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Ultra-severe plastic deformation: Evolution of microstructure, phase transformation and hardness in immiscible magnesium-based systems

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ABSTRACT

Although severe plastic deformation (SPD) alters the microstructure and phase transformation at the early stages of straining, the microstructural features finally saturate to the steady states at large shear strains. However, from the atomic point of view, to achieve the steady state in immiscible systems with positive heat of mixing, the minimum shear strain should be so high that the thickness of sheared phases becomes comparable to one atomic distance. In this study, ultrahigh shear strains up to ~70,000 are introduced in different Mg-based immiscible systems by high-pressure torsion (HPT) method for up to 1500 turns. New metastable phases are formed in most of the selected magnesium alloys by ultra-SPD, in good agreement with the first-principles calculations. However, the microstructural/structural saturation hardly occurs in many alloys even at ultrahigh strains. The materials processed by ultra-SPD exhibit unique hardness-strain and tensile behaviors which cannot be observed after conventional SPD.

1. Introduction

Severe plastic deformation (SPD) techniques [1,2] are currently used to achieve two main microstructural and structural features: (i) refine grains to enhance the mechanical and functional properties [3], and (ii) control phase transformation and mechanical alloying [4]. Numerous studies showed that despite the microstructure and phase evolutions at the early stages of straining, the microstructural and structural features finally become saturated at large strain, where a steady state is achieved [5]. Although the occurrence of steady states at large strains is expected in single-phase metals [6] because of the contribution of dynamic recovery [7], dynamic recrystallization [8], grain-boundary rotation [9] and/or grain-boundary migration [5], it is not still well understood why and when a steady state is reached in multiple-phase materials with immiscible phases [10,11].

When pure shear strain is introduced in a multiple-phase system with immiscible phases, the phases are elongated in the shear direction and their thicknesses are continuously reduced. Therefore, to achieve the saturation in an immiscible system under pure shear deformation mode, the strain should be increased so that the thicknesses of sheared phases are reduced to the sub-nanometer level or ideally to one atomic distance. For example, the shear strain should be at least 10,000 to achieve the saturation in an immiscible system with initial phase sizes of 10 μm. However, since the fragmentation, rotation and/or sliding of phases occur practically during the SPD process and the co-deformation of phases does not follow an ideal and homogenous pattern, the shear strain should be even higher than the one calculated above.

Among numerous SPD methods developed in recent decades [1–3], the high-pressure torsion (HPT) provides a unique opportunity for the fundamental study of the behavior of different materials under very large shear strain [12,13]. Since the material in HPT processing is constrained between two rotating anvils under high pressure, the shear strain ($\gamma = 2\pi rN/h$, γ: shear strain, r: distance from disc center, N: number of HPT turns, h: thickness of disc [2]) can be significantly

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increased with increasing the numbers of HPT turns without any limitation. Moreover, the extent of strain is controllable and the contamination of sample is minor during HPT, and thus it is basically more appropriate than ball milling for investigation of immiscible systems [14]. Although the HPT method has been widely used in the past to control the phase transformations in different kinds of metallic and non-metallic materials [15], the significance of ultra-high shear strains (N = 1000 turns or higher) on phase transformations, mechanical alloying and properties has not received appreciable attention, except in a recent publication on the immiscible Mg-Zr system [16].

In this study, thus, different immiscible Mg-based systems, which are of interest for hydrogen storage or structural applications, are processed by HPT method for up to 1500 turns, and ultrahigh shear strains (up to 70,000) are introduced in the materials. Mechanical mixing of elements at the atomic scale and formation of new phases are reviewed together with the evolution of microstructure and mechanical properties.

2. Experimental materials and procedures

Several immiscible Mg-based systems were selected for this study, as shown in Table 1: (1) Mg − 25% V − 25% Sn, (2) Mg − 25% V − 25% Pd, (3) Mg − 25% V − 25% Ni, (4) Mg − 50% Zr, (5) Mg − 17% Ni − 17% Sn, (6) Mg − 17% Ni − 17% Pd, and (7) Mg − 25% Li (all compositions are in atom%). These compositions were originally selected for possible applications as hydrogen storage materials (based on some first-principles calculations in Ref. [17]), although their performance for hydrogen storage is still under investigation. It should be noted that since the evolution of microstructure in Mg-Zr system were studied in Refs. [16] and [18], respectively, only their mechanical properties were reported in this study. The mechanical properties of Mg-Li system after processing by HPT for 5 turns were investigated in Ref. [19], but the material was investigated after processing by HPT for much larger number of turns in this study.

For the first three compositions (Mg-V-based systems), MgH_2 powders were mixed with the powders of V (99.5%), Sn (99.99%), Pd (99.9%) and Ni (99.99%) with particle sizes smaller than ~44 μm (325 mesh). MgH_2 was intentionally used as a source of Mg because it is harder than metallic Mg and can be mixed easier with other selected elements. For the fourth composition (Mg-Zr alloy), Mg and Zr powder mixtures with particle sizes smaller than ~44 μm were used. For the fifth and sixth compositions (Mg-Ni-based systems), the elements were melted under controlled atmosphere and casted into the form of ingots (plates with $200\times100\times13$ mm^3 for Mg-Ni-Sn and a rod with 10 mm diameter and 10 mm length for Mg-Ni-Pd). The last composition (Mg-Li) was prepared by casting under controlled atmosphere followed by extrusion at 373 K with an extrusion speed of 1 mm/s and an extrusion ratio of 25:1 (final diameter: 10 mm).

Almost 0.5 g of powder mixtures for Mg-V-based and Mg-Zr systems were processed by HPT under a pressure of 3 GPa for N = 0 (pure compression), 10, 100, 1000 or 1200 turns to produce discs with 14 mm diameter and ~0.8 mm thickness. For the Mg-Ni-based systems, discs with 10 mm diameter and ~0.8 mm thickness were processed by HPT under a pressure of 6 GPa for N = 0 (as-cast condition), 20, 100, 300, 500 and 1500 turns. For the Mg-Li alloy, the HPT was conducted on 10 mm diameter and ~0.8 mm thick discs for N = 0 (as-cast condition), 5, 50, 200 and 1000 turns. The processing speed was ω = 1 rpm, and the processing temperature was room temperature for all selected compositions. The temperature rise was less than 100 K even after processing for 1500 turns because of slow rotation speed and due to the small size of sample (as the heat source) compared to the size of anvils and other large metallic parts of the HPT facility (as the heat sinks). Details concerning the temperature rise during HPT were discussed in Refs. [20,21].

Table 1
Composition of selected systems and their initial form before HPT processing.

Composition (in atom%)	Initial Form
Mg − 25% V − 25% Sn	MgH_2 + V + Sn powder mixture
Mg − 25% V − 25% Pd	MgH_2 + V + Pd powder mixture
Mg − 25% V − 25% Ni	MgH_2 + V + Ni powder mixture
Mg − 50% Zr	Elemental powder mixture
Mg − 17% Ni − 17% Sn	As-cast ingot
Mg − 17% Ni − 17% Pd	As-cast ingot
Mg − 25% Li	Extruded bar

Following the HPT processing, the discs were first polished and the Vickers microhardness was measured in four radial directions from the disc center to periphery. The hardness could not be measured for the Mg-V-based systems because of the presence of many cracks.

Second, the chemical homogeneity was examined at the middle of discs using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS).

Third, the phase transformations were studied by X-ray diffraction (XRD) analyses using the Cu Kα radiation.

Fourth, for examination of microstructure, transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were conducted using the accelerating voltages of 300 kV and 200 kV, respectively. Thin foils were prepared from the middle or edge of the discs using a focused ion beam system. For making the TEM foils from the Mg-Li alloy, a twin-jet electro-chemical polishing system with a solution of 5 vol% $HClO_4$, 25 vol% $C_3H_5(OH)_3$ and 70 vol% C_2H_5OH was used at 263 K.

Fifth, for examination of tensile properties, tensile specimens with gauge dimensions of $1.5\times0.3\times0.7$ mm^3 were cut from the discs at 2–2.5 mm away from the disc center and pulled to failure using an initial strain rate of $\dot{\varepsilon} = 4\times10^{-3}$ s^{-1}. The only material that could be examined by tensile test was Mg-Li because of the absence of cracks.

3. Calculation methods

In this study, the crystal structure of severely deformed Mg − 17% Ni – 17% Sn and Mg − 17% Ni − 17% Pd alloys were examined by first-principles calculations. The B2-type structure was selected as the initial structure for the structure optimization because this structure was experimentally detected for Mg-Ni-Pd. The initial structure was modeled by the special quasirandom structure (SQS) [22] based on the $3\times3\times3$ (54 atoms) supercell of the unit cell of the B2-type structure. In the SQS model, body-center sites in the B2 unit cells were fully occupied by Mg atoms, while the corner sites were occupied by the same numbers of Mg, Ni, and Sn or Pd as randomly as possible under the periodic boundary conditions of the supercells. The SQS used in this study was obtained by simulated annealing [23,24] as implemented in the CLUPAN code [25,26]. To analyze the optimized atomic positions of the alloys, the radial distribution function (RDF) was calculated using the following equation as linear combinations of the Dirac delta functions, which are broadened by a normal Gaussian function with the standard deviation of 0.05 Å.

$$g(r) = \frac{1}{N}\frac{1}{\rho}\frac{1}{4\pi r^2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\delta(r-|\mathbf{r}_j-\mathbf{r}_i|) \quad (1)$$

In this equation, $g(r)$ is the RDF, r is the distance, N is the number of atoms in a simulated cell (54 in this study), ρ is the density of atoms of the optimized structure, i and j are the indices for atoms in the cell, and $\mathbf{r}_i$ and $\mathbf{r}_i$ are the position of the ith and jth atoms, respectively.

For calculations, the plane-wave basis projector augmented wave (PAW) method [27] was employed in the framework of density functional theory (DFT) within the generalized gradient approximation of the Perdew-Burke-Ernzerhof form [28] as implemented in the VASP (Vienna Ab initio simulation package) code [29–31]. A plane-wave energy cutoff of 350 eV was used. The 3s electrons for Mg, the 3d and 4s