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Formation of long-period stacking fault structures in magnesium alloys

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ABSTRACT

We developed a Ginzburg-Landau model of long-period stacking order (LPSO) lamellar structure observed in magnesium alloys. Contrary to other models, we do not treat LPSO as a homogeneous stoichiometric phase but as a chemically modulated heterogeneous structure of parallel plates of two phases with different compositions and degrees of ordering. The Turing instability that is, existence of a finite-wavelength linear-instability mode was identified as the origin of formation of LPSO structure. The process of LPSO formation can be understood as a process of finding local minima and saddle points on the free energy landscape of the system. The model explained transformation between the two most common LPSO structures, 18R and 14H, and their general resistance to coarsening. The model can be used for the design of new LPSO materials.

1. Background

A novel group of Mg-based alloys discovered 15 years ago [1,2] is considered for potential applications in many different industries due to their excellent mechanical and thermal properties. This group of alloys is characterized by the structural order with long periods along the c-axis of the hexagonal close-packed planes of Mg matrix. This feature was called *long-period stacking order* (LPSO). All the alloys of the group have similarities in composition and processing that lead to formation of LPSO [1–8]. These are ternary Mg-TM-RE (TM-Transition Metal: zinc, copper, etc.; RE-Rear Earth: yttrium, gadolinium, etc.) alloys with a small overall concentration of the heavy elements. The distinct features of LPSO in Mg-2 at.% Y-1 at.% Zn—the most prominent member of the group—are the following [1–8]:

1. LPSO structures emerge either directly after the process of rapid solidification or/and after hot extrusion of the alloy. Both processes have large driving force of transformation.
2. The as-cast/extruded microstructures are composed of grains of two types and intermetallic particles along the grain boundaries. The Mg-Y grains have hcp structure and are featureless. The Mg-Y-Zn grains have fine-lamellar features with characteristic 18R structure.
3. LPSO is a strictly periodic lamellar structure of coexisting, alternating plates of hcp α-Mg solid solution and fcc phase with intrinsic stacking faults of the close-packed planes.
4. There is strong synchronization between the periodicity of the lamellae and chemical modulations in the plates with the α-Mg being almost completely void of the heavy elements and the fcc phase having practically fixed concentration of Zn and Y in the inner close-packed planes.
5. LPSO is practically a one-dimensional structure with the main variations in the c-direction of the α-Mg crystalline lattice.
6. LPSO structures, characterized as 18R-type, are made of building blocks that have the same stacking orientations while those of 14H-type are made of the building blocks that are in twin-orientation relationship.
7. 18R-type structure is highly resistant to change during heat treatment or overall variation in alloy composition. However, annealing at 500 °C transforms the 18R-type structure to the 14H-type structure through the intermediate 24R-type structure.

2. Ginzburg-Landau model of LPSO structure formation

2.1. Basic ideas

In this Section we propose a theoretical model of the LPSO structure of Mg-Zn-Y alloys. Main questions to be addressed by the model are: What is the phase content of the LPSO structure? Why is the structure strictly periodic and chemically synchro-

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nized? Why does this highly heterogeneous structure not coarsen quickly?

According to our model LPSO is not aphase but a *two-phase structure*, which consists of alternating plates of the disordered α-Mg solid solution (α-phase) and ordered fcc phase with intrinsic stacking faults and composition $Mg_{1-X\beta}(Y_4Zn_3)_{X\beta}$ (β-phase). Alloying Mg (atomic radius 0.16 nm) with Y (atomic radius 0.18 nm) and Zn (atomic radius 0.14 nm) in proportions close to 4/3 practically removes the local strain since the average size of (Y + Zn) atoms is close to that of Mg [7]. This creates a virtual-solute species and a *quasi-binary alloy* with a very small amount of internal (built-in) stress. The remaining mismatch of atomic radii introduces *shear strain* between the atomic planes, which gives rise to the stacking faults in the crystalline lattice and two different orientations of the β-phase. In this regard, LPSO structure has strong similarities with the martensitic structure [6].

The LPSO structure forms in the precipitate particles in a process with large driving force of transformation. Formation of LPSO structure is not due to the mechanism of spinodal decomposition. It is rather a result of the so-called *Turing instability* when the structures emerge as a synchronous interplay of the two competing processes: in this case—ordering and diffusion [9–12]. Periodicity of the emerging structure in the precipitate particle is dictated by the most unstable mode of the fluctuations of order and composition. Initial period of the emerging structure grows because, overall, structural homogenization decreases the total free energy of the system. The 18R-type structure forms when the driving force for coarsening becomes not enough to overcome the barrier due to discreteness of the crystalline lattice. If the temperature of the system is raised, the free energies of the structures increase and the coarsening may resume, leading to the formation of a coarser structure with larger period (14H-type). This process may be called *LPSO coarsening*.

2.2. Phase-field theory of diffusional transformations

In this Section, we recall the basic principles of the phase-field theory of diffusional transformations, which will be used below for the LPSO modeling [13,14]. The Gibbs free energy of a two-component system is expressed by a Ginzburg-Landau functional [15]:

$$G\{\eta, X\} = \int_V d^3x \left\{ g(\eta, X) + \frac{1}{2}\kappa_\eta(\nabla\eta)^2 + \frac{1}{2}\kappa_X(\nabla X)^2 \right\} \tag{1}$$

where g is the Gibbs free energy density of a homogeneous system (we consider its molar density to be constant), η(**x**, t) and X(**x**, t) are, respectively, continuously distributed *order parameter* (OP) and concentration fields, κ_η and κ_X are the order-parameter and composition gradient-energy coefficients and V is the volume. Dynamics of the system is described by the time-dependent Ginzburg-Landau equation (TDGLE) for the order-parameter field evolution:

$$\frac{d\eta}{dt} = -\gamma\frac{\delta G}{\delta\eta} \tag{2a}$$

and Cahn-Hilliard equation (CHE) for the evolution of the concentration field [14,15]:

$$\frac{dX}{dt} = \nabla M \nabla \frac{\delta G}{\delta X} \tag{2b}$$

where γ is the relaxation coefficient and M is the species mobility. Equilibrium states of the system described by Eqs. (1) and (2) satisfy equations: $\delta G/\delta\eta = \delta G/\delta X = 0$. As known [13,14], the set of homogeneous solutions of these equations contains phases of the system and the potential barriers, represented by the saddle points. In this work we are looking at a system consisting of two phases, e.g., α-phase (η_α, X_α) and β-phase (η_β, X_β) where the latter may have two orientation variants: β_+ and β_-. The heterogeneous solutions of the equilibrium equations can be classified based on their dimensionalities. The set of one-dimensional (1D) solutions contains equilibrium two-phase *interfaces*, critical plates, and periodic solutions, sometimes called *periodons*. (2D and 3D solutions will not be of interest in this publication.) An interface is a transition zone of finite thickness. A critical plate is a localized excitation of order of finite amount. A periodon consist of interacting plates of finite thickness. All 1D equilibrium structures are characterized by the free-energy excess per unit area measured in the direction perpendicular to the direction of variation of the structures (the c-direction in our case) [14]:

$$\sigma_{1D} = \int_{-\infty}^{+\infty} \left\{ \kappa_\eta \left(\frac{d\eta}{dx}\right)^2 + \kappa_X \left(\frac{dX}{dx}\right)^2 \right\} dx \tag{3}$$

For the two-phase equilibrium interface, this amounts to the interfacial energy σ. The free-energy excess makes the periodic structures unstable and gives rise to the coarsening mechanism, which is significantly different from the traditional Lifshitz-Slyozov one. The driving force of the latter is the curvature of the interphase interfaces; it vanishes when the interfaces are flat. The driving force of the former is the free-energy excess itself; it exists even when all interfaces are flat. The difference in the driving forces leads to the difference in structural evolutions of the systems.

The homogeneous equilibrium states of thesystem may be stable, metastable or unstable. Transformation out of a metastable state proceeds via a process of nucleation. An unstable state decomposes, so to speak, by itself that is, due to small fluctuations, which are always present in thesystem. To examine initial stages of the *decomposition* of a homogeneous unstable equilibrium state ($g_{\eta\eta} < 0$), we superimpose on it adisturbance in the form of a *linear mode* $\{\Delta\eta, \Delta X\} = \{H, \Theta\}\exp(\beta t + i\,\mathbf{k}\cdot\mathbf{x})$ where β is an amplification rate and **k** is a 3D wave-vector, substitute it into Eq. (2), linearize them and find that, for the mode to be a solution, the following characteristic equation must be satisfied:

$$\left(\frac{\beta}{\gamma} + \kappa_\eta k^2 + g_{\eta\eta}\right)\left\{\frac{\beta}{M} + (\kappa_X k^2 + g_{XX})k^2\right\} = g_{\eta X}^2 k^2 \tag{4}$$

where $k = |\mathbf{k}|$. The characteristic Eq. (4) has two branches. If $g_{\eta X} = 0$, these are the transformation branch $\beta_\gamma = -\gamma(g_{\eta\eta} + \kappa_\eta k^2)$ and diffusive branch $\beta_M = -M(g_{XX} + \kappa_\eta k^2)k^2$ that is, the processes proceed independently. Spinodal decomposition is an important limiting case of this regime when $g_{XX} < 0$ (miscibility gap) and $\kappa_X \neq 0$ (uphill diffusion). If $g_{\eta X} \neq 0$, the transformation and diffusion processes interact and the branches morph into $\beta_+(k)$ and $\beta_-(k)$ with $\beta_+(k) \geqslant \beta_-(k)$. The more important branch $\beta_+(k)$ has the following characteristic modes: the uniform ($k_0 = 0$, $\beta_0 \geqslant 0$), the cutoff ($k_c \neq 0$, $\beta_c = 0$), and the most unstable (k_T, $\beta_T = \max$). The latter dominates initial structure formation during decomposition of an unstable homogeneous system. The case when the most unstable mode is not uniform that is, $k_T > 0$ is called *Turing instability* [9,10].

Let us look at the decomposition of unstable states ($g_{\eta\eta} < 0$) of a binary system without the miscibility gap ($g_{XX} > 0$). In such system the uphill diffusion is not important and we can disregard the concentration gradient-energy coefficient ($\kappa_X = 0$). Then the uniform and cutoff modes are characterized by:

$$\beta_0 = -\gamma g_{\eta\eta} \tag{5a}$$

$$k_c^2 = -\frac{g_{\eta\eta}}{\kappa_\eta}(A + 1) \tag{5b}$$

$$A \equiv -\frac{g_{\eta X}^2}{g_{\eta\eta} g_{XX}} \tag{5c}$$