Crystal Structures and Mechanical Properties of Fe–Zn Intermetallic Compounds Formed in the Coating Layer of Galvannealed Steels

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The crystal structures of all intermetallics of the Fe–Zn system have been investigated by synchrotron X-ray diffraction combined with atomic-resolution scanning transmission electron microscopy, in order to elucidate a basic principle based on which these crystal structures are constructed. The plastic deformation behavior of all these Fe–Zn intermetallics have also been investigated by micropillar compression testing at room temperature, with the use of small-scale pillar specimens of micrometer size, in order to elucidate operative slip systems and their critical resolved shear stress values. The observed deformation behavior is discussed in the light of the deduced building principle of the crystal structures.

KEY WORDS: crystal structure; icosahedron; plastic deformation; deformability; dislocation.

1. Introduction

Galvannealed (GA) steels, which have widely been used in the automobile industry,^{1–3)} are usually produced by hot-dip galvanizing, in which steel strips are immersed into a molten zinc bath, followed by heat-treatment to form an intermetallic coating layer through thermal diffusion in the zinc coating and the substrate iron. The coating layer of GA steels usually consists of five intermetallic compounds, Γ (Fe_4Zn_9), Γ_1 ($\text{Fe}_{11}\text{Zn}_{40}$), δ_{1k} (FeZn_7), δ_{1p} ($\text{Fe}_{13}\text{Zn}_{126}$) and ζ (FeZn_{13}) phases in the decreasing order of the Fe content, according to the Fe–Zn binary phase diagram (Fig. 1).^{4–11)} However, problems called powdering and flaking are known sometimes to occur in the steel forming process in the automobile industry.²⁾ Powdering is known to occur by particle formation through intracoating failure when the annealing is made excessively so that the Fe content in the coating layer is high. This is usually ascribed to the brittleness of Γ and Γ_1 phases. On the other hand, flaking is known to occur by the formation of flat particles through the decohesion of the coating-substrate interface when the annealing is made insufficiently so that the Fe content in the coating layer is low. This is usually ascribed also to the brittleness of Γ and Γ_1 phases as well as the softness of the ζ phase. The intermediate annealing condition is thus usually used to prevent from powdering and flaking so that the main

constituent phases of the coating layer are δ_{1k} and δ_{1p} , and that the experience in the industry assumes that these two phases are the most ductile.

These problems called flaking and powdering cannot be solved without knowledge on the mechanical properties (deformation, elastic, fracture and so on) for each of the five intermetallic compounds^{1,8,9,12–23)} as well as their thermodynamic properties (phase diagram/relationships).^{4–7)} However, almost nothing is known about the physical and

Fig. 1. Reported partial binary phase diagram in the Fe–Zn system.^{4,11,37)} (Online version in color.)

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mechanical properties of these intermetallic phases in the Fe–Zn system. There is actually no direct evidence to indicate the brittleness or ductility for any of the phases of question. In this perspective, the crystal structure information for these intermetallics is fundamentally very important to consider elementary processes of plastic deformation such as slip planes, slip directions, dislocation Burgers vectors and dislocation dissociation.^{18,19,24,25)} The crystal structures of all the Fe–Zn intermetallics, except for that of the δ_{ik} phase, have long been investigated by X-ray diffraction in the past.^{26–34)} In general, all of them have a very complex crystal structures comprising coordinated polyhedra such as icosahedra. There seem some discrepancies in their reported crystal structures in terms of what kinds of polyhedra exist, how these polyhedra are linked to one another, and how Fe and Zn atoms occupy particular crystallographic sites of these polyhedra.^{26–34)} The complexity of the crystal structures as well as the small difference in the X-ray/electron scattering factors for Fe and Zn atoms may be one of the major reasons for the discrepancies. In addition, the difficulties in obtaining large-sized single crystals arising from the fact that all the phases are formed through a series of peritectic or peritectoid reactions^{4,11)} may be partly responsible for the discrepancies. However, we have recently shown that synchrotron X-ray diffraction (XRD) combined with atomic-resolution scanning transmission electron microscopy (STEM) is very powerful in crystal structure refinement of the intermetallic of the δ_{ip} phase.^{9,35)} We have applied this combined technique to crystal structure refinement of the other intermetallics of the Fe–Zn system,^{8,36,37)} in order to solve the discrepancies in their reported crystal structures; what kinds of polyhedra exist, how these polyhedra are linked to one another and how Fe and Zn atoms occupy particular crystallographic sites of these polyhedra. On the other hand, the plastic deformation behavior of any of these intermetallics of the Fe–Zn system has never been explored in detail. This is due mainly to the difficulties in obtaining large-sized single and polycrystals of any single-phase by the reasons described above. On top of that, plastic flow is not believed to occur at ambient temperature for these intermetallics because of their very complex crystal structures. We have, however, recently shown that plastic flow occurs by slip deformation, at least, for two intermetallics, Γ and ζ , in compression for micrometer-sized specimens.^{18,38)} With the use of the micropillar compression testing method, we may be able to obtain fundamental knowledge about the strength and ductility at ambient temperature for each of the five Fe–Zn intermetallics of the coating layer.

In the present paper, we review the results of our investigation on the crystal structures of all these intermetallics of the Fe–Zn system by the above-mentioned combined technique, in order to elucidate a building principle of the crystal structures. We also review the results of our investigation on the plastic deformation behavior of each of these intermetallics in micropillar compression at ambient temperature, so that the observed plastic deformation behavior is correlated with the building principle of the crystal structures.

2. Crystal Structures

2.1. Geometrical Principles in Frank-Kasper Polyhedra

Frank and Kasper^{39,40)} described the crystal structures of a number of complex close-packed phases in terms of sphere packing with the basic stacking units of 12-, 14-, 15- and 16-coordinated polyhedra. Although the locally densest packing is achieved by tetrahedral packing, the space cannot be filled only with regular tetrahedral packing. Then, the regular tetrahedra are distorted to achieve the possibly densest local packing, leading to the formation of many different coordinated polyhedra described above, as observed in many of the Fe–Zn intermetallics. Which of polyhedra is formed depends on the atomic radius ratios of the constituent elements.

If an icosioctahedron (16-coordinated polyhedron) is formed with two different constituent atoms (one at the center and the other at the vertex positions), the larger atom should reside at the center and the densest packing is achieved when the larger atom at the center has the atomic radius ratio of 1.345 (Fig. 2(a)). For the Fe–Zn binary system, this will be achieved with the Zn atom residing at the center, when referring to the Goldschmidt radii of Fe (0.124 nm) and Zn (0.133 nm). On the other hand, if an icosahedron (12-coordinated polyhedron) is formed with two different constituent atoms in a similar way, the smaller atom should reside at the center and the densest packing is achieved when the smaller atom at the center has the atomic radius ratio of 0.902 (Fig. 2(b)). For the Fe–Zn binary system, this will be achieved with the Fe atom residing at the center of the icosahedron. Yet, this is not the case for the crystal structure of the δ_{ip} phase determined previously by Belin *et al.*³³⁾ In their crystal structure model, the center of icosahedra is always the larger Zn atom, and Fe atoms are allocated to the vertex positions in the so-called disordered icosahedron.³³⁾ This is not consistent with the geometrical principles of the Frank-Kasper polyhedra.

Fig. 2. Geometries of locally dense packed (a) icosioctahedron and (b) icosahedron. (Online version in color.)

2.2. Crystal Structures of the Five Phases in the Fe–Zn Binary System

A solution growth method was employed to grow large crystal grains ($> 300 \mu\text{m}$) of the Γ , δ_{Ik} , δ_{Ip} and ζ phase while a solid-state reaction of Zn and Fe powder was employed for the Γ_1 phase.^{4,11)} Experimental details of the crystal growth are described elsewhere.^{8,9,19,37)}

2.2.1. ζ Phase (FeZn_{13})

The crystal structure of the ζ phase was first refined by Brown²⁷⁾ and then by Gellings *et al.*,³¹⁾ both of who assigned a base-centered monoclinic unit cell, failing to determine the Fe atomic positions in the unit cell. Belin *et al.*³⁴⁾ subsequently refined the Fe positions to be exclusively at the center of the Zn_{12} icosahedron, although their lattice setting does not conform with the international convention that the oblique angle β should be non-acute but be as close as 90° .⁴¹⁾ Fe-centered Zn_{12} icosahedra are the structural unit and they are linked to one another by vertex-sharing to form a chain of Zn_{12} icosahedra along the c -axis, and isolated Zn atoms are located between the chains as if they act as glue among the chains in the C -centered monoclinic lattice (with the space group of $C2/m$), giving rise to the chemical formula of FeZn_{13} (**Fig. 3**).^{19,34)} If we take the origin of the monoclinic lattice shifted by half the c axis, the crystal structure of the ζ phase can be described as being made up of Zn_{12} icosahedron with their central Fe atoms being located at the C -centered monoclinic lattice points together with the Zn atoms that act as glue among the icosahedra.

Some of isolated Zn atoms located between the chains of Fe-centered Zn_{12} icosahedra may be substituted with Fe atoms so that some solid-solubility range occurs in the Fe-rich side of the stoichiometric composition (FeZn_{13} : Zn-7.1 at.%Fe). Yet, the solid-solubility range of the ζ phase is reported to extend in the Zn-rich side of the stoichiometry.⁴⁾ This is not easily understood, since the extension of the solid-solubility range in the Zn-rich side indicates that some Fe atoms allocated to the center of the Zn_{12} icosahedron are substituted by Zn atoms, which is not consistent with the geometrical principles in Frank-Kasper polyhedra (icosahedra). Indeed, the solid-solubility range of the ζ phase has recently been revised to extend in the Fe-rich side of the stoichiometry as shown in Fig. 1.¹¹⁾ The ζ phase in the coating layer usually exhibits columnar grains elongated along the $[001]$ directions, while no orientation relationship is found with the underlying δ_{Ik} phase.¹⁹⁾

2.2.2. δ_{Ip} Phase ($\text{Fe}_{13}\text{Zn}_{126}$)

Belin *et al.*³³⁾ refined the crystal structure of the δ_{Ip} phase by X-ray diffraction and reported that the huge hexagonal unit cell contains 556 atoms, of which 52 are Fe atoms although the chemical formula of the δ_{Ip} phase of their model is designated as FeZn_{10} (**Fig. 4(a)**). The characteristic features of their model are that in addition to icosahedra, icosioctahedra and pentagonal prisms are included as coordinated polyhedra and that in the so-called disordered icosahedron, while a Zn atom is allocated to the center, Fe atoms are allocated to the vertex positions. The latter is not consistent with the geometrical principles of the Frank-Kasper polyhedra. Indeed, our results of direct observations of atoms in the δ_{Ip} phase are not consistent with Belin's

Fig. 3. (a) The crystal structure of the ζ phase. The Fe-centered Zn_{12} icosahedra are shown in light blue. (b) $[010]$ and (c) $[001]$ projections of the unit cells.¹⁹⁾ The four widest interplanar distances are shown in (b) and (c). (Online version in color.)

model, as shown in Fig. 4(b). When the STEM images are calculated based on the atomic coordinates given by Belin *et al.*,³³⁾ some bright spots corresponding to atoms in the experimental images are found to be missed in the calculated images and vice versa (**Fig. 5**). Then, crystal structure refinement can be done combining with STEM observations through comparing experimental and calculated images until the best matching is obtained. Our combined analysis of the δ_{Ip} phase indicates that Fe atoms at vertices of disordered icosahedron in Belin's model are transferred to the center of the icosahedron and that Zn atoms at vertices of pentagonal prisms and icosahedron are transferred to vertices of the Fe-centered icosahedron. The net result is that (1) no pentagonal prism is included, (2) Fe atoms are never allo-

Fig. 4. The crystal structure model of the δ_p phase by (a) Belin *et al.*³³⁾ and (b) Okamoto *et al.*⁹⁾ (Online version in color.)

Fig. 5. (a) HAADF and (b) ABF images of a quarter unitcell of the δ_p phase simultaneously taken along the $[1\bar{1}00]$ zone axis with the spherical-aberration-corrected STEM. (c) HAADF and (d) ABF images calculated with the structural parameters reported by Belin *et al.*³³⁾ (f) HAADF and (g) ABF images calculated with the structural parameters refined in our study.⁹⁾ The corresponding portion of $[1\bar{1}00]$ projection of the structural models (e) reported by Belin *et al.*³³⁾ and (h) refined in our study.⁹⁾ (Online version in color.)

cated at vertices of icosahedra, but (3) these Fe atoms are allocate at the center of Zn_{12} icosahedra. The structural unit is therefore the Fe-centered Zn_{12} icosahedron, as in the case of the ζ phase. In both the ζ and δ_p phases, the vertex sites

Fig. 6. (a) SEM backscattered electron image, (b) magnified image of interface, and (c) EBSD orientation mapping of a cross section of coating (δ_p/δ_k) of post heat-treated GA steel. (d) Pole Fig. of growth direction of the δ_p and δ_k phases. (Online version in color.)

of Fe-centered icosahedra are occupied exclusively by Zn atoms, forming a pure Zn_{12} icosahedron so as to encapsulate an Fe atom at the center.^{9,19,34)} The large hexagonal unit cell of the δ_p phase with the space group of $P6_3/mmc$ comprises more or less regular (normal) Zn_{12} icosahedra, disordered Zn_{12} icosahedra, Zn_{16} icosioctahedra, and isolated Zn atoms.⁹⁾ The unit cell contains 52 Fe and 504 Zn atoms so that the compound is expressed with the chemical formula of $\text{Fe}_{13}\text{Zn}_{126}$, instead of FeZn_{10} .⁹⁾ Normal icosahedra are linked to one another by face- and vertex-sharing forming two types of basal slabs, which are bridged with each other by face-sharing with icosioctahedra, whereas disordered icosahedra with positional disorder at their vertex sites are isolated from other polyhedra.^{9,35)}

2.2.3. δ_k Phase

The crystal structure of the δ_k phase has yet to be refined until now, although the phase is known to locate in the Fe-rich side next to the δ_p phase, so that the compound is expressed with the chemical formula of FeZn_7 .⁴²⁾ Hong and Saka¹⁶⁾ reported that the δ_k phase has a superlattice structure based on the δ_p phase having a tripled periodicity along the a -axis direction of the δ_p phase from the inspection of electron diffraction patterns. The tripled periodicity along the a -axis direction is believed to be due to higher-order chemical ordering of Fe atoms in excess of the solubility limit of the Fe content in the δ_p phase, although the atomic coordinates have never been clarified. Because of this, the stoichiometric composition of this compound, which is sometimes described to be FeZn_7 , is still an open question. However, the higher-order chemical ordering of Fe atoms in the parent δ_p phase seems reasonable when judged from the formation sequence of the two phases as well as the existence of the orientation relationship between the two phases keeping their mutual a - and c -axis directions parallel to each other (Fig. 6). We believe that the structural unit of this compound is still Fe-centered Zn_{12} icosahedron linked to one another by face- and vertex-sharing. There still exist some argument about the order (either the first- or second-order) of phase transformation between the two phases,^{7,43)}

although recently the first-order transformation is claimed to occur at least in the temperature range 450–500°C.¹¹⁾

Because of the tripled periodicity along the a -axis direction, three different equivalent stacking positions are generated in stacking an atomic slab with the thickness corresponding to the c -axis dimension of the parent δ_{lp} phase (Fig. 7). Then, multiplicity is generated for the stacking sequence of these atomic slabs along the c -axis direction.⁸⁾ The crystal structure can then be described in terms of the order–disorder (OD) theory^{8,44,45)} with these atomic slabs being called ‘OD layer’. Depending on the stacking order, the crystal structure of the δ_{lk} phase can be ordered with various periodicities along the stacking direction (along the c -axis) or completely disordered. Based on the OD

theory,^{8,44,45)} 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_{lk} phase. The most stable MDO polytype in the OD family of the δ_{lk} phase is determined experimentally to be the MDO2 polytype.⁸⁾ However, the δ_{lk} phase may have a high chance to exhibit one-dimensional stacking disorder along the c -axis direction if the annealing condition is far from the equilibrium, as in the practice of GA steel production.

2.2.4. Γ_1 Phase ($\text{Fe}_{21.2}\text{Zn}_{80.8}$)

The Γ_1 phase in the Fe–Zn binary system is reported to crystallize into one of the so-called γ' -brass structures (space group $F43m$),³²⁾ whose crystal structures are usually described as a $2 \times 2 \times 2$ superstructure based on the γ -brass structure with a doubled lattice constant of the cubic unit cell so that the unit cell volume for the γ' -brass structure is eight times that for the γ -brass structure, into which the Γ phase compound crystallizes.^{46–49)} Koster and Schoone,³²⁾ made a first refinement of crystal structure of the intermetallics of the Γ_1 phase in the Fe–Zn system. According to the atomic coordinates reported by Koster and Schoone,³²⁾ the crystal structure of the Γ_1 -phase compound whose chemical composition is determined to be $\text{Fe}_{11}\text{Zn}_{40}$ can be considered to consist of $(\text{Zn,Fe})_{12}$ icosahedra as in the case of other compounds in the Fe–Zn system. Some Fe atoms start to occupy the vertex sites of icosahedra to form $(\text{Zn,Fe})_{12}$ icosahedra because of the increased Fe content in the compound. However, the central site of some of the constituting icosahedra are occupied not only by Fe but also by Zn atoms. This is somewhat questionable when referring to the geometrical principles in Frank–Kasper polyhedra. Indeed, our results by synchrotron X-ray diffraction have indicated that the Γ_1 -phase compound consists of Zn_{12} and $(\text{Zn,Fe})_{12}$ icosahedra whose central site is *exclusively* occupied by Fe atoms (Fig. 8).³⁷⁾ That is, while an Fe atom exclusively occupy the center of icosahedra, vertices of some icosahedra are occupied exclusively by Zn atoms but those of others are occupied not only by Zn but also by Fe atoms. This leads to the formation of both Fe-centered Zn_{12} and Fe-centered $(\text{Zn,Fe})_{12}$ icosahedra as the structural units (Fig. 8). They are connected to one another by vertex- and face-sharing, respectively, with isolated Zn atoms forming a Zn_4 tetrahedron between the agglomerated polyhedra.³⁷⁾ The unit cell contains 408 atoms (Pearson symbol $cF408$), of which 84.8 are Fe atoms, and 323.2 Zn atoms. The Γ_1 phase is formulated thus to be $\text{Fe}_{21.2}\text{Zn}_{80.8}$ instead of $\text{Fe}_{11}\text{Zn}_{40}$ as previously described by Koster and Schoone.³²⁾ The chemical composition corresponding to the formula of $\text{Fe}_{21.2}\text{Zn}_{80.8}$ is very close to the peritectic composition of the Γ_1 phase in the recently revised phase diagram (Fig. 1).¹¹⁾

2.2.5. Γ Phase (Fe_4Zn_9)

The intermetallic of the Γ phase, the most Fe-rich compound in the Fe–Zn system, is known to crystallize into the so-called γ -brass structure^{26,28,29,48)} that comprises $(\text{Zn,Fe})_{12}$ icosahedra (Fig. 9). Vertices of all icosahedra are occupied not only by Zn but also by Fe atoms, because of the Fe-rich composition. The structural unit of the Γ phase is thus the Fe-centered $(\text{Zn,Fe})_{12}$ icosahedron. However, there are some discrepancies in the results of crystal structure refine-

Fig. 7. Schematic illustrations of stacking manners of the structural blocks with the thickness of $c^{(p)}/2$ in the (a) δ_{lp} and (b–d) δ_{lk} phases, respectively.⁸⁾ There are three different stacking manners in the δ_{lk} phase. (e) HAADF-STEM images of the δ_{lk} phase taken along the $[1\bar{1}00]_p$ direction. The solid frame indicates the unit cell of the δ_{lp} phase. Single and double arrows in (b) indicate slightly darker and brighter atomic columns. The intensity profile along the dashed line X–Y is shown in the bottom of (e). (Online version in color.)

Fig. 8. Agglomerated polyhedra constituting the crystal structure of the Γ_1 phase.³⁷⁾ (a) Four Fe4-centered $(\text{Fe,Zn})_{12}$ icosahedra connected with one another by face-sharing. (b) Four Fe2-centered Zn_{12} icosahedra connected with one another by vertex-sharing. (c) Four Fe1-centered $(\text{Fe,Zn})_{12}$ icosahedra connected with one another by face-sharing. (d) Zn_4 tetrahedron filling the remained space which is not occupied by the agglomerated polyhedra. (Online version in color.)

Fig. 9. Unit cell of the Γ phase³⁷⁾ described in (a) the nested cluster model^{46,48)} and (b) the coordination polyhedra model. (a) Unit cell of the γ -brass structure consisting of two γ -brass type (26 atoms) clusters residing at the cell corner and body centre.²⁶⁾ (b) Unit cell of the Γ phase consists of the agglomerated Fe-centred $(\text{Zn,Fe})_{12}$ icosahedra. (Online version in color.)

ment made in the past by four research groups in the Fe and Zn occupancy behaviors especially for the central site of these $(\text{Zn,Fe})_{12}$ icosahedra. While exclusive occupancy by Zn atoms was claimed by Johansson *et al.*,²⁸⁾ exclusive occupancy by Fe atoms was claimed by Brandon *et al.*,²⁹⁾ Belin *et al.*,³³⁾ and Xie *et al.*⁵⁰⁾ Our results of crystal structure refinement of the Γ phase compounds with some different chemical compositions by synchrotron X-ray diffraction have indicated that the central site of $(\text{Zn,Fe})_{12}$ icosahedra is occupied *exclusively* by an Fe atom regardless of chemical compositions (Fig. 9). The Γ phase compound consists of Fe-centered $(\text{Zn,Fe})_{12}$ icosahedra that connect with one another by face-sharing. The icosahedral vertex sites of

Fig. 10. Crystal structures and connecting behaviour of the coordination polyhedra (Fe-centered $(\text{Fe,Zn})_{12}$ icosahedra) in the Fe–Zn intermetallic compounds, (a) ζ , (b) δ_{1p} , (c) Γ and (d) Γ_1 .³⁷⁾ (Online version in color.)

the shared triangle faces are occupied by Fe and Zn atoms to form a $(\text{Fe,Zn})_4$ tetrahedral core and the Fe occupancy increases with the increase in the Fe content of the compounds (Fig. 9). The stoichiometry of the Γ phase occurs at the peritectic composition and is expressed as Fe_4Zn_9 (Zn-30.77 at.%Fe), where the center of the icosahedra and the vertices of the shared triangle faces are all occupied exclusively by Fe atoms while the other vertex sites by Zn atoms. The chemical composition corresponding to the formula of Fe_4Zn_9 is indeed very close to the peritectic composition of the Γ phase in the recently revised phase diagram (Fig. 1).¹¹⁾

Some reports described the cube-on-cube orientation relationships among the three phases (α , Γ and Γ_1).^{51,52)} This is consistent with the expectation from the fact that the crystal structure of the Γ -phase compound is sometimes described as a $3 \times 3 \times 3$ superlattice structure based on the BCC (body-centered cubic) structure with the tripled lattice constant²⁶⁾ and that of the Γ_1 -phase compound is regarded as a $2 \times 2 \times 2$ superlattice structure based on the structure of the Γ -phase compound.^{49,53)} On the other hand, there are other reports to show no orientation relationships among the three phases.^{54–56)} Our study indicates that generally, there is no orientation relationship both between the Γ and Γ_1 phases and between the α (BCC-Fe) and Γ phases in the coating layer of GA steel sheet.³⁷⁾

2.3. Building Principle of the Crystal Structures

In the ζ phase, the most Fe-lean compound in the Fe–Zn system (Fig. 10(d)), Fe-centered Zn_{12} icosahedra are linked to one another by vertex-sharing to form a chain of Zn_{12} icosahedra along the c -axis,³⁴⁾ and isolated Zn atoms are located between the chains¹⁹⁾ (Fig. 10(d)). In the δ_{1p} phase, located next to the ζ phase in the Fe-rich side in the Fe–Zn binary phase diagram (Fig. 10(c)), the structural unit is again the Fe-centered Zn_{12} icosahedron and these Fe-centered Zn_{12} icosahedra are connected to one another by vertex- and

face-sharing with isolated Zn atoms between vertex- and face-shared Fe-centered Zn_{12} icosahedron (Fig. 10(c)).^{9,35)} In both the ζ and δ_{1p} phases, the vertex sites of Fe-centered icosahedra are occupied exclusively by Zn atoms, forming pure Zn_{12} icosahedron so as to encapsulate an Fe atom at the center.^{9,34,35)} In the Γ_1 phase, located next to the δ_{1p}/δ_{1k} phases in the Fe-rich side in the Fe–Zn binary phase diagram, while the center of icosahedra is exclusively occupied by an Fe atom, vertices of some icosahedra are occupied exclusively by Zn atoms but those of other icosahedra are occupied not only by Zn but also by Fe atoms. This occurs because Fe atoms that cannot be allocated to the center of icosahedra occupy some vertex sites. This leads to both Fe-centered Zn_{12} and Fe-centered $(\text{Zn,Fe})_{12}$ icosahedra as the structural units (Fig. 10(b)). They are connected to one another by vertex- and face-sharing, respectively, with isolated Zn atoms forming a Zn_4 tetrahedron between the agglomerated polyhedra (Fig. 8(d)). In the Γ phase, the most Fe-rich compound in the Fe–Zn system, while the center of icosahedra is exclusively occupied by an Fe atom, vertices of these icosahedra are occupied by both Zn and Fe atoms. The structural unit of the Γ phase is thus the Fe-centred $(\text{Zn,Fe})_{12}$ icosahedron and they are connected with one another in a tetrahedrally close-packed arrangement by face-sharing (Fig. 10(a)).

The variation of the crystal structures of all these Fe–Zn compounds with chemical composition can be best understood by considering the packing of coordinated polyhedra with the common structural unit being the Zn_{12} and/or $(\text{Zn,Fe})_{12}$ icosahedron whose central site is *exclusively* occupied by an Fe atom (Fig. 10). Exclusive occupancy of an Fe atom at the center of the Zn_{12} and/or $(\text{Zn,Fe})_{12}$ icosahedron is consistent with the geometrical principles in Frank-Kasper polyhedra, in which the smaller atom (Fe in this case) is concluded to reside at the center of the icosahedron formed by the larger atoms (Zn in this case) for the formation of icosahedron with two constituent elements with different atomic radii. When the Fe content is increased so that all Fe atoms cannot be accommodated in the central sites of these icosahedra, these excess Fe atoms occupy vertices of some icosahedra together with Zn atoms, forming $(\text{Zn,Fe})_{12}$ icosahedron. As a whole, the building principle of the crystal structures of the Fe–Zn intermetallics is described as follows. As the Fe content of the Fe–Zn intermetallics increases, (i) the linkage geometry among Fe-centered icosahedra changes from vertex-sharing to face-sharing, (ii) the atoms occupancy (either Zn or Fe atoms) at the face-sharing sites changes from exclusive occupancy by Zn atoms to mixed occupancy by Zn and Fe atoms and to exclusive occupancy by Fe atoms, and (iii) the fraction of isolated Zn atoms tends to decrease (7.1% (ζ) $\rightarrow$ 9.4% (δ_{1p}) $\rightarrow$ 3.9% (Γ_1) $\rightarrow$ 0% (Γ)).³⁷⁾

3. Mechanical Properties

3.1. Prediction of Plasticity Based on the Peierls–Nabarro Model

Plasticity (deformability) of materials is sometimes predicted based on the Peierls–Nabarro (PN) model,^{57,58)} in which the shear stress required to move an edge dislocation is expressed with the interplanar distance of slip plane

(h) and the magnitude of Burgers vector (b), as described below.

$$\tau_p = \frac{2\mu}{1-\nu} \exp\left(-\frac{2\pi h}{(1-\nu)b}\right), \dots\dots\dots (1)$$

where μ and ν are the shear modulus and Poisson's ratio. According to Eq. (1), the slip system with a large value of the h/b ratio is expected to operate more easily, since the value of τ_p is expected to be smaller as the h/b ratio increases. The low value of the h/b ratio leads to the high Peierls–Nabarro stress to move dislocations, generally resulting in material brittleness. The h/b ratios for all these Fe–Zn intermetallic compounds (0.058–0.183) are considerably smaller than that for iron (0.817) (Table 1), suggesting the brittleness for all these Fe–Zn intermetallics. However, some (at least) of these intermetallics should exhibit some deformability, since GA steels can be bent, stretched and drawn under optimized forming conditions without serious coating failure.

3.2. Micropillar Compression Testing

Recent advances in fabrication processes with precise control of material dimensions down to the nanometer level, for example, with the focused ion beam (FIB) method have made it possible to investigate mechanical properties at these small scales using a nano-indenter with a flat punch.^{59–62)} This testing method is called micropillar compression testing and has used for a number of different materials.^{63–67)} We investigate the compression deformation behavior of FIB-fabricated micropillar specimens cut from each of the five intermetallic phases in the GA coating at room temperature, in order to elucidate the mechanical properties for the respective phases. Our compression experiments of polycrystalline micropillars of each of the five phases prepared from the thin coating layer ($\sim 10 \mu\text{m}$) of the GA steels have shown that the Γ and ζ phases are deformable while Γ_1 , δ_{1k} and δ_{1p} phases are all considerably brittle.^{18,38)} This is somewhat consistent with Table 1 in that the Γ and ζ phases have higher h/b ratios than the others, although these h/b ratios were calculated without taking account of detailed mechanisms such as dislocation dissociation (shorter Burgers vector length). With the knowledge of the deformability for the respective phases, crack initiation and propagation in the coating of GA steel upon forming can be discussed, as was done in our previous study.¹⁸⁾

We have extended the work on micropillar compression of polycrystals to single crystals to explore operative slip systems and their bulk critical resolved shear stress (CRSS) values. We have found during the course of single-crystal micropillar compression tests that the δ_{1p} and δ_{1k} phases are also deformable, as in the case of the Γ and ζ phases. This may be reasonable in view of the fact that the optimum formability of GA steels is achieved when the coating layer consists mostly of the δ_1 (δ_{1k}/δ_{1p}) phase. The details of the plastic deformation behavior of each of the five phases will be described in the following sections.

3.3. Plastic Deformation Behavior of the Five Phases in the Fe–Zn Binary System

3.3.1. ζ Phase¹⁹⁾

Significant large strains (more than 10%) are usually

Table 1. Crystal structure parameters, Burgers vectors, and interplanar distances of slip planes for the Fe–Zn intermetallic compounds and pure iron.¹⁸⁾

	Formula	Pearson symbol	Space group	Lattice constant (nm)	Burgers vector, <i>b</i>	Interplanar distance, <i>h</i>	<i>h/b</i>	Plastic deformation in polycrystalline micropillars
Γ ^a	Fe ₄ Zn ₉	<i>cI</i> 52	$\bar{I}43m$	<i>a</i> = 0.8976	$1/2\langle 111 \rangle^f$ 0.777 nm	$\{110\}^f$ 0.135 nm	0.174	Yes
Γ ₁ ^a	Fe _{21.2} Zn _{80.8}	<i>cF</i> 408	$F\bar{4}3m$	<i>a</i> = 1.7989	$1/2\langle 110 \rangle^g$ 1.272 nm	$\{111\}^g$ 0.137 nm	0.108	No
δ _{ik} ^b	FeZn ₇	—	(higher-ordered structure based on δ _{ip})	<i>a</i> = 2.2148	$1/3\langle 1120 \rangle^f$ 2.222 nm	$(0001)^f$ 0.1298 nm	0.058	No
δ _{ip} ^c	Fe ₁₃ Zn ₁₂₆	<i>hP</i> 556	<i>P</i> 6 ₃ / <i>mmc</i>	<i>a</i> = 1.2830 <i>c</i> = 5.7286	$1/3\langle 1120 \rangle^f$ 1.283 nm	$(0001)^f$ 0.1298 nm	0.101	No
ζ ^d	FeZn ₁₃	<i>mC</i> 28	<i>C</i> 2/ <i>m</i>	<i>a</i> = 1.0862 <i>b</i> = 0.7608 <i>c</i> = 0.5061 β = 100.32°	$1/2\langle 112 \rangle^{f,h}$ 0.770 nm	$\{110\}^{f,h}$ 0.1412 nm	0.183	Yes
Fe ^e	—	<i>cI</i> 2	<i>Im</i> $\bar{3}m$	<i>a</i> = 0.2867	$1/2\langle 111 \rangle$ 0.2483 nm	$\{110\}$ 0.2027 nm	0.817	Yes

^aN. L. Okamoto *et al.*³⁷⁾^bN. L. Okamoto *et al.*⁸⁾^cN. L. Okamoto *et al.*⁹⁾^dR. Belin *et al.*³⁴⁾^eR. Kohlhaas *et al.*⁷³⁾^fSlip systems were determined via compression tests of single-crystal micropillars.^gThe shortest Burgers vector and the plane with the largest interplanar distance were selected for the anticipated operative slip system.^hN. L. Okamoto *et al.*¹⁹⁾

observed in micropillar compression at room temperature for single crystals of many different orientations (**Fig. 11(a)**). Deformation markings are easily observed on deformed micropillar specimens so that the slip plane is determined through trace analysis on two orthogonal surfaces (Figs. 1(b) and 1(c)). The slip direction is also easily determined if the possible slip direction is intended to lay on one of the side surfaces (Fig. 11(d)). The major slip system, $\{110\}\langle 11\bar{2} \rangle$ is identified in that way to be operative in a very wide range of crystal orientation. In a narrow orientation range where $\{110\}\langle 11\bar{2} \rangle$ slip cannot be operative, another slip system, (100)[001] is identified to operate. The CRSS value tends to increase with the decrease in the specimen size according to a power-law scaling. The bulk CRSS values deduced by extrapolating the inverse-power law size dependence of CRSS to the specimen size of 20–30 μm are ~70 MPa for $\{110\}\langle 11\bar{2} \rangle$ slip and ~240 MPa for (100)[001] slip.

The slip systems observed to operate in the ζ phase are predicted respectively to be only the fourth and sixth easiest slip systems from the *h/b* ratio, if (110), (010), (100) and $\bar{0}01$ are considered as possible slip planes and [001], $[11\bar{0}]$, $[11\bar{2}]$ and $[1\bar{1}\bar{2}]$ as possible slip directions. Slip on $\{110\}[001]$, (010)[001] and $\{110\}\langle 11\bar{2} \rangle$ are predicted for the three easiest slip systems. The selection of slip planes and directions is believed to be closely related to the arrangement of Fe-centered Zn₁₂ icosahedra in the C-centered monoclinic lattice. In view of the fact that the average bonding distance between Fe and Zn atoms in the icosahedron (0.2590 nm) is much shorter than that between Zn atoms at vertex sites of the icosahedron (0.2782 nm), the bonding between Fe and Zn atoms is so strong that slip deformation occurs so as not to destroy the Fe-centered Zn₁₂ icosahedron. In other words, each individual Fe-centered

Fig. 11. Stress–strain curves obtained for seven micropillar specimens of the ζ phase compound with the orientations A–G.¹⁹⁾ The edge length is ~4 μm for all specimens. The mark × indicates the occurrence of failure. (b–d) SEM secondary electron images of deformation structures in the micropillar with the orientation E ([7 4 15]). (a) and (b) were taken along a direction inclined by 30° from the loading axis, while (c) was taken along the loading axis. (Online version in color.)

Zn₁₂ icosahedron behaves as if it is a large-sized atom during slip deformation so that the slip plane is determined as one that does not break any atomic bonding within the Fe-centered Zn₁₂ icosahedra during slip. This can be realized in the ζ phase compound, since in the crystal structure, Fe-centered Zn₁₂ icosahedra (the structural unit) are linked

to one another by vertex-sharing to form a chain of Zn_{12} icosahedra along the c -axis. This means that the slip plane to be selected should not destroy the vertex-shared c -axis chains of Fe-centered Zn_{12} icosahedra. The $\{110\}$ plane is such a plane with the widest interplanar distance and the (100) plane has the second widest (Fig. 3(c)), as reflected in the difference in the CRSS values for these two slip systems.

There are some other possible slip vectors on the (110) slip plane. Those include $[001]$ and $\frac{1}{2}\langle 1\bar{1}0 \rangle$, both of which are actually shorter than $\frac{1}{2}\langle 1\bar{1}2 \rangle$. In view of the magnitude of the slip vector, the shorter is favorable. Nevertheless, $\frac{1}{2}\langle 1\bar{1}2 \rangle$, which is not the shortest translation vector, is selected as the slip vector on the (110) slip plane. The selection of the slip vector is indeed closely associated with the dislocation dissociation, since the magnitude of the Burgers vector for dislocations with $b = \frac{1}{2}\langle 1\bar{1}2 \rangle$ can be shortened as a result of dissociation. TEM observations (Fig. 12) have clearly indicates dislocation dissociation into three collinear superpartials, as described below.

$$\frac{1}{2}[1\bar{1}2] \rightarrow 1/5[1\bar{1}2] + 1/5[1\bar{1}2] + 1/10[1\bar{1}2] \dots\dots (2)$$

This is further confirmed by calculation of the overlapping atomic volume along the slip direction on the slip plane.

3.3.2. δ_{ip} Phase

Since both the a - and c -axis lengths (1.283 and 5.729 nm, respectively) of the hexagonal unit cell of the δ_{ip} phase compound are very large,⁹⁾ the occurrence of slip deformation is hard to expect in the δ_{ip} phase. This is particularly the case for slip along the direction containing the c -axis component. However, slip along the a -axis direction may be possible if dislocation dissociation occurs so that the Burgers vector length for each of the relevant partial dislocations is sufficiently short. In single-crystal micropillar compression, we indeed observed the operation of slip along the a -axis

direction on two different slip systems; $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ and $\{01\bar{1}0\}\langle 2\bar{1}\bar{1}0 \rangle$. Of the two systems, the $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ basal slip system is the major slip system having a much lower CRSS value. The bulk CRSS values deduced in a similar way are ~ 330 MPa for $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ basal slip and ~ 750 MPa for $\{01\bar{1}0\}\langle 2\bar{1}\bar{1}0 \rangle$ prism slip, indicating the operation of $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ basal slip in a much wider orientation range. Both basal and prism slip occurs involving the motion of many dislocations in *avalanche* on a single slip plane accompanied by a significantly large strain burst in the stress-strain curve, so that the specimen can be looked as if failed by slip plane failure after deformation. That is the reason why we mistakenly concluded in our previous study on polycrystals¹⁸⁾ that the δ_{ip} phase does not plastically deform but fails in a brittle manner.

When the CRSS values of the easiest slip systems in the ζ and δ_{ip} phases are compared, the CRSS value for $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ slip in the δ_{ip} phase (~ 330 MPa) is obviously considerably higher than that for $\{110\}\langle 1\bar{1}2 \rangle$ slip in the ζ phase (~ 70 MPa). We believe that the difference in the linkage mode among Fe-centered Zn_{12} icosahedra, which are the common structural unit in the ζ and δ_{ip} phase compounds, is reflected to the difference in the CRSS values. While Fe-centered Zn_{12} icosahedra are linked to one another by vertex-sharing in the ζ phase, normal Fe-centered Zn_{12} icosahedra are linked to one another by face- and vertex-sharing forming two types of basal slabs, which are bridged with each other by face-sharing with icosioctahedra in the δ_{ip} phase. Then, because of the incorporation of face-sharing in the linkage mode among Fe-centered Zn_{12} icosahedra in the δ_{ip} phase, Fe-centered Zn_{12} icosahedra have to be inevitably destroyed, breaking chemical bondings between Fe and Zn atoms in the icosahedra during slip, whatever the slip plane is. $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ slip inevitably destroy Fe-centered Zn_{12} icosahedra, breaking chemical bondings between Fe and Zn atoms in the icosahedra during slip. We believe that this is the reason for the higher CRSS value of $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ slip in the δ_{ip} phase. This is also the case for $\{01\bar{1}0\}\langle 2\bar{1}\bar{1}0 \rangle$ prism slip. Of significance to note, however, is that basal slip may occur along the slip plane where Fe–Zn atomic bondings within the Fe-centered Zn_{12} icosahedra as well as Zn–Zn atomic bondings in the Zn-centered Zn_{16} icosioctahedra are broken, while prism slip needs to break much more Fe–Zn atomic bondings within the Fe-centered Zn_{12} icosahedra. We believe that this is the reason for the higher CRSS value for prism slip than for basal slip.

3.3.3. δ_{ik} Phase

In view of the fact the δ_{ik} phase has a superlattice structure based on the δ_{ip} phase with a tripled periodicity along the a -axis direction of the δ_{ip} phase accompanied by one-dimensional disorder in the stacking along the c -axis direction, it is very hard to expect plasticity for this compound. Yet, we have recently observed plastic flow of the slip-plane-failure type in the δ_{ik} phase compound oriented favorably for $(0001)\langle 2\bar{1}\bar{1}0 \rangle$ basal slip, as in the δ_{ip} phase compound. Significantly large strain burst is usually observed in the stress-strain curve, indicating the involvement of the motion of a large number of dislocations in *avalanche*. The bulk CRSS is deduced to be ~ 450 MPa, which is much higher than that (~ 330 MPa) for

Fig. 12. (a) Dark-field TEM image of a typical dislocation structure observed in a ζ crystallite embedded in the Zn matrix.¹⁹⁾ The image was taken with g (reflection vector) = $2\bar{4}2$ and the beam direction (B) was close to $[2\bar{1}0]$. (b) Weak-beam TEM image taken with $g = \bar{1}10$ to reveal the dissociation scheme of the dislocation with $b = \frac{1}{2}[1\bar{1}2]$.

(0001) $\langle 2\bar{1}10 \rangle$ slip in the δ_{1p} phase. Since the atomic coordinates have yet to be deduced for the δ_{1k} phase compound, any detailed explanation for this in terms of the linkage mode of Fe-centered Zn_{12} icosahedra is difficult to make. In view of the tripled a -axis length, dislocations carrying slip along the $\langle 2110 \rangle$ direction are expected to dissociate into a number of partial dislocations. This has yet to be clarified. The occurrence of $\{0110\}\langle 2\bar{1}10 \rangle$ prism slip has also yet to be clarified for the δ_{1k} phase compound, although the multiplied c -axis dimension arising from one-dimensional stacking disorder is expected to make the operation of prism slip difficult.⁸⁾

3.3.4. Γ_1 Phase

The Γ_1 phase compound has a cubic crystal structure with the face-centered lattice. The lattice constant is huge (1.7989 nm),³⁷⁾ amounting to about six times that of the underlying BCC lattice. Plastic flow is therefore expected to be difficult to occur in the Γ_1 phase. This is consistent with what is observed in experiment. Premature fracture occurs without showing any evidence of plasticity at a very high stress level usually exceeding to 1 GPa. The observed high (fracture) strength is understandable when referring to the characteristics of the crystal structure. Because of the increased Fe content, excess Fe atoms that cannot be accommodated in the central sites of Fe-centered icosahedra occupy vertices of some icosahedra together with Zn atoms forming $(Zn,Fe)_{12}$ icosahedra in the Γ_1 phase.³⁷⁾ Since these $(Zn,Fe)_{12}$ icosahedra are connected to one another not only by vertex-sharing but also by face-sharing, many strong Fe–Zn bondings have to be broken during slip deformation, in addition to breaking Fe–Zn bondings within the Fe-centered $(Zn,Fe)_{12}$ icosahedra.

3.3.5. Γ Phase

The Γ phase has been believed to be very brittle from experience in the industry that the problem called ‘powdering’ occurs more frequently when annealing is made excessively so that the Fe content, *i.e.*, the volume fraction of the Γ (Γ/Γ_1) phase in the coating layer is high.^{68–70)} This is understandable from the complex crystal structure of the Γ phase compound with the body-centered cubic lattice and a large lattice constant (0.898 nm). However, we have found plastic flow in the Γ phase compound in micropillar compression.^{18,25)} Two different slip systems, $\{110\}\langle 111 \rangle$ ²⁵⁾ and $\{110\}\langle 001 \rangle$, are identified with the $\{110\}\langle 111 \rangle$ slip system being the major slip system having a much lower CRSS value. The bulk CRSS values deduced are ~240 MPa for $\{110\}\langle 111 \rangle$ slip and ~550 MPa for $\{110\}\langle 001 \rangle$ slip, indicating the operation of $\{110\}\langle 111 \rangle$ slip in a much wider orientation range. The CRSS values for the two slip systems operative in the Γ phase are a little smaller than those in the δ_{1p} phase. This may be due to the fact that the crystal structure of the Γ phase cannot be regarded as that comprises with the structural unit of Fe-centered Zn_{12} and/or $(Zn,Fe)_{12}$ icosahedron anymore because of the increased Fe content that makes (1) Fe atoms to occupy not only the center of icosahedra but also the vertex sites of these icosahedra and (2) the triangle face sites to share icosahedra by face-sharing to be occupied by more Fe atoms. This means that in the course of plastic deformation, the Γ -phase com-

pound behaves more or less as a general compound with a complex crystal structure, and the characteristic feature in the crystal structure to be described with packing of coordinated polyhedra (icosahedra) is not important to describe the plastic deformation behavior.

3.4. Correlation of Plastic Behavior with Building Principle of Crystal Structure

The variation of CRSS (for slip deformation), hardness and fracture toughness with intermetallics compounds in the Fe–Zn system are illustrated in Figs. 13(a)–13(c), respectively. The CRSS values plotted in Fig. 13(a) are from our micropillar compression tests.^{19,68)} Plastic flow is observed for four intermetallics (ζ , δ_{1p} , δ_{1k} and Γ) except for Γ_1 . Three intermetallics, ζ , δ_{1p} and Γ , have two operative slip systems. In the plot of the hardness values (Fig. 13(b)) taken from

Fig. 13. Variation of (a) CRSS values,¹⁹⁾ (b) hardness⁷¹⁾ and (c) fracture toughness⁷²⁾ of the intermetallic compounds in the Fe–Zn system. As the dashed curve in Fig. 13(a) indicates, the trend in the variation of the CRSS values for the major slip system with compounds is very similar to the hardness trend. (Online version in color.)

Ref. 71, the value for the δ_1 phase is plotted without differentiating δ_{1p} and δ_{1k} . The fracture toughness values plotted in Fig. 13(c) are from our microbeam bending tests, whose results as well as experimental procedures are described in detail in a separate paper⁷²⁾ in this special issue. If we take the CRSS value for the major slip system (with the lower CRSS value) for each of the four intermetallics, the trend for CRSS values (dashed curve in Fig. 13(a)) is surprisingly very similar to the hardness trend explored a long time ago by Bastin *et al.*⁷¹⁾ (Fig. 13(b)). This may indicate that the hardness value also reflects the variation of chemical bonding in the compounds, as described in the following.

The bonding between Fe and Zn atoms is so strong that slip deformation occurs at a low stress level if any of Fe-centered Zn_{12} icosahedra are not destroyed during slip deformation. This is possible for the ζ phase compound, since in the crystal structure, Fe-centered Zn_{12} icosahedra are linked to one another by vertex-sharing to form a chain of Zn_{12} icosahedra along the c -axis. So, the $\{110\}$ plane is selected so as not to destroy the vertex-shared c -axis chains of Fe-centered Zn_{12} icosahedra, and the lowest CRSS value was observed for the corresponding slip. The CRSS value increases for the δ_{1p} phase, in which normal Fe-centered Zn_{12} icosahedra are linked to one another by face- and vertex-sharing forming two types of basal slabs, which are bridged with each other by face-sharing with icosioctahedra. Because of the incorporation of face-sharing in the linkage mode among Fe-centered Zn_{12} icosahedra in the δ_{1p} phase, Fe-centered Zn_{12} icosahedra have to be inevitably destroyed, breaking chemical bondings between Fe and Zn atoms in the icosahedra during slip, whatever the slip plane is. This is the reason for the higher CRSS value of $(0001)\langle 2110 \rangle$ slip in the δ_{1p} phase. However if the Fe content increases considerably as in the Γ phase so that Fe atoms occupy not only the center of icosahedra but also the vertex sites of these icosahedra to form Fe-centered $(Zn,Fe)_{12}$ icosahedra and the triangle face sites to share icosahedra by face-sharing are occupied mostly by Fe atoms, the description of the crystal structure by the packing of coordinated polyhedra becomes less important and the crystal structure can be better described simply as a general compound with a complex crystal structure. Then, the characteristic feature in the crystal structure to be described with packing of coordinated polyhedra (icosahedra) is not important to describe the plastic deformation behavior. We believe this is the reason for the smaller CRSS value in the Γ phase than in the δ_{1p} phase.

Of importance to notice is that the δ_{1p} phase, the major constituent phase in the coating layer of GA steels in practical use, possesses plasticity as well as the fracture toughness value which is the highest among the five intermetallics (Fig. 13(c)).⁷²⁾ This means that the microstructure of the coating layer with the δ_{1p} phase being the major (thickest) constituent phase is indeed a very reasonable choice of microstructure. However, the CRSS value (strength) of the δ_{1p} phase seems to be a bit too high when compared with those of the other intermetallics in the Fe–Zn system. If the strength of the δ_{1p} phase is reduced, we may expect better formability of GA steels without being bothered by the problem called ‘powdering’. This may be achieved by changing the crystal structure of the δ_{1p} phase, for example by alloying, so that the extent of vertex-sharing (instead

of face-sharing) among Fe-centered Zn_{12} icosahedra is increased as in the case of the ζ phase, or that the crystal structure becomes more complicated to behave as a general compound as in the case of the Γ phase.

4. Conclusions

(1) There is a building principle of the crystal structures for intermetallics of the Fe–Zn system. The crystal structures of all the Fe–Zn intermetallics can be best understood by considering the packing of coordinated polyhedra with the common structural unit being the Zn_{12} and/or $(Zn,Fe)_{12}$ icosahedron whose central site is *exclusively* occupied by an Fe atom. When the Fe content is increased so that all Fe atoms cannot be accommodated in the central sites of these icosahedra, these excess Fe atoms occupy vertices of some icosahedra together with Zn atoms forming $(Zn,Fe)_{12}$ icosahedron. As the Fe content of the Fe–Zn intermetallics increases, (i) the linkage geometry among the Fe-centered icosahedra changes from vertex-sharing to face-sharing, (ii) the atoms occupancy (either Zn or Fe atoms) at the face-sharing sites changes from exclusive occupancy by Zn atoms to mixed occupancy by Zn and Fe atoms and to exclusive occupancy by Fe atoms, and (iii) the fraction of isolated Zn atoms decreases.

(2) Plastic deformation occurs in four intermetallic compounds, Γ , δ_{1p} , δ_{1k} and ζ phases. The variation of CRSS values with intermetallics can be well correlated with the building principle of the crystal structures described above. The selection of slip planes is closely related to the arrangement of Fe-centered Zn_{12} icosahedra. The slip plane is determined so as not to break any Fe–Zn atomic bondings within the Fe-centered Zn_{12} icosahedra during slip. This is particularly the case for the intermetallics with a lesser Fe content, the ζ phase, in which the linkage mode among Fe-centered Zn_{12} icosahedra is only vertex-sharing. But, once face-sharing occurs in the linkage mode among Fe-centered Zn_{12} icosahedra as in the δ_{1p} phase, some Fe–Zn atomic bondings within the Fe-centered Zn_{12} icosahedra are inevitably broken during slip, resulting in the higher CRSS value.

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