Contents lists available at ScienceDirect

Acta Materialia



journal homepage: www.elsevier.com/locate/actamat

Binary ZnY porous materials through integrated high-throughput approach

Xiangrui Feng ^{a,b,1}, Meng Liu ^{a,b,1}, Jun Li ^a, Ao Zhang ^a, Ji Zhang ^a, Yvwei Liang ^a, Yongzheng Zhang ^{b,*}, Zhen Lu ^{a,c,**}, Weihua Wang ^{a,d}

^a Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

^b School of Physics and Physical Engineering, Qufu Normal University, Qufu 273165, China

^c School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

^d Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China

ARTICLE INFO

Keywords: Supergravity-induced solidification High-throughput Vapor phase dealloying Intermetallic nanoporous materials Dealloying kinetics

ABSTRACT

Porous materials, characterized by their important applications in catalysis, energy storage, and conversion, are predominantly derived from binary alloy systems due to the compositional complexity and the limited availability of phase diagrams for multi-component alloys. In this work, supergravity-induced solidification, a highthroughput approach, is employed to construct ternary MgZnY combinatorial libraries in a near-equilibrium state. This method utilizes the differences in densities and melting points among metal phases, where denser phases with higher melting points solidify and migrate towards the bottom, while lighter phases precipitate successively as the temperature decreases, resulting in samples with compositional and structural gradients along the centrifugal direction. Subsequently, a high-throughput vapor phase dealloying technique is developed based on the above bulk gradient samples, selectively volatilizing elements with high saturated vapor pressures and leaving behind residual elements that evolve into porous structures. Through the integrated high-throughput approach, we have successfully identified multiple precursor alloys capable of constructing intermetallic nanoporous Zn₂Y₁ (atomic percentage, at.%) with diverse morphologies. Furthermore, we have meticulously fabricated several alloys using the aforementioned high-throughput techniques. These alloys demonstrate consistent nanoporous compositions, underscoring the efficacy of our high-throughput approaches. This integrated highthroughput method significantly simplifies the exploration and development of porous materials, offering an innovative route to exploit the capabilities of multi-component alloy systems in a broad range of applications.

1. Introduction

Porous materials exhibit widespread applications across various fields such as aerospace material engineering, catalysts, fuel cells, medical science, optical communications, and environmental purification [1-6] on account of their low relative density, high specific strength, high specific surface area, sound insulation, heat insulation, and good permeability [7-10]. Dealloying offers a straightforward and versatile approach for constructing nanoporous structure, utilizing techniques like chemical dealloying (CD), electrochemical dealloying (ECD), liquid metal dealloying (LMD), and vapor phase dealloying (VPD), etc. [11-13]. CD or ECD is characterized by the selective dissolution of more active components while preserving the relatively stable ones in the presence of an appropriate electrolyte. This technique is particularly

effective for fabricating noble and easily-passivated porous materials, including metals like Cu, Ni, Pt, Au and Pd [14-17]. LMD is a recently developed method to fabricate nanoporous metals through the miscibility difference between alloy components and metallic melts. Due to its relatively high dealloying temperatures, refractory metals (Ta, Mo, Nb, etc.) and even high entropy alloys can be constructed into nanoporous structures [18-21]. However, chemical etching is inevitable for the above two approaches, which will induce severe environmental issues. Recently, VPD has emerged as a versatile and environmentally-friendly method to build open nanopore structures by selectively evaporating elements with high saturated vapor pressures (SVPs), capitalizing on the variance in SVP among constituent elements [13,22,23].

Despite significant advancements, the fabrication of porous metallic materials is primarily focused on binary systems [23-25], with limited

¹ These authors contributed equally: Xiangrui Feng, Meng Liu

https://doi.org/10.1016/j.actamat.2024.120048

Received 12 March 2024; Received in revised form 23 May 2024; Accepted 24 May 2024 Available online 28 May 2024



^{*} Corresponding author.

^{**} Corresponding author at: Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

E-mail addresses: yzzhang@qfnu.edu.cn (Y. Zhang), zhenlu@iphy.ac.cn (Z. Lu).

^{1359-6454/© 2024} Acta Materialia Inc. Published by Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.



Fig. 1. (a) Simplified schematic of the high-speed centrifugal melting machine. (b) Schematic diagram of the centrifugal rotation and heating procedures for supergravity-induced solidification process. (c)-(e) Photographs of the cross-sections of $Mg_{45}Zn_{45}Y_{10}$, $Mg_{63}Zn_{27}Y_{10}$ and $Mg_{70}Zn_{25}Y_5$ after supergravity-induced solidification, respectively.

exploration into multicomponent systems. Multicomponent porous materials have the potential to harness synergistic effects among elements to promote mechanical and electrochemical performances [26-28], yet the complexity of exploring such materials and the limited availability of multicomponent phase diagrams pose significant challenges to achieving nanoporous structures. As a result, there is an urgent requirement for the development of high-throughput methods tailored for the fabrication of nanoporous materials in multicomponent systems. Magnetron co-sputtering represents a conventionally high-throughput approach to fabricate alloy libraries with a wide range of compositional variations [29]. Nonetheless, this technique significantly deviates from equilibrium states, characterized by an equivalent cooling rate of approximately 10⁹ K/s [30]. Such rapid cooling rate leads to the formation of materials that substantially deviate from their bulk counterparts, as the obtained structures may not adequately represent or perform similarly to their bulk counterparts.

In this work, we proposed an innovative supergravity-induced solidification approach, in which an alloy is heated above its liquidus temperature in advance and subsequently cooled below the crystallization temperature at a cooling rate of 2 K/min while under continuous centrifugation. This process facilitates the formation and growth of crystalline phases from the liquid phase during cooling, which are then segregated due to the centrifugal effect, resulting in bulk combinatorial libraries with compositional and structural gradients. A high-throughput VPD concept is subsequently applied to process the generated alloy libraries, selectively volatilizing elements with high SVPs and leaving behind residual elements that evolve into porous structures. Through these systematic high-throughput avenues, an intermetallic Zn₂Y₁ (atomic percentage, at.%) with diverse morphologies was successfully discovered, which was further verified by specific synthesizing alloys. This composite high-throughput methodology provides an efficient and straightforward path of screening potential compositions for the development of porous materials.

2. Methods

Ternary precursor alloys with nominal compositions of $Mg_{45}Zn_{45}Y_{10}$, Mg₆₃Zn₂₇Y₁₀, and Mg₇₀Zn₂₅Y₅ (at.%) were synthesized using a vacuum induction melting furnace from pure Mg (99.99 %), pure Zn (99.99 %) and pure Y (99.99 %) blocks under an argon atmosphere. Before induction melting, the oxidized layers of the pure metals were carefully removed, followed by ultrasonic cleaning in alcohol to eliminate surface impurities. To achieve homogeneous alloy melts, an additional heating duration of 10 min was employed during the melting process. Subsequently, these melts were cast into graphite crucibles with a diameter of 13 mm. The resulting alloy rods were cut with a length of 3.5 cm, and the surface was carefully polished to further remove oxide layers. Due to the reactivity of Mg with quartz glass tubes, the polished rods were initially placed into boron nitride (BN) tubes, and subsequently sealed within quartz glass tubes under a vacuum better than 4×10^{-4} Pa. The sealed ternary alloys were subjected to a high-speed centrifugal melting machine for supergravity-induced solidification. The melting points of three alloys were determined by simultaneous thermal analyzer (STA, PerkinElmer STA 8000) at a constant heating rate of 20 K/min with 20 mL/min flowing pure argon.

Three supergravity-induced solidified samples were cut along the radial direction and carefully polished for metallographic and compositional analyses. High-throughput VPD was performed after systematical characterizations. The Mg₄₅Zn₄₅Y₁₀ supergravity-induced solidified sample was placed in a high-vacuum tube furnace. It was heated to 693.15 K at a heating rate of 10 K/min and maintained at this temperature for 12 h under a vacuum of better than 2×10^{-4} Pa. After the heat treatment, the sample was cooled naturally while still under a high vacuum environment. The dealloyed high-throughput sample was then carefully polished to expose a fresh cross-section for further characterization of its morphologies, composition and dealloying depth. Mg₃₄Zn₅₇Y₉ and Mg₁₆Zn₆₆Y₁₈, obtained from high-throughput VDP screening, were particularly synthesized using a vacuum induction



Fig. 2. EDS mappings of the cross-section of the supergravity-induced solidified sample of $Mg_{45}Zn_{45}Y_{10}$.

melting furnace, the synthesis procedures were the same as those described above. These samples were also subjected to heat treatment in a high-vacuum tube furnace at 693.15 K with a heating rate of 10 K/min under a vacuum of better than 2×10^{-4} Pa for various durations to study the dealloying kinetics and the evolution of porous structures.

The crystal structures of these supergravity-induced solidified and dealloyed samples were characterized using X-ray diffraction (XRD) with Cu-K α radiation (DX-2700-BH). Field emission scanning electron microscopy (SEM, HITACHI SU5000, 15 keV) equipped with X-Ray energy dispersive spectroscopy (EDS, BRUKER XFlash6160) was employed to reveal the microstructure and chemical compositions of samples. The pore sizes, dealloying depths and compositions of the dealloyed samples were characterized and measured by SEM and EDS. Additionally, the proportions and spatial distributions of eutectic phases within the cross-section areas of the samples were meticulously analyzed using a metallographic microscope at a magnification of 50X.

3. Results

3.1. Fabrication of high-throughput libraries with compositional gradient

Fig. 1a illustrates a schematic of the self-designed high-speed centrifugal melting machine [31]. Samples sealed in quartz tubes were placed into the sample furnace and the other furnace with the same weight was symmetrically mounted on the opposite side. The supergravity field is created by a centrifugal force $G = r\omega^2$, where r is the distance between the rotation-system center and the sample, and ω is the rotating angular velocity. The centrifugal rotation and heating procedures are illustrated in Fig. 1b. Three ternary alloys were heated to a temperature 50 K above their melting points at a heating rate of 10 K/min and maintained for 20 min, effectively attaining superheated and relative equilibrium states (Supplementary Fig. S1). Subsequently, the furnaces were rotated with a rotating speed of 1745 r/min to generate a supergravity of 1000 g (g is the standard gravitational acceleration). Following a 20 min holding period, the furnaces were methodically cooled at a controlled rate of 2 K/min. The supergravity-induced solidification experiments were terminated once the temperature fell below the solidification temperature of 100 K (Supplementary Fig. S2). The solidified samples were then cut along the radial direction and carefully polished for metallographic and compositional analyses. Figs. 1c-e exhibit the cross-sectional photographs of Mg₄₅Zn₄₅Y₁₀, $Mg_{63}Zn_{27}Y_{10}$ and $Mg_{70}Zn_{25}Y_5,$ respectively. Distinctly, all three samples present a noticeable structural gradient along the direction of



Fig. 3. (a) (b) and (c) The distribution of the area ratio of eutectic phases for supergravity-induced solidified $Mg_{45}Zn_{45}Y_{10}$, $Mg_{63}Zn_{27}Y_{10}$ and $Mg_{70}Zn_{25}Y_5$, respectively.

centrifugal force. The bevels observed on the left side of the samples are likely induced by the gravitational forces.

Fig. 2 showcases the EDS mappings of the cross-section area of the supergravity-induced solidified Mg45Zn45Y10 sample, revealing the spatial distributions of its constituent elements. The varying proportions of these elements across different regions are evident, indicating the heterogeneous nature of samples via supergravity-induced solidification approach. Additionally, these EDS mappings correlate well with the polished cross-section photograph of the $Mg_{45}Zn_{45}Y_{10}$ sample (Fig. 1c). Detailed chemical line analyses were conducted to quantitatively determine the elemental distribution, with the resulting profiles overlaid on the EDS mappings, as depicted in Fig. 2. In addition, EDS mappings and line distribution analyses for the Mg₆₃Zn₂₇Y₁₀ and Mg₇₀Zn₂₅Y₅ samples are also provided in Supplementary Figs. S3 and S4, respectively. These results elucidate the gradient elemental variations within these samples, also demonstrating a close match with their corresponding polished cross-sectional photographs. Mg, characterized by its low density and melting point, demonstrates a concentration decrease in the direction of supergravity, implying that metal phases with higher density and melting points solidify first and move towards the bottom preferentially. Subsequently, phases with lower density and melting points precipitate successively with the decreasing temperature. The supergravity-induced solidification procedure thus generates gradient alloy libraries, wherein compositional variations are systematically arranged across the sample [32], offering a valuable tool for high-throughput screening of alloys and facilitating the targeted exploration of bulk materials with specific properties.

The gradient metallographic structures of the solidified samples confirm that the supergravity field facilitates the stratified crystallization. However, on account of the complexity of crystallization procedures and the considerable size of samples, it is challenging to ascertain the distribution of crystal phases rapidly and visually. Eutectic phases with representative lamellar structure are easily characterized by a metallographic microscope, which provides a straightforward approach to assess the influence of the supergravity field on the crystallization process [33,34]. The metallographic phases of the cross-sections for all three samples were imaged using an optical microscope at 50X magnification under consistent optical conditions. The area ratios of the eutectic phases were extracted from the captured images, which were then quantitatively analyzed using the ImageJ software [35]. Fig. 3 displays the eutectic phase distribution across the three alloys, depicted as color matrix maps. Notably, the distribution of the area ratio of eutectic phases exhibits analogical morphology with photographs and EDS mappings (Figs. 1c-e, Fig. 2, Supplementary Figs. S3-S4). These eutectic phases exhibit the uniform composition of Mg78Zn20Y2 for all



Fig. 4. (a) (b) (c) and (d) The low magnification SEM images of the Region I, Region II, Region III, and Region IV of the supergravity-induced solidified sample, respectively. (e) (f) (g) and (h) The high magnification SEM images of the Region I, Region II, Region III, and Region IV of the supergravity-induced solidified sample, respectively.

three samples, revealed by EDS measurements. The presence of eutectic phases increases with the magnesium content in the precursor alloy and tends to aggregate towards the bottom of the samples as shown in Fig. 3. This observation suggests that the supergravity-induced solidification approach generates high-throughput libraries with hierarchical structures, where the eutectic phase serves as an effective identifier for fast screening the structural distributions. In contrast, $Mg_{45}Zn_{45}Y_{10}$ solidified at normal gravity with the same heating procedures exhibits relatively uniform morphologies and componential distributions (Supplementary Fig. S5). Although $Mg_{63}Zn_{27}Y_{10}$ and $Mg_{70}Zn_{25}Y_5$ samples exhibit apparent heterogeneous structures, carefully compositional and structural analyses reveal that supergravity-induced solidified samples exhibit broader compositional gradients and benefit the construction of alloy libraries (Supplementary Figs. S6-S7).

In the comprehensive analysis of cross-section polished images (Figs. 1c-e), EDS mappings (Fig. 2) and the distribution of eutectic ratio (Fig. 3), the supergravity-induced solidified samples can be divided into four distinct regions (Fig. 3a). Particularly, we have systematically investigated the supergravity effect on the solidification behaviors of Mg₄₅Zn₄₅Y₁₀ focusing on detailed structures and compositions analyses on account of the relative pronounced gradient structure. Region I at the bottom of the metal alloy predominantly consists of Zn-rich phases with an average composition of $Mg_{16}Zn_{65}Y_{19}\!,$ attributed to the relatively higher atomic mass of Zn and Y compared to Mg. Under the action of centrifugal force, Zn and Y tend to accumulate towards the bottom. In detail, Region I contains three representative phases, $Mg_{16}Zn_{66}Y_{18}$, Mg₂Zn₇₆Y₂₂ and Mg₉Zn₅₃Y₃₈, as shown in Figs. 4a and e. As an intermediary zone, Region II features a mix of eutectic and Zn-rich phases with an average composition of Mg₅₅Zn₃₇Y₈ (Figs. 4b and f). The Zn-rich phase in Region II is identified as Mg₁₆Zn₆₆Y₁₈, which is also distributed in Region I. This phase, characterized by a relatively high concentration of Mg, possesses a lower melting temperature and density, allowing it to coexist in Regions I and II. The irregular eutectic phase Mg78Zn20Y2 in Region II is composed of two compositions, Mg₃₄Zn₅₇Y₉ and Mg₉₇Zn₃. The average composition of Region III is identified as Mg₈₀Zn₁₉Y₁, predominantly consisting of the eutectic phase with the composition of Mg₇₈Zn₂₀Y₂ (Figs. 4c and g). Furthermore, the eutectic structures are interspersed with the Mg97Zn3 phase, which appears as dark gray regions in Fig. 4c. Although the composition of the eutectic phases in both Regions II and III are identical, Region III exhibits a finer and more regular eutectic structure (Figs. 4f and g). This difference may result from the dynamics of the centrifugation process that a portion of the

eutectic phase solidifies first and is propelled to Region II by centrifugal force. Following this, the surrounding un-solidified alloy melt undergoes a post-solidification process and releases significant latent heat of crystallization, which might result in the coarsening and irregularity of this eutectic in Region II [36]. Finally, Region IV is characterized by two Mg-rich phases of Mg₇₀Zn₃₀ and Mg₉₇Zn₃ (Figs. 4d and h). These phases, having a higher concentration of Mg, exhibit lower density and melting point, consequently leading to their solidification at the top of the sample.

Upon analyzing the other two supergravity-induced solidified alloys of Mg₆₃Zn₂₇Y₁₀ and Mg₇₀Zn₂₅Y₅, the eutectic phases of both alloys exhibit the same composition of Mg78Zn20Y2 that are composed of two phases of Mg34Zn57Y9 and Mg97Zn3 (Supplementary Fig. S8). This suggests that the eutectic phase may be unique in the MgZnY ternary system, thus further demonstrating the relevance of the three eutectic distribution maps (Fig. 3). The polished cross-section photographs in Figs. 1c-e and the whole EDS mappings in Fig. 2 reveal the existence of a buffer zone between Regions II and III, the maximum width of the buffer zone is approximately 3 mm. This region exhibits complex compositions, characterized by the presence of 4-5 phases as shown in Supplementary Fig. S9a and b. The interface region between Regions I and II forms relatively loose and fragile structures (Supplementary Fig. S9c), while the interface region between Regions III and IV consists of eutectic and Mg-rich phases (Supplementary Fig. S9d). The presence of these phases could be attributed to the influence of stresses during the supergravityinduced solidification process, leading to an intermingling of different metal phases within this area. However, further investigation is required to fully elucidate the nature and implications of these phenomena.

3.2. High-throughput VPD approach

Due to the varying activities and SVPs of Mg, Zn and Y, highthroughput dealloying strategy is prospectively realized using highthroughput libraries to quickly explore the effects of compositions on the formation, evolution, and morphologies of porous structures [37]. Considering the different chemical properties and SVP values of Mg, Zn and Y, CD/ECD and VPD emerge as two viable approaches to construct porous structures. Supplementary Fig. S10 displays SEM images of the supergravity-induced solidified $Mg_{45}Zn_{45}Y_{10}$ samples treated with various solutions including acid, alkali, and salt. In all cases, significant surface corrosion is observed in all four conditions, which does not lead to the formation of any porous structure in the $Mg_{45}Zn_{45}Y_{10}$ system. The



Fig. 5. The spatial distribution of porous structures in the eutectic distribution map of $Mg_{45}Zn_{45}Y_{10}$ (a) The cross-sectional SEM image at Region I of the dealloyed supergravity-induced solidification sample. (b) and (c) The cross-sectional SEM images at the Region II of the dealloyed supergravity-induced solidification sample. (d) The typical SEM image of the dealloyed supergravity-induced solidification sample at the buffer region and the interface region between Regions I and II. (e) The cross-sectional SEM image at Region III of the dealloyed supergravity-induced solidification sample. (f) The typical SEM image of the dealloyed supergravity-induced solidification sample. (f) The typical SEM image of the dealloyed supergravity-induced solidification sample. (f) The typical SEM image of the dealloyed supergravity-induced solidification sample. (f) The typical SEM image of the dealloyed supergravity-induced solidification sample. (f) The typical SEM image of the dealloyed supergravity-induced solidification sample at Region IV and the interface region between Regions III and IV.

absence of porosity can be attributed to the multi phases of the $Mg_{45}Zn_{45}Y_{10}$ sample, possessing different electric potentials that predominantly induce a corrosion procedure rather than the development of porous structures. In contrast, VPD solely relies on the differences in SVPs among constituent elements without involving elemental activity, which represents a naturally high-throughput approach for constructing porous structures via combination samples.

In order to clearly demonstrate the influence of precursor structure on the morphology of dealloying products, we have combined the porous morphology images from different representative regions with the Mg₄₅Zn₄₅Y₁₀ supergravity-induced solidification eutectic distribution maps (Fig. 3a) as shown in Fig. 5. Fig. 5a illustrates the porous structure observed in Region I of the supergravity-induced solidified sample, which was dealloyed at 693.15 K and 2×10^{-4} Pa for 12 h. The cross-section images distinctly reveal the formation of a porous structure with an average pore size of 550 nm and a depth of approximately 12 µm (Fig. 5a and Supplementary Fig. S11). The corresponding EDS mappings (Supplementary Fig. S12) indicate that Mg is barely visible with a concentration lower than 5 at.%, while Zn and Y display a uniform distribution. The porous composition is determined to be Zn₂Y₁ through the selected EDS analysis. Despite the presence of three distinct pristine metal-phases in Region I (Mg₁₆Zn₆₆Y₁₈, Mg₂Zn₇₆Y₂₂ and Mg₉Zn₅₃Y₃₈), only a single porous structure is formed. Considering the high SVP of Zn, it is theorized that Zn would volatilize firstly and be completely evaporated during the VPD process conducted at 693.15 K and 2×10^{-4} Pa for 12 h. However, a substantial concentration of residual Zn (Zn₂Y₁) remains stably entrenched within the resultant porous structure.

Based on the Zn-Y phase diagram and the corresponding XRD results (Supplementary Fig. S13), the observed porous structure aligns with the intermetallic Zn₂Y₁ phase with a high melting temperature of 1081 °C [38]. Since the atomic ratio of Mg is low in Region I, the phase evolution during dealloying can be approximately interpreted through the binary Zn-Y phase diagram. Atomic ratios of Zn and Y in phases Mg₁₆Zn₆₆Y₁₈ and Mg₂Zn₇₆Y₂₂ fall between Zn₃Y₁ and Zn₁₁Y₃, while Mg₉Zn₅₃Y₃₈ aligns between ZnY and Zn₂Y₁ [38]. Let's consider phase evolutions of Mg16Zn66Y18 and Mg2Zn76Y22 firstly, both Zn and Mg evaporate from $Mg_{16}Zn_{66}Y_{18}$ and $Mg_2Zn_{76}Y_{22}$ phases under high temperature and vacuum conditions, resulting in a compositional shift towards a lower Zn content. Subsequently, the formation of the Zn_3Y phase occurs; however, this phase demonstrates instability due to its relative high concentration of Zn and low melting temperature, which will be transformed into a more stable Zn_2Y_1 phase upon further volatilization of Zn. In contrast, the concentration of Zn in the Mg9Zn53Y38 phase is lower than that in Zn₂Y₁, implying that this phase should be developed



Fig. 6. The integrated plot combines the concentration map of residual Mg and the morphological and compositional characteristics of the dealloyed supergravityinduced solidification alloy $Mg_{45}Zn_{45}Y_{10}$ at 693.15 K and 2×10^{-4} Pa for 12 h. Region II contains two representative phases that can form porous structures, the widely distributed $Mg_{16}Zn_{66}Y_{18}$ phase forms unimodal pore with the composition of Zn_2Y_1 and the small amount of $Mg_{34}Zn_{57}Y_9$ evolves into unimodal pore with the composition of $Mg_{8}Zn_{62}Y_{30}$ (marked by diamond symbols). The gray areas are cavities formed during the supergravity-induced solidification process.

into the ZnY phase. However, the absence of ZnY product in both XRD and EDS analyses (Supplementary Figs. S12 and S13) suggests that Zn might diffuse from Zn-rich to Zn-poor phases driven by concentration gradient through a bulk diffusion mechanism and finally yield a single Zn₂Y₁ intermetallic nanoporous structure. Percolation theory posits that the nanoporous Zn₂Y₁ should be destabilize when the residual concentration of Zn in Zn₂Y₁ phase surpasses the percolation threshold [39]. Nonetheless, the intermetallic effect [40], characterized by chemical ordering, reduces the surface diffusivity and significantly upgrades the percolation threshold, thereby stabilizing the nanoporous Zn₂Y₁ structure.

Region II exhibits two types of porous structures after dealloying at 693.15 K and 2×10^{-4} Pa for 12 h, as shown in Figs. 5b and c. Initially, the Mg-rich Mg97Zn3 component within the eutectic phase is completely evaporated, leading to the formation of large channels (Supplementary Fig. S14) that allow for a deeper dealloying process and result in a substantial dealloying depth around 200 µm. The remaining Mg₃₄Zn₅₇Y₉ component in the eutectic phase evolves into a porous structure with an average composition of $Mg_8Zn_{62}Y_{30}$ and a pore size of about 1 μm (Fig. 5b). The residual Mg is gradient vary from 15 at.% at the dealloying front to 0 at.% at the surface, while the atomic ratio of Zn and Y consistently approximates 2. The significant dealloying depth (approximately 250 µm) and substantial ligament size hinder the evaporation and migration of Mg, leading to its incomplete volatilization from the dealloyed structure. Concurrently, the other Mg₁₆Zn₆₆Y₁₈ phase evolves into a porous structure with a pore diameter of about 550 nm (Fig. 5c). Due to the relatively small ligament size, Mg is thoroughly evaporated, resulting in a structure that also exhibits a composition of Zn₂Y₁, as same as the composition of the porous structure at Region I. The buffer region at the intersection of Regions II and III, and the interface region between Regions I and II, are constituted by complex fine crystalline grains with different compositions (Supplementary Fig. S9). After the dealloying

process, only discrete particles of several micrometers with an average composition of $Mg_{24}Zn_{42}Y_{34}$ are formed, which do not evolve into a continuous porous structure (Fig. 5d).

Since Region III predominantly consists of eutectic phases, exhibiting a dealloying mechanism akin to that observed in Region II. The Mg-rich $Mg_{97}Zn_3$ phase, embedding in the eutectic matrix, is thoroughly removed in advance, generating extensive pore channels of several micrometers (Fig. 5e). Then the Mg97Zn3 component within the eutectic phase will remove firstly, followed by the complete evaporation of Mg and portion volatilization of Zn from the Mg34Zn57Y9 component, ultimately resulting in a composition of Zn₂Y₁. Given the refined microstructure of the original eutectic phases in Region III, the resultant porous structure derived from the Mg34Zn57Y9 phase exhibits a finer nanoporous structure with an average pore size of approximately 250 nm. The absence of residual Mg in this region can be attributed to the delicate eutectic structure, which facilitates the complete volatilization of Mg. The formation of the intermetallic Zn₂Y₁ phase could reduce the surface diffusion and significantly suppress the coarsening of the nanoporous structure [40], yielding a hierarchical porous structure by one-step VPD procedure (Fig. 5e).

Region IV of the supergravity-induced solidification samples primarily consists of Mg-rich phases, $Mg_{97}Zn_3$ and $Mg_{70}Zn_{30}$, which are incapable of forming porous structures (Fig. 5f). The absence of porosity can be attributed to the low melting points and high SVPs of Mg and Zn, leading to the complete evaporation of all elements during the VPD process and thereby precluding the formation of porous structures. The resulting morphology is constituted by the not-yet-volatilized phases with an average composition of nearly pure Mg, which will fully evaporate with extended heating time (Fig. 5f).

Because the average pore size is around hundreds of nanometers and the high-throughput sample size is several centimeters, it is difficult to compose a morphological map that directly presents the spatial



Fig. 7. (a) The EDS mappings of $Mg_{34}Zn_{57}Y_9$ precursors with homogeneously elements distribution. (b) The cross-sectional SEM images of $Mg_{34}Zn_{57}Y_9$ dealloyed for 6 h under 693.15 K and 2 × 10⁻⁴ Pa. (c) The relation between dealloying depth and time for $Mg_{34}Zn_{57}Y_9$ at 2 × 10⁻⁴ Pa and 693.15 K. (d) The relation between pore size and dealloying time for $Mg_{34}Zn_{57}Y_9$ at 2 × 10⁻⁴ Pa and 693.15 K.

distribution of the appearances of porous structures like the compositional maps (Fig. 2). A compositional map combined with morphological features of the dealloyed sample is a direct approach to demonstrate the structural and compositional evolution of a supergravity-induced solidification sample during dealloying. Since the atomic ratio of Zn and Y in the dealloyed porous structures consistently approximates 2 (Zn₂Y₁), the residual concentrations of Mg can be used to reveal the spatial compositional distribution of the dealloyed supergravity-induced solidified $Mg_{45}Zn_{45}Y_{10}$ sample. In consequence, we have drawn a model map of the residual concentrations of Mg after dealloying and listed the corresponding compositional and morphological characteristics to well expose the evolution of the supergravity-induced solidified $Mg_{45}Zn_{45}Y_{10}$ sample during dealloying as shown in Fig. 6.

4. Evaluating the efficacy of the high-throughput VPD approach

The effect of the initial phases on the porous compositions and structures has been carefully examined by means of the high-throughput VPD. $Mg_{34}Zn_{57}Y_9$ and $Mg_{16}Zn_{66}Y_{18}$, identified via high-throughput screening, are particularly selected to study the dealloying kinetics. $Mg_{16}Zn_{66}Y_{18}$ is widely existed in Regions I and II of the supergravity-induced solidified sample, and $Mg_{34}Zn_{57}Y_9$ is a component found within the eutectic phase, distributed across the eutectic phases of both Regions II and III. The precursor $Mg_{34}Zn_{57}Y_9$ and $Mg_{16}Zn_{66}Y_{18}$ alloys were precisely prepared by induction melting, and the porous formation and evolution behaviors were thoroughly investigated via VPD.

The structural characteristics of the precisely prepared Mg₁₆Zn₆₆Y₁₈

and Mg34Zn57Y9 precursor alloys have been carefully analyzed using XRD profiles (Supplementary Fig. S16a-b). The diffraction peaks can be roughly matched to the PDF standard cards PDF#36–1274 ($Mg_3Zn_6Y_1$) for $Mg_{34}Zn_{57}Y_9$ and PDF#97-009-9224 ($Mg_{6.6}Zn_{21.8}Y_{7.6}$) for Mg₁₆Zn₆₆Y₁₈. Although the compositions of the Mg₁₆Zn₆₆Y₁₈ and Mg₃₄Zn₅₇Y₉ precursor alloys slightly differ from those of the PDF standard cards, the good match suggests the structural uniformity of the precursor alloys. Supplementary Fig. S16c presents the XRD curves of the precisely prepared Mg₁₆Zn₆₆Y₁₈ and Mg₃₄Zn₅₇Y₉ samples, as well as Region II in the supergravity-induced solidification Mg₄₅Zn₄₅Y₁₀ alloy. The primary diffraction peaks are marked by diamond and star symbols for the Mg₁₆Zn₆₆Y₁₈ and Mg₃₄Zn₅₇Y₉ samples, respectively. The diffraction peaks marked by spade symbols are from pure Mg (PDF#35-0821). Distinctly, the XRD curve of Region II can be well decomposed into the diffraction peaks of Mg₁₆Zn₆₆Y₁₈, Mg₃₄Zn₅₇Y₉ and pure Mg (PDF#35-0821), demonstrating that the precisely prepared alloys share the same phases in the high-throughput sample. Similarly, the XRD profile of Region III can also be well matched by the XRD signals of Mg34Zn57Y9 and pure Mg (PDF#35-0821) as shown in Supplementary Fig. S16d. These results demonstrate that the precisely prepared $Mg_{16}Zn_{66}Y_{18}$ and $Mg_{34}Zn_{57}Y_9$ alloys exhibit the same structure as the high-throughput sample.

Fig. 7a displays the EDS mappings of $Mg_{34}Zn_{57}Y_9$ alloy, where Mg, Zn, and Y are uniformly distributed in the precursor alloys. Fig. 7b is the SEM cross-sectional images of the $Mg_{34}Zn_{57}Y_9$ alloy dealloyed at 693.15 K and 2×10^{-4} Pa for 6 h. The cross-section can be categorized into three distinct regions, the left side retains the pristine region with the same



Fig. 8. (a) The EDS mappings of $Mg_{16}Zn_{66}Y_{18}$ precursors with homogeneously elements distribution. (b) The cross-sectional SEM images of $Mg_{16}Zn_{66}Y_{18}$ dealloyed for 12 h at 693.15 K and 2 × 10⁻⁴ Pa. (c) The relation between dealloying depth and time for $Mg_{16}Zn_{66}Y_{18}$ at 2 × 10⁻⁴ Pa and 693.15 K. (d) The relation between pore size and dealloying time for $Mg_{16}Zn_{66}Y_{18}$ at 2 × 10⁻⁴ Pa and 693.15 K.

composition of precursor alloy. The upper left SEM image of Fig. 7b presents the amplified dealloyed intermediate region, which exhibits a distinct porous structure with an average pore size of 550 nm. EDS analysis indicates a variable residual concentration of Mg, vielding an average composition of Mg8Zn62Y30 as shown in Supplementary Fig. S17. The top right SEM image in Fig. 7b shows a finer porous structure at the edge side of the dealloyed region with a pore size of around 250 nm, the composition is determined strictly to be Zn₂Y₁ (Supplementary Fig. S18). According to the variation in residual Mg concentrations across the porous region, the Mg₃₄Zn₅₇Y₉ sample firstly forms a Mg-residual nanoporous structure due to the incomplete dealloying procedure. A more prolonged dealloying period results in the complete removal of Mg, resulting in the final Zn₂Y₁ porous structure. Notably, the compositional evolution of the particular prepared Mg34Zn57Y9 sample exhibits similar behavior of the Mg34Zn57Y9 component within the eutectic phase of Region II in the supergravityinduced solidified sample.

Dealloying kinetics of the Mg₃₄Zn₅₇Y₉ sample were investigated by measuring the time dependence of dealloying depth at different time (Supplementary Fig. S19) as shown in Fig. 7c. At a constant dealloying temperature and pressure of 693.15 K and 2×10^{-4} Pa, the dealloying depth increases gradually with time and shows a linear relationship in the beginning, suggesting that the dealloying front migration is primarily dominated by an interface diffusion and reaction mechanism. However, after 10 h, the curve deviates from linear relation, which demonstrates a transition in dealloying kinetics from interface-limited kinetics to diffusion-limited kinetics [37]. Moreover, the ligament size of Zn_2Y_1 in the edge region remains essentially constant even after 15 h, indicating the temperature and time stability of the intermetallic nanoporous Zn_2Y_1 structure (Fig. 7d).

Fig. 8a exhibits EDS mappings for the Mg₁₆Zn₆₆Y₁₈ sample, showing a uniform distribution of Mg, Zn and Y within the alloy. Fig. 8b shows the SEM cross-sectional image of the Mg16Zn66Y18 sample after dealloying at 693.15 K and 2 \times 10⁻⁴ Pa for 12 h. The inset presents an enlarged SEM image of the resultant porous structure, featuring pore sizes ranging from 500 nm-600 nm (Fig. 8b). The minimal Mg concentration within the porous region and the Zn to Y atomic ratio of 2:1 indicates that the porous structure of Zn₂Y₁ is directly evolved from the pristine Mg₁₆Zn₆₆Y₁₈ alloy (Supplementary Fig. S20). Supplementary Fig. S21 shows SEM images of Mg₁₆Zn₆₆Y₁₈ alloy dealloyed at the same temperature and pressure conditions for 6 h, 8 h, 10 h, and 15 h, and the relation between dealloying depth and time reveals a linear to power law transition (Fig. 8c) [37]. Moreover, the consistency in pore size and morphology (Fig. 8d) underscores the stability of the intermetallic nanoporous Zn₂Y₁ structure, akin to that observed in the Mg₃₄Zn₅₇Y₉ sample.

Both the $Mg_{34}Zn_{57}Y_9$ and $Mg_{16}Zn_{66}Y_{18}$ alloys possess capable of forming porous structures composed of the intermetallic compound of Zn_2Y_1 under sufficient dealloying time. However, the higher Mg content in the $Mg_{34}Zn_{57}Y_9$ alloy prevents the complete evaporation of Mg in the early stages of dealloying, leading to the formation of a transitional porous region with residual Mg. As dealloying progresses, all Mg is eventually evaporated, resulting in a pure Zn_2Y_1 porous structure. In contrast, the $Mg_{16}Zn_{66}Y_{18}$ alloy, with its reduced Mg content, permits the immediate evaporation of Mg, thus directly leading to the formation of a Zn_2Y_1 porous structure. Additionally, the presence of a small amount of sacrificial components in $Mg_{16}Zn_{66}Y_{18}$ generates a slower dealloying velocity (Figs. 7c and Fig. 8c) and larger ligament size (Figs. 7d and Fig. 8d) compared to the $Mg_{34}Zn_{57}Y_9$ alloy [41].

5. Conclusion

We synthesized a ternary MgZnY bulk combinatorial libraries using a supergravity-induced solidification approach, where alloy phases with different densities and melting points solidify and migrate accordingly as the temperature decreases along the centrifugal direction, resulting in samples with compositional and structural gradient. By virtue of these combinatorial libraries, high-throughput VPD approach is naturally designed, which capitalizes on differences in SVPs rather than the chemical properties among constituent elements. These integrated highthroughput techniques swiftly identified Mg₃₄Zn₅₇Y₉ and Mg₁₆Zn₆₆Y₁₈ alloys capable of forming a nanoporous Zn₂Y₁ structure. The relatively high residual concentration of Zn in the nanoporous structure demonstrates an intermetallic effect, which diminishes surface diffusivity and significantly enhances the percolation threshold for dealloying, leading to a nearly constant pore size as dealloying time increases. By synthesizing specific alloy compositions, an interface-limited to diffusionlimited kinetics transition is revealed. This combined material exploration and microstructure construction high-throughput methodology promises the rapid development of precursor alloys that exhibit capacity for porous material fabrication.

CRediT authorship contribution statement

Xiangrui Feng: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. Meng Liu: Data curation, Formal analysis, Investigation, Methodology. Jun Li: Data curation, Formal analysis. Ao Zhang: Investigation. Ji Zhang: Data curation. Yvwei Liang: Data curation. Yongzheng Zhang: Conceptualization, Funding acquisition, Supervision. Zhen Lu: Conceptualization, Formal analysis, Funding acquisition, Investigation, Project administration, Supervision, Writing – original draft, Writing – review & editing. Weihua Wang: Conceptualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank Jing Jiang and Zhichao Zhao for inspiring discussion. This work was sponsored by the National Key R&D Program of China (grant number 2021YFB3802900), the National Natural Science Foundation of China (grant numbers 52192604, 52371166 and 62104131), the Higher Educational Youth Innovation Science and Technology Program Shandong Province (2021KJ022), Taishan Scholars Program (tsqn201909107), Natural Science Foundation of Shandong Province (ZR2020QF077). This work was supported by the Center for Materials Genome and the Synergetic Extreme Condition User Facility (SECUF).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.actamat.2024.120048.

References

- [1] C. Li, L. Qi, J. Fei, J. Yan, Z. Wu, T. Zhang, H. Li, Construction of polydopamine functionalized porous carbon network structure in polymer composites for excellent mechanical and electromagnetic interference shielding properties, Carbon N Y 217 (2024) 118620.
- [2] S. Fajal, S. Dutta, S.K. Ghosh, Porous organic polymers (POPs) for environmental remediation, Mater. Horizons 10 (2023) 4083–4138.
- [3] K.J. Korman, M.R. Dworzak, G.P.A. Yap, E.D. Bloch, Porous salts as platforms for heterogeneous catalysis, Small 19 (2023) 2207507.
- [4] H. Xu, B. Chen, P. Tan, W. Cai, W. He, D. Farrusseng, M. Ni, Modeling of all porous solid oxide fuel cells, Appl. Energy 219 (2018) 105–113.
- [5] S. Wu, S. Luo, Z. Cen, Q. Li, L. Li, W. Li, Z. Huang, W. He, G. Liang, D. Wu, M. Zhou, Y. Li, All-in-one porous membrane enables full protection in guided bone regeneration, Nat. Commun. 15 (2024) 119.
- [6] Q. Li, G. Liu, J. Yu, J.Yang G.Wang, L. Zhang, A perovskite/porous GaN crystal hybrid structure for ultrahigh sensitivity ultraviolet photodetectors, J. Mater. Chem. C 10 (2022) 8321–8328.
- [7] L. Yu, Y. Wang, Y. Sun, Y. Tang, Y. Xiao, G. Wu, S. Peng, X. Zhou, Nanoporous crystalline materials for the recognition and applications of nucleic acids, Adv. Mater. (2023) 2305171.
- [8] D. Zhao, T. Zhao, Pore engineering for high performance porous materials, ACS Cent. Sci. 9 (2023) 1499–1503.
- [9] J. Wang, Z. Li, R. Li, H. Wang, Y. Wu, X. Liu, Z. Lu, Nanoporous metals based on metallic glasses: synthesis, Structure and Functional Applications, Acta Metall, Sin. (Engl. Lett.) 36 (2023) 1573–1602.
- [10] Z. Su, T. Chen, Porous noble metal electrocatalysts: synthesis, performance and development, Small 17 (2021) 2005354.
- [11] I. McCue, E. Benn, B. Gaskey, J. Erlebacher, Dealloying and dealloyed materials, Annu. Rev. Mater. Sci. 46 (2016) 263–286.
- [12] Y. Shi, W. Yang, Q. Bai, J. Qin, Z. Zhang, Alloying/dealloying mechanisms, microstructural modulation and mechanical properties of nanoporous silver via a liquid metal-assisted alloying/dealloying strategy, J. Alloys Compd. 872 (2021) 159675.
- [13] Z. Lu, C. Li, J. Han, F. Zhang, P. Liu, H. Wang, Z. Wang, C. Cheng, L. Chen, A. Hirata, T. Fujita, J. Erlebacher, M. Chen, Three-dimensional bicontinuous nanoporous materials by vapor phase dealloying, Nat. Commun. 9 (2018) 276.
- [14] T. Fujita, L.-H. Qian, K. Inoke, J. Erlebacher, M.-W. Chen, Three-dimensional morphology of nanoporous gold, Appl. Phys. Lett. 92 (2008) 251902.
- [15] J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Evolution of nanoporosity in dealloying, Nature 410 (2001) 450–453.
- [16] Q. Yang, S. Liang, B. Han, J. Wang, R. Mao, Preparation and properties of enhanced bulk nanoporous coppers, Mater. Lett. 73 (2012) 136–138.
- [17] M. Hakamada, M. Mabuchi, Preparation of nanoporous Ni and Ni–Cu by dealloying of rolled Ni-Mn and Ni–Cu–Mn alloys, J. Alloys Compd. 485 (2009) 583–587.
- [18] L. Lai, P.-A. Geslin, A. Karma, Microstructural pattern formation during liquid metal dealloying: phase-field simulations and theoretical analyses, Phys. Rev. Mater. 6 (2022) 093803.
- [19] I. McCue, B. Gaskey, P.-A. Geslin, A. Karma, J. Erlebacher, Kinetics and morphological evolution of liquid metal dealloying, Acta Mater 115 (2016) 10–23.
- [20] G. Greenidge, J. Erlebacher, Porous graphite fabricated by liquid metal dealloying of silicon carbide, Carbon N Y 165 (2020) 45–54.
- [21] S.-H. Joo, H. Kato, I.V. Okulov, Evolution of 3D interconnected composites of highentropy TiVNbMoTa alloys and Mg during liquid metal dealloying, Compos. B. Eng. 222 (2021) 109044.
- [22] O. Yakovenko, V. Sokolskii, N. Golovataya, T. Kulik, G. Cieslak, O. Roik, Preparation of porous Cu material using vapor phase dealloying, Mater. Lett. 331 (2023) 133486.
- [23] J. Han, C. Li, Z. Lu, H. Wang, Z. Wang, K. Watanabe, M. Chen, Vapor phase dealloying: a versatile approach for fabricating 3D porous materials, Acta Mater 163 (2019) 161–172.
- [24] S. Ibrahim, A. Dworzak, D. Crespo, F.U. Renner, C. Dosche, M. Oezaslan, Nanoporous copper ribbons prepared by chemical dealloying of a melt-spun ZnCu alloy, J. Phys. Chem. C 126 (2021) 212–226.
- [25] Y. Li, X. Han, Z. Lu, L. Ying, X. Wang, Y. Zeng, Y. Gao, Q. Chen, P. Liu, Crystal plane-orientation dependent phase evolution from precursor to porous intermediate phase in the vapor phase dealloying of a Co–Zn alloy, Acta Mater 245 (2023) 118617.
- [26] A. Cai, H. He, Q. Zhang, Y. Xu, X. Li, F. Zhang, X. Fan, W. Peng, Y. Li, Synergistic effect of N-doped sp² carbon and porous structure in graphene gels toward selective oxidation of C-H bond, ACS Appl. Mater. Interfaces 13 (2021) 13087–13096.
- [27] J. Zeng, J. Liu, S.S. Siwal, W. Yang, X. Fu, Q. Zhang, Morphological and electronic modification of 3D porous nickel microsphere arrays by cobalt and sulfur dual synergistic modulation for overall water splitting electrolysis and supercapacitors, Appl. Surf. Sci. 491 (2019) 570–578.
- [28] X. Shi, B. Cao, J. Liu, J. Zhang, Y. Du, Rare-earth-based metal–organic frameworks as multifunctional platforms for catalytic conversion, Small 17 (2021) 2005371.
- [29] M.-X. Li, S.-F. Zhao, Z. Lu, A. Hirata, P. Wen, H.-Y. Bai, M. Chen, J. Schroers, Y. Liu, W.-H. Wang, High-temperature bulk metallic glasses developed by combinatorial methods, Nature 569 (2019) 99–103.
- [30] Y. Li, C. Wang, D. Ma, X. Zeng, M. Liu, X. Jiang, Y.X. Leng, Nano dual-phase CuNiTiNbCr high entropy alloy films produced by high-power pulsed magnetron sputtering, Surf. Coat. Technol. 420 (2021) 127325.
- [31] G. Hu, Y. Li, L. Zhang, Solidification and remelting of aluminum though alumina preform under a centrifugal force field, Scr. Mater. 56 (2007) 1039–1042.

X. Feng et al.

Acta Materialia 275 (2024) 120048

- [32] Q. Liu, Y. Yang, Z. Hu, Theoretical analysis of the particle gradient distribution in centrifugal field during solidification, Metall Mater Trans B 27 (1996) 1025–1029.
- [33] A. MCWILLIAM, La Métallographie Microscopique, Nature 84 (1910) 295.
- [34] P. Hedström, S. Baghsheikhi, P. Liu, J. Odqvist, A phase-field and electron microscopy study of phase separation in Fe–Cr alloys, Mater. Sci. Eng. A 534 (2012) 552–556.
- [35] R. Gerst, Z. Cseresnyés, M.T. Figge, JIPipe: visual batch processing for ImageJ, Nat. Methods 20 (2023) 168–169.
- [36] J. Zhang, Y. Zhang, F. Zhang, D. Cui, Y. Zhao, H. Wu, X. Wang, Q. Zhou, H. Wang, Dendrite growth and grain "coarsening" in an undercooled CoNi equiatomic alloy, J. Alloys Compd. 816 (2020) 152529.
- [37] Z. Lu, F. Zhang, D. Wei, J. Han, Y. Xia, J. Jiang, M. Zhong, A. Hirata, K. Watanabe, A. Karma, J. Erlebacher, M. Chen, Vapor phase dealloying kinetics of MnZn alloys, Acta Mater 212 (2021) 116916.
- [38] M. Aljarrah, J. Alnahas, M. Alhartomi, Thermodynamic modeling and mechanical properties of Mg–Zn–{Y, Ce} alloys: review, Crystals 11 (2021) 1592.
- [39] D.M. Artymowicz, J. Erlebacher, R.C. Newman, Relationship between the parting limit for de-alloying and a particular geometric high-density site percolation threshold, Philos. Mag. 89 (2009) 1663–1693.
- [40] R. Song, J. Han, M. Okugawa, R. Belosludov, T. Wada, J. Jiang, D. Wei, A. Kudo, Y. Tian, M. Chen, H. Kato, Ultrafine nanoporous intermetallic catalysts by hightemperature liquid metal dealloying for electrochemical hydrogen production, Nat. Commun. 13 (2022) 5157.
- [41] P.-A. Geslin, I. McCue, B. Gaskey, J. Erlebacher, A. Karma, Topology-generating interfacial pattern formation during liquid metal dealloying, Nat. Commun. 6 (2015) 8887.