

1 Article

2 Effect of the addition of molybdenum on the structure 3 and corrosion resistance of zinc–iron plating

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12 **Abstract:** Zn–Ni plating is indispensable in various industries because of its high corrosion
13 resistance. However, Ni has been reported to trigger allergies; thus, an alternative Ni-free plating is
14 desired. Zn–Fe plating is considered to be a promising candidate, albeit its corrosion resistance still
15 needs to be improved. The corrosion resistance of Zn–Fe plating is expected to increase by the
16 addition of Mo as the third alloying element as it is more noble than Zn and Fe. In this study, Zn–
17 Fe–Mo plating with a corrosion resistance nearly equivalent to that of the Zn–Ni plating was
18 fabricated. Zn–Fe–Mo plating was electrically deposited from continuously agitated plating baths
19 prepared by mixing ZnSO₄, FeSO₄, Na₂MoO₄, Na₃C₆H₅O₇, and Na₂SO₄ using Fe or Ni plates as the
20 substrate. The surface morphology, composition, crystal phase, and electronic state of Mo of the
21 platings were investigated by SEM-EDS, XRD, and XPS. The anti-corrosion performance was
22 evaluated by Tafel extrapolation method. Formation of plating comprising a Mo containing alloy
23 phase was found to be crucial for improving corrosion resistance. The Zn–Fe–Mo plating
24 demonstrates promise for replacing anti-corrosion Zn–Ni platings.

25 **Keywords:** Zn–Ni plating; Zn–Fe plating; anti-corrosion performance; Mo addition; alloy
26 formation

28 1. Introduction

29 Metals such as steel and cast iron are typically used as the major components of architecture
30 and machines in daily life [1]. In several cases, these metals are exposed to harsh environments, and
31 protection against corrosion is a critical issue particularly where high reliability is required. The
32 application of corrosion-resistant alloys, including stainless steels, is an effective solution; however,
33 the high cost hinders its applications for daily use [2]. Another promising method to improve
34 corrosion resistance is protection by Zn plating or so-called galvanization [3]. It protects the
35 underlying steel or cast iron by the sacrificial corrosion protection effect, and its considerably lower
36 cost has led to its widespread use in various fields.

37 Currently, protection coatings with a high corrosion resistance are desired to extend the life of
38 industrial products for realizing a sustainable society and for withstanding a more severe
39 environment to meet industrial demands. Alloying with iron-group elements such as Fe and Ni is
40 well known in improving the corrosion resistance of Zn platings [4–8]. By the formation of alloys of
41 Zn with iron-group elements, the standard electrode potential of the alloy becomes closer to that of
42 the substrate metal. The smaller potential difference between the plating and substrate decreases the
43 driving force for the corrosion of the plating, which, in turn, improves its corrosion resistance. In
44 particular, Zn–Ni plating has demonstrated to exhibit five to six times greater corrosion resistance
45 compared with that of Zn plating according to salt spray tests [8]. Thus, Zn–Ni plating has become

46 indispensable for various applications, including aircraft and automotive parts, where conventional
 47 Zn plating cannot be applied [9].

48 Meanwhile, in recent years, Ni allergies have become a social concern. In fact, allergic contact
 49 dermatitis in children is caused by nickel [10]. Nickel ions released from various alloys are potent
 50 allergens or haptens that can trigger skin inflammation [11]. Therefore, an alternative nontoxic
 51 Ni-free plating with a corrosion resistance equivalent to or higher than that of Zn–Ni plating is
 52 desired. Zn–Fe plating is considered to be promising because of its cost-effectiveness and
 53 nontoxicity. However, it exhibits insufficient corrosion resistance, corresponding to only one-third
 54 of that of the Zn–Ni plating [12]. Meanwhile, the addition of noble elements such as Mo and W into
 55 plating has been reported to improve the corrosion resistance via the stabilization of the passive film
 56 [13,14]. Mo and W cannot be electrically deposited from solutions alone, but these elements have
 57 been reported to undergo co-deposition with iron-group elements [15,16]. This result indicated that
 58 these elements are also possibly co-deposited into Zn–Fe platings; however, studies of Zn–Fe–Mo
 59 plating have been rarely reported thus far to the best of our knowledge [17–21]. In this study, Zn–Fe–
 60 Mo plating was electrically deposited by the addition of Mo into the plating bath, and its effect on
 61 corrosion resistance was investigated. Furthermore, the possibility of using Zn–Fe–Mo platings to
 62 replace conventional Zn–Ni platings was discussed.

63 2. Materials and Methods

64 2.1. Bath preparation

65 Table 1 shows the composition of the bath, which was prepared by mixing zinc sulfate
 66 heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Nacalai Tesque, Inc.), iron(II)sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$,
 67 Nacalai Tesque, Inc.), sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, Kishida Chemical Co., Ltd.),
 68 trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, Nacalai Tesque, Inc.), and sodium sulfate (Na_2SO_4 ,
 69 Nacalai Tesque, Inc.). Typically, 60 mL of distilled water (DI) was first added into a 100-mL Pyrex
 70 glass beaker, and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 , $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were
 71 added in the order mentioned. Second, the pH was adjusted using sodium hydroxide (NaOH,
 72 Nacalai Tesque, Inc.) and sulfuric acid (H_2SO_4 , Nacalai Tesque, Inc.) solutions, respectively, and the
 73 total bath volume was adjusted to 100 mL by the addition of distilled water. All procedures were
 74 carried out under continuous agitation. Finally, oxygen was removed from the bath by bubbling
 75 with Ar for 30 min before use.

76 **Table 1.** Bath compositions used in this study

77

78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 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83 using a magnetic stirrer at room temperature (25 °C). A potential/galvanostat (HZ-7000, Hokuto
 84 Denko Co.) was utilized to control the electrolysis potential and analyze data. A Ni plate (NI-313374,
 85 Nilaco) or an Fe plate (B-60-P01, Yamamoto-Ms) and a Pt coil were used as the cathode and anode,
 86 respectively. Ag/AgCl in saturated KCl was used as the reference electrode. The cathode was
 87 degreased with ethanol, pickled with 10% H₂SO₄, and masked with an insulation tape (PES-01, AS
 88 ONE), leaving a space of 400 mm² (20 mm × 20 mm) for electrodeposition prior to the experiment.

89 *2.3. Characterization and evaluation of the platings*

90 Scanning electron microscopy (SEM; JSM-6330F, JEOL) equipped with energy-dispersive
 91 spectroscopy (EDS; JED2140-GS, JEOL) was employed to examine the surface morphology and
 92 composition of the plating. X-ray diffraction (XRD, Ultima IV, Rigaku) was employed to examine the
 93 crystalline phase. X-ray photoelectron spectroscopy (XPS, ESCA-3300, Shimadzu Corporation) was
 94 employed to examine the electronic state of Mo. Ar etching was performed for 3 min to confirm the
 95 electronic state of Mo inside the plating. Current efficiency (C_{eff}) was calculated from the mass
 96 change and plating composition, as shown in (1).

$$C_{eff} = \frac{Z_{Zn}n_{Zn}F + Z_{Fe}n_{Fe}F + Z_{Mo}n_{Mo}F}{Q}. \quad (1)$$

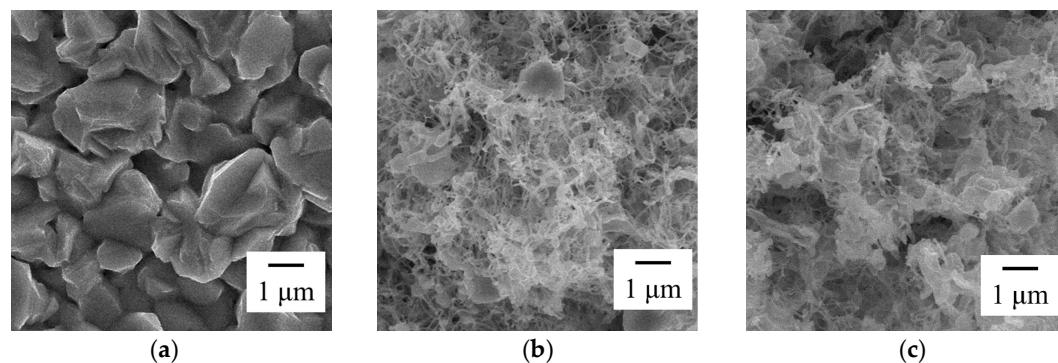
97 Here, Z_X (X = Zn, Fe, or Mo) is the ionic valence of each element, n_X is the molar amount obtained
 98 from EDS analysis, F is the Faraday constant, and Q is the amount of electricity passed.

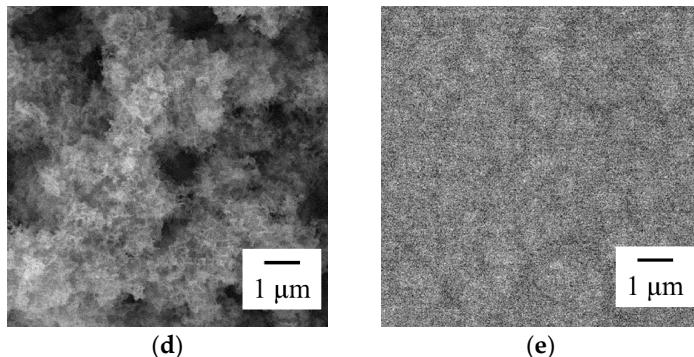
99 The corrosion resistance was evaluated by anode polarization tests. A 3 mass% sodium chloride
 100 (NaCl, Nacalai Tesque, Inc.) solution degassed with Ar was used as the test solution, with a sweep
 101 rate of 1 mVs⁻¹ for the polarization measurement. The potential at 0.1 mAcm⁻² in the anode
 102 polarization curve was defined as the corrosion potential (E_{corr}). Zn, Zn–Fe, and Zn–Ni plating were
 103 prepared and evaluated as a reference.

104 **3. Results and Discussions**

105 *3.1. Effect of bath pH on Zn–Fe–Mo platings*

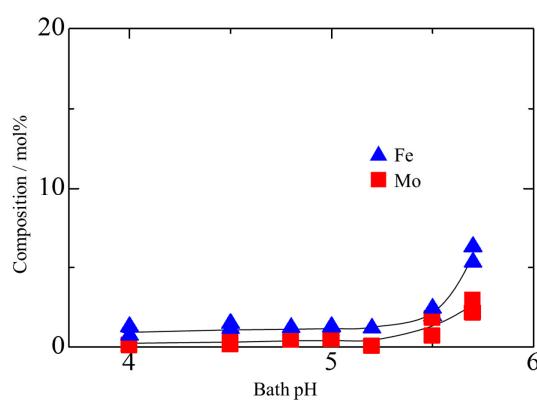
106 Zn–Fe–Mo plating was electrically deposited at various pH values. The current density was
 107 fixed at 10 mAcm⁻². A black precipitate with low adhesion was formed on the substrate during
 108 electrodeposition at a pH greater than 5.7. Thus, the pH range was selected from 4.0 to 5.7. Figure 1
 109 shows the SEM images of the platings deposited in the baths at different pH values. The surface
 110 morphology clearly changed. The plating obtained from the bath at pH 4 comprised granules of c.a.
 111 2 μm (Figure 1(a)), whereas that obtained from pH 4.5 to 5.5 changed to a fibrous structure (Figure
 112 1(b–d)). Finally, that from pH 5.7 exhibited a smooth structure comprising fine grains (Figure 1(e)).





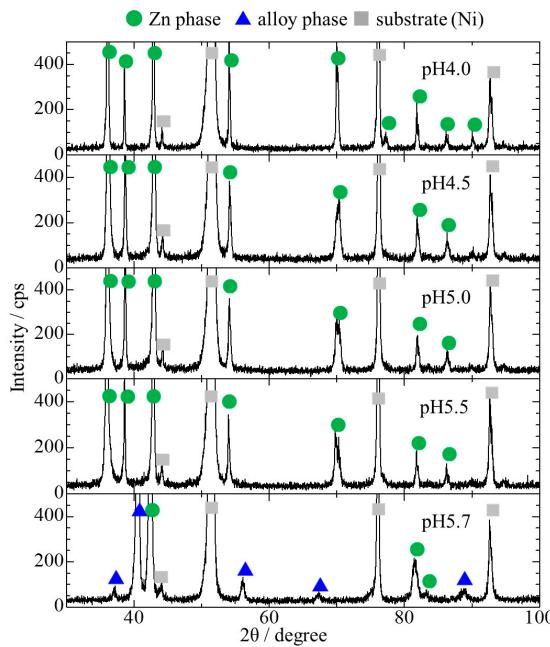
115 **Figure 1.** SEM images of the Zn–Fe–Mo platings deposited at various pH values.
 116 (a) pH 4.0, (b) pH 4.5, (c) pH 5.0, (d) pH 5.5, and (e) pH 5.7
 117

118 Figure 2 shows the composition of the platings deposited at various pH values. Ni substrates
 119 were used in this experiment to avoid the detection of Fe from the substrate. A majority of the
 120 platings exhibited a high Zn content, with only trace Fe and Mo, indicating that the current
 121 conditions are categorized as “anomalous codeposition” [22]. Although Mo was barely observed for
 122 the plating prepared by electrical deposition at pH between 4.0 and 5.2, the amount of Mo increased
 123 with further increasing pH. Moreover, at a pH of 5.7, the plating exhibited 3 at% Mo, probably
 124 related to the difference in the present form of Mo. In solution, Mo exists as oxyanions, which is
 125 known to form various polyoxoanion at low pH and mono-oxyanions at pH greater than around 6.
 126 Therefore, the deposition of Mo is thought to occur with the decrease in the size of oxyanions, which
 127 allows for the easier deposition of Mo [23,24].
 128



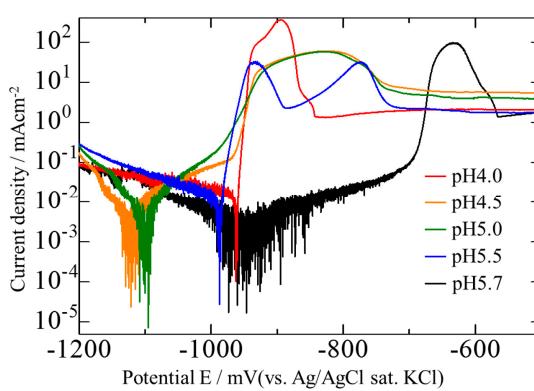
129 **Figure 2.** Content of Fe and Mo in Zn–Fe–Mo plating deposited at various pH values
 130

131 Figure 3 shows the XRD patterns of the platings deposited at various pH values. Intense peaks
 132 were observed for all platings, indicative of the deposition of a crystalline structure. Reflections only
 133 corresponding to the Zn phase and the substrate were observed in the platings deposited at pH 4.0–
 134 5.5; however, with increasing pH, a slight shift toward low angles was observed, in addition to peak
 135 broadening. The incorporation of Fe atoms into the Zn lattice was anticipated to lead to a distorted
 136 Zn structure. Peaks other than Zn were observed for the plating obtained at pH 5.7. These are
 137 expected to correspond to reflections from a FeMo based alloy phase since similar peaks have been
 138 observed for FeMo alloys in previous studies [25,26].
 139



140 **Figure 3.** XRD patterns of the Zn-Fe-Mo plating deposited at various pH values
141

142 Figure 4 shows the anodic polarization curves of platings deposited at various pH values. The
143 plating deposited at pH 4.0 exhibited a sharp increase in current density at around -960 mV,
144 whereas that deposited at pH values of 4.5 exhibited a slight increase at around -1100 mV and a
145 drastic increase at around -960 mV. At pH 5.0 and 5.5, a gradual increase between -1100 mV to -920
146 mV and a similar behavior to that at pH 4.0 was observed with a sharp change at around -990 mV,
147 respectively. This indicated a low corrosion potential for the fibrous structure. For the platings
148 deposited at pH 5.7, a change at -950 mV and a drastic change at -700 mV were observed. The
149 plating with the supposed Fe₃Mo based alloy phase exhibited higher corrosion resistance than those
150 of the others comprising the Zn phase. From these experiments, a pH of 5.7 is selected for the
151 remaining experiments.
152



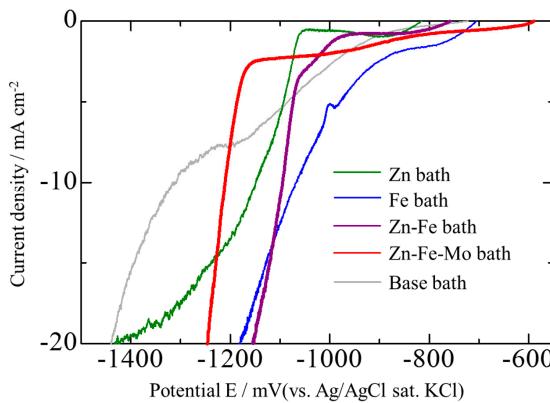
153 **Figure 4.** Anodic polarization curves of the Zn-Fe-Mo plating deposited at various pH values
154

155 *3.2. Effect of current density on Zn-Fe-Mo platings*

156 A cathodic polarization measurement was carried out to consider the range of current density.
157 Figure 5 shows the measured cathodic polarization curves at a pH of 5.7 and a sweep rate of 5 mV/s.
158 The deposition of Zn and Fe started at approximately -1080 and -980 mV from baths containing Zn

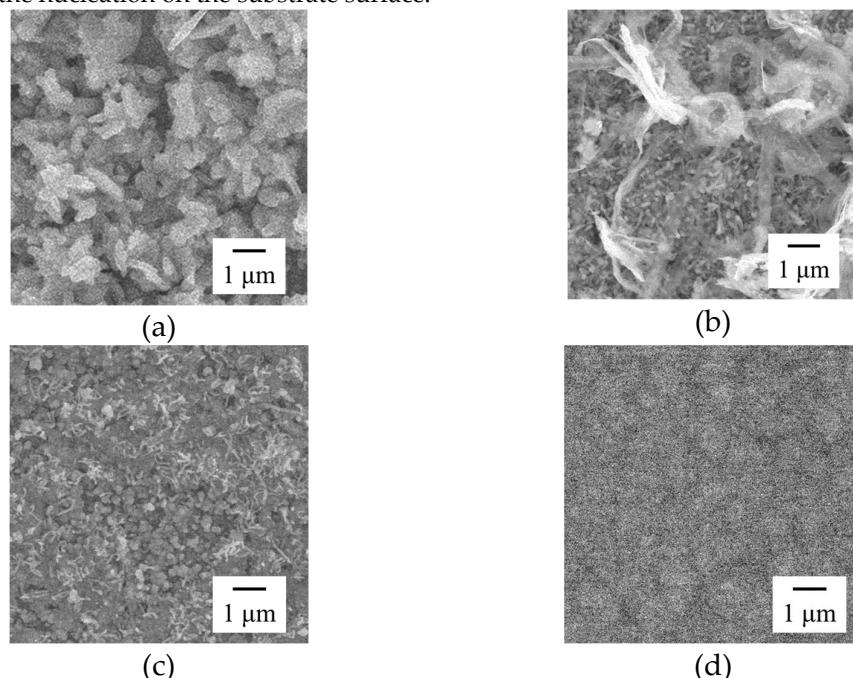
159 or Fe alone (Zn and Fe baths), respectively. Meanwhile, when using the plating bath containing
 160 both Zn and Fe (Zn-Fe bath), a small peak at -980 mV and a second large peak were observed at
 161 -1080 mV, corresponding to the deposition of Fe and Zn, respectively. Finally, from the bath
 162 containing Zn, Fe, and Mo, two peaks were again observed at -800 mV, possibly corresponding to
 163 the co-reduction of Fe and Mo, and at -1200 mV, related to Zn deposition. These shifts in potential
 164 are likely to be explained by the presence of noble Mo, shifting the reduction of Fe to higher
 165 potentials through co-reduction of Mo while shifting the Zn deposition to lower potential by
 166 avoiding the deposition of Zn via the adsorption of oxyanions on substrate surface.

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 168



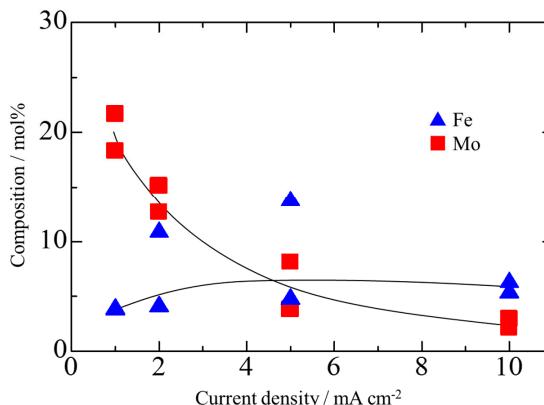
169 **Figure 5.** Cathodic polarization curves obtained from different baths
 170

171 From the results obtained from the cathodic polarization curves, current densities of 1, 2, 5, and
 172 10 mA cm^{-2} were selected. Figure 6 shows the SEM images of the platings deposited at different
 173 current densities. At low current densities, the plating surface comprised bulky granules (Figure
 174 6(a)). The size decreased with increasing current density, probably because a high current density
 175 promoted the nucleation on the substrate surface.



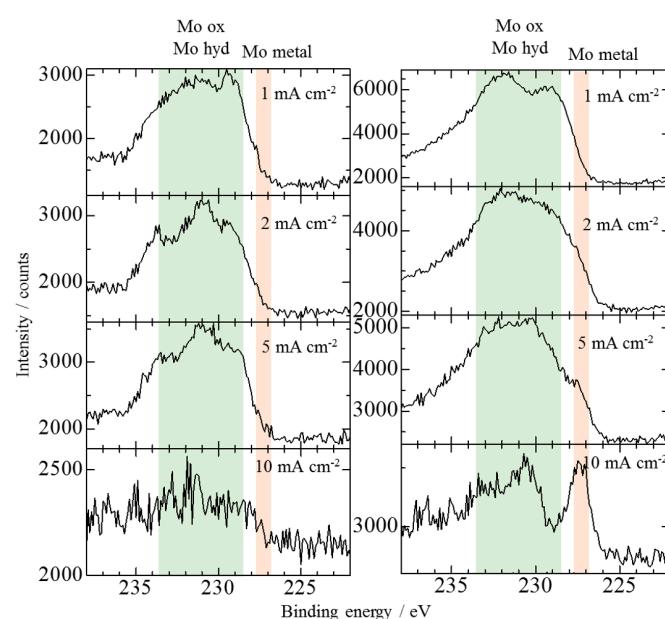
176 **Figure 6.** SEM images of the Zn-Fe-Mo plating deposited at various current densities
 177 (a) 1 mA cm^{-2} , (b) 2 mA cm^{-2} , (c) 5 mA cm^{-2} , and (d) 10 mA cm^{-2}

178 Figure 7 shows the relationship between the plating composition and current density. The
 179 content of Mo in the plating decreased with increasing current density, possibly corresponding to a
 180 high deposition rate of the plating and an insufficient feed rate of the Mo ions. The extremely high
 181 deposition rate must have led to the depleted Mo layer near the substrate surface, thereby leading to
 182 the slow reduction of Mo [27].
 183



184 **Figure 7.** Content of Fe and Mo in the Zn–Fe–Mo plating deposited at various current densities
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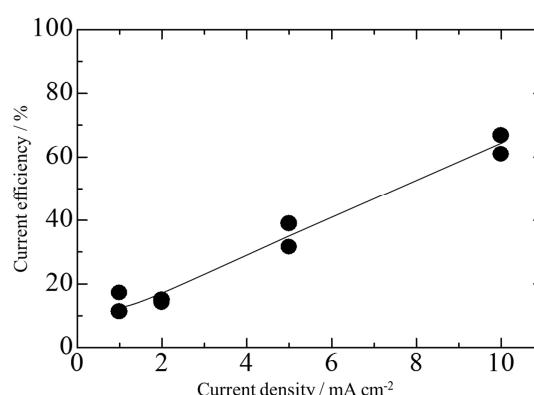
186 Figure 8 shows the result obtained from the XPS analysis of platings deposited at different
 187 current densities. The peaks around 227 to 228 eV corresponds to metal Mo (Mo (0)) and 229 to 234
 188 eV corresponds to Mo in the oxide or hydroxide state. Mo (0) was not observed on the plating
 189 surface. For the platings deposited at 1 and 2 mA cm⁻², changes were not observed even after Ar-ion
 190 etching; however, Mo (0) was observed for plating at 5 and 10 mA/cm² after Ar-ion etching,
 191 indicating that a relatively high current density is required to reduce Mo, which is necessary for
 192 co-deposition to occur. The low generation rate of atomic hydrogen at the substrate surface may be
 193 responsible for this phenomenon since Mo is proposed to be reduced by the generation of atomic
 194 hydrogen in previous studies [27,28]. Similar results have been reported for electroplating in a Ni–
 195 Mo system [27].
 196
 197



198 **Figure 8.** XPS analysis results of the Zn–Fe–Mo platings deposited at various current densities

199

200 Figure 9 shows the relationship between the current density and current efficiency. The current
 201 efficiency increased with current density. As the amount of electricity was constant, a low current
 202 density is equivalent to a long electrodeposition time. The decrease in the current efficiency at low
 203 current density is assumed to be related to the dissolution of oxygen from the atmosphere into the
 204 plating bath, leading to necessity of extra electricity to reduce the dissolved oxygen in the bath.
 205

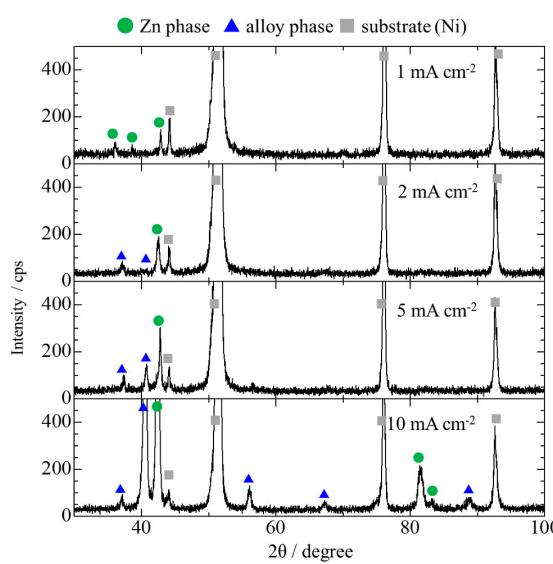


206 **Figure 9.** Relationship between current density and current efficiency

207

208

209 Figure 10 shows the XRD patterns of the platings deposited at various current densities. With
 210 increasing current density, peaks corresponding to the alloy phase were observed. The peak of the
 211 alloy phase became more intense as the current density increased. Even though a large amount of
 212 Mo was detected in platings deposited at low current densities, Mo could not be reduced to form
 213 alloys and could only exist as oxides or hydroxides.



214 **Figure 10.** XRD patterns of the Zn-Fe-Mo platings deposited at various current densities

215

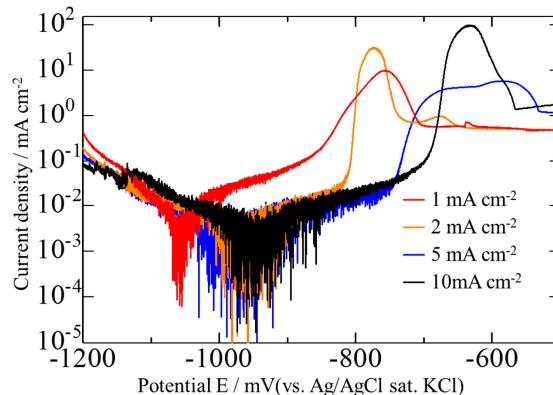
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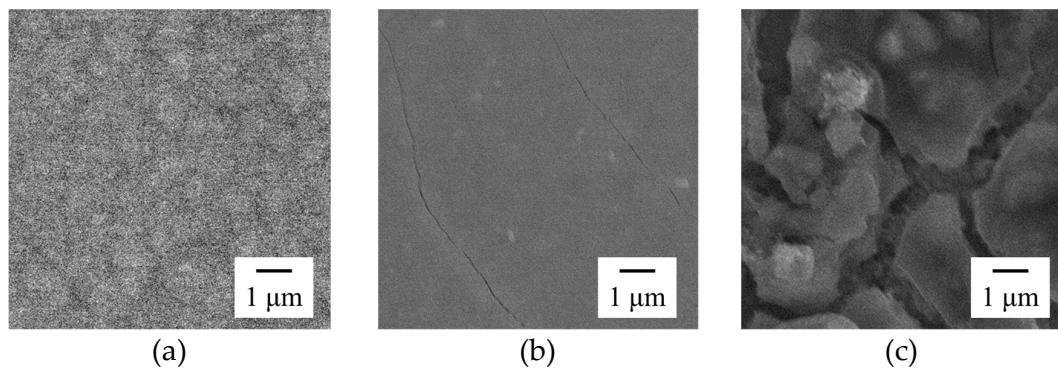
216 Figure 11 shows the anodic polarization curves of platings deposited at various current
 217 densities. With increasing current density, the potential shifted to a more noble value. The presence
 218 of an alloy phase is indicated to be crucial as anticipated in Section 3.1.
 219



220 **Figure 11.** Anodic polarization curves of the Zn–Fe–Mo platings deposited at various current
 221 densities
 222

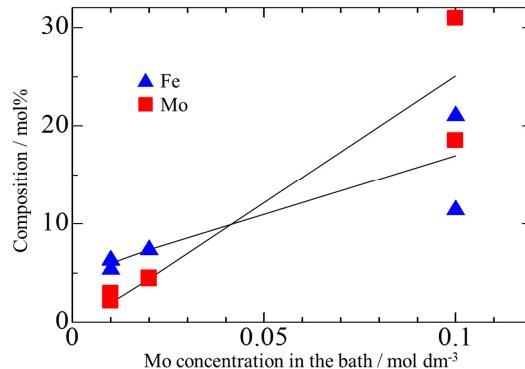
223 *3.3. Effect of Mo concentration of plating bath on Zn-Fe-Mo platings*

224 The SEM image of platings obtained when using plating baths with different Mo concentration
 225 is shown in Figure 12. The Mo concentration was 0.01, 0.02 and 0.1 mol dm^{-3} . The plating obtained
 226 from the 0.01 mol dm^{-3} Mo containing bath showed smooth and homogeneous surface; however,
 227 small cracks were observed by increasing the Mo concentration to 0.02 mol dm^{-3} and a rough
 228 surface with even more cracks were observed by further increasing the Mo concentration to 0.1
 229 mol dm^{-3} . An increase in Mo concentration of the plating bath seems to have negative effect on
 230 plating quality.
 231



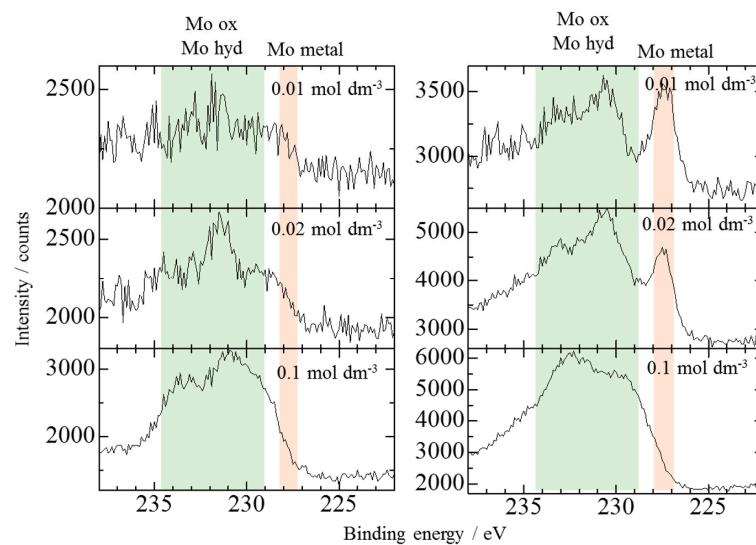
232 **Figure 12.** SEM image of Zn-Fe-Mo plating deposited at various Mo concentration
 233 (a) 0.01 mol dm^{-3} (b) 0.02 mol dm^{-3} (c) 0.1 mol dm^{-3}
 234

235 The composition of Mo content in the platings are shown in Figure 13. An increase in the
 236 content of Fe and Mo in the platings was observed by increasing the Mo concentration of the plating
 237 bath. This is because more MoO_4^{2-} were supplied and adsorbed onto the surface of the substrate
 238 along with the increase in Mo concentration in the plating bath.
 239



240 **Figure 13.** Content of Fe and Mo in the Zn–Fe–Mo plating deposited from a plating bath with
 241 different Mo concentration
 242

243 Figure 14 shows the result obtained from the XPS analysis of platings deposited from plating
 244 baths with different Mo concentrations. Again, Mo (0) was not observed on the plating surface. After
 245 Ar-ion etching, Mo (0) was observed for plating deposited from baths containing 0.01 and 0.02
 246 mol dm^{-3} Mo; however, not from baths containing 0.1 mol dm^{-3} Mo. At low Mo concentration, both
 247 Fe and hydroxide of Mo by reduction of MoO_4^{2-} shall coexist on the surface of the substrate and Mo
 248 may be thus reduced since the atomic hydrogen can be held at the unpaired 3d electrons on the Fe
 249 metals [28]. In contrast, at high Mo concentrations, the surface of the substrate will be covered with
 250 excess hydroxides of Mo, making it difficult for Fe to approach the plating surface. Thus, further
 251 reduction of hydroxides of Mo must be prevented due to the lack of Fe; i.e., the lack of atomic
 252 hydrogen. Zn must have been prevented as well by the hydroxide of Mo.
 253



254 **Figure 14.** XPS analysis results of the Zn–Fe–Mo plating deposited from a plating bath with different
 255 Mo concentration
 256

257 Figure 15 shows the relationship between the Mo concentration in the plating bath and current
 258 efficiency. The current efficiency decreased by increasing the Mo concentration in the plating bath.
 259 The increasing formation of hydroxide of Mo on the surface prevents Fe deposition, resulting in a
 260 lower current efficiency [29]. The trend of current efficiency seems to support this expectation.
 261

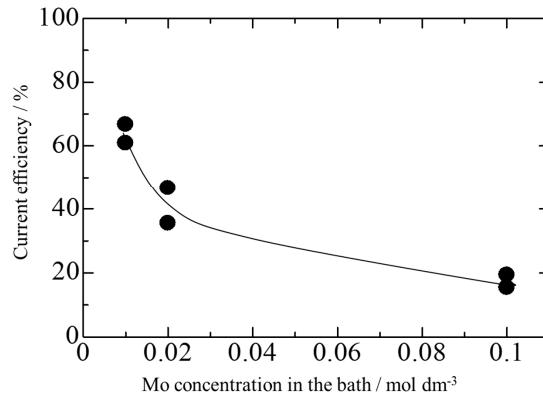
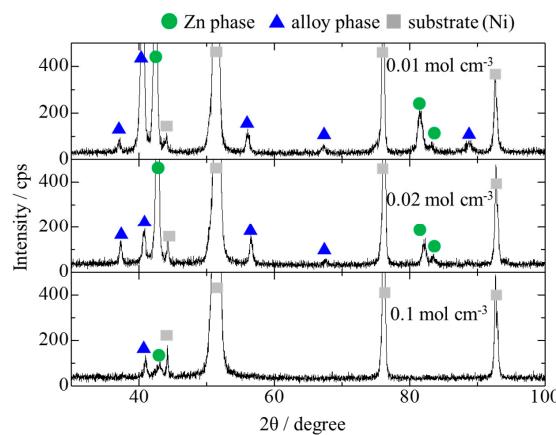


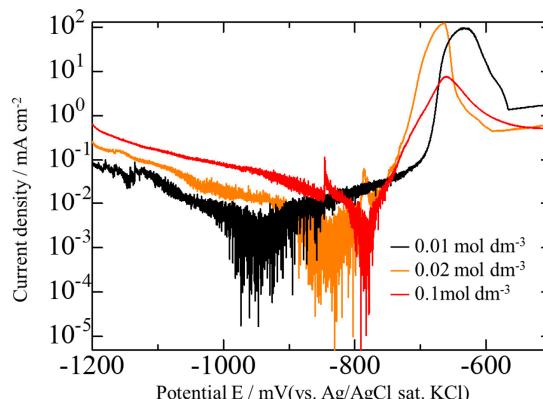
Figure 15. Relationship between Mo concentration and current efficiency

262
263
264 Figure 16 shows the XRD patterns of the platings deposited from baths of various Mo
265 concentrations. The intense peaks of alloy phase were detected as decreasing the Mo concentration.
266 This also supports the idea that Mo in the plating existed in the Mo (0) form and lower Mo
267 concentration led to enhanced formation of Mo (0).
268



269 **Figure 16.** XRD patterns of the Zn-Fe-Mo plating deposited from a plating bath with different Mo
270 concentration
271

272 Figure 17 shows the anodic polarization curves of platings deposited from baths with various
273 Mo concentrations. All three platings showed relatively noble potentials. A decrease in Mo
274 concentration of the plating bath, corresponding to more intense peaks of alloy phase, shifted the
275 potential to a more noble value. Again, the results support the idea that presence of alloy phase is
276 importance.
277

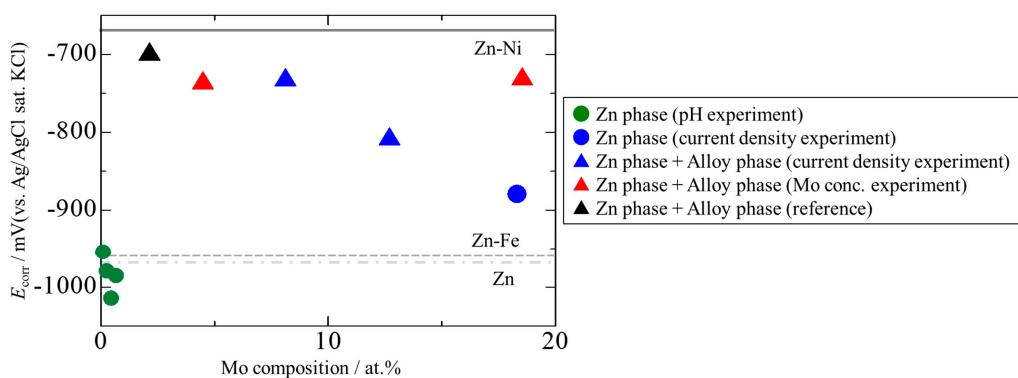


278 **Figure 17.** Anodic polarization curves of the Zn–Fe–Mo platings deposited at various Mo
 279 concentration
 280

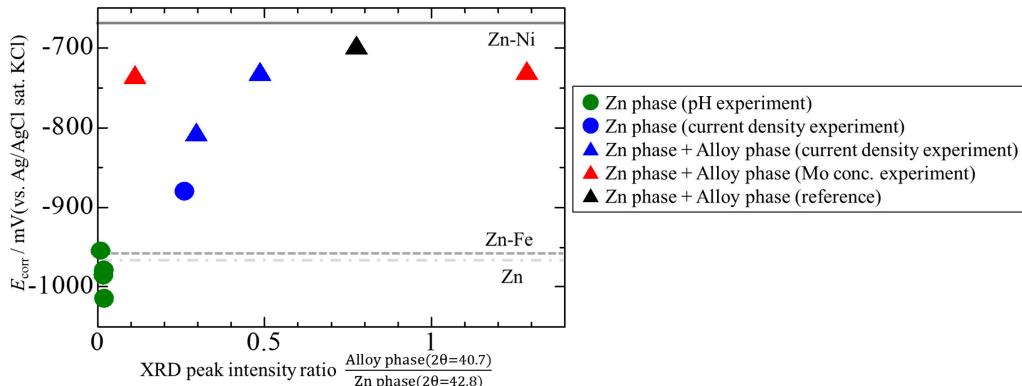
281 *3.4. Corrosion potentials of the Zn–Fe–Mo platings*

282 Figure 18 shows the relationship between the content of Mo in the plating and E_{corr} , as well as
 283 the E_{corr} values for Zn, Zn–Fe, and Zn–Ni plating. A low Mo content led to high E_{corr} ; however, it was
 284 not proportional to the content of Mo in the plating. This indicated that the Mo content in the
 285 plating is not the primary factor improving the corrosion resistance of the plating.

286 Figure 19 shows the relationship between the peak intensity ratio of the alloy and Zn phases
 287 from XRD and E_{corr} to discuss the effect of alloy phase. Peaks corresponding to the alloy and Zn
 288 phases were observed at 2θ values of 40.7° and 42.8° , respectively, apparently indicating that the
 289 deposition of the alloy phase is crucial for high corrosion resistance.
 290



291 **Figure 18.** Relationship between the content of Mo in the plating and E_{corr}
 292



293 **Figure 19.** Relationship between the peak intensity ratio of the alloy phase and Zn phase from the
 294 XRD and E_{corr}
 295

296 **4. Conclusions**

297 In this study, the addition of Mo into the Zn–Fe platings was considered to improve its
 298 corrosion resistance. The following results were obtained.

299 1. The Zn–Fe–Mo platings obtained by this experiment exhibited high corrosion resistance when
 300 the electrically deposited layer formed a Fe_3Mo based alloy phase.

301 2. The best plating exhibited high corrosion resistance comparable with that of Zn–Ni platings,
 302 revealing promise for Zn–Fe–Mo platings as potential alternatives for Zn–Ni platings.

303 3. For the co-deposition of Mo, it is crucial to control the pH to approximately 5.7 to ensure that
 304 Mo does not form large polyoxides and Zn does not form hydroxides.

305 4. Co-deposition does not effectively occur at low current densities, and a high Mo concentration
 306 in the bath as Mo (IV) cannot be efficiently reduced to Mo (0).

307

308 **Author Contributions:** D. Kosugi mainly performed the experiments and analyses; T. Hagio considered the
 309 data and wrote the paper; Y. Kamimoto gave important advice throughout the experiments; and R. Ichino
 310 conceived and designed the experiments.

311 **Conflicts of Interest:** The authors declare no conflict of interest.
 312

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