Effect of orientation and lamellar spacing of Fe₂B on interfaces and corrosion behavior of Fe-B alloy in hot-dip galvanization

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Abstract: The effects of orientation and lamellar spacing on the interface microstructure and corrosion behavior of a directionally solidified (DS) Fe-B alloy in a hot-dip galvanization bath were investigated. The results indicated that the microstructure of the DS Fe-B alloy consisted of oriented α -Fe and Fe₂B grains. The oriented Fe₂B with [002] preferred growth orientation displayed low-angle grain boundaries on the Fe₂B (001) basal plane. The DS Fe-B alloy with Fe₂B vertical to the corrosion interface possessed the best corrosion resistance to liquid zinc owing to the formation of an interface-pinning multilayer induced by the Fe₂B orientation. The epitaxially grown columnar ζ -FeZn₁₃ products were controlled by the geometric constraint of Fe₂B grain orientation and size, and a mechanism model that explains the interfacial orientation-pinning behavior is discussed in detail. Transmission electron microscopy (TEM) results revealed that the possible orientation relationships of the oriented Fe₂B and columnar ζ -FeZn₁₃ products are (001)_{Fe₂B} // (-402) _{ζ -FeZn₁₃} and [002]_{Fe₂B} // [110] _{ζ -FeZn₁₃}. The corrosion damage of the DS Fe-B alloy with Fe₂B [002] orientation vertical to the corrosion interface in liquid zinc was governed by the competitive mechanisms of Fe₂B/FeB transformation and microcrack-spallation resistance, which is proposed as being the result of a multiphase synergistic effect in the micro-structures.

Keywords: Crystallographic orientation; Corrosion; Transmission electron microscopy; Interface structure; Phase transformation.

1. Introduction

Galvanized steels are widely used in the automotive industry because of their atmospheric corrosion resistance and inexpensive production [1-3]. However, a significant problem in hot-dip galvanization is the rigorous corrosion of submerged equipment (i.e., rolls, supporting bearings, sinkers, supporting roll arms and snout tips) [4-7]. The degradation and frequent failure of this equipment result in significant production downtime and high maintenance costs. Therefore, research on superior corrosion-resistant materials in hot-dip galvanization baths has recently been allotted a high priority in the field of liquid metal corrosion [8].

Previous studies have revealed that the orientation and size of grains have a significant influence on the plastic deformation and wear of materials, especially in terms of thermal expansion [9-11]. Coronado found that the elastic modulus and fracture toughness of carbides in transverse direction for 7.39 wt.% Cr cast iron, as well as the abrasive wear resistance, are higher than those in longitudinal direction [9]. Tezvergil et al. investigated the effect of fiber orientation on the thermal expansion coefficients of various composites [10], whereas Roebuck et al. investigated the hardness of hexagonal tungsten carbide as a function of orientation [11]. Many studies also revealed that crystal orientation has a strong impact on the corrosion and cracking resistance of materials owing to the interfacial films generated and the grain boundaries of the materials [12-15]. For example, Li et al. investigated the effect of orientation and grain boundaries on the cracking behavior of copper bicrystals [12]. Bauer et al. revealed the influence of various grain boundaries on liquid

1 metal-induced embrittling behavior in bcc iron [13], Shahryari et al. showed the effect
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3 of orientation on pit corrosion susceptibility [14], and Lu et al. investigated the
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5 influence of orientation on stress corrosion cracking [15]. The orientation effect
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7 mentioned above stems from the close-packed planes of the crystal, whose high
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9 atomic coordination and binding energy lead to good material properties [16]. In
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11 addition, Song et al. studied zinc coating/steel substrate interface cracking behavior,
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13 and the results revealed that the orientation and size of the zinc coating have an
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15 obvious impact on the adhesion. For instance, the stress levels in grains with the
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17 [0001] direction parallel to the interface are much lower than in grains with the [0001]
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19 direction perpendicular to the interface [16]. Furthermore, the adhesion of the
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21 coating/substrate interface can be affected by the segregation of alloying elements,
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23 surface roundness and interfaces [17-20]. Nevertheless, there is little literature looking
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25 into the effect of crystal orientation on the adhesive layer of films in microstructures.
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29 Based on the aforementioned investigations, it can be inferred that the crystal
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31 orientation and grain size of an Fe-B alloy may affect the interface structures and the
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33 corrosion resistance of the alloy in hot-dip galvanization bath. Although some
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35 previous works revealed that the grain orientation can affect corrosion resistance to
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37 liquid metal [16, 21, 22], the microstructural regulation and synergy of the as-received
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39 interfaces of alloys need to be studied and clarified. Therefore, in the present work,
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41 the interfacial characteristics and corrosion behavior of a directionally solidified Fe-B
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43 alloy in liquid zinc, as well as the alloy's interfacial adhesion capability, were
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45 extensively investigated. The effect of Fe₂B grain orientation and the lamellar spacing
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of the Fe-B alloy on the corrosion mechanism are also discussed in order to understand the relationships between interface structures and the degradation of the properties of boride-containing alloys in terms of liquid metal corrosion damage.

2. Experimental procedures

2.1 Sample preparation of directionally solidified Fe-B alloy

A directionally solidified (DS) Fe-B alloy containing 3.5wt.% B was fabricated in a ZG-5-type vacuum induction melting furnace approximately 1 Pa. The initial charge materials were clean pure iron and an Fe-19.55 wt.% B ferro-alloy. Fig. 1 schematically illustrates the setup of directional solidification with a longitudinal thermal gradient to prepare the directionally solidified Fe-B alloy (Fig. 1a). The figure also shows the corrosion ways of the directionally solidified Fe-B alloy in liquid zinc under static conditions (Fig. 1b and c named in vertical and parallel samples, respectively). The directional solidification in the vacuum melting furnace consisted of a permanent copper mold with recirculating cooling water and a wrapper of sodium silicate-CO₂-bonded sand with exothermal materials. Once the alloy was melted at 1450-1480 °C, it was poured into the mold to solidify, resulting in Y-block ingots of the directionally solidified Fe-B alloy. The directional region near the chilled copper mold, where the sample with a solidification rate of approximately 15 °C/s was measured by a thermocouple (Fig. 1a), was cut into individual samples. Small, non-oriented grains next to the chilled wall (i.e., equiaxed and random grain zones) were removed approximately 6 mm from the surface of the lower part of the Y-block, and only the straightly columnar zones were utilized for the liquid zinc corrosion test.

The long axis of Fe₂B grains in the columnar samples corroded in liquid zinc was either perpendicular to the corrosion interface (labelled as the Fe₂B ⊥ interface, i.e., the vertical sample) or parallel to the corrosion interface (labelled as the Fe₂B // interface, i.e., the parallel sample). The chemical composition of the DS Fe-B alloy analyzed via a spark emission spectrometer is listed in Table 1.

2.2 Corrosion test

Immersion corrosion tests of all samples in a 460 °C liquid zinc bath were carried out in a graphite crucible placed in the vertical electric resistance furnace. The sample were ground using 2000-mesh carborundum paper, and the size of all tested samples was 75 mm × 10 mm × 4 mm. They were then dipped into the liquid zinc to a depth of 40 mm. The initial thickness between the two side faces of the samples was obtained from the average value after being measured 10 times at multiple locations using a micron micrometer. After each sample was corroded for 12 h, it was taken from the liquid zinc and embedded in resin. Then the thickness of each corroded sample was microscopically measured at 1 mm intervals through its cross-section [5, 23]. From these thickness measurements, the average thickness loss for each sample was obtained to evaluate the corrosion rate. The equation used to calculate the corrosion rate of the tested alloy is given as follows [4, 5, 7, 21, 22]:

$$R = \frac{a - b}{2t} \quad (1)$$

where R is the corrosion rate (mm·h⁻¹), a is the original thickness (mm), b is the final thickness (mm), and t is the corrosion time (h). The factor of 1/2 in the equation was used to reflect the fact that the average thickness change of the sample was caused by

corrosion of both faces of the sample.

2.3 Microstructure characteristics

The microanalysis of the samples was carried out by using scanning electron microscopy [SEM, JEOL JSM-6360LV microscope (JEOL, Tokyo, Japan) and a Noran System SIX microscope (Noran Instruments, Middleton, WI, USA], a backscattered electron (BSE) imaging, X-ray diffraction (XRD), electron probe microanalysis (EPMA, JEOL JXA-8100) equipped with energy dispersive X-ray (EDX), and wavelength dispersive X-ray (WDX) analysis to identify the microstructures. For metallographic observations, all samples were etched in a 4 vol.% nital solution. XRD was performed using a MXP21VAHF diffractometer with Cu K α radiation as the X-ray source using continuous scanning at 40 kV and 200 mA. The corroded sample was scanned in the 2θ range from 20° to 60° with a scanning speed of 2°/min and a step space of 0.02°.

Electron backscatter diffraction (EBSD) analysis was carried out to analyze the grain orientation and disorientation of the DS Fe-B alloy. The sample for EBSD measurement was prepared using electro-polishing and chemical etching with a solution of acetic acid and perchloric acid.

Thin foil specimens for TEM examination in a JEOL JEM-2100F field emission transmission electron microscope equipped with EDX analysis were prepared by punching 3 mm discs from wafers cut from large blocks, which were then mechanically ground by hand to a thickness of 50 μ m. These specimens were twin-jet electropolished to an electron transparency at 50 V in a mixture of 5 vol% perchloric

acid, 20 vol% glycerol, and 75 vol% methanol. The solution was cooled to 0 °C with liquid nitrogen following the standard techniques of thin foil used for TEM.

3. Results

3.1 Microstructures of directionally solidified Fe-B alloy

Fig. 2 illustrates the relationship between the lamellar spacing of Fe₂B in the longitudinal direction of the DS Fe-B alloy and the distance of the sample surface close to the chilled wall. Obviously, the average lamellar spacing of Fe₂B in the DS Fe-B alloy ranging from 1.78 μm to 3.42 μm can be obtained from the ingots near the chilled surface distance of approximately 8 mm to 41 mm. The columnar Fe₂B in this region, which had a mean grain size of 2.1 μm, displayed a straight morphology and strong orientation growth.

Fig. 3 shows the dual-phase (α-Fe plus Fe₂B) oriented microstructures of the DS Fe-B alloy. It can be seen that the DS Fe-B alloy has typical lamellar structures in the longitudinal direction (Fig. 3a). Moreover, a large number of rod-like oriented Fe₂B grains become long and straight opposite to the heat extracted direction, exhibiting strong orientation and compact distribution. The transverse morphology of Fe₂B in the DS Fe-B alloy was a regular quadrilateral, as shown in Fig. 3b, which is different from the three-dimensional (3-D) network or interconnected skeleton of the Fe₂B morphology in ordinary solidification of an Fe-B alloy [24 , 25]. The inset in Fig. 3b shows the extracted transverse morphology of primary Fe₂B after the DS process.

Fig. 4 reveals the XRD patterns of the DS Fe-B alloy in the transverse and longitudinal directions. It is clear that the DS Fe-B alloy is mainly composed of α-Fe

1 and Fe₂B. The (002) crystallographic plane of the oriented Fe₂B in transverse
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3 direction is markedly strong, and it was accurately detected at the 2θ diffraction angle
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5 of 42.527°. Nevertheless, the (002) crystallographic plane completely disappeared in
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7 longitudinal direction, which indicates that the preferred growth direction of Fe₂B is
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9 the [002] orientation owing to its body-centered tetragonal structure (i.e. C16,
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11 Cu₂Al-type structure, $a = b = 0.5109$ nm, $c = 0.4249$ nm) [25, 26]. Also, the
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13 accurately detected α -Fe matrix under DS process revealed that it can grow along the
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15 [110] direction. This implies that the orientation relationship between Fe₂B and α -Fe
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17 may be $[002]_{\text{Fe}_2\text{B}} // [110]_{\alpha\text{-Fe}}$.
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25 **3.2 Corrosion characteristics of various corrosion methods**

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27 Fig. 5 shows the corrosion depth (i.e., corrosion thickness loss) and corrosion rate
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29 as a function of corrosion time for the DS Fe-B alloy with various orientations of
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31 Fe₂B in liquid zinc. From Fig. 5a, it is clearly seen that the corrosion depth displays a
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33 linearly increasing relationship. The DS Fe-B alloy with the long axis of Fe₂B
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35 oriented perpendicular to the corrosion interface in the liquid zinc shows lower
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37 corrosion thickness loss, which may be a function of the different interface
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39 microstructures. The mean corrosion rate of the DS Fe-B alloy with the long axis of
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41 Fe₂B perpendicular to the corrosion interface is nearly one time as low as the DS Fe-B
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43 alloy with the long axis of Fe₂B parallel to the corrosion interface (Fig. 5b).
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53 **3.3 Interfacial morphologies and XRD analysis**

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55 Fig. 6 shows the interfacial morphologies of the DS Fe-B alloy subjected to
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57 different corrosion methods in liquid zinc. From Fig. 6a, it is obvious that columnar
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corrosion products (i.e., ζ -FeZn₁₃) exist among the oriented Fe₂B grains. They grow along the [002] orientation of Fe₂B (i.e., in the direction of the long axis) accompanied by some vertical microcracks. Moreover, a corrosion-resistant Fe₂B skeleton with a width of approximately 40 μ m protrudes at the interface, thus showing a pinning layer, and there is only minimal flaking as Fe₂B spalls off into the corrosion layer (Fig. 6a). However, many small granular corrosion products distributed randomly (i.e., ζ -FeZn₁₃) were found in the corrosion layer, and no Fe₂B skeleton zone was found at the interface (Fig. 6b). The columnar Fe₂B may peel off from the matrix layer by layer upon corrosion of the iron matrix. This peeling can cause the premature failure and insufficient corrosion resistance of Fe₂B in liquid zinc. In addition, more flakes of Fe₂B become wrapped in the corrosion layer, as shown in the inset of Fig. 6b.

Fig. 7 shows the XRD patterns of the corrosion products in the oriented (the red spectrum) and non-oriented (the black spectrum) layers. It is clear that except for η -Zn (JCPDS 04-0831) and a little residual Fe₂B (JCPDS 36-1332), a significant amount of ζ -FeZn₁₃ compound is found [7]. The obvious peak of the (-402) plane for the accurately indexed columnar ζ -FeZn₁₃ is very strong only in the oriented product layer, and it exhibits epitaxial growth and maintains consistent orientation of Fe₂B grains in the structure. The XRD results imply that the (-402) plane for epitaxially grown columnar ζ -FeZn₁₃ is likely coherent, with the (002) plane of oriented Fe₂B on the grain boundaries under structural constraints [27-29]. The results indicate that ζ -FeZn₁₃ grows directionally owing to the template effect for epitaxial growth or

controlled growth [27-31]. The proved orientation results reveal that a possible relationship between oriented Fe₂B and columnar ζ-FeZn₁₃ is (-402)_{FeZn13} // (002)_{Fe2B}.

4. Discussion

4.1 EBSD characterization of as-cast DS Fe-B alloy

Fig. 8 shows the EBSD grain orientation and disorientation map of the transverse DS Fe-B alloy. From Fig. 8a, the orientations of the grains are represented by the different colors, and they are indexed to α-Fe and Fe₂B. The grain boundary distribution map in Fig. 8b reveals the misorientation of different grains. Fig. 8 (c and d) show the misorientation angle distributions of the Fe₂B and α-Fe phases, respectively, in the transverse DS Fe-B alloy. The misorientation angles of the Fe₂B phase are mainly distributed near 10° except for very small misorientation angles at approximately 59°. However, some misorientation angles of the α-Fe phase are less than 10° and others range from 35° to 50°. The misorientation-angle distribution results indicate that the types of grain misorientation for the oriented Fe₂B belong to low-angle grain boundaries on the (002) plane, whereas those of the α-Fe phase consist of some low-angle and high-angle grain boundaries in the DS Fe-B alloy [32].

4.2 Effect of Fe₂B orientation on corrosion interface micro-structures

Fig. 9 shows the interface morphologies of the vertical sample, which had the best corrosion resistance to liquid zinc. It is clear that there was a skeleton of oriented Fe₂B at the interface. Some compact columnar ζ-FeZn₁₃ grew along the orientation of Fe₂B (Fig. 9a), which reveals the “template effect” of orientation growth characteristics (i.e., structural inherited characteristics). In other words, the oriented

1 Fe₂B and the epitaxially induced grown ζ -FeZn₁₃ compound can generate a corrosion
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3 reaction film, which can effectively obstruct the diffusion and infiltration of liquid
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5 zinc, preventing further attack. Moreover, partially oriented Fe₂B displayed some
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7 tubercular or pitting corrosion (Fig. 9a), which indicates that dense layers of oriented
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9 Fe₂B skeletons can suffer from strong liquid zinc corrosion, even after it resisting
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11 corrosion for a long period of time. Meanwhile, a significant number of sliding
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13 deformations along various directions (Fig. 9a) and transverse microcracks in the
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15 epitaxially grown ζ -FeZn₁₃ compound were clearly found. Fracture of the oriented
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17 Fe₂B at the interface also occurred (Fig. 9a).
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25 From the SEM image, shown in Fig. 9b, it was found that some oriented Fe₂B
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27 ruptured and that the average sliding width of the deformed zone in the ζ -FeZn₁₃
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29 compound was approximately to 600 nm. The flaking and deformation in the
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31 as-received corrosion reaction film (i.e., Fe₂B plus ζ -FeZn₁₃, constituting a corrosion
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33 interfacial film) revealed very high growth stress between the oriented Fe₂B and the
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35 epitaxial ζ -FeZn₁₃ compound [33-35].
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44 corresponding selected area diffraction pattern (SADP). From Fig. 10a, it is clearly
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46 revealed that significant slipping deformation took place in the columnar ζ -FeZn₁₃
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48 compound, and that a large number of dislocations occurred in the ζ -FeZn₁₃.
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50 Dislocation lines 45° to the horizontal direction were parallel to each other, and the
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52 average distance between two dislocation lines was approximately 650 nm (Fig. 10b),
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54 which indicates that dislocations may be important for adhesion [34, 35]. The SADP
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of ζ -FeZn₁₃ at the pinning interface indicates that slipping deformation occurred on the (110) plane of ζ -FeZn₁₃ (Fig. 10a). Further SADP analysis of the Fe₂B/ ζ -FeZn₁₃ interface revealed that possible orientation relationships between oriented Fe₂B and columnar ζ -FeZn₁₃ at the pinning interface are $(001)_{\text{Fe}_2\text{B}} // (-402)_{\zeta\text{-FeZn}_{13}}$ and $[002]_{\text{Fe}_2\text{B}} // [110]_{\zeta\text{-FeZn}_{13}}$ (Fig. 10b). The results indicate that a strong Fe₂B/ ζ coherent interface induced by orientation may have formed, which is in agreement with the XRD results [36-41].

Generally, the interface growth stress in oxide films may be formed by the intrinsic growth stresses resulting from the chemical nature of multicomponent film transformation, induced growth stresses from the differences in volume of the films and metals, thermally included stresses resulting from temperature changes and the different thermal expansion coefficients of the metals and the films/oxides, and external stresses from operation or constraints in the structures [33, 43]. According to the present microstructural orientations, the volume change of the compounds and the geometric constraint of oriented Fe₂B which can induce the growth stress of reaction films are the dominant causes of the interface stress. The interface stress can be characterized by the well-known Pilling-Bedworth ratio (PBR, $R_{\text{P-B}}$) shown in the following equation [16, 32, 33, 43]:

$$R_{\text{P-B}} = \frac{V_{\text{com}}}{V_{\text{M}}} = \frac{M_{\text{com}} \cdot \rho_{\text{m}}}{n \cdot A \cdot \rho_{\text{com}}} \quad (1-1)$$

where V_{com} and V_{M} are the molar volumes of the compound and metal matrix, respectively, M_{com} and A are the respective molar and atomic weights of the compound and the metal, ρ_{com} and ρ_{m} are the respective compound and metal densities,

and n is the number of metal atoms in the compound molecules. In the present study, the directionally solidified Fe-B alloy was exposed to liquid zinc, and thus the R_{P-B} values of the main Fe-Zn compounds such as δ -FeZn₁₀ and ζ -FeZn₁₃ were be estimated to be 13.83 and 17.76, respectively. Consequently, the corrosion products grew inwardly and took root in the gaps of the oriented Fe₂B, which is attributed to the microstructural orientation-induced effect. In this case, the volume of the corrosion products expanded among the columnar Fe₂B grains, which implied that the corrosion products next to the metal matrix and columnar Fe₂B were compact. The generation and growth of the corrosion products resulted in very high stress among the columnar Fe₂B grains, which theoretically should generate a significant amount of spallation and microcracks based on the general models of the PBR value calculated.

Nevertheless, a dense and compact corrosion interface comprising orientated Fe₂B and a columnar ζ -FeZn₁₃ compound can form, and this in turn increases the corrosion product adherence, thus greatly suppressing the interface spallation. The work of adhesion between intermetallics (such as at the FeZn₁₃/Fe₂Al₅ interface) is naturally lower than that of the interface/steel interface, and element segregation may somewhat improve the adhesion owing to the wetting interface [2, 3, 18, 20, 44]. However, the present interface under such large PRB values can well adhere to the substrate, which is attributed to the orientation-pinning effect on the interface. Such a strong orientation-induced pinning interface (i.e., interface-pinning effect resulting from orientation grains of Fe₂B and epitaxial ζ -FeZn₁₃) affects the interfacial geometry, enhancing the interface contact area, fixation effect, and pinning force of

1 interface products. This orientation-pinning interface generates significantly larger
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3 interfacial adhesion according to the comparison of pinning and non-pinning
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5 interfaces in our peel tests [44]. In addition, the differences between the misfit stress
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7 (approximately 725 MPa) and the residual stress (approximately 100 MPa) resulted
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9 from the release of plastic deformation at the interfaces (i.e., sliding and rupture
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11 behavior) [18, 44]. Therefore, the forceful combination of the oriented Fe₂B grains
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13 and microexpanded epitaxial ζ -FeZn₁₃ on the corrosion interface had a significant
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15 impact on the corrosion product adherence derived from the multi-phase geometric
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17 constraints of the microstructures, which can well explain the experimental results
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19 [18-20, 37, 43].
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27 **4.3 Effect of Fe₂B lamellar spacing on corrosion resistance to liquid zinc**

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29 The present work indicates that the grain orientation of an anticaustic Fe₂B phase
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31 can induce the formation of oriented ζ -FeZn₁₃ corrosion products and give rise to an
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33 interfacial-pinning effect, which improves the adherence and corrosion resistance of
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35 the interfaces. However, the orientation-pinning effect of directional Fe₂B grains is
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37 governed by the lamellar spacing of Fe₂B, as well as by the grain size. Fig. 11 shows
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39 the average lamellar spacing of directional Fe₂B as a function of corrosion
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41 performance and the residual Fe₂B skeleton existing at the interfaces. Here, the
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43 lamellar spacing, $\lambda_{\text{Fe}_2\text{B}}$, is equal to the marginal distance of columnar Fe₂B between
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45 the broad side, schematically shown in Fig. 11a. In order to ensure the same grain
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47 thickness of Fe₂B as much as possible, the proper location of the DS ingot tested was
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49 selected. From Fig. 11a, it is clearly found that the small lamellar spacing of
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directional Fe₂B, with $\lambda_{\text{Fe}_2\text{B}}$ below 2.4 μm , can reduce the corrosion depth and rate of the Fe-B alloy in liquid zinc, whereas the corrosion rate increases with increasing lamellar spacing of the directional Fe₂B. That is to say, the smaller the lamellar spacing, the better the corrosion resistance. The changes of the corrosion performance can be attributed to the interface structures and intensities of the orientation-pinning effect, which depends on the lamellar spacing of Fe₂B. This orientation-pinned interface can act as a buffer layer to resist the liquid zinc diffusion and corrosion. The residual skeleton width of corroded Fe₂B at the interfaces shown in Fig. 11b further reveals that the interfacial-pinning effect caused by the oriented Fe₂B and columnar $\zeta\text{-FeZn}_{13}$ is dominantly controlled by the lamellar spacing of directional Fe₂B. A large lamellar spacing and weak orientation may reduce the interfacial-pinning effect. The typical interface morphologies of the directional Fe-B alloy with various Fe₂B lamellar spaces are shown in Fig. 11 (c and d). The alloy with a small lamellar spacing resulted in a dense, oriented layer that possessed beneficial pinning effects. Also, many pitting corrosion and tuberculous pits were found, which indicates that slight dissolution and corrosion of the oriented Fe₂B at the pinning zone occurred because of the high liquid zinc concentration in these areas [22, 44]. Moreover, the corrosion pits joined together, which led to the degradation and phase transition of Fe₂B. Many zinc atoms dissolved into the Fe₂B crystal, causing it to decompose into a transition layer (EDX spectra in Fig. 11d) [21, 42].

Therefore, the control of the lamellar spacing and orientation of Fe₂B, which is determined by configuration of the microstructural parameters, may govern the

interface microstructure and corrosion resistance of Fe-B alloys in liquid zinc.

4.4 Phase transition of Fe₂B intermetallic during liquid zinc corrosion

The improved corrosion resistance of the DS Fe-B alloy in liquid zinc may be derived not only from the lamellar spacing of Fe₂B but also from the Fe₂B grain orientation, which can influence the orientation-pinning effect at the interface. However, a number of oriented Fe₂B grains retained at the corrosion interface for long periods of time can continue to be corroded by liquid zinc, resulting in cracks and spalls off the substrate [22, 33, 43]. Fig. 12 shows the damage to a corroded Fe₂B skeleton at the interface and interface transports. As discussed above, the rigorous corrosion of the Fe₂B skeleton can promote microcrack initiation and propagation, thus leading to large flakes (Fig. 12a). Thereafter, subsequent films comprising the skeleton layer of oriented Fe₂B and epitaxial products may appear in the flaking zone, causing a repeat of the orientation-pinning effect at the interface.

Because of lengthy resistance to liquid zinc corrosion, the anticaustic Fe₂B phase can transform into a transitional phase at the oriented Fe₂B/ ζ -FeZn₁₃ interface (shown in the grey transition region in Fig. 12). Based on the Zn-Fe-B ternary system [45], three phases, ζ -FeZn₁₃, Fe₂B, and FeB, can coexist in thermodynamic equilibrium at 450 °C in a liquid zinc bath [22, 45]. Obviously, this indicates that the corrosion interface can be divided into three zones (Fig. 12b), namely, I-zone containing uncorroded Fe₂B, II-zone, with corroded Fe₂B, denoted as the transition phase (i.e., FeB), and III-zone, with epitaxially grown columnar ζ -FeZn₁₃, which takes root in the gaps of the Fe₂B grains. That is to say, the Fe₂B phase in an interfacial-pinning zone

may transform into a transition phase. The compositional profiles measured by WDX quantitative analysis through the three zones are shown in Fig. 12c. Obviously, the Fe concentration in the transition layer is lower than that in the Fe₂B layer, which indicates that the transition layer is FeB phase containing some zinc [21]. Previous researches also revealed that bulk pure Fe₂B can transform into the FeB phase owing to the physicochemical reaction under high zinc chemical potential [22, 45]. In this phase-transition process, the strong seepage force of zinc atoms at 460 °C results in the initial excessive dissolution and subsequent further lattice distortion. Then, many diffusion-induced vacancies in the Fe₂B crystal occur, which is ultimately attributed to the higher diffusion coefficient of liquid zinc ($D_{\text{liquid zinc atom in } c \text{ axis}} = 1.8 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$, $D_{\text{Fe in liquid zinc}} = 9.8 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) and high zinc chemical potential as driving forces of the diffusion reaction in dynamics [21].

In addition, the similar atomic structures and chemical properties of Fe and Zn atoms powerfully promote the phase transformation of Fe₂B under high liquid zinc concentrations [21, 22]. On one hand, the Fe₂B/FeB phase transformation is essentially derived from the induced atomic reorganization of Fe₂B crystals at high zinc concentrations because the spatial bonding distribution of Fe₂B crystals is primarily heterogeneous. For instance, the bonding energy for the B-B atoms of Fe₂B along the [002] direction is only 4.5052 kJ·mol⁻¹, but it is 15.7372 kJ·mol⁻¹ bonding energy for Fe-Fe atoms of Fe₂B along the [220] direction) [21, 46]. On the other hand, the larger diffusion coefficient of boron in Fe₂B crystals may compel and govern the lattice reorganization of Fe₂B crystals, thus leading to the formation of a FeB phase

($D_{\text{B in Fe}_2\text{B}} = 4.67 \times 10^{-9} \text{ cm}\cdot\text{s}^{-1}$ and $D_{\text{B in FeB}} = 2.33 \times 10^{-9} \text{ cm}\cdot\text{s}^{-1}$) [42]. It is also revealed that, thermodynamically, the $\text{Fe}_2\text{B}/\text{FeB}$ transformation process may occur naturally because of the excess Gibbs energy (e.g. $-14.58 \text{ kJ}\cdot\text{mol}^{-1}$) [22, 46].

Actually, the corrosion of Fe_2B may be controlled by dissolution and diffusion through the solid Fe_2B /liquid zinc interface. The dissolution rate constant, k_d , and the mass transfer coefficient, k_m , were estimated according to the Nernst-Shchukarev equation [47, 48] and Higbie's Penetration theory [49, 50], and the results are shown in Fig. 12d. Obviously, the dissolution rate constant is much lower than the mass transfer coefficient when the temperature of the liquid zinc increases, and the value of the latter is approximately 25 times higher than that of the former at liquid zinc temperature of 460°C . It can, therefore, be inferred that the orientation-pinning interfaces in liquid zinc may be governed by the mass transfer process [48-50].

4.5 Interfacial orientation-pinning effect and corrosion-resistant mechanism

On the basis of the aforementioned analyses, the orientation and size of the anticaustic Fe_2B phase have a significant effect on the corrosion interface morphologies. It is further inferred that geometric pinning of the interface can significantly inhibit flaking and spallation, thus improving the corrosion resistance to liquid zinc. The strong pinning effect of the interface relies on the geometric constraints, volume expansion, and size effect, as schematically represented in Fig. 15 according to the present work. The results of this study may provide us a method for controlling boride in the working layer of components that form a pinned interface.

The confirmed differences in corrosion resistance of an Fe-B alloy with different

1 Fe₂B morphologies stem from the corrosion interface structures and Fe₂B damage that
2
3 peels off. The interfacial morphologies of Fe₂B oriented perpendicular to the
4
5 corrosion interface show that significant amounts of residual anticaustic Fe₂B is
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7 retained at the corrosion interface. This retention results from the microstructural
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9 synergistic effect of the strong orientation of the Fe₂B grains and the epitaxially
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11 grown ζ-FeZn₁₃ compound, which results in interfacial orientation-pinning effects.
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13 Undoubtedly, the level of corrosion interface-pinning effect depends on the
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15 orientation and size of Fe₂B, as mentioned previously. The strong orientation-pinning
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17 effect may be ascribed to the geometric fixation of Fe₂B and the interface coherency
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19 between columnar Fe₂B and ζ-FeZn₁₃, which results in highly adhered reaction films
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21 and prevents further corrosion.
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31 Fig. 16 shows the elemental mapping distribution of the Fe-B alloy with various
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33 Fe₂B morphologies corroded in liquid zinc. It can be seen that different interfacial
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35 structures and spalling modes appear. The multipath effect of liquid zinc corrosion of
36
37 a netlike boride barrier results in the anticaustic Fe₂B phase losing the support of the
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39 iron matrix, thus peeling off the substrate and displaying a mesh-flaking mode (Fig.
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41 16a) [7, 21, 22]. This is different the case in which boride parallel to the corrosion
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43 interface spalls off and loses its barrier protection early by the corrosion of the iron
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45 matrix, which is therefore failure through a layer-by-layer mode (Fig. 16b). In these
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47 two cases, the remarkable intergranular corrosion of liquid zinc takes place easily. The
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49 severe spallation of Fe₂B cannot offset the anticorrosion of Fe₂B. On the contrary, the
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51 boride protrudes at the interface, and there is scarcely any peeling of Fe₂B vertical to
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corrosion interface owing to the strong interface-pinning effect (Fig. 16c). Obviously, the strong pinning effect on the interface is derived from the microstructural orientation synergy and geometric consistency of the multiphase at the interfaces (e.g. the film of columnar Fe_2B plus $\zeta\text{-FeZn}_{13}$). The results therefore show a competing failure model between the $\text{Fe}_2\text{B}/\text{FeB}$ phase transition and subsequent massive spalling and flaking of borides that are constantly inhibited by the pinning interface.

It is observed that the pinning interface can well adhere to the substrate, forming a buffer and resisting the diffusion of liquid zinc and thus decreasing the corrosion rate. However, microcracks may be partially induced by the large thermal misfit existing at the interfaces owing to differences of the thermal expansion coefficients for the multilayer [18]. Moreover, the phase transition from Fe_2B to FeB at the $\text{Fe}_2\text{B}/\zeta$ interface accelerates crack initiation and propagation [22, 42, 46], significantly destroying the interface structures by further corrosion damage.

Based on the XRD and TEM examinations of the interfaces, it is indicated that the FeZn_{13} grows directionally in corrosion interface of the vertical sample and forms a possible orientation relationship, i.e., $[002]_{\text{Fe}_2\text{B}} // [110]_{\text{FeZn}_{13}}$. The orientation of Fe_2B controls the interfacial morphologies and influences its failure behavior, thus leading to differences in corrosion resistance to liquid zinc. Therefore, it is also inferred that the grain orientation and size have high microstructural sensitivity and specificity in terms of corrosion and spallation resistance of the alloy in a hot-dip galvanization bath.

5. Conclusions

1 This work reveals the corrosion interface control and the directional solidification
2
3 of an Fe-B alloy in liquid zinc, as well as the effect of orientation on corrosion
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5 resistance. The main conclusions can be drawn as follows:
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9 (1) The microstructure of the DS Fe-B alloy consists of α -Fe and Fe₂B. The
10
11 oriented Fe₂B, with [002] preferred growth orientation, displays a tetragonal
12
13 morphology in transverse direction. The oriented Fe₂B possesses low-angle grain
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15 boundaries, and the orientation relationship in the DS Fe-B alloy may be $[002]_{\text{Fe}_2\text{B}} //$
16
17 $[110]_{\alpha\text{-Fe}}$.
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23 (2) The DS Fe-B alloy with Fe₂B vertical to the corrosion interface possesses the
24
25 best corrosion resistance to liquid zinc, and interface-pinning films can generate a
26
27 buffer that resists the corrosion of liquid zinc, thus improving the corrosion and
28
29 spallation resistance of Fe-B alloys.
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34 (3) The sliding deformation of orientation-induced columnar ζ -FeZn₁₃ on the (110)
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36 plane takes place at the interface, and epitaxially grown ζ -FeZn₁₃ is controlled by the
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38 geometric constraints of oriented Fe₂B. The orientation and lamellar spacing of Fe₂B
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40 can strongly affect the interfacial structure and pinning effect of Fe-B alloys in liquid
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42 zinc.
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48 (4) XRD and TEM results revealed that the possible orientation relationships of
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50 oriented Fe₂B and epitaxially grown columnar ζ -FeZn₁₃ products are $(001)_{\text{Fe}_2\text{B}} //$
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52 $(-402)_{\zeta\text{-FeZn}_{13}}$ and $[002]_{\text{Fe}_2\text{B}} // [110]_{\zeta\text{-FeZn}_{13}}$, which may be generated by the strong
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54 geometric constraints of the multiphase in the structures.
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59 (5) The corrosion damage mechanism of the DS Fe-B alloy in liquid zinc is
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governed by the Fe₂B grain morphologies. The formation of a pinning interface can lead to the transformation of Fe₂B into FeB and a microcrack-spallation process owing to the high zinc chemical potential.

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List of Table Captions

Table 1 Chemical compositions analyzed via spark emission spectrometer (wt.%)

List of Figure Captions

Figure 1 The set-up of directional solidification (DS) equipment of Fe-B alloy and corrosion manners of DS Fe-B alloy in liquid zinc: (a) Device of DS; (b) Vertical sample with Fe_2B [002] orientation perpendicular to corrosion interface (Labelled as $\text{Fe}_2\text{B} \perp$ interface); (c) Parallel sample with Fe_2B [002] orientation parallel to corrosion interface (Labelled as $\text{Fe}_2\text{B} //$ interface).

Figure 2 Relationship between grain size of DS Fe-B alloy in longitudinal section and the distance from the chill.

Figure 3 Microstructure of DS Fe-B alloy: (a) Longitudinal; (b) Transverse.

Figure 4 XRD patterns of as-cast DS Fe-B alloy.

Figure 5 Corrosion depth and rate of DS Fe-B alloy as a function of corrosion time.

Figure 6 Corrosion morphologies of DS Fe-B alloy in liquid zinc: (a) Vertical sample; (b) Parallel sample.

Figure 7 XRD results of corrosion layers for Fe-B alloy with oriented and non-oriented Fe_2B in liquid zinc

Figure 8 EBSD analysis of DS Fe-B alloy in transverse: (a) orientation map; (b) disorientation map; (c) Misorientation angle distribution of Fe_2B ; (d) Misorientation angle distribution of α -Fe.

Figure 9 Interface morphologies of pinning zone for the vertical sample in liquid zinc: (a) BSE image; (b) SEM image.

Figure 10 TEM analysis of ζ - FeZn_{13} existing at pinning interface and corresponding selected area diffraction pattern (SADP): (a) TEM micrograph of ζ at pinning zone; (b)

1 Parallel dislocation in ζ and the SADP for $\zeta/\text{Fe}_2\text{B}$ interface.

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3 Figure 11 Relationships between lamellar spacing of Fe_2B ($\lambda_{\text{Fe}_2\text{B}}$) and interface
4 characteristics: (a) Lamellar spacing $\lambda_{\text{Fe}_2\text{B}}$ vs. corrosion performance; (b) Lamellar
5 spacing $\lambda_{\text{Fe}_2\text{B}}$ vs. residual Fe_2B skeleton at interface; (c) Pinning interface ($\lambda_{\text{Fe}_2\text{B}} =$
6 $2.45 \mu\text{m}$); (d) Pitting corrosion ($\lambda_{\text{Fe}_2\text{B}} = 2.85 \mu\text{m}$).
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9 Figure 12 Analysis of the corroded Fe_2B skeleton lain at the interface and interface
10 transports: (a) Spallation and reproductive film of pinning interface consisting of
11 oriented Fe_2B and epitaxial $\zeta\text{-FeZn}_{13}$; (b) FeB transition layer on $\text{Fe}_2\text{B}/\zeta$ interface; (c)
12 Compositional profile through the $\text{Fe}_2\text{B}/\zeta$ interface; (d) Dissolution constant and mass
13 transfer coefficient vs. temperature.
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16 Figure 13 Schematically representation for verticality of $[002]$ orientation to interface
17 and lamellar spacing of Fe_2B as a function of the interface-pinning zone.
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20 Figure 14 Elemental mapping distribution of Fe-B alloy with various Fe_2B
21 morphologies corroded in liquid zinc: (a) Net-like Fe_2B for Fe and Zn; (b) Parallel
22 Fe_2B for Fe and Zn; (c) Vertical Fe_2B for Fe and Zn.
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Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 7

Figure 8a

Figure 8b

Figure 8c

Figure 8d

Figure 9a

Figure 9b

Figure 10a

Figure 10b

Figure 11a

Figure 11b

Figure 11c

Figure 11d

Figure 12a

Figure 12b

Figure 12c

Figure 12d

Figure 13

Figure 14

Table 1

Table 1 Chemical compositions analyzed via spark emission spectrometer (wt.%)

Element	B	Cr	Si	C	S	P	Fe
Specimen	3.51	0.55	0.36	0.14	0.014	0.023	Bal.