Fracture Toughness of the Fe–Zn Intermetallic Compounds Measured by Bend Testing of Chevron-Notched Single-Crystal Microbeams

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The fracture toughness values of the five intermetallic compounds in the Fe–Zn system have been investigated through bend testing of chevron-notched single-crystal microbeams. The intermetallic compounds of the Fe-lean phases, $\delta_{1p}$ and $\zeta$, exhibit fracture toughness values higher than the other compounds of the Fe-rich phases, $\Gamma_1$, $\Gamma$, and $\delta_{1k}$. The $\delta_{1p}$ phase exhibits a strong anisotropy in fracture toughness while the other four compounds exhibit almost no anisotropy. The compositional dependence of fracture toughness is discussed in terms of the surface energies estimated by ab initio calculations as well as the capability of stress relaxation around a crack by dislocation emission. The $\Gamma$ phase with a relatively wide solid solubility range exhibits no compositional dependence of the fracture toughness. The fracture toughness value of $\Gamma$-phase microbeams that include a grain boundary at the chevron-notch position is comparable to that of the $\Gamma$-phase single-crystal microbeams, indicating that the grain boundaries in the $\Gamma$ phase may not be particularly weak.

KEY WORDS: galvannealed steel; crystal anisotropy; surface energy; grain boundary; focused ion beam; electron back scatter diffraction; ab initio calculations.

1. Introduction

Galvannealed (GA) steel sheets are used in a wide variety of industrial fields because of their excellent corrosion-resistance, weldability and paintability. The coating layer usually consists of multilayers of the five intermetallic compounds in the Fe–Zn system: $\Gamma$, $\Gamma_1$, $\delta_{1k}$, $\delta_{1p}$ and $\zeta$ in decreasing order of the Fe content. Due to their complex crystal structures comprising the common structural unit, Fe-centered Zn$_{12}$ or (Zn,Fe)$_{12}$ icosahedron these intermetallic compounds have been considered to be brittle. When the heat-treatment is excessive, the coating consists mainly of the Fe-rich $\Gamma$ and $\Gamma_1$ phases with high hardness, resulting in intracoating cracking to form fine particles (powdering). When the heat-treatment is insufficient, on the other hand, the coating consists mostly of the soft $\zeta$ phase and unalloyed zinc, resulting in flaking-off of the coating layer from the substrate (flaking). Thus, the steel making industry has generally adopted moderate heat-treatment conditions to achieve the optimum formability of GA steels, avoiding the above two problems. In this case, the coating layer consists mostly of the $\delta_1$ ($\delta_{1k}/\delta_{1p}$) phase. Therefore, the $\delta_1$ ($\delta_{1k}/\delta_{1p}$) phase has been believed to be relatively ductile while the $\Gamma$ phase has been empirically considered significantly brittle based on the positive correlation between the thickness of the $\Gamma$ phase and the extent of the powdering. However, Munekane et al. reported that both the $\Gamma_1$ and $\delta_1$-phase compounds exhibit plastic flow under uniaxial compression of GA steels, while Inoue et al. have recently reported that the $\Gamma_1$ and $\delta_1$($\delta_{1k})$-phase compounds exhibit similarly low values of fracture toughness from the measurement on a single-phase polycrystalline layer of the $\Gamma$ or $\delta_{1k}$ phase formed on a steel sheet. In addition, Ploypech et al. have reported that cracks nucleated in the $\delta_1$-phase layer propagate as to penetrate to the surface, inferring the low fracture toughness of the $\delta_1$ phase. On the other hand, Shi et al. indicated that the most brittle region in the coating is between the $\Gamma$- and $\delta_1$-phases (presumably the $\Gamma_1$- or $\delta_{1k}$-phase layer). These disagreements may be attributed to the difficulties in distinguishing the $\Gamma$/$\Gamma_1$ and $\delta_{1k}/\delta_{1p}$ phases in the multilayer coating of GA steels, or to the fact that they have not been actually distinguished in most investigations of the mechanical properties of the intermetallic compounds, because the structural differences between the phases have relatively recently been revealed.

In order to advance the knowledge about the mechanical properties (plastic deformability, fracture toughness, etc.), it is necessary to carry out mechanical tests on single-phase (and single-crystal if allowed) specimens of each of the intermetallic phases to directly compare their mechanical properties. However, the mechanical properties of...
single-phase specimens have rarely been elucidated because each phase formed in the coating layer of GA steel is very thin (at most a few micrometers in thickness), and also because it is difficult to obtain a single-phase microstructure or large single crystals of each of the intermetallic phases due to their peritectic/peritectoid reactions.\(^{2,6}\) However, the recent development of microfabrication with the use of the focused ion beam (FIB) method and nanoindentation techniques have made it possible to carry out mechanical testing on small specimens at the micrometer scale.\(^{24-28}\) We have applied this microscale testing to all these five intermetallics and found that the \(\Gamma\)-phase compound is the most deformable in compression in the polycrystalline form among the five intermetallic compounds in the Fe–Zn system,\(^{29}\) which seems incompatible with the empirical knowledge that the \(\Gamma\)-phase compound is significantly brittle. We have also found that micropillars of the \(\zeta\), \(\delta_1\), and \(\delta_3\) phases exhibit plasticity in compression in the single-crystal form.\(^{30-32}\) In addition to the compression deformability, however, the fracture toughness of each of the intermetallic compounds is essential to improve the understanding of the coating failure in GA steels. In the present study, therefore, we measure the fracture toughness values of each of the compounds by bend testing of chevron-notched single-crystal cantilever microbeams,\(^{33}\) which are FIB-machined from polycrystals with a relatively large grain size.

2. Experimental Procedures

2.1. Crystal Growth

A solution growth method was employed to grow large crystal grains of the \(\Gamma\), \(\delta_1\), \(\delta_3\), and \(\zeta\) phases taking advantages of their peritectic reactions while a solid-state reaction of Zn and Fe powder was employed for the \(\Gamma_1\) phase because of its peritectoid reaction.\(^{2,6}\) Experimental details of the crystal growth are described elsewhere.\(^{7,8,11,30}\) Although we failed to grow large single crystals of the \(\Gamma\), \(\Gamma_1\), and \(\zeta\) phases, relatively large crystallites (from several ten to hundred micrometers in diameter) are obtained.\(^{11,30}\) On the other hand, we obtained large single crystals (~10 mm) of the \(\delta_1\) and \(\delta_3\) phases containing many microcracks.\(^{7,8}\) The chemical compositions measured on several crystals by energy dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (SEM) were Zn-22.4\(\pm\)0.3 at.%Fe (\(\Gamma\)), Zn-20.6\(\pm\)0.4 (\(\Gamma_1\)), Zn-13.0\(\pm\)0.4 (\(\delta_1\)), Zn-9.7\(\pm\)0.4 (\(\delta_3\)), Zn-8.4\(\pm\)0.3 at.%Fe (\(\zeta\)), respectively.

2.2. Bend Testing of Single-crystal Cantilever Microbeams

We employed bend testing on chevron-notched cantilever microbeams to obtain fracture toughness values because no fatigue precrack is needed to be introduced and a chevron-notched specimen will self-precrack without specially designed fixtures of a stiff loading system.\(^{33,34}\) During loading on a chevron-notched cantilever beam, a crack is nucleated at the apex of the ligament and propagates in a stable manner (precrack) before the load reaches the maximum followed by unstable crack propagation. The fracture toughness value \(K_{IC}\) of a chevron-notched specimen is calculated only from the maximum test load \(P_{max}\) and the geometric parameters \((B, W, S, a_0, \text{ and } a_1)\) as indicated in

\[
K_{IC} = \frac{P_{max}}{BW^{0.5}} Y' (a, a_0, a_1, B, W, S)_{\mu=ac} \quad \text{(1)}
\]

where \(Y'\) is the dimensionless geometric factor of a chevron-notched specimen determined by specimen compliance and \(ac\) is the critical crack length (distance between the top of the cantilever beam and the crack tip at the transition from stable to unstable crack propagation, see Fig. 1(b)). Both \(Y\) and \(ac\) are functions only of the geometric parameters and are independent of material properties.\(^{37}\)

Single-crystal microbeams with a chevron notch as schematically shown in Fig. 1 were machined from the grown crystallites (\(\Gamma, \Gamma_1, \zeta\)) or single crystals (\(\delta_1, \delta_3\)) with a JEOL JIB-4000 focused ion beam (FIB) apparatus at an operating voltage of 30 kV. The weakest Ga\(^+\) ion beam current (5 pA) was used to introduce a sufficiently sharp chevron notch into microbeams. In order to investigate the crystal anisotropy of fracture toughness, the low-indexed Miller plane with the largest interplanar distance and higher-indexed Miller planes with smaller interplanar distances are selected to be parallel to the chevron-notch plane for each of the five intermetallic compounds, because the surface energy of the low-index plane with the largest interplanar distance is expected to be the smallest at a first approximation, exhibiting the lowest fracture toughness.

Bend testing were conducted for the chevron-notched single-crystal microbeams with a cube-corner diamond indenter using a Nanomechanics\(^{6}\) G200 nanoindentation apparatus at room temperature and at a displacement rate of 5 nm/s. Displacement control is managed by utilizing a feedback method though nanoindentation testing is usually operated under force control. Deformed and fractured specimens were observed by SEM.

3. Results

3.1. \(\Gamma\) Phase

The \(\Gamma\) phase crystallizes in the so-called \(\gamma\)-brass structure of body-centered cubic symmetry.\(^{11,12}\) The chevron-notch plane was selected to be parallel to the (110) plane with the largest interplanar distance ((110)\(\text{Zn-ic}\): 0.135 nm as shown in Fig. 2(a) as well as to a higher-indexed Miller plane, (234), to investigate the anisotropy of fracture toughness. As shown in the selected load-displacement curves of Fig. 3(a), the single-crystal microbeams of the \(\Gamma\) phase fractured in the linear elastic region. Figure 3(b) indicates a typical SEM secondary electron image (SEI) of the (110) chevron-notched microbeam after the bend test as well

![Fig. 1. Schematic illustrations of (a) a chevron-notch cantilever microbeam and (b) the notch shape.](image-url)
as a magnified frontal image of the fracture surface. The crack propagated parallel to the notched plane and the fracture surface is almost perfectly flat. This is also the case for the (234) chevron-notched microbeams (not shown), indicating that the fracture occurred in a brittle manner without preferential cleavage planes for the phase. The geometric parameters and maximum test load for selected single-crystal microbeams and fracture toughness values averaged over microbeams with the same notch plane are tabulated in Table 1. The fracture toughness values for the (110) and (234) chevron-notched microbeams are almost identical with each other, showing no anisotropy in fracture toughness of the phase.

### 3.2. \(\gamma\)-\(\delta\) Phase

\(\gamma\) phase crystallizes in the so-called \(\gamma\)'-brass structure of face-centered cubic symmetry, which is recognized as the doubled \((2\times2\times2)\) superstructure of the \(\gamma\)-brass structure (\(\Gamma\) phase).

The chevron-notch plane was selected to be parallel to the (110) plane with the largest interplanar distance ((110)Fe-Zn: 0.137 nm as shown in Fig. 2(b)) as well as to a higher-indexed Miller plane, (124), to investigate the for the (234) chevron-notched microbeams (not shown), indicating that the fracture occurred in a brittle manner without preferential cleavage planes for the \(\Gamma\) phase. The geometric parameters and maximum test load for selected single-crystal microbeams as well as the fracture toughness value averaged over microbeams with the same notch plane are tabulated in Table 1. The fracture toughness values for the (110) and (234) chevron-notched microbeams are almost identical with each other, showing no anisotropy in fracture toughness of the \(\Gamma\) phase.

#### Table 1. Geometric parameters \((B, W, S, a_0, a_1)\), critical crack length \((a_C)\) and the first local maximum load \((P_{\text{max}})\) for selected single-crystal microbeams, and fracture toughness averaged over microbeams with the same notch plane.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Notch plane</th>
<th>(B) ((\mu m))</th>
<th>(W) ((\mu m))</th>
<th>(S) ((\mu m))</th>
<th>(a_0) ((\mu m))</th>
<th>(a_1) ((\mu m))</th>
<th>(a_C) ((\mu m))</th>
<th>(P_{\text{max}}) ((mN))</th>
<th>Fracture toughness (K_{IC}, K_{Q}) ((\text{MPa}\cdot\text{m}^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma)</td>
<td>(110)</td>
<td>3.80</td>
<td>5.02</td>
<td>9.11</td>
<td>2.54</td>
<td>3.84</td>
<td>3.03</td>
<td>0.208</td>
<td>0.45±0.01</td>
</tr>
<tr>
<td></td>
<td>(234)</td>
<td>3.21</td>
<td>4.58</td>
<td>9.99</td>
<td>0.85</td>
<td>2.20</td>
<td>1.23</td>
<td>0.269</td>
<td>0.40±0.07</td>
</tr>
<tr>
<td>(\Gamma_1)</td>
<td>(110)</td>
<td>3.06</td>
<td>4.96</td>
<td>9.62</td>
<td>1.89</td>
<td>3.33</td>
<td>2.42</td>
<td>0.223</td>
<td>0.39±0.05</td>
</tr>
<tr>
<td></td>
<td>(124)</td>
<td>3.36</td>
<td>4.50</td>
<td>11.16</td>
<td>1.69</td>
<td>2.71</td>
<td>2.10</td>
<td>0.199</td>
<td>0.40±0.02</td>
</tr>
<tr>
<td>(\delta_k)</td>
<td>(0001)</td>
<td>3.44</td>
<td>4.32</td>
<td>9.20</td>
<td>1.90</td>
<td>3.36</td>
<td>2.39</td>
<td>0.180</td>
<td>0.44±0.07</td>
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<tr>
<td></td>
<td>(11(\overline{2})9)</td>
<td>3.31</td>
<td>4.22</td>
<td>9.23</td>
<td>1.17</td>
<td>2.71</td>
<td>1.67</td>
<td>0.214</td>
<td>0.37±0.02</td>
</tr>
<tr>
<td>(\delta_p)</td>
<td>(0001)</td>
<td>3.00</td>
<td>4.22</td>
<td>9.14</td>
<td>1.79</td>
<td>3.35</td>
<td>2.29</td>
<td>0.315</td>
<td>1.16±0.19</td>
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<tr>
<td></td>
<td>(11(\overline{2})0)</td>
<td>2.99</td>
<td>4.18</td>
<td>8.58</td>
<td>0.53</td>
<td>2.02</td>
<td>0.87</td>
<td>0.490</td>
<td>0.57±0.03</td>
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<tr>
<td></td>
<td>(1(\overline{1})00)</td>
<td>3.01</td>
<td>4.78</td>
<td>8.82</td>
<td>1.86</td>
<td>3.37</td>
<td>2.39</td>
<td>0.400</td>
<td>0.81±0.07</td>
</tr>
<tr>
<td></td>
<td>(11(\overline{2})9)</td>
<td>3.21</td>
<td>4.94</td>
<td>9.26</td>
<td>2.44</td>
<td>4.16</td>
<td>2.98</td>
<td>0.430</td>
<td>1.16±0.20</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>(110)</td>
<td>3.48</td>
<td>5.20</td>
<td>9.33</td>
<td>1.02</td>
<td>2.76</td>
<td>1.52</td>
<td>0.752</td>
<td>0.64±0.05</td>
</tr>
<tr>
<td></td>
<td>(14(\overline{2})3)</td>
<td>3.89</td>
<td>4.74</td>
<td>9.61</td>
<td>1.64</td>
<td>3.19</td>
<td>2.18</td>
<td>0.394</td>
<td>0.71±0.14</td>
</tr>
</tbody>
</table>

*Only one microbeam specimen was tested for the notch plane.*
anisotropy of fracture toughness. Similarly to the $\Gamma$ phase, the single-crystal microbeams of the $\Gamma_1$ phase fractured in the linear elastic region as shown in Fig. 3(a). The crack propagated parallel to the notched plane and the fracture surface is almost perfectly flat as shown in Fig. 3(c) not only for the (110) chevron-notched microbeams but also for the (234) ones (not shown), indicating that the fracture occurred in a brittle manner without preferential cleavage planes for the $\Gamma_1$ phase. The fracture toughness value averaged over microbeams with the same notch plane for the $\Gamma_1$ phase are also tabulated in Table 1. The fracture toughness values for the (110) and (124) chevron-notched microbeams are almost identical with each other within the margin of error, showing no anisotropy in fracture toughness of the $\Gamma_1$ phase.

### 3.3. $\delta_k$ Phase

The $\delta_k$ phase possesses a tripled ($\sqrt{3}a \times \sqrt{3}a$) superlattice structure based on the hexagonal structure of the $\delta_p$ phase. However, the $\delta_k$ phase lacks a translational symmetry along the hexagonal c-axis, resulting in the so-called order-disorder (OD) structure. Thus, the Miller index notation cannot be applied rigorously to the $\delta_k$ phase. Nonetheless, we referred to the hexagonal Miller index notation of the $\delta_p$ phase to express planes in the $\delta_k$ phase. Although the detailed atomic arrangement in the $\delta_k$ phase has yet to be determined, the (0001) basal plane is expected to have the largest interplanar distance as in the case of the $\delta_p$ phase (next section, see Fig. 2(c)). Thus, the (0001) plane was selected as the chevron-notch plane. The (1129) pyramidal plane, a higher-index Miller plane, was also selected as the chevron-notch plane. The results of the bend testing of the (0001) and (1129) chevron-notched microbeams of the $\delta_k$ phase are very similar to those of the previous $\Gamma$ and $\Gamma_1$ phases: exhibiting brittle fracture without preferential cleavage planes and no anisotropy in fracture toughness.

### 3.4. $\delta_p$ Phase

The $\delta_p$ phase crystallizes in a large hexagonal unitcell with a large $c/a$ axis ratio ($c/a = 4.47$), containing 52 Fe and 504 Zn atoms. The chevron-notch plane was selected to be parallel to the (0001) basal plane with the largest interplanar distance ([0001]$_{\text{Fe}-\text{Zn}}$: 0.126 nm as shown in Fig. 2(c)) as well as to the (1129) pyramidal plane, as a higher-indexed Miller plane. The (1120) and (1100) prism planes were also selected as the chevron-notch plane to investigate the anisotropy of fracture toughness. Selected load-displacement curves for bend testing of the chevron-notched microbeams of the $\delta_p$ phase are shown in Fig. 4(a). The load initially increases linearly against the indenter displacement and starts to deviate from the linearity, which is associated with crack nucleation and stable crack extension. Then, the load reaches a local maximum as indicated by arrow (Fig. 4(a)) followed by a gradual decrease. Further, the load smoothly goes up and down repeatedly followed by final catastrophic fracture during load increase. The first local maximum load was taken as $P_{\text{max}}$ in Eq. (1) to calculate fracture toughness values because the load drop is considered to correspond to unstable crack propagation. Figures 4(b)–4(d) show typical perspective images and magnified frontal images of the fracture surface for the (0001), (1120), and (1129) chevron-notched microbeams after the bend testing, respectively. While the fracture surface for the (0001) specimen is almost parallel to the notched plane (Fig. 4(b)), those for the (1120) and (1129) specimens are inclined from the notched plane by $\sim 20^\circ$ (Figs. 4(c), 4(d)). While the fracture surface for the (1120) specimen is almost flat (Fig. 4(c)), those for the (0001) and (1129) specimens near the apex of the triangle ligament are relatively rough showing river markings, typical morphological features of quasi-brittle fracture (Figs. 4(b), 4(d)). This implies that plastic deformation is involved in the fracture process in the $\delta_p$ phase. The fracture toughness value averaged over microbeams with the same notch plane are tabulated in Table 1. The fracture toughness values for the (0001) and (1129) chevron-notched microbeams (1.16 MPa m$^{1/2}$) are more than twice larger than that for...
the (1120) specimen (0.57 MPa·m^{1/2}), showing significant anisotropy in fracture toughness of the δ_{1p} phase.

3.5. ζ Phase

The ζ phase crystallizes in the smallest unit cell among the five Fe–Zn intermetallic compounds, containing 28 atoms per unit cell although the crystal system is monoclinic of low symmetry.13,30) The chevron-notch plane was selected to be parallel to the (110) plane with the largest interplanar distance ([110]_{Zn–Zn}: 0.141 nm as shown in Fig. 2(d)) as well as to the (1423) plane, a higher-index Miller plane. The results of the bend testing of the ζ phase are somewhat similar to those of the previous δ_{1p} phase: the load-displacement curves exhibit a local maximum as indicated by arrow in Fig. 5(a) followed by final catastrophic fracture. As shown in Figs. 5(b) and 5(c), the fracture surface near the apex of the notch ligament are relatively rough showing river markings, indicating quasi-brittle fracture. The fracture toughness values calculated by taking the first local maximum load as \( P_{\text{max}} \), averaged over microbeams with the same notch plane, are tabulated in Table 1.

4. Discussions

4.1. Validity of the Fracture Toughness Values

The derivation of the fracture toughness in this work is within the linear elastic fracture mechanics, which assume infinite local stresses at the crack tip. In reality, a microscopic plastic deformation zone is formed near the crack tip even in brittle materials, mitigating the infinitely large stress concentration. For bulk-size specimens, the elastic deformation region which is not affected by the stress concentration around the crack rim (linear regime) is dominant. For micrometer-size specimens, however, it is not necessarily guaranteed that the microscopic plastic deformation zone is small enough compared to the specimen size (small-scale yielding condition). In addition, the specimen should satisfy the plane strain condition because the fracture toughness values are independent of the specimen size under the plane strain condition while they depend on the specimen size and are overestimated under plane stress condition. The specimen size requirement to obtain the size-independent fracture toughness given by the ASTM standard E-130441) is expressed with the following inequality:42)

\[ B \geq 1.25 \left( \frac{K_o}{\sigma_Y} \right)^2 \]

where \( \sigma_Y \) is the material’s 0.2% offset yield strength and \( K_o \) is the conditional fracture toughness obtained by using Eq. (1) (“conditional” means that the toughness value calculated with Eq. (1) may not be valid as a plane-strain fracture toughness value \( K_{IC} \) unless the tested specimen satisfies the above size requirement). Here, the 0.2% offset yield strength or fracture strength obtained by polycrystalline micropillar compression testing29) were used as \( \sigma_Y \) and tabulated in Table 2. The minimum specimen size calculated for the ζ, \( \Gamma \), \( \Gamma_1 \), \( \delta_1 \) and \( \delta_{1p} \) phases are smaller than 1 \( \mu m \), which is much smaller than the microbeam width \( B \) (large than 3 \( \mu m \) for all tested microbeams), indicating that the fracture toughness values obtained for the four phases are valid and can be regarded as \( K_{IC} \). However, the required minimum specimen size for the ζ phase is significantly large (42.53 \( \mu m \)) due to its relatively low yield strength, which is far larger than the specimen size, indicating that the conditional fracture toughness value obtained for the ζ phase is not valid and cannot be regarded as \( K_{IC} \).

In the derivation of the fracture toughness value (Eq. (1)), the thickness (gap) of the chevron notch, caused by the broadness of the FIB ion beam, is not taken into consideration. Kolhe et al.35) have evaluated the allowable

![Fig. 5.](image)
chevron-notch thickness $t_c$ by a 3-dimensional finite element method:

$$t \leq t_c = \frac{ac - a_0}{2} \quad \quad \quad \quad \quad \quad (3)$$

The values of $t_c$ for the microbeam specimens tested in the present study were between 0.17 and 0.27 μm. We confirm that the chevron-notch thickness of any of the tested microbeam specimens was kept below 0.15 μm by the usage of the weakest Ga$^+$ ion beam and is smaller than the allowable thickness.

4.2. Composition Dependence of Fracture Toughness

4.2.1. Composition Dependence Over the Five Intermetallic Compounds

The fracture toughness values averaged over microbeams with the same notch plane are summarized in a bar graph shown in Fig. 6(a) (K IC for the Γ, Γ1, δ1k, and δ1p phases and K O for the ζ phase). As an overall trend, the fracture toughness values for the Fe-rich phases (Γ, Γ1, δ1k) are smaller than those for the Fe-lean (Zn-rich) phases (δ1p, ζ). A similar trend is observed in the fracture toughness values of the Γ, δ1k and δ1p phases (0.40, 0.44 and 0.75 MPa m$^{1/2}$, respectively) reported by Inoue et al. It is somewhat surprising that the δ1p phase with the huge unitcell exhibits the largest fracture toughness among the five compounds. We discuss this compositional dependence of fracture toughness in terms of the surface energy $\gamma_s$, a measure of the resistance against the crack propagation, as well as the plastic deformability in the small scale regime around the crack tip in the following paragraphs.

The stress intensity factor near the crack tip, so-called local stress intensity factor $K_I^{local}$, can be considered to be the sum of the contribution from an external tensile stress ($K_I$) and that from dislocations emitted from the crack tip ($k_D$):

$$K_I^{local} = K_I + k_D \quad \quad \quad (4)$$

The fracture toughness $K IC$ is the critical value of $K_I$ when the strain energy release rate $G$ expressed with the following equation,

$$G = \frac{1}{E} \left( K_I^{local} \right)^2 \quad \quad \quad (5)$$

reaches twice the surface energy ($2\gamma_s$), where $E$ is Young’s modulus and $v$ is Poisson’s ratio. At the critical point, the local stress intensity factor $K_I^{local}$ equals $\sqrt{2E\gamma_s/(1-v^2)}$. Thus, the fracture toughness can be expressed with the following equation:

$$K IC = \sqrt{\frac{2E\gamma_s}{1-v^2}} - k_D \quad \quad \quad (6)$$

The $k_D$ value is usually negative in sign because the stress field of the dislocations emitted from the crack tip is compressive to mitigate the tensile stress concentration around the crack induced by the external stress. Thus, the magnitude of the fracture toughness is determined by the crystal bonding strength (first term) as well as the ability of stress relaxation by dislocations (second term).

Since no experimental data of the surface energies of the Fe–Zn intermetallic compounds have been available, we carried out density functional theory (DFT) calculations to theoretically estimate the surface energies for the Γ, Γ1, δ1p, and ζ phases$^1$ by using the projector augmented wave method$^{46}$ and the electronic exchange correlation effects were described by the generalized gradient approximation$^{47}$ within the Perdew-Burke-Ernzerhof functional as implemented in the Vienna Ab initio Simulation Package (VASP).$^{48}$ Three or four crystallographic planes of low index and/or of large interplanar distance (Fig. 2 and Table 3) were selected as the surface. Supercells of corresponding crystals with two surfaces as well as a vacuum layer thicker than 1.6 nm were built. A plane wave energy cut-off of 480 eV was used. The $k$-point meshes were chosen to ensure a convergence of the total energy within 1 meV per atom for the Γ and ζ phases while the $k$-point calculation was done for the Γ1 and δ1p phase with the huge unitcell.$^{7,11,38}$ Atomic relaxations were performed for the original unitcell until the energy and forces converged to 10$^{-5}$ eV and 10$^{-2}$ eVnm$^{-1}$, respectively, while they were not performed on the supercells with surfaces. The calculated surface energies for each of the surface planes are tabulated in Table 3. As an overall trend, the surface energy increases with the increase in the Fe content (Γ > Γ1 > δ1p > ζ). This is attributed to the fact that the Fe–Fe and Fe–Zn atomic bonds are stronger

\footnote{The calculation of surface energy of the δ1k phase cannot be carried out not only because the atomic positions have not been determined yet but also because it lacks the translational symmetry along the c-axis direction.$^{36}$}
than the Zn–Zn atomic bonds and the ratio of the stronger bonds is larger for the Fe-rich phases.\(^{11,30}\) Within the same phase, the surface energy for the surface terminated with mostly Fe atoms (“Fe–Zn” is denoted as a subscript to the phase, the surface energy for the surface terminated with only or mostly Zn atoms (“Zn–Fe”, respectively) regardless of the interplanar distance: for example, the surface energy of the (0001)Zn–Fe plane in the δ\(_p\) phase with the larger interplanar distance is larger than the Zn–Zn plane in the δ\(_p\) phase.

The first term of the right side \(\sqrt{2E_S/\left(1-v^2\right)}\) in Eq. (6) is calculated by using the surface energy, and Young’s modulus\(^{21,49}\) and assuming Poisson’s ratio to be 0.3 for all the intermetallic compounds (see Table 4). The value of \(\sqrt{2E_S/\left(1-v^2\right)}\) tends to increase with the increase in the Fe content \((\Gamma > \Gamma_1 > \delta_{\text{lp}} > \zeta)\) because both the surface energy and Young’s modulus increase with increasing Fe content as tabulated in Table 4. However, this tendency of the value of \(\sqrt{2E_S/\left(1-v^2\right)}\) is opposite to that of the measured fracture toughness, which tends to decrease with increasing Fe content (Fig. 6(a)). This results from the stress intensity factor contributed from dislocations \((k_D)\), which tends to increase from negative to positive values as the Fe contents increases, although the value of \(k_D\) is usually negative in sign as mentioned previously.\(^2\) In other words, the ability of stress relaxation by plastic deformation decreases with increasing Fe content. This is consistent with our recent results of single-crystal micropillar compression for the \(\Gamma, \delta_{\text{Ik}}, \delta_{\text{lp}}\) and \(\zeta\) phases that the CRSS value almost monotonically increases with increasing Fe content \((\delta_{\text{Ik}}\) and \(\delta_{\text{lp}}\) were pre-strained by Vickers indentation before the FIB-machining of the micropillars.\(^{30–32}\)

4.2.2. Composition Dependence within the \(\Gamma\)-phase Solid Solubility Range

The \(\Gamma\) phase possesses a relatively wide solid solubility range (22–32 at.%Fe).\(^{6,11}\) In order to investigate whether the \(\Gamma\) phase exhibits the composition dependence of fracture toughness, we carried out bend testing of chevron-notched single-crystal microbeams of the \(\Gamma\) phase with the Fe-rich composition (Zn-30.4 at.%Fe). The growth method of the Fe-rich crystallite is described elsewhere.\(^{11}\) As shown in Fig. 6(b), the fracture toughness value of the Fe-rich \(\Gamma\) phase (30.4 at.%Fe) is virtually identical with that of the Fe-lean one (22.4 at.%Fe) described previously.

4.2.3. Difference between the \(\delta_{\text{lp}}\) and \(\delta_{\text{Ik}}\) Phases

As is often the case, the \(\delta_{\text{lp}}\) and \(\delta_{\text{Ik}}\) phases have not been distinguished but treated as the “\(\delta\)” phase in both research and industrial fields. This will be because it is very difficult to distinguish them by optical microscopy or SEM due to the subtle morphological and compositional differences. Electron diffraction\(^{23}\) and scanning transmission electron microscopy\(^{30}\) make the distinction between the two phases easier and revealed that the difference in the crystal structures of the phases is not marginal as described in Section 3.3. The fact that the \(\delta_{\text{Ik}}\) phase lacks the translational symmetry along one direction seems to reduce its fracture toughness desperately. The large difference in the fracture toughness between the \(\delta_{\text{lp}}\) and \(\delta_{\text{Ik}}\) phases manifests that the two phases must definitely be distinguished in considering the mechanical properties of the coating layer of GA steel.

4.3. Grain Boundary Strength of the \(\Gamma\) Phase

Inoue et al.\(^{19}\) have adroitly fabricated a single-phase polycrystalline layer of the \(\Gamma\) phase formed on a steel sheet and measured its fracture toughness as a function of average grain size by evaluating the crack interval in the \(\Gamma\)-phase layer after uniaxial tensile testing of the \(\Gamma\)/steel sheet. The fracture toughness values for polycrystals with an average grain size of 0.87 and 2.97 \(\mu\)m are 0.41 and 0.22 MPa m\(^{1/2}\), respectively (Fig. 6(b)).\(^{19}\) The former value with the smaller grain size is comparable to that of the single crystals obtained in the present study (0.42 ± 0.06

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**Table 3.** Surface energies for the \(\Gamma, \Gamma_1, \delta_{\text{lp}}, \) and \(\zeta\) phases calculated by the DFT calculations.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Plane</th>
<th>Interplanar distance (nm)</th>
<th>Surface energy (J/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma)</td>
<td>(110)Zn-Fe</td>
<td>0.135</td>
<td>1.23</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>(110)Zn-Zn</td>
<td>0.129</td>
<td>1.89</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>(100)Zn-Fe</td>
<td>0.095</td>
<td>1.79</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>(100)Zn-Zn</td>
<td>0.046</td>
<td>1.74</td>
</tr>
<tr>
<td>(\delta_{\text{lp}})</td>
<td>(0001)Zn-Zn</td>
<td>0.126</td>
<td>1.43</td>
</tr>
<tr>
<td>(\delta_{\text{lp}})</td>
<td>(0001)Zn-Fe</td>
<td>0.008</td>
<td>1.22</td>
</tr>
<tr>
<td>(\delta_{\text{lp}})</td>
<td>(11\overline{2}0)</td>
<td>0.093</td>
<td>1.39</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>(110)Zn-Fe</td>
<td>0.141</td>
<td>0.93</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>(110)Zn-Zn</td>
<td>0.136</td>
<td>1.23</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>(100)Zn-Fe</td>
<td>0.082</td>
<td>1.01</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>(100)Zn-Zn</td>
<td>0.064</td>
<td>0.80</td>
</tr>
</tbody>
</table>

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**Table 4.** Averaged fracture toughness, surface energy, Young’s modulus, local stress intensity factor at the critical point, and stress intensity factor contributed from dislocations emitted from the crack tip.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(K_{\text{IC}}, K_{\text{QD}}) (MPa m(^{1/2}))</th>
<th>(\gamma_S) (J/m(^2))</th>
<th>(E) (GPa)</th>
<th>((2E/\gamma_S)\left(1-v^2\right)) (MPa m(^{1/2}))</th>
<th>(k_D) (MPa m(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma)</td>
<td>0.42</td>
<td>1.23–1.89</td>
<td>151(^a)</td>
<td>0.64–0.79</td>
<td>0.22–0.37</td>
</tr>
<tr>
<td>(\Gamma_1)</td>
<td>0.39</td>
<td>1.54–1.87</td>
<td>118</td>
<td>0.63–0.70</td>
<td>0.24–0.30</td>
</tr>
<tr>
<td>(\delta_{\text{lp}})</td>
<td>0.97</td>
<td>1.22–1.43</td>
<td>110(^b)</td>
<td>0.54–0.59</td>
<td>−0.43–0.38</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>0.70</td>
<td>0.80–1.01</td>
<td>82.4(^c)</td>
<td>0.38–0.47</td>
<td>−0.32–0.27</td>
</tr>
</tbody>
</table>

\(^a\) Chakrabarty et al.\(^{49}\)

\(^b\) Ployssen et al.\(^{21}\)

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\(^2\) The surface energies might be overestimated by the DFT calculations.
Inoue et al.\textsuperscript{50} have also reported that the grain boundaries of the $\Gamma$-phase polycrystals are weak, resulting in the low fracture toughness. In order to investigate whether the grain boundaries are particularly fragile and the determinant of the low fracture toughness of the $\Gamma$ phase, we carried out additional bend tests of microbeams in which a grain boundary is located at the chevron notch. Polycrystalline specimens of the $\Gamma$ phase with a relatively large average grain size ($\sim 30$ $\mu$m) coexisting with the $\Gamma_1$ phase were fabricated by a solid-state reaction of Zn and Fe powder (Zn:Fe=75:25 in at.\%). Figure 7(a) shows an orientation map of the $\Gamma$-phase polycrystals obtained by electron back scatter diffraction (EBSD). A microbeam was FIB-machined from the region indicated by white rectangle in the figure. Figure 7(b) shows the FIB-machined microbeam with a chevron notch being introduced at the grain boundary position and being almost parallel to the grain boundary. The microbeam with grain boundary fractured in the linear elastic region as in the case of the single-crystal microbeam (Figs. 3(a) and 3(b)) as exemplified by the load-displacement curve shown in Fig. 7(c). The fracture surface is almost perfectly flat as shown in Fig. 7(d). The crack seems to propagate along the grain boundary because the apex of the triangle ligament is unclear unlike the cases of the $\Gamma$, $\Gamma_1$, and $\delta_1$ phases (see Figs. 3(b)–3(d)). The fracture toughness value calculated with the maximum load and averaged over three microbeams with grain boundary is $0.40 \pm 0.07$ MPa m\textsuperscript{1/2}, which is comparable to that of the single-crystal microbeam (Fig. 6(b)). This indicates that the grain boundaries in the $\Gamma$ phase may not be particularly fragile. Nonetheless, it should be noted that the difference in the grain boundary strength between our results (not particularly weak) and the previous reports (weak)\textsuperscript{17,50} might be attributed to the fabrication process of specimens of the $\Gamma$ single-phase compound, as the grain boundary strength in intermetallic compounds is known to be significantly sensitive to impurity segregation\textsuperscript{51} and/or grain boundary structures.\textsuperscript{52} To put it the other way around, it may be possible to control the grain boundary properties of the $\Gamma$-phase compound in the coating of GA steel sheets through optimization of the manufacturing process.

### 4.4. Optimization of the Coating Structure of GA Steel Sheets

The bend testing of single-crystal microbeams have shown that the Fe-lean (Zn-rich) phases, $\delta_1$ and $\zeta$, exhibit relatively high fracture toughness and possess high resistance against crack propagation compared to the other Fe-rich phases, $\Gamma$, $\Gamma_1$, and $\delta_1$. Industrially, GA steel sheets are produced by moderate heat treatment so that the coating consists mainly of the $\delta_1$ phase with the $\zeta$ or $\delta_1$ phase being the outermost layer. This is probably because of the higher resistance of the $\delta_1$ and $\zeta$ phases against crack propagation. Cracks that have nucleated and/or propagated in the Fe-rich brittle phases may be hindered by the $\delta_1$ and/or $\zeta$ phases to suppress severe powdering. In order to further improve the powdering/flaking resistance of GA coating, it is considered effective to avoid or minimize the formation of the $\delta_1$ phase of low fracture toughness compared to the $\delta_1$ phase with the distinction of the $\delta_1$ phases having the similar compositions and metallographic morphologies. It will be also important to suppress the formation of the $\Gamma$ and $\Gamma_1$ phases of low fracture toughness.

### 5. Conclusions

1. The fracture toughness values of the intermetallic compounds in the Fe–Zn system have been measured by bend testing of chevron-notched single-crystal microbeams. The Fe-lean compounds, $\delta_1$ and $\zeta$, exhibit fracture toughness values higher than the other Fe-rich compounds, $\Gamma$, $\Gamma_1$, and $\delta_1$. The hexagonal $\Gamma_1$-phase compound exhibits anisotropy in the fracture toughness while the other four compounds exhibit almost no anisotropy.

2. The $\delta_1$ and $\delta_1$-phase compounds exhibit markedly different fracture toughness values although they have the similar compositions and metallographic morphologies. The large difference in the fracture toughness between the two phases may be attributed to the lack of the translational symmetry along one direction in the $\delta_1$ phase, reducing its fracture toughness desperately, and manifests that the two phases must definitely be distinguished in considering the mechanical properties of the coating layer of GA steel.

3. The $\Gamma$ phase with a relatively wide solid solubility range exhibits no compositional dependence of the fracture toughness.

4. The fracture toughness value of the $\Gamma$-phase microbeams including a grain boundary at the chevron-notch position is comparable to that of the corresponding single-crystal microbeams, indicating that the grain boundaries in the $\Gamma$ phase are not particularly fragile.

5. The surface energies of the intermetallic compounds in the Fe–Zn system except the $\delta_1$ phase have been estimated by the DFT calculations. The surface energy tends to increase with the increase in the Fe content ($\Gamma > \Gamma_1 > \Gamma_b > \delta_1 > \zeta$). This is attributed to the higher ratio of the Fe–Fe solubility for the $\delta_1$ and $\zeta$ phases.
and Fe–Zn atomic bonds which are stronger than the Zn–Zn atomic bonds for the Fe-rich phases.

(6) The compositional dependences of the fracture toughness and the surface energies suggest that the ability of stress relaxation around the crack by plastic deformation decreases with increasing Fe content.

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