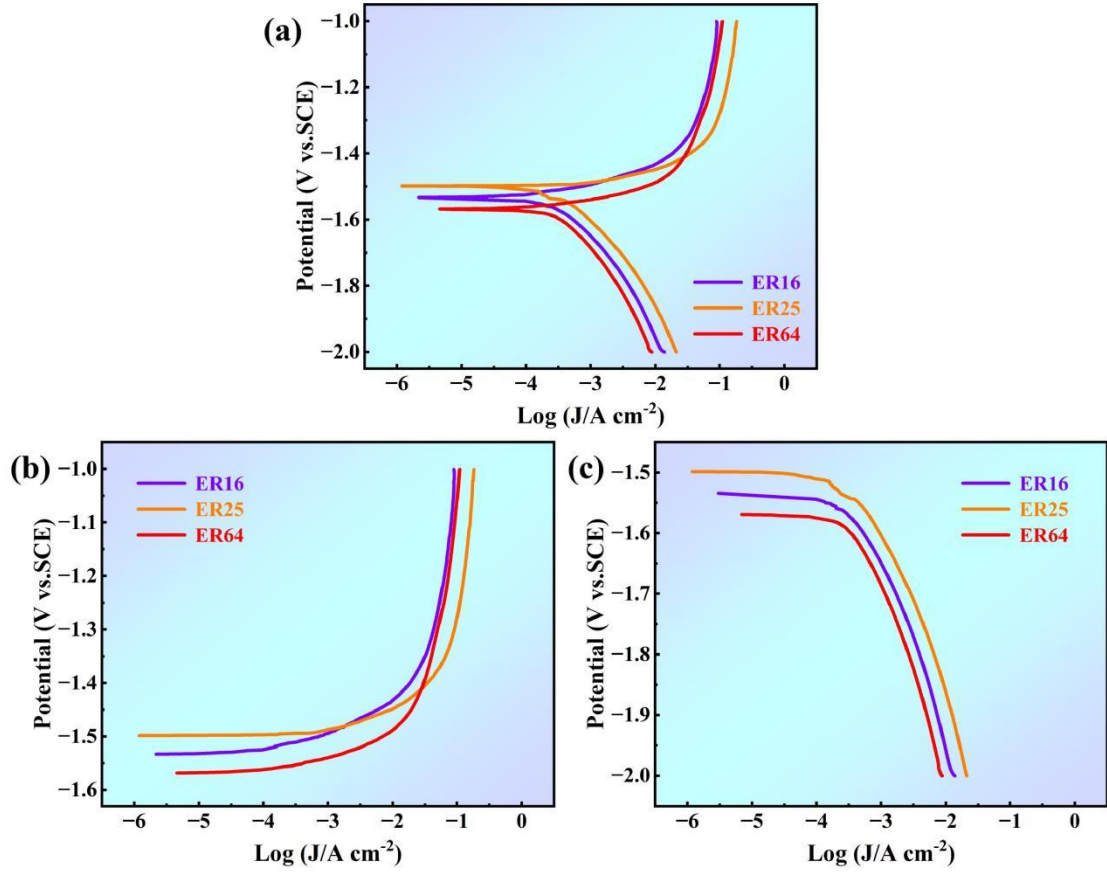


Fig. 10 Electrochemical test results of Mg-Sn-Bi-Gd alloys with different extrusion ratios: (a) polarization curve, (b) cathode branch, (c) anode branch.

Tab. 1 Electrochemical test results of Mg-Sn-Bi-Gd alloys with different extrusion ratios:

| Nominal codes | $E_{\text{corr}}$ (V) | $J_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ ) | $\beta_a$ (mV) | $\beta_c$ (mV) | $R_p$ ( $\Omega/\text{cm}^2$ ) |
|---------------|-----------------------|-------------------------------------------------|----------------|----------------|--------------------------------|
| ER64          | -1.568                | 248.9                                           | 20.828         | 4.856          | 68                             |
| ER25          | -1.498                | 813.4                                           | 9.236          | 5.362          | 41                             |
| ER16          | -1.533                | 194.7                                           | 13.569         | 5.543          | 117                            |

Figure 11 presents the Nyquist plots and corresponding fitted curves of Mg-Sn-Bi-Gd alloys with different extrusion ratios (ER16, ER25, and ER64). The electrochemical parameters obtained from equivalent circuit fitting are summarized in Table 2, providing quantitative insight into the

impedance characteristics and interfacial reaction kinetics. The solution resistance ( $R_s$ ) reflects the ionic conductivity of the electrolyte. A lower  $R_s$  indicates more efficient ion transport in the solution. As shown in Table 2, the  $R_s$  values for ER64 ( $4.435 \Omega \cdot \text{cm}^2$ ), ER25 ( $4.495 \Omega \cdot \text{cm}^2$ ), and ER16 ( $3.909 \Omega \cdot \text{cm}^2$ ) exhibit only minor differences, suggesting that the electrolyte conductivity remains essentially unchanged under all testing conditions and does not dominate the electrochemical response. In contrast, the charge transfer resistance ( $R_{ct}$ ) is a critical parameter governing interfacial reaction kinetics. A lower  $R_{ct}$  corresponds to faster charge transfer across the electrode/electrolyte interface and thus higher electrochemical activity. Notably, the ER64 sample exhibits the lowest  $R_{ct}$  value ( $13.74 \Omega \cdot \text{cm}^2$ ), significantly smaller than those of ER25 ( $29.32 \Omega \cdot \text{cm}^2$ ) and ER16 ( $34.59 \Omega \cdot \text{cm}^2$ ). This result indicates that a high extrusion ratio markedly enhances interfacial charge transfer capability, which can be attributed to microstructural homogenization, extensive dynamic recrystallization, and grain boundary stabilization. The constant phase element ( $\text{CPE}_1$ ) and its exponent ( $n_1$ ) are used to describe the non-ideal capacitive behavior of the electrical double layer, which is closely related to surface roughness and local heterogeneity. For the ER64 sample, a moderate  $\text{CPE}_1$  value combined with an  $n_1$  value close to 0.91 suggests a highly uniform, near-ideal capacitive response, indicating a homogeneous and stable electrochemical interface. In contrast, ER25 and ER16 exhibit larger  $\text{CPE}_1$  values and lower  $n_1$  values, implying increased surface roughness and interfacial heterogeneity. Such non-uniformity may lead to localized variations in charge transfer and increased local current density. From a microstructural perspective, the superior impedance response at high extrusion ratio originates from the nearly complete dynamic recrystallization, uniform grain size, and highly consistent crystallographic orientation. The transformation of low-angle grain boundaries into high-angle grain boundaries, along with the significant reduction in KAM values and dislocation density, indicates effective release of stored strain energy. Furthermore, the uniform activation of prismatic and pyramidal slip systems ensures homogeneous strain distribution within grains, thereby promoting coordinated electrochemical reactions across the electrode surface. As a result, interfacial heterogeneity is minimized, leading to a reduced  $R_{ct}$  and a more ideal capacitive response. This microstructural optimization is directly reflected in the polarization behavior, where a better balance between hydrogen evolution and uniform anodic dissolution is achieved. Consequently, the corrosion current density is reduced, and both Tafel slopes and polarization resistance exhibit more favorable kinetic characteristics. In summary, the ER64 sample demonstrates the smallest Nyquist semicircle diameter and the lowest  $R_{ct}$ , indicating the highest interfacial charge transfer efficiency. This is attributed to its uniform microstructure, high recrystallization fraction, coordinated slip activity, and homogeneous dislocation distribution, which collectively create a highly active and uniform electrochemical interface. In contrast, the ER16 and ER25 samples exhibit larger grain size heterogeneity, higher fractions of low-angle grain boundaries, and non-uniform slip activation, resulting in restricted charge transfer, increased  $R_{ct}$ , and heterogeneous electrochemical activity. Overall, the extrusion ratio effectively tailors the electrochemical impedance characteristics and interfacial reaction

kinetics of Mg alloys through systematic microstructural regulation, thereby providing a fundamental basis for optimizing their corrosion and discharge performance.

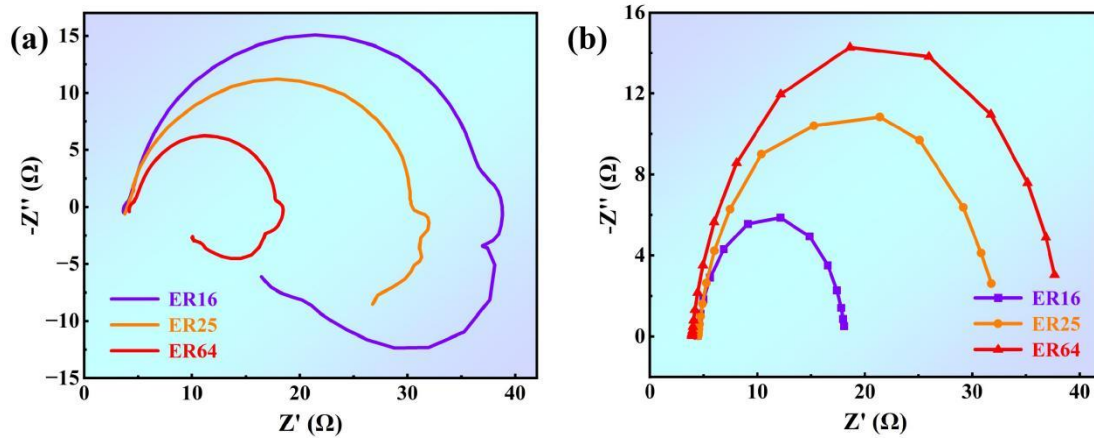


Fig. 11 Electrochemical impedance spectroscopy (EIS) results of Mg-Sn-Bi-Gd alloys with different extrusion ratios (ER16, ER25, and ER64): (a) Nyquist plots and (b) corresponding fitted curves derived from the equivalent circuit model

Tab. 2 Parameters for impedance fitting

| Nominal codes | $R_s$ | $R_{ct}$ | $CPE_1$              | $n_1$   |
|---------------|-------|----------|----------------------|---------|
| ER64          | 4.435 | 13.74    | $2.203 \times 10^4$  | 0.90534 |
| ER25          | 4.537 | 28.27    | $3.268 \times 10^4$  | 0.87832 |
| ER16          | 3.909 | 34.59    | $2.2461 \times 10^4$ | 0.88726 |

Figure 12 illustrates the variation of hydrogen evolution volume as a function of immersion time for ER16, ER25, and ER64 samples in 3.5 wt.% NaCl solution. It is evident that the hydrogen evolution volume of all samples increases continuously over the 180 min testing period, while the evolution rate differs significantly. The ER16 sample exhibits the highest hydrogen evolution volume, whereas the ER64 sample shows the lowest, indicating a substantial reduction in corrosion-induced hydrogen evolution with increasing extrusion ratio. From a microstructural perspective, hydrogen evolution is predominantly initiated at the grain boundary [40]. At a low extrusion ratio (ER16), the alloy exhibits a bimodal grain structure characterized by heterogeneous grain size distribution and a relatively low recrystallization fraction. The large grain interior volume fraction, combined with a high density of low-angle grain boundaries and dislocations, results in localized

strain concentration. Moreover, prismatic and pyramidal slip systems are only partially activated, leading to poor intragranular deformation compatibility. In addition, the segregation tendency of Gd at grain boundaries enhances the potential difference between grain interiors and boundaries, thereby accelerating localized hydrogen evolution. These factors collectively contribute to the highest hydrogen evolution rate observed in the ER16 sample. At an intermediate extrusion ratio (ER25), the microstructure is dominated by deformed grains with a limited fraction of recrystallized grains. The increased density of low-angle grain boundaries and the active but non-uniform activation of prismatic and pyramidal slip systems result in pronounced strain accumulation in localized regions. Consequently, hydrogen evolution remains relatively high and spatially heterogeneous. This behavior is consistent with the electrochemical results, where moderate corrosion current density and intermediate charge transfer resistance are observed in both polarization and EIS analyses. In contrast, at a high extrusion ratio (ER64), the alloy exhibits a fully recrystallized microstructure with fine and uniformly distributed grains. The increased fraction of high-angle grain boundaries, reduced KAM values, and lower dislocation density indicate effective strain relaxation and enhanced structural homogeneity. Furthermore, the uniform activation of prismatic and pyramidal slip systems improves intragranular deformation compatibility. This microstructural uniformity suppresses excessive hydrogen evolution within grains and promotes a balanced relationship between cathodic hydrogen evolution and anodic dissolution. As a result, the ER64 sample exhibits the lowest hydrogen evolution rate, consistent with the reduced corrosion current density in polarization curves and the smallest Nyquist semicircle in EIS measurements, indicating superior interfacial charge transfer efficiency. Overall, the extrusion ratio effectively regulates hydrogen evolution behavior by tailoring grain structure, recrystallization extent, grain boundary characteristics, and slip mechanisms. The ER64 sample achieves an optimal balance between high discharge activity and suppressed hydrogen evolution corrosion. This microstructural optimization directly enhances the overall electrochemical performance of the Mg–air battery anode, establishing its superiority as an advanced anode material.

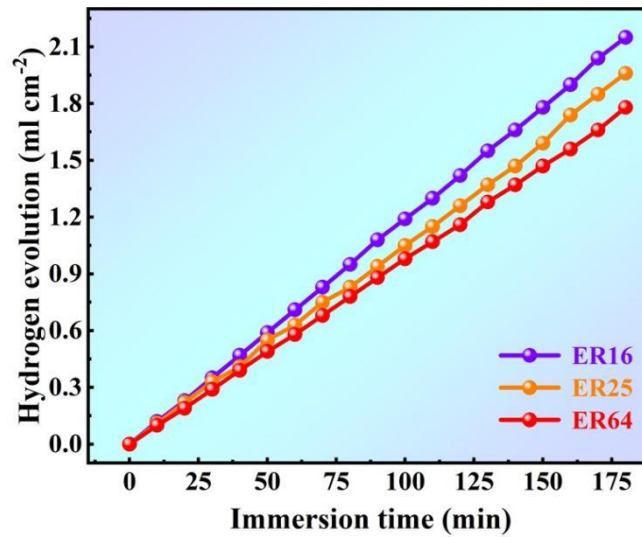


Fig. 12 Hydrogen evolution process diagram of Mg Sn Bi Gd alloy.

### 3.3 Discharge performance

Figure 13 is a schematic diagram of the discharge mechanism of magnesium alloy air batteries. During discharge, the Mg alloy anode undergoes oxidation, releasing electrons and generating  $Mg^{2+}$  ions, while oxygen at the cathode is reduced in the presence of water to produce hydroxide ions ( $OH^-$ ) [41]. These ions react at the anode to form magnesium hydroxide ( $Mg(OH)_2$ ), which gradually deposits on the surface. The accumulation of  $Mg(OH)_2$  diminishes the effective active area and, combined with concurrent hydrogen evolution, accelerates anodic dissolution. Electron transfer in the electrolyte reduces water to  $H_2$ , enhancing local corrosion and decreasing discharge efficiency.

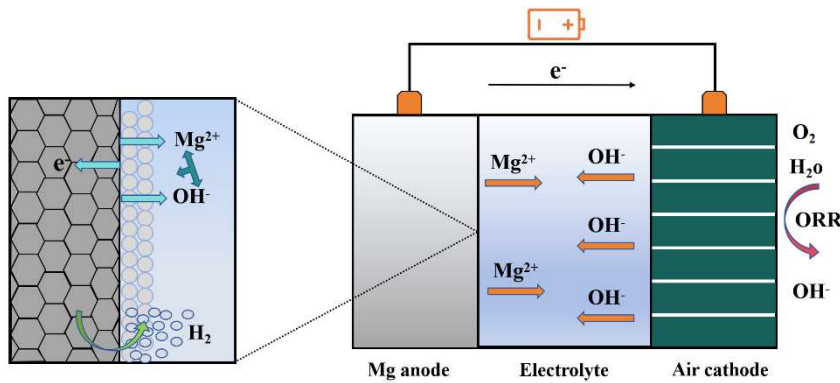


Fig. 13 is a schematic diagram of the discharge mechanism of mag air batteries

Figure 14 presents the constant-current discharge behavior and anode efficiency of ER16, ER25, and ER64 Mg–Sn–Bi–Gd alloys in an air battery configuration. Fig. 14(a) shows the discharge curves in 3.5 wt.% NaCl at a current density of  $2.5 \text{ mA cm}^{-2}$ . During the initial stage, all alloys exhibited a rapid voltage drop, primarily due to the breakdown of the stable surface oxide

layer on the Mg alloy, followed by the formation of discharge products that transiently reduced the electrode potential. Around 1000 s, the formation and detachment of these products reached a dynamic equilibrium, resulting in a relatively stable discharge voltage. Subsequent voltage fluctuations reflected differences in the adhesion and removal of discharge products: smaller fluctuations indicated balanced formation and detachment, while larger fluctuations suggested local product accumulation or sudden detachment. Among all alloys, ER16 displayed the highest and most stable voltage, indicating uniform detachment of discharge products that maintained continuous electrolyte–anode contact and stable output. Fig. 14(b) compares the anode efficiencies ( $\eta$ ) of the three alloys. All exceeded 35%, with ER16 achieving the highest value of 36.2%, reflecting more uniform matrix dissolution and minimized electrolyte blockage due to localized product accumulation, thereby enhancing anode utilization. Figures 14(c–e) show the surface morphologies after 3 h of discharge. All samples were covered by a relatively thick layer of discharge products; notably, the ER16 surface exhibited extensive cracks and deep pores, facilitating electrolyte penetration through the product layer to maintain continuous matrix contact. This microstructural feature promoted uniform matrix dissolution and loose deposition of discharge products, enabling high anode utilization and stable discharge. Mechanistically, a thin initial layer of discharge products forms at the matrix–electrolyte interface. Only when this layer is perforated by hard secondary phases can the matrix maintain continuous electrolyte contact, allowing the gradual accumulation of a thick, porous product layer. Thin and dense product layers restrict matrix–electrolyte interaction, causing pronounced voltage fluctuations, whereas thick and porous layers sustain continuous contact and stable voltage output. These observations correlate with the previously reported hydrogen evolution and corrosion behavior: a porous discharge layer facilitates timely hydrogen release, reduces local blockage, and ensures uniform surface dissolution, thus maintaining stable discharge performance. It should be noted that, although ER64 exhibits optimal discharge behavior, its relatively high hydrogen evolution rate and moderate corrosion activity could accelerate local degradation during long-term operation, promote passive layer accumulation, and reduce the effective active area, potentially limiting anode lifespan. In applications requiring sustained current output or repeated discharge cycles, this may impact overall performance and system reliability. Therefore, while ER16 achieves the best balance in single-cell operation, its long-term stability may require further enhancement via surface modification, electrolyte optimization, or multi-element alloying strategies.

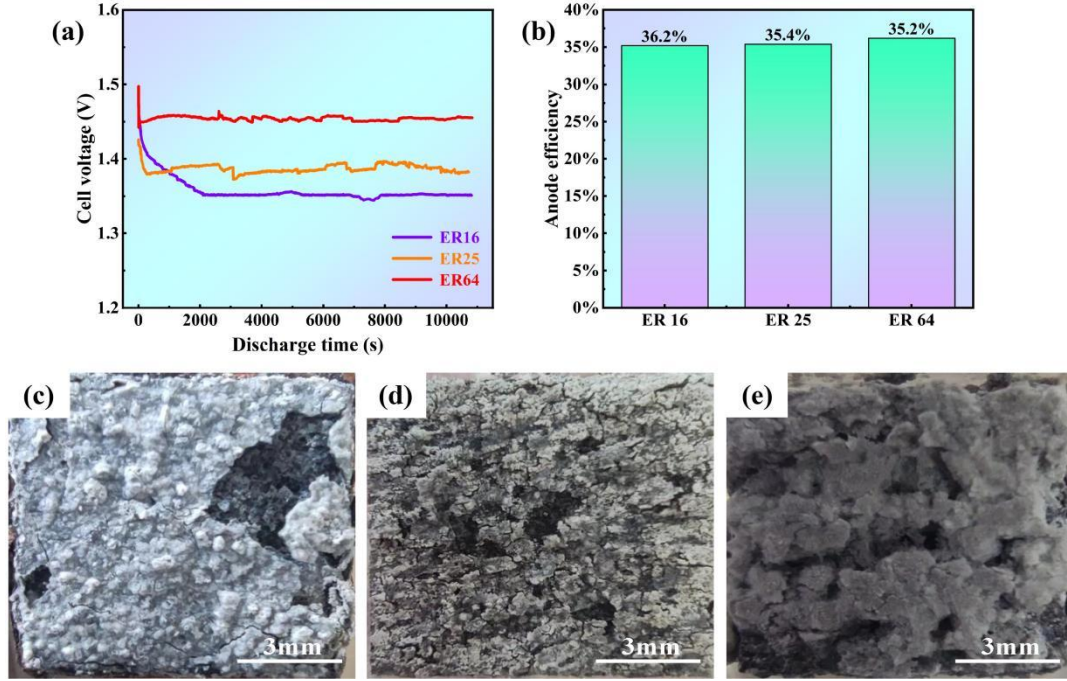


Fig. 14 Constant current discharge curves (a) and anode efficiency (b) of Mg-Sn-Bi-Gd alloy with different extrusion ratios and their macroscopic morphology after discharge (c-e): (a) constant current discharge curve; (b) anode efficiency, (a) ER64,(b) ER25, (c) ER16

In 3.5 wt.% NaCl, the discharge behavior of Mg-Sn-Bi-Gd alloys is strongly influenced by extrusion-induced microstructural changes. Adjusting the extrusion ratio modifies grain size, grain boundary distribution, and the morphology and dispersion of secondary phases, which in turn affect the contact between the Mg matrix and the electrolyte. As shown in Figure 15, a moderate extrusion ratio (ER25) refines grains, creating a continuous interface that promotes even matrix dissolution, stable formation and partial detachment of discharge products, and thus maintains steady voltage and improved anode efficiency. At low extrusion ratios (ER16), coarse grains lead to incomplete or blocked contact with the electrolyte. The resulting thin, dense product layers detach unevenly, causing localized over-dissolution, current concentration, voltage fluctuations, and reduced overall performance. At high extrusion ratios (ER64), further grain refinement with surface microcracks and pores, allowing sustained electrolyte access through the product layer. This structure ensures uniform dissolution, forms thicker but porous discharge layers, moderates hydrogen evolution, and maximizes voltage stability and anode utilization. However, prolonged high hydrogen evolution may accelerate local degradation, indicating the need to balance extrusion ratio, hydrogen release, and durability. Overall, extrusion ratio governs grain structure, secondary phase distribution, and product-layer morphology, controlling the uniformity of anode dissolution and discharge stability: moderate extrusion favors uniform corrosion and stable performance, while excessively low or high ratios risk localized over-dissolution or hydrogen-induced degradation, reducing battery efficiency and lifetime.

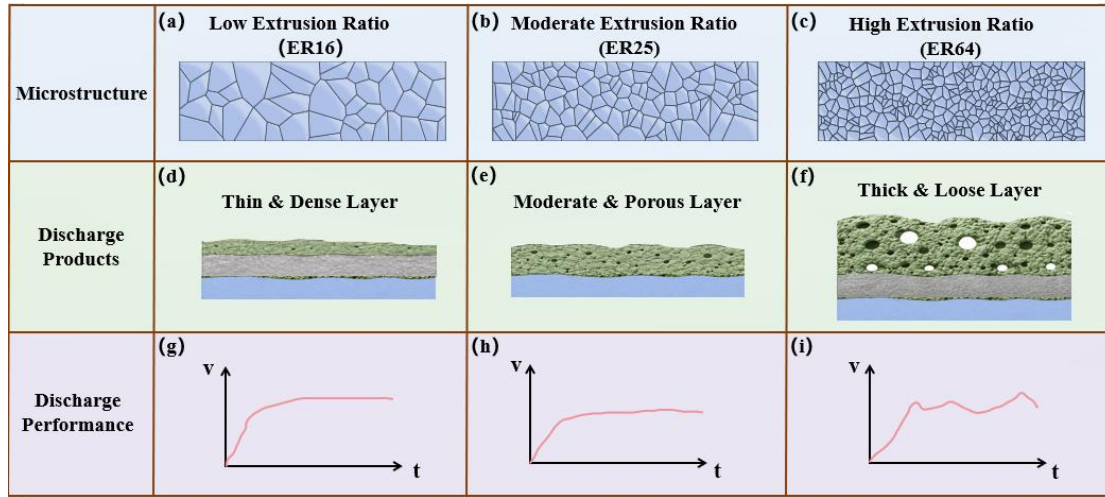


Fig. 15 Schematic diagram of anode discharge characteristics of air battery alloy

## 4. Conclusion

This study systematically investigates the influence of extrusion ratio (ER) on the microstructural evolution and electrochemical behavior of Mg–Sn–Bi–Gd alloys. By integrating EBSD analysis, polarization curves, electrochemical impedance spectroscopy, and hydrogen evolution measurements, the intrinsic relationships among grain structure, recrystallization behavior, texture evolution, dislocation density, and slip mechanisms were elucidated. A comprehensive “processing–microstructure–electrochemical performance” correlation model was established, providing critical theoretical guidance for optimizing Mg–air battery anode materials.

(1) As the extrusion ratio increased from ER16 to ER64, the alloy microstructure transformed from an incompletely dynamically recrystallized bimodal structure to a predominantly fully recrystallized and homogeneous structure. The recrystallization fraction rose markedly from 45.9% to 87.1%. Grain size exhibited a non-monotonic trend (9.83  $\mu\text{m}$ , 9.32  $\mu\text{m}$ , 14.41  $\mu\text{m}$ ), reflecting a competitive interplay between dynamic recrystallization and grain growth. Concurrently, low-angle grain boundaries gradually evolved into high-angle boundaries, stabilizing the overall grain boundary network. High extrusion ratios thus enhanced structural uniformity and grain orientation consistency, laying a solid foundation for performance optimization.

(2) KAM analysis revealed that the average misorientation first increased from  $0.55^\circ$  to  $1.12^\circ$  and then decreased to  $0.39^\circ$  with increasing ER, while the corresponding dislocation density rose from  $2.14 \times 10^{15} \text{ m}^{-2}$  to  $4.65 \times 10^{15} \text{ m}^{-2}$  before decreasing to  $1.39 \times 10^{15} \text{ m}^{-2}$ . This indicates substantial strain accumulation at intermediate extrusion ratios, whereas high ER enables effective dislocation release through dynamic recrystallization. Schmidt factor analysis showed that basal slip became increasingly constrained, while prismatic and pyramidal slips dominated, transitioning from localized activation to uniform and coordinated deformation. This process significantly enhanced intergranular plastic compatibility and reduced strain localization, thereby promoting homogenized

interfacial electrochemical reactions.

(3) Electrochemical measurements demonstrated that the ER64 alloy exhibited the lowest charge transfer resistance  $13.74\ \Omega\cdot\text{cm}^2$  and reduced corrosion current density, coupled with the slowest hydrogen evolution rate, indicating superior interfacial reaction stability. Under constant-current discharge, ER64 achieved the highest and most stable voltage, with an anode efficiency of 36.2%. Microscopically, the uniform fine grains and high recrystallization fraction facilitated the formation of a thick yet porous  $\text{Mg}(\text{OH})_2$  product layer, allowing continuous electrolyte penetration and dynamic product detachment, thereby sustaining stable discharge output. Overall, the ER64 alloy achieves an optimal balance between electrochemical activity and structural stability.

## Acknowledgements

This research was funded by Project of Enhancing the Innovation Capabilities of Small and Medium-sized Sci-tech Enterprises in Shandong Province. [No. 2024TSGC2041, No. 2024TSGC0733], Supported by the Fundamental Research Foundation for Universities of Heilongjiang Province (No. 2023-KYYWF-0132), project Multiscale Interface Control of the Impact Mechanical Behavior and Strengthening Mechanism in Layered Heterogeneous Magnesium Alloys supported by Shandong Provincial Natural Science Foundation (ZR2024QE006)

## CRediT authorship contribution statement

**Yinzhu Wang:** Conceptualization, Methodology, Data curation, Visualization, Funding acquisition, **Hongze Xu:** Writing-Original draft preparation and Editing. **Xiaofang Yuan:** Supervision, Resources, Data Curation, Conceptualization, Funding acquisition Investigation. **Fangyu Jing:** Writing- Reviewing and Editing, Conceptualization. **Zehua Yan:** Supervision, Data Curation, Project administration, Writing-Reviewing and Editing, Funding acquisition. **Lei Li:** Data Curation, Project administration, Funding acquisition.

## References

- [1] J.M.V. Nsanzimana, L. Cai, Z.Q. Jiang, B.Y. Xia, T. Maiyalagan, Engineering bifunctional catalytic microenvironments for durable and high-energy-density metal–air batteries, *Nano-Micro Lett.*, 17 (2025) 294.
- [2] J.Y. Liang, Y.Q. Zhu, H. Yang, H. Zhao, D. Jin, B.Z. Guo, H.B. Liu, W.X. Zhang, S.B. Tian, C.B. Cao, M.S. Zou, Structural design and active-site modulation of bifunctional electrocatalysts and electrolyte chemistry for zinc-air batteries, *Adv. Funct. Mater.*, 35 (49) (2025) 10535.

- [3] Y. Shabeer, S.S. Madani, S. Panchal, M. Mousavi, M. Fowler, Different metal–air batteries as range extenders for the electric vehicle market: a comparative study, *J. Batteries*, 11 (1) (2025) 11010035.
- [4] Y.H. Zhang, Y.J. Fu, Y.K. Lv, Z.Y. Song, L.H. Gan, M.X. Liu, Carbonyl-rich organic cathodes for advanced aqueous batteries: progress and perspectives, *Chem. Commun.*, 61 (76) (2025) 14611-14624.
- [5] S. Wu, W.J. Liu, Q. Wang, Q. Ye, H.B. Yang, S. Zhao, L.K. Liu, B. Jiang, A comparative study of the discharge performance of Mg-0.6Gd-1.3Y alloy at two states as anodes for Mg-air batteries, *J. Energy Storage*, 126 (2025) 117097.
- [6] S.B. Šoštarić, N. Tomašić, V. Bohanek, N. Gizdavec, S. Miko, Croatian Critical Mineral Commodity Letters: Magnesium, *Geologia Croatica*, 78 (1) (2025) 87-101.
- [7] J.C. Long, Z. He, G. Zhang, Y. Ding, J.Y. Zhang, P. Liu, H.T. Xu, R. Wang, S.S. Tan, Q. y.An, L.Q. Mai, Solvation chemistry of nonaqueous electrolytes for rechargeable magnesium batteries, *Adv. Mater.*, 37 (40) (2025) e10488.
- [8] Q. X. Yan, L.F. Hou, J.L. Sun, D.H. Li, J.L. Song, X.D. Liu, Q. Wang, Y.H. Wei, Regulating the localized corrosion of grain boundary and galvanic corrosion by adding the electronegative element in magnesium alloy, *Corros. Sci.*, 244 (2025) 112667.
- [9] D. Mei, Y.S. Tian, S. Y.Mao, T.C. Kong, Z.P. Liu, J.X. Liu, H.T. Xie, Y. Xiao, L.G. Wang, S.J. Zhu, S.K. Guan, The inhibitory effect of caffeic acid on localized corrosion of LAZ931 Mg alloy, *Corros. Sci.*, 252 (2025) 112949.
- [10] X. Cheng, B.B. Sun, T.T. Wei, J.M. Dong, X. Cao, J.X. Zhang, Y.H. Zhang, T. Wang, Y.H. Liu, F. Zhong, M. Liang, J.F. Li, The effect of lithium content on the discharge and electrochemical performance of Mg-Li-Zn-Y alloys for primary Mg-air batteries, *J. Mater. Chem. A*, 13 (12) (2025) 8642-8653.
- [11] W.Y. Hu, T.H. Le, S.H. Chen, Y.J. Zhang, Influence of La alloying on the electrochemical corrosion and discharge performance of Mg-0.5Sn-1Ca-0.3Mn alloy as Mg-air battery anodes, *J. Mater. Today Commun.*, 46 (2025) 112586.
- [12] Q.Y. Xie, P.Y. Ma, Y.X. Gu, Z.X. Wang, J.H. Jiang, A.B. Ma, S. Lu, Effect of trace In on the discharge behavior of Mg-0.1Ge-xIn anode for Mg-air battery, *Journal of Alloys and Compounds*, 1039 (2025) 183141.
- [13] Y.T. He, P. Sun, L. Wu, M.Y. Sun, J.A. Sun, Z.C. Wang, Y. Yuan, G.Z. Wu, Y.L. Ma, J.X. Wang, J.F. Wang, F.S. Pan, Effect of trace amount of Sn on the corrosion and discharge performance of Mg-Sn as an anode for Mg-air battery, *J. Corrosion Science*, 256 (2025) 113223.

- [14] M. J. Deviprasad, B. Rikhari, A Review on influence of alloying elements: microstructures, mechanical properties, and biocompatibility of Mg-based alloys for biomedical application, *Journal of Bio-and Tribo-Corrosion*. 11(4) (2025) 130.
- [15] X. Z. Chen, S. H. Wei, F. L. Tong, M. P. Taylor, P. Cao, Electrochemical performance of Mg-Sn alloy anodes for magnesium rechargeable battery, *J. Electrochimica Acta*, 398 (2021) 139336.
- [16] M. J. Song, H. Gao, Z. H. Zhong, Recent Progress in Bi-Based Anodes for Magnesium Ion Batteries, *J. Molecules*, 27(22) (2022) 7751.
- [17] C. Wang, G. Z. Lv, T. G. Zhang. Review: progress in magnesium alloy research for magnesium-air batteries[J]. *J. Mater. Sci.*, 61 (2026) 1467-1497.
- [18] Y.H. Chen, W.L. Cheng, X.J. Gu, H. Yu, H.X. Wang, X.F. Niu, L.F. Wang, H. Li, Discharge performance of extruded Mg-Bi binary alloys as anodes for primary Mg-air batteries, *J. Alloys Compd.* 886 (2021) 161271.
- [19] H. Azzeddine, A. Hanna, A. Dakhouche, L. Rabahi, N. Scharnagl, M. Dopita, F. Brisset, A.-L. Helbert, T. Baudin, Impact of rare-earth elements on the corrosion performance of binary magnesium alloys, *J. Alloys Compd.* 829 (2020) 154569.
- [20] J.F. Han, W. T. Guo, X. J. Liu, Q.W. Bai, Z.Y. Chen, Effect of rare earth Ce and Y on solidification microstructure and fluidity of AZ91D magnesium alloy, *J. Alloys Compd.* 1047 (2025) 184885.
- [21] Q.H. Wei, L. Yuan, X. Ma, M.Y. Zheng, D.B. Shan, B. Guo, Strengthening of low-cost rare earth magnesium alloy Mg-7Gd-2Y-1Zn-0.5Zr through multi-directional forging, *Mater. Sci. Eng: A*, 831 (2022) 142144.
- [22] Y.C. Zhu, N.L. Wang, Z.B. Chu, Y. Niu, L. Ma, L. Qin, Study of the corrosion mechanism of Mg-Gd based soluble magnesium alloys with different initial texture states, *Corros. Rev.* 41(6) (2023) 659–672.
- [23] Q.H. Wang, Z. Q. Huang, Y. C. Zhu, L. Qin, J. F. Zou, L. F. Ma, Study of Corrosion Behavior of Mg-Gd-Based Soluble Magnesium Alloys, *Metals* 15(1) (2025) 35.
- [24] Z. Xu, W.J. Liu, S. Wu, H.B. Yang, Q. Ye, Z.K. Zhu, J.F. Song, B. Jiang, Improving the discharge performance of as-extruded Mg-Gd alloy anode for Mg-air battery by tailoring the Gd content, 1048(2025)185193.
- [25] Y.Z. Xu, J.Y. Li, M.F. Qi, J.B. Gu, The influence of Gd content on the microstructure, mechanical properties, corrosion behavior and corrosion film deposition mechanisms of as-extruded Mg-Zn-Mn-Sr-Gd alloys for biomedical applications, *J. Mater. Sci.* 57(3) (2022) 2053–2072.
- [26] H. Yao, S.B. Wang, Y. Xiong, X.Y. Shi, H. Singh, M. Huttula, W. Cao, Enhanced mechanical

properties and corrosion resistance by minor Gd alloying with a hot-extruded Mg alloy, *J. Mater. Eng. Perform.* 31 (2022) 9997–10009.

[27] Y. Zhang, H.J. Wang, X. Dai, Y. Liu, W. Liu, Y.Q. Tian, L.S. Chen, Microstructure characteristics and corrosion mechanism of Mg-Gd-Ag-Y-Zn with the hot-rolling multiple-passes deformation, *Mater. Chem. Phys.* 359(2026)132507.

[28] M. J. Deviprasad, B. Rikhari, Microstructural and corrosion rate evolution of Mg-Nd-Zr alloy during multiaxial forging processing, *J. Alloys Metall. Syst.* 13 (2026) 100240.

[29] Y.Z. Zuo, H.F. Xiang, Y. Xiang, T. H. Gao, Q. S. Lu, Y. H. Guo, F. J. Shi, W. G. Yang, J. H. Peng, Y. Cheng, Corrosion behaviors of GYZ65K magnesium alloy after shear extrusion: Microstructure evolution and localized corrosion mechanisms, *J. Alloys Compd.* 1059 (2026) 187206.

[30] Z.H. Xu, W.J. Liu, S. Wu, H.B. Yang, Q. Ye, Z.K. Zhu, J.F. Song, B. Jiang, Improving the discharge performance of as-extruded Mg-Gd alloy anode for Mg-air battery by tailoring the Gd content, *J. Alloys Compd.* 1048,(2025),185193.

[31] W.Y. Huang, Z. Jiang, P.F. Wu, W. Qiu, W. Chen, J. Chen, Tailoring the electrochemical behavior and discharge performance of Mg–Al–Ca–Mn anodes for Mg-air batteries by different extrusion ratios, *J. Mater. Res. Technol.* 28 (2024) 3494–3506.

[32] Z. H. Yan, X. Ping, J. B. Zhang, F. Y. Jing, W. Zhang, Gd micro-alloying enhances microstructure and electrochemical performance of extruded Mg-1.5Sn-1.5Bi alloy for Mg-air battery anodes, *Mater. Chem. Phys.* 346 (2025) 131359.

[33] M. Yuasa, X.S. Huang, K. Suzuki, M. Mabuchi, Y. Chino, Discharge properties of Mg–Al–Mn–Ca and Mg–Al–Mn alloys as anode materials for primary magnesium–air batteries, *J. Power Sources* 297(30) (2015) 449–456.

[34] M.C. Lin, C.Y. Tsai, J.Y. Uan, Electrochemical behaviour and corrosion performance of Mg–Li–Al–Zn anodes with high Al composition, *Corros. Sci.* 51(10) (2009) 2463–2472.

[35] W. L. Cheng, S.S. Park, B.S. You, B.H. Koo, Microstructure and mechanical properties of binary Mg-Sn alloys subjected to indirect extrusion, *Materials Science and Engineering: A*, 527(18-19)(2010) 4650-4653.

[36] H. Lv, L. Li, Z.Z. Wen, C.R. Liu, W. Zhou, X. Bai, H.L. Zhong, Effects of extrusion ratio and temperature on the microstructure and mechanical properties of Mg–Zn–Yb–Zr extrusion alloys, *Materials Science and Engineering: A*, 833(2022) 142521.

[37] F.R. Cao, N.P. Guo, P.N. Xu, G.M. Xu, Room temperature strengthening and quasi-superplasticity behavior in superlight Mg-3.11 Li-2.31 Al-1.95 Sn-0.94 Y-0.45Er alloy processed by

multidirectional forging and asymmetric rolling, Transactions of Nonferrous Metals Society of China, 35(3)(2025) 800-818.

[38] W.Z. Wang, X. Chen, Y.Q. Hong, G.S. Huang, X.H. Chen, J.B. Li, K.H. Zheng, B. Jiang, F.S. Pan, Modified Schmid factor analysis and calculation of magnesium crystals under three-dimensional stress states, Journal of Materials Research and Technology, 36(2025) 5115-5127.

[39] J.C. Sha, Q. Wang, X. Li, Z.L. Liu, Y.Q. Yang, J.X. Bao, L.H. Li, J. Tian, W.L. Chen, W.H. Liu, Z.Q. Zhang, Trifluoroacetamide additive-driven solvation structure regulation and interfacial adsorption for wide-temperature hydrogen-evolution-suppressed aqueous magnesium-air batteries, Journal of Colloid and Interface Science, 699(1)(2025) 138170.

[40] P. Bhuyan, S. Sanyal, G.V. Fortunato, S. Mandal, A.M. Mingers, M. Ledendecker, Grain boundary engineering for improved performance: A case study with Ni-superalloy on the hydrogen evolution reaction, Materials & Design, 260,(2025) 115262.

[41] Y.H. Zhang, Y.B. Wang, Z.B. Chen, C.Z. Hu, J.H. Qu, Recovering nutrients and unblocking the cake layer of an electrochemical anaerobic membrane bioreactor, Nature communications, 15,(2024) 9111.