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Order–disorder structure of the δ_{1k} phase in the Fe–Zn system determined by scanning transmission electron microscopy

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Abstract

The crystal structure of the δ_{1k} phase in the Fe–Zn system was investigated by scanning transmission electron microscopy. The δ_{1k} phase has a superlattice structure based on the δ_{1p} phase having a tripled periodicity along the *a*-axis direction of the δ_{1p} phase, accompanied by one-dimensional stacking disorder of structural blocks (called order–disorder (OD) packets) along the *c*-axis direction. The crystal structure can be described crystallographically in terms of the OD theory so as to belong to the category IV OD structures composed of two types of non-polar OD layers (L_{2n} and M_{2n+1}). The tripled periodicity along the *a*-axis direction is due to chemical ordering of the constituent Fe and Zn atoms in the OD layer M_{2n+1}. Because of the tripled periodicity of the OD layer M_{2n+1}, three different equivalent stacking positions are generated in stacking an OD layer M_{2n+1} on top of the OD layer L_{2n}. Depending on the stacking order, the crystal structure of the δ_{1k} phase can be ordered with various periodicities along the stacking direction or completely disordered. Based on the OD theory, two maximum degree of order (MDO) polytypes belonging to the space groups of $P6_3/mcm$ (MDO1) and $R3c$ (MDO2) are deduced for the δ_{1k} phase. The most stable MDO polytype in the OD family of the δ_{1k} phase is determined experimentally to be the MDO2 polytype.
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1. Introduction

Hot-dipped galvannealed (GA) steels have been widely used in the automobile industry because of their high corrosion resistance, weldability and paintability [1]. GA steels are produced by immersing steel strips into a molten zinc bath followed by heat-treatment to alloy the zinc coating with the substrate iron through thermal diffusion. The coating layer usually consists of five intermetallic compounds – Γ (Fe_3Zn_{10}), Γ_1 ($Fe_{11}Zn_{40}$), δ_{1k} ($FeZn_7$), δ_{1p} ($Fe_{13}Zn_{126}$) and ζ ($FeZn_{13}$) phases [2–6] – which appear in the zinc-rich domain of the Fe–Zn binary phase diagram. When GA steels are deformed under severe conditions such as press-forming operations, the coating layer occasionally fails by decohesion at the coating/substrate interface (flaking) or by intracoating cracking to form fine particles (powdering). Such coating failure is known empirically to be mitigated when the coating layer consists largely of the δ_1 (δ_{1k}/δ_{1p}) phase [7]. The δ_1 (δ_{1k}/δ_{1p}) phase has thus long been considered to be relatively ductile, playing an important role in deformation of the coating in the forming process of GA steels. However, we have recently revealed from micropillar compression tests made for polycrystals that both of the δ_{1k} and δ_{1p} phases are extremely brittle, exhibiting no appreciable plastic strain prior

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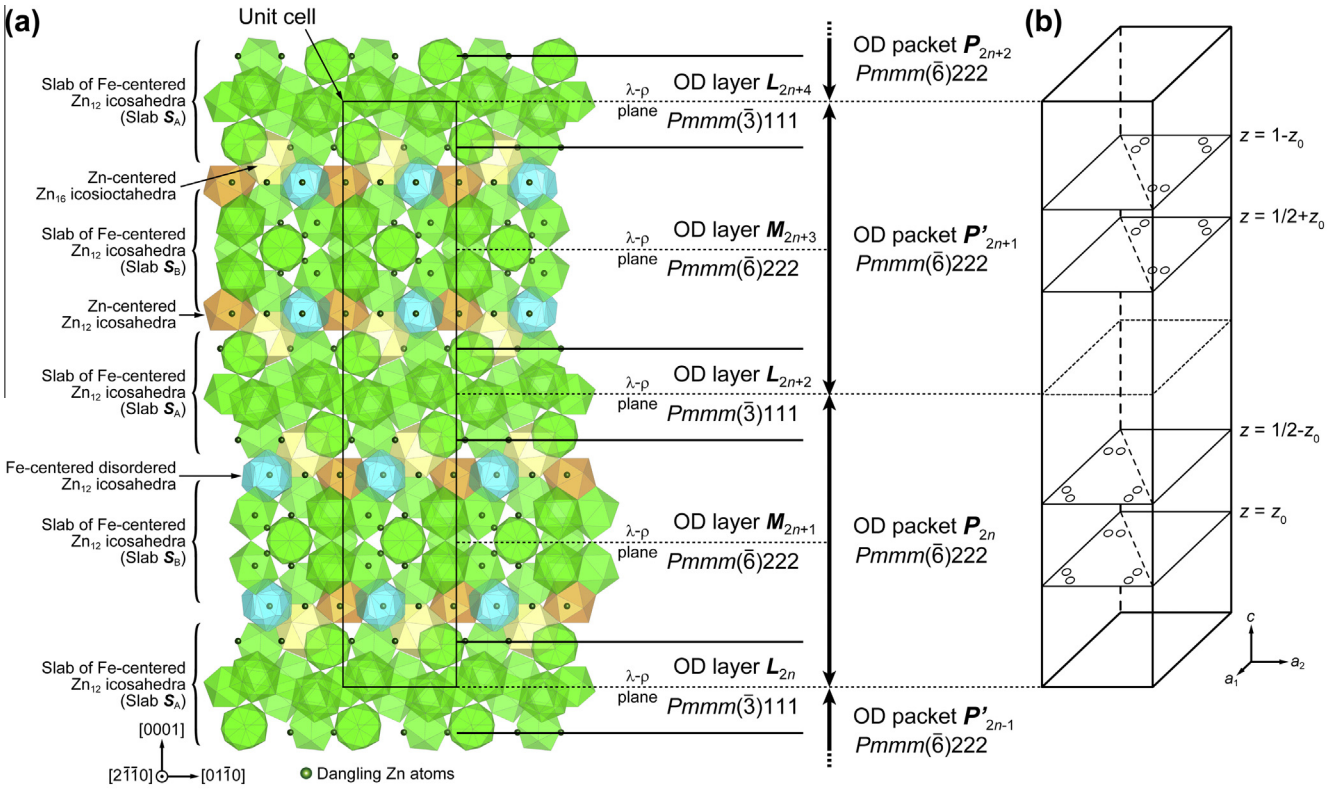

Fig. 1. (a) Crystal structure of the δ_{1p} phase projected along the $[2\bar{1}\bar{1}0]_p$ direction. The constituting OD layers and packets are described in the right-hand of the figure. (b) Schematic illustration of the 24*l* Wyckoff sites, the general positions in the space group of $P6_3/mmc$.

to premature fracture [8]. Although thermodynamics and crystallography of the relevant phases in the Fe–Zn binary system have been intensively investigated for several decades [3–5,9–25], the information about the crystal structure of the δ_{1k} and δ_{1p} phases is very much limited. It is only relatively recently that the crystal structure of the δ_{1p} phase has been refined by X-ray diffraction (XRD) [22], while the crystal structure of the δ_{1k} phase has yet to be refined until now. Hong and Saka [20] have reported that the δ_{1k} phase has a superlattice structure based on the δ_{1p} phase with the *a*-axis dimension three times that of the δ_{1p} phase, since they observed additional streaks in selected-area electron diffraction (SAED) patterns of the δ_{1k} phase at the corresponding positions. However, they neither explained the origin of the additional streaks (instead of diffraction spots) nor made any further structure refinement for the δ_{1k} phase [20]. The existence of structural disorder, which can easily be inferred from diffraction streaks, is considered to have prevented detailed structural analyses of the δ_{1k} phase by XRD. Very recently, we have refined the crystal structure of the δ_{1p} phase by synchrotron XRD combined with scanning transmission electron microscopy (STEM) [25], elucidating that the δ_{1p} phase comprises coordination polyhedra including Fe-centered normal and disordered Zn_{12} icosahedra[1], and Zn-centered Zn_{12} icosahedra and Zn_{16} icosioctahedra (as described in detail in the next section), but that Zn_{12} bicapped pentagonal prisms are not included, unlike in the model of Belin and Belin [22]. We have planned to refine the crystal structure of the δ_{1k} phase similarly by synchrotron XRD combined with STEM.

In the present study, we investigate the structure of the δ_{1k} phase using STEM at an ultra-high spatial resolution (~0.08 nm) to elucidate structural relationships between the δ_{1k} and δ_{1p} phases, paying special attention to the origin of additional streaks in SAED patterns. The results of crystal structure refinement by synchrotron XRD will be published elsewhere [26].

2. Crystal structure of the δ_{1p} phase

The crystal structure of the δ_{1p} phase [25] is described here, since the crystal structure of the δ_{1k} phase is considered to be a superlattice structure based on the δ_{1p} phase. The δ_{1p} phase contains 556 atoms in a large hexagonal unit cell ($a^{(p)} = 1.28297$ nm, $c^{(p)} = 5.72860$ nm) with the space group of $P6_3/mmc$. The structure can be best described by considering the packing of coordination polyhedra, including Fe-centered normal and disordered Zn_{12} icosahedra, and Zn-centered Zn_{12} icosahedra and Zn_{16} icosioctahedra (Fig. 1a). Fe-centered normal icosahedra are linked with one another so as to form two types of slabs (slabs S_A and S_B) parallel to the *c*-plane (Fig. 1a). These two types of slabs are stacked alternately along the *c*-axis, being

[1] In disordered Zn_{12} icosahedra, positional disorder exists at the vertex sites with the occupancy of 1/3.

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