Differences in pitting growth kinetics between Zr$_{60}$Ni$_{25}$Al$_{15}$ and Zr$_{60}$Cu$_{25}$Al$_{15}$ metallic glasses exposed to a 0.6 M NaCl aqueous solution

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1. Introduction

Metallic glasses (MGs) with structurally amorphous features exhibit superior corrosion resistance in corrosive media because of their chemical homogeneity, lack of lattice defects, and considerably beneficial characteristics in long-range disordered solid solutions [1,2]. Zirconium-based MGs are well known to exhibit excellent corrosion resistance in halide-free solutions because of the formation of a uniform surface passive film mainly comprising zirconium oxides. Unfortunately, such passive films are susceptible to deterioration in chloride-containing aqueous solutions. Typically, multicomponent Zr–Ni–Cu–Al, Zr–Ti–Ni–Cu, and Zr–Ti–Ni–Cu–Be bulk metallic glasses (BMGs) are highly susceptible to pitting corrosion [3–8]. Besides passive elements such as zirconium, titanium, and aluminium, the pitting corrosion resistance of Zr-based MGs chemically depends on the incorporated species of late transition metals (LTMs) such as copper, cobalt, and nickel. These elements are required to render the glass-forming ability of BMGs. For the alloys with one LTM, Ni-bearing Zr$_{55}$Ti$_{4}$Ni$_{22}$Al$_{13}$ BMG exhibits a pitting potential $\sim$ 400 mV greater than that of Cu-bearing Zr$_{61}$Ti$_{4}$Cu$_{25}$Al$_{12}$ BMG in a 0.6 M NaCl solution [8], indicative of a significantly enhanced pitting resistance. However, the intrinsic sources responsible for this compositional effect of LTM on the pitting resistance are still unclear.

In conventional crystalline metals [9–12], the evolution of corrosion pits is well known to apparently occur in several distinct stages, including the passivity breakdown, metastable pitting, and pit growth. To understand the overall picture of the pitting behaviour, it is necessary to characterise the pit evolution processes. However, to the best of our knowledge, a few studies have reported the pit evolution processes of Zr-based MGs. Recently, our group [8] has reported that the electrochemical characteristics, composition, and thicknesses of the surface passive films of Zr$_{61}$Ti$_{4}$Cu$_{25}$Al$_{12}$ and Zr$_{55}$Ti$_{4}$Ni$_{22}$Al$_{13}$ BMGs are similar. The LTM elements in the BMGs are not incorporated into the passive film to form oxides. Thus, differences in the passivity breakdown process between these two alloys are thought to not crucially affect the pitting resistance of Zr-based MGs. Previous studies [5–8,13] have reported the selective dissolution of elements such as zirconium, titanium, and aluminium over copper in Cu-bearing Zr-based MGs during pitting growth. In contrast, no selective dissolution occurs in Ni-bearing Zr-based MGs [8]. Thus far, the effect of the selective dissolution behaviour caused by different LTMs in these alloys on the kinetics of stable pitting growth is not clear. Clarifying the pit growth kinetics of Zr-based MGs is essential for understanding the chemical effect of LTM on the pitting resistance of Zr-based MGs and designing highly corrosion-resistant BMGs.

During pit growth, the metal cations from the pitting dissolution undergo hydrolysis, accompanied with the simultaneous production of metal hydroxide(s) and hydrogen ions. These processes generate a sufficiently aggressive acidic pit solution, which can depassivate the material via destabilising passive films on the metal surface [9–11]. Burstein et al. [12,14] have suggested that stable pitting growth is controlled by the diffusion of metal cations from the pit bottom to the pit mouth. The pit depth inevitably serves as a sufficient diffusion barrier. In addition, the local acidic solution dynamically leads to the enhanced Cl$^-$ concentration because these anions migrate to the pit to simultaneously maintain the charge neutrality. Because of the high metal cation and Cl$^-$ concentrations, a salt film is precipitated at the pit mouth. The pit depth inevitably serves as a sufficient diffusion barrier. In addition, the local acidic solution dynamically leads to the enhanced Cl$^-$ concentration because these anions migrate to the pit to simultaneously maintain the charge neutrality. Because of the high metal cation and Cl$^-$ concentrations, a salt film is precipitated at the pit mouth. The pit depth inevitably serves as a sufficient diffusion barrier.
bottom as a resistive layer [15–18]. Furthermore, based on the one-dimensional pit growth model, a minimum critical value of cation flux, expressed as the product of the current density \( i \) and pit depth \( d \), is theoretically required for the pit to maintain a critical chemistry, and thus sustainable spontaneous pitting growth [19]. Moreover, the stable growth of an open hemispherical pit is feasible only under the condition that the product of current density and pit depth \( (i_d)_{\text{pit}} \) exceeds a critical value [9,20,21]. For stainless steels (SS) exposed to chloride solutions, this value has been reported to be 0.3–0.6 A/m [9].

Artificial pit electrodes, fabricated by embedding a wire-shaped metal in an insulator such as epoxy, are typically used to examine the pit dissolution kinetics in naturally assembled pit environments [18,22–26]. This approach exhibits advantages in several aspects, including (i) attaining a unidirectional pit geometry, (ii) excluding potential multiple pits, and (iii) only monitoring the active pit surface. In fact, artificial pit electrodes have been widely utilized to examine the pitting growth behaviour of SS, such as rate-determining factors, salt film formation, and physical meaning of the pitting potential [18,22,23,27–31]. Recently, Kelly et al. [26,32,33] have developed a cyclic electrochemical technique, introducing a rapid, high-throughput extraction of key kinetic parameters, such as the pit stability product under a salt film \( (i_d)_{\text{salt}} \) and the repassivation potential \( E_{rp} \), by single artificial pit testing. Regarding the MGs, Scully et al. [24,25] have utilized the artificial pit approach and examined the pit stabilisation of several nanocrystalline-containing Al-based MGs and the effect of micro-earthing with nickel on the stable pitting growth of Al–Cu–Mg-based MGs.

In this study, two LTM-bearing Zr-based MGs, Zr_{60}Ni_{25}Al_{15} and Zr_{60}Cu_{25}Al_{15}, are selected to investigate the growth kinetics of stable pits with artificial pit electrodes exposed to 0.6 M NaCl solution. Maintaining an equal stoichiometry of nickel and copper in the glassy alloys ensures that the LTM concentration effect on the pitting growth is exclusive. By the characterisation of current transient events and the growth kinetics parameters, the effect of the selective dissolution behaviour on the stable pit growth is expected to be revealed. Finally, the chemical effect of LTM on the pitting resistance of Zr-based MGs is discussed by comparing the differences in several perspectives between two Zr-based MGs.

2. Experimental

2.1. Materials

Two ternary Zr–LTM–Al alloys with nominal compositions of Zr_{60}Ni_{25}Al_{15} and Zr_{60}Cu_{25}Al_{15} (in atomic percentage) were selected to fabricate MG ribbons, denoted as ZNA and ZCA hereafter, respectively. Elemental pieces with a purity greater than 99.9 wt% were used as starting materials. Master alloy ingots were prepared by arc melting in an alumina container under a Perkin-Elmer differential scanning calorimeter (DSC diamond) with an alumina container under flowing purified argon at a heating rate of 20 K/min. A second run under identical conditions was carried out to determine the baseline after each run. To confirm the reproducibility of the data, at least three samples taken from independent sites of the ribbon were examined for each alloy. All of the measured glass transition temperatures \( T_g \) and onset temperature of crystallisation \( T_c \) were reproducible within an error of ± 1K.

2.2. Electrochemical setup

The as-prepared MG ribbons as the working electrode were electrically connected with copper wires, followed by mounting between two glass microscope cover slips with a thin epoxy layer. The detailed processing of this sandwiched-like electrode is described elsewhere [24]. The surface exposed to electrolyte is the cross section of the MG ribbon. Then, pit growth in the ribbon took place along the longitudinal direction. Such a sample architecture is desirable to permit the ex situ visualisation of the grown pit under an optical microscope. The electrode surface exposed to the electrolyte was polished to up to 2000 grit using SiC abrasive papers and immediately dipped into the unbuffered 0.6 M NaCl solution with the electrode surface facing upward. The exposed area of the electrode was approximately \( 2 \times 10^{-4} \) cm². The pH of the test electrolyte was maintained at 6.0 ± 0.1. The temperature during testing was maintained at 25 ± 1 °C using a water bath.

The experimental setup comprised a conventional three-electrode electrochemical cell with a platinum foil and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. Electrochemical measurements were carried out on an EG & G Princeton Applied Research Model 2273 electrochemical workstation. Potentiodynamic polarisation curves were recorded at a potential sweep rate of 1 mV/s after holding at the steady open circuit potential (OCP) for a period of 600 s in the electrolyte. To create artificial pits, pitting was initiated by the application of an anodic potential of +1.5 V vs. SCE for 10 s. Once the pit was initiated, the applied potential was reduced to +1 V vs. SCE and held for a certain duration to manipulate the pit growth process. Once a desired depth was established, rapid cathodic polarisation scanning was immediately conducted at a scan rate of 25 mV/s to a final potential of −1 V vs. SCE. To determine the resistance inside the pits, high-frequency impedance measurements were carried out at frequencies ranging from \( 10^5 \) Hz to 1 Hz. For each alloy, electrochemical acquisition was repeated four times for five electrodes (i.e. 20 measurements in total) to obtain data for statistical analysis.

The current transient analysis was counted by the peak analyser of Origin 9.0 software. In this study, the criterion to identify the current transients is defined as the condition under which the peak current is at least three folds greater than the amplitude of the background current. All of the parameters used to characterise the transient response are determined from four repeated measurements.

2.3. Pit morphology observation

After making the artificial pits, the cross-sectional morphologies of the pits was observed ex situ by confocal laser scanning microscopy (CLSM, OLYMPUS LEXT OLS4000, Japan). The corroded samples for scanning electron microscopy (SEM) observation were mounted between two pieces of adhesive tape using a resin. After pit growth, one side of the adhesive tape was torn off, and dipped into the resin solubilizer. By this treatment, the species inside the pit were stuck to the remaining side of the adhesive tape, retaining majority of the pit environment. The samples were then coated with gold and dried in a desiccator prior to characterisation. The morphology and chemistry of the samples were characterized using a Zeiss Supra™ 55 Sapphire field-emission SEM (FESEM, Carl Zeiss Group, Germany), equipped with a 20 X-Max® energy-dispersive spectrometer (EDS, Oxford Instruments, UK).

3. Results

3.1. Characterisation of the amorphous nature

Fig. 1(a) shows the XRD patterns of the as-prepared glassy ribbons of ZNA and ZCA alloys. The diffraction patterns for both alloys consist
only of a broad diffuse peak, with no distinct crystalline diffraction lines, indicative of the formation of a completely amorphous phase. Fig. 1(b) shows the DSC curves of glassy ribbons of two alloys. With isochronous heating, the curves of the two alloys exhibit a well-defined endothermic plateau associated with the glass transition event, and sharp exothermic peaks related to the crystallisation of the amorphous phase are observed. The $T_g$ and $T_x$ are 697 K and 790 K and 684 K and 758 K for ZNA and ZCA MGs, respectively, indicating that the Ni-bearing MG is more thermally stable than the Cu-bearing MG. The temperature extensions of the supercooled liquid ($\Delta T_s = T_x - T_g$) for the ZNA and ZCA MGs are 93 K and 74 K, respectively, indicative of a typical glassy feature. The crystallisation entropy $\Delta S_x$ values for ZNA and ZCA are obtained by the integral of heat release of the crystallisation peak are 5.7 kJ/mol and 4.6 kJ/mol, respectively.

3.2. Pitting potential

Fig. 2(a) shows the typical potentiodynamic polarisation curves of ZNA and ZCA MGs exposed to a 0.6 M NaCl solution. Notably, no significant differences in the passive current density ($j_{pass}$) and corrosion potential ($E_{corr}$) between two MGs are observed. These values are on the order of several $\mu$A/cm$^2$ and approximately $-570$ mV vs. SCE, respectively. During upward scanning, both MGs exhibit typical pitting appearance is observed (not shown). For the ZNA MG, significant residual element species along the pit are not detected (Fig. 4(a)). Regarding the scatter of the recorded $E_{pit}$ values for a given alloy, the distribution of $E_{pit}$ from a number of measurements is more significant.

Fig. 2(b) shows the cumulative probability plot of $E_{pit}$ which reflects the probability of a given potential at or below the value on the x-axis. The $E_{pit}$ for ZNA is statistically much greater than that for ZCA. The dashed lines and shadow areas represent the average values and variation ranges (standard deviation) for the recorded $E_{pit}$ values, respectively. The average $E_{pit}$ values are 325 and $-160$ mV vs. SCE for ZNA and ZCA, respectively. Notably, the average $E_{pit}$ of ZNA is 485 mV greater than that of ZCA. Several definitions of $E_{pit}$ have been proposed, namely (i) the potential above which the stable pits propagate or a potential required to maintain a salt film inside a pit [18], (ii) a potential at which the chemistry of the pit solution is so sufficiently aggressive that it makes the passive film locally unstable and then suppresses repassivation [34], or (iii) the minimum potential at which metastable pits become stable [35]. Essentially, the magnitude of $E_{pit}$ reflects a critical state for a pit to sustain stable growth. In this sense, the Cu-bearing ZCA MG has been primarily thought to reach such a state considerably easier than Ni-bearing ZNA.

3.3. Artificial pit growth

According to the obtained $E_{pit}$ values, it is necessary to select an appropriate potential to control the growth of artificial pits. This potential should meet two basic requirements. First, it must be sufficiently greater than the $E_{pit}$ of each MG to ensure the diffusion-controlled pit growth. Newman et al. [18] have suggested that pit growth at a high potential is controlled by diffusion, accompanied by the formation of a metal salt film at the pit bottom, whereas mixed activation or ohmic control occurs at a low potential. Second, the selected potential should be less than the potential of oxygen evolution on the electrode surface to prevent the involvement of any additional anodic reaction. For Zr-based MGs, the oxygen evolution reaction typically occurs at around 1.2 V vs. SCE [3]. Considering these issues, the growth of artificial pits was maintained at 1 V vs. SCE.

The characterisation of the artificial pit covers two distinct stages [26,27], including potentiostatic polarisation at 1 V vs. SCE to establish diffusion-controlled pit dissolution and subsequent dropping the potential to $-1$ V vs. SCE to dissolve the salt film and render repassivation. Fig. 3 shows the data of potential and current versus the exposure time for artificial pits of two MGs with potentiostatic polarisation for 1800 s and subsequent potential backscanning. In the potentiostatic polarisation regime, the current rapidly decreases during the initial 300 s, which is associated with the proceeding of diffusion-controlled pit dissolution [26]. With increasing polarisation time, a near-steady state is attained. Notably, the current–time curves show a number of current transient events (Fig. 3), which are analysed in Section 3.5 in detail. The significance of data within the potential backscanning regime is further discussed in Section 3.6.

3.4. Pit depth and current efficiency

Fig. 4 shows the optical microscopy images recorded for the artificial pits of two MGs, which are subjected to potentiostatic polarisation in a 0.6 M NaCl solution for different times, including 600 s, 1200s, and 1800s. At polarisation times of 300 s, 900 s, and 1500 s, similar appearance is observed (not shown). For the ZNA MG, significant residual element species along the pit are not detected (Fig. 4(a)–(c)). In contrast, for the ZCA MG, considerable amounts of elemental Cu are left over along the pit because of the selective dissolution of Zr and Al (Fig. 4(d)–(f)). Fig. 5 shows the SEM images and element maps of the artificial pit for the ZCA MG subjected to a potentiostatic polarisation time of 1800 s. The enrichment of Cu (Fig. 5(e)) and depletion of Zr and Al (Fig. 5(b) and (d)) within the pit with respect to the bulk matrix are observed. The ratio of $[\text{Cu}] / ([\text{Zr}] + [\text{Cu}] + [\text{Al}])$ inside the pit increases up to 80 at%, where $[\text{Cu}]$ is the atomic percentage of element Cu. In addition, a small amount of Zr and Al as well as Cl (Fig. 5(e)) are detected inside the pit, probably originating from the Cl$^-$-concentrated pit.
solution. A large amount of O (even concentrated to ∼40 at%) in the pitting corrosion products inside the pit is observed, indicative of considerable hydrolysis of metal cations inside the pit [36]. The pit depth measured by OM, denoted as \(d_{\text{OM}}\), is plotted as data points in Fig. 6(a). With increasing polarisation time, the pit depth monotonically increases in both cases. Notably, at a given polarisation time, the \(d_{\text{OM}}\) of ZCA is approximately 1.4 folds greater than that of ZNA, indicating that the pit growth rate of ZCA is slightly greater than that of ZNA.

Alternatively, the pit depth can be calculated by Faraday’s law, denoted as \(d_{\text{Faraday}}\),

\[
d_{\text{Faraday}} = \frac{V}{A} = \frac{M}{A \rho z F} \int I \, dt
\]

where \(I\) is the current, \(t\) is the time, \(\int I \, dt\) is the dissolution charge, \(M\) is the average molecular weight of the alloy, \(A\) is the electrode area, \(\rho\) is the mass density, \(z\) is the number of the transferred electrons, and \(F\) is the Faraday’s constant. For the ZNA MG, a direct calculation is made using Eq. (1) because of the absence of any selective dissolution. Thus, \(M\), \(\rho\), and \(z\) are taken as the weighted average values of the constituent elements in the MG based on the rule of mixture, as 73.46 g/mol, 6.54 g/cm³, and 3.35, respectively. For the ZCA, however, the scenario is subtly complex. First, as only Zr and Al are dissolved, it is necessary to consider the values of \(M\), \(\rho\), and \(z\) for a Cu-free equivalent alloy with a nominal composition of (Zr60Al15)100/75, i.e. Zr80Al20, which are 78.38 g/mol, 5.76 g/cm³, and 3.80, respectively. Next, because of the effect of residual Cu, the actual dissolution volume, \(V\), is correlated to the apparent pit volume, \(V_{\text{app}}\), as follows

\[
V = V_{\text{app}} \left( r_{\text{Zr}} + r_{\text{Cu}} + r_{\text{Al}} \right) = 0.70V_{\text{app}} = 0.70d_{\text{Faraday}}A
\]

where \(r_{\text{Zr}}\), \(r_{\text{Cu}}\), and \(r_{\text{Al}}\) are the atomic radii of Zr, Cu, and Al, which are 0.16 nm, 0.128 nm, and 0.143 nm, respectively. By combining Eqs. (1) and (2), the \(d_{\text{Faraday}}\) of the ZCA MG is obtained. The \(d_{\text{Faraday}}\) of two MGs are shown as lines in Fig. 6(a). Because of the continuous \(I\)-\(t\) curves, the \(d_{\text{Faraday}}\) at each polarisation time can be obtained. Notably, the evolution trend of \(d_{\text{Faraday}}\) is comparable to the corresponding \(d_{\text{OM}}\). Similarly, the pit depth of ZCA is also approximately 1.4 folds greater than that of ZNA at a given polarisation time.

By comparing the ratio of \(d_{\text{Faraday}}\) to \(d_{\text{OM}}\), the current efficiency of pit dissolution for two MGs is determined. Fig. 6(b) shows the linear relationship between \(d_{\text{Faraday}}\) and \(d_{\text{OM}}\) for two MGs. The current efficiencies for the ZNA and ZCA MGs obtained from the slopes by linear fitting are 96% and 97%, respectively, indicating that only 4% and 3% of the anodic current is consumed by the cathodic reaction. Therefore, the current efficiency during pit growth appears to not be strongly related to the alloy composition and atomic-scale structure.
3.5. Transient current responses under potentiostatic polarisation

Notably, a number of current transient events are observed during potentiostatic polarisation at 1 V vs. SCE (Fig. 3(a) and (b)). In addition, similar transient responses are observed for the electrodissolution of iron, copper, and 304 SS in chloride-containing solutions. Such behaviour is physically related to the alternate build-up and breakdown of an unstable porous nonprotective salt film [29, 38–40]. After the breakdown of the salt film, the acceleration of localised dissolution leads to the formation of secondary pits. Fig. 7 shows the OM images of the observed secondary pits at the dissolving frontier of two MGs subjected to a transient response. Notably, the length of secondary pits for two MGs are quite comparable, with a maximum depth of ∼20 μm.

Fig. 8(a) and (b) shows the typical current transient response within a time interval of 200 s for two MGs. Fig. 8(c) and (d) shows the typical line profile of a single transient in two cases. Several parameters are
used for quantitative characterisation, including the transient peak current $I_{\text{peak}}$, transient growth time $t_g$, transient recovery time $t_r$, and transient lifetime $t_{\text{lifetime}}$. Apparently, three significant distinctions are observed: (i) the number of current transients for ZCA is greater than that for ZNA, (ii) the magnitude of current transients for ZNA is greater than that for ZCA, and (iii) the transients of ZCA show typical characteristics of a sudden jump followed by a gentle decay.

As the current transient is correlated to the salt film breakdown, the salt film breakdown frequency $\lambda$ is defined as

$$\lambda = \frac{N}{A \cdot t_{\text{interval}}}$$

where $N$ is the transient number at a certain time interval, $t_{\text{interval}}$, and $A$ is the surface area. Fig. 9 shows the $\lambda$ of two MGs at a $t_{\text{interval}}$ of 50 s. The scattered data reflect that the breakdown of the salt film is a highly stochastic process. $\lambda$ decreases with the increase of the pit growth time in both cases, probably corresponding to the thickening of the salt film and high difficulty for breakdown [41]. At a given time, the $\lambda$ of ZCA is several folds greater than that of ZNA, indicating that the salt film breakdown is more favourable on ZCA compared to ZNA. Furthermore, the current transient of ZNA rarely occurs after the pit growth lasts for ~600 s, roughly corresponding to a pit depth of 250 μm. For ZCA, the pit growth lasts for 1200 s to reach the same scenario, with a corresponding pit depth of ~510 μm.

By selecting a single transient with intervals of 30 s and 60 s, a total of 20 transients are counted for ZNA and ZCA MGs, respectively. The statistical analysis of $I_{\text{peak}}$, ratio of the transient recovery time to lifetime ($t_r/t_{\text{lifetime}}$), and secondary pit radius ($r_p$) is performed. Table 1 summarizes the average values and standard deviation for these parameters. Fig. 10(a) shows the cumulative distribution of $I_{\text{peak}}$ for the two MGs. The $I_{\text{peak}}$ of ZNA is greater than that of ZCA with statistical significance. The average $I_{\text{peak}}$ values for ZNA and ZCA are 0.35 mA and 0.16 mA, respectively, indicating that the accelerated localised dissolution of ZNA is more rapid compared to ZCA. Fig. 10(b) shows the cumulative distribution of $t_r/t_{\text{lifetime}}$ for the two MGs. The $t_r/t_{\text{lifetime}}$ for ZCA is greater than that for ZCA, indicating that the salt film on ZCA is considerably more difficult to be regenerated compared to that on ZNA. By the combination of integral charges for the current transient and Faraday’s law, the volume of secondary pits can be estimated. Based on the assumption that secondary pits are shaped as a semi-circular column (inset in Fig. 10(c)), the radius of the secondary pit ($r_p$) is calculated by the following equation,

$$r_p = \sqrt{\frac{2}{\pi d} \frac{M}{\rho zF} \int I \, dt}$$

where $d$ is the thickness of the ribbon sample, taken as 50 μm. Here, it is necessary to consider the effect of the selective dissolution behaviour for ZCA. Fig. 10(c) shows the cumulative distribution of the secondary pit radius for the two MGs. Notably, the $r_p$ of two MGs is quite comparable without significant differences, at a level of ~20 μm.

### 3.6. Kinetic parameters of pit growth

Fig. 11 shows the backscanning potentiodynamic polarisation curves of the two MGs after the completion of pit growth for several periods. Decreasing the potential leads to the dissolution of the salt film and the repassivation of MGs. For the ZNA MG, an apparent repassivation transition occurs. At the repassivation potential ($E_{\text{rp}}$), the current density suddenly decreases by two orders of magnitude. However, no obvious transition is observed for ZCA. For comparison, the potential at which the current density decreases by two orders of magnitude is determined as $E_{\text{rp}}$. Fig. 12 shows a plot of $E_{\text{rp}}$ against the pit growth time of the two MGs. Notably, the $E_{\text{rp}}$ of ZNA is around ~180 mV vs.
after the pit growth lasts for 300 s. With extending pit growth time, the \( E_{rp} \) is stabilized at a plateau of around \( -330 \text{ mV vs. SCE} \). The \( E_{rp} \) decreases with the increase in the anodic charge passed during pit growth (equivalent to the pit depth), and when a sufficiently large quantity of charge is passed, the \( E_{rp} \) becomes independent of pit depth, maintaining a constant level [26]. For the ZCA, however, all of the \( E_{rp} \) values attain a constant level, around \( -570 \text{ mV vs. SCE} \). In other words, when the pit growth lasts for 300 s, sufficient anodic charge has passed to attain a constant value of \( E_{rp} \). The \( E_{rp} \) of ZNA is 240 mV greater than that of ZCA, reflecting a considerably higher propensity to repassivation for the ZNA.

For both MGs, in the potential range of 1 V vs. SCE to \( \sim 0 \text{ V vs. SCE} \), a current density plateau is observed, implying that the dissolution at the pit bottom is controlled by diffusion once again [26,32,33]. Hence, the corresponding current density at the plateau indicates the diffusion-limited current density \( i_L \), which is taken at 0.5 V vs. SCE hereafter. With the increase in the pit growth time (or the pit depth), \( i_L \) decreases from \( \sim 0.45 \text{ A/cm}^2 \) to \( \sim 0.15 \text{ A/cm}^2 \). No significant differences in \( i_L \) between the two MGs is observed. By combining \( i_L \) with the pit depth as discussed in Section 3.4, another kinetic parameter, i.e. the pit stability product \( i_L \cdot d \), can be obtained. \( i_L \) shows a linear plot with the reciprocal of the pit depth \( d_{OM} \), where the slope of the line provides the \( i_L \cdot d \) value (Fig. 13). The \( i_L \cdot d \) values are 1.2 A/m and 1.7 A/m for ZNA and ZCA, respectively. Based on pitting theory suggested by Burstein [9], the pit stability product \( i_L \cdot d \) during stable pitting growth is approximately constant. For example, for 304 SS, \( i_L \cdot d \) ranges from 0.3 to 0.6 A/m. Moreover, Woldemedhin et al. [32] have calculated \( i_L \cdot d \) to be 0.4–0.9 A/m for 304 and 316 SS exposed to various Cl\(^-\)-containing solutions using artificial pit electrodes. The \( i_L \cdot d \) for SS is less than that of the current Zr-based MGs. In addition, Lucente et al. [24] have examined the pit stabilisation of Al\(_{90}\)Fe\(_{5}\)Gd\(_{5}\) MG and estimated an \( i_L \cdot d \) of \( \sim 1.6 \text{ A/m} \) when an artificial pit grows at 0.1 V vs. SCE. This value is comparable to those obtained herein for ZCA MG.

As the \( i_L \) of the two MGs reaches a magnitude of several tenths of A/cm\(^2\), it is necessary to consider the effect of potential drop caused by the
resistance of the pit solution and salt film inside the pit. The apparent resistance $R_{\text{app}}$ is obtained by high-frequency impedance measurements at a range from $10^5$ Hz to 1 Hz. Fig. 14(a) shows a plot of $R_{\text{app}}$ versus different pit growth times. For both MGs, $R_{\text{app}}$ increases with the pit growth times, corresponding to the accumulated pit solution and salt film thickening [41]. Notably, there is no significant difference in $R_{\text{app}}$ between the two MGs, ranging from 2 to 9 Ω·cm². Aburada et al. [25] have calculated an $R_{\text{app}}$ of $\sim$2.9 Ω·cm² inside the pit for (Al$_{75}$Cu$_{17}$Mg$_{8}$)$_{97}$Ni$_{3}$ MG. This value is comparable to that obtained for the Zr-based MGs herein. Using the product of $i_L$ and $R_{\text{app}}$, $i_L R_{\text{app}}$, the potential drop inside the pit is estimated (Fig. 14(b)). The potential drop fluctuates around a mean value of 1.2 V. Similarly, Isaacs [15] has calculated the potential across the surface resistive layer of 304 SS in a 1 M NaCl solution to be $\sim$1.1 V when the pit grow under 1 V vs. SCE. Also, Pickering and Frankenthal [42] have measured the potential inside the pit using a microprobe providing that the changes in the potential from the bulk surface to the pit bottom is $\sim$1 V.

4. Discussion

4.1. Estimation of local acidification with Galvele’s model

Generally, mass transport in solution mainly occurs by diffusion, electromigration, and liquid convection [19,42,43]. For the pit growth, liquid convection within the occlusion region is negligible. The effect of
Men in Eq. 10 is taken from an equivalent binary MG with a nominal in the bulk solution and HO M (OH) Hn 2 (n-1) is the amount (6) and is obtained as follows:

\[ \text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn} \]

\[ \text{Mn}^{2+} + \text{H}_2 \text{O} \rightarrow \text{M(OH)}^{(n-1)+} + \text{H}^+ \]

Meanwhile, the equilibrium of hydrolysis is assumed to be rapidly attained. Regarding Eq. (6), the flux equations of the species containing O, H, and M atoms are expressed as follows,

\[ D_i \frac{dC_i}{dx} + D_{MOH} \frac{dC_{MOH}^{(n+1)}}{dx} = 0 \]

\[ 2D_i \frac{dC_{iH}}{dx} + D_{MOH} \frac{dC_{MOH}^{(n+1)}}{dx} + D_{iF} \frac{dC_{iF}}{dx} = 0 \]

\[ D_M \frac{dC_{M^+}}{dx} + D_{MOH} \frac{dC_{MOH}^{(n+1)}}{dx} = \frac{i_j}{zF} \]

where \( D_j \) is the diffusion coefficient of species \( j \) and \( C_j \) is the concentration of species \( j \). In Eq. (9), the right-hand term \( \frac{i_j}{zF} \) is the amount of freshly generated metal cation. Combining Eqs. (7), (8), and (9) and eliminating the terms of the H2O and M(OH)\(^{(n-1)+} \) species, the flux equation of the metal cation and H\(^+ \) is expressed as follows

\[ D_M \frac{dC_{M^+}}{dx} + D_{iF} \frac{dC_{iF}}{dx} = \frac{i_j}{zF} \]

By taking the line integral along the pit depth, the relationship between \( C_{M^+}^{sat} \) and \( C_{iF} \) is obtained as follows:

\[ D_M \frac{dC_{M^+}}{dx} + D_{iF} \frac{dC_{iF}}{dx} = \frac{i_j}{zF} + x_1 \]

where \( x_1 \) is the boundary condition when \( d = 0 \), which is the product of \( C_{iF} \) in the bulk solution and \( D_{iF} \). Generally, the solution at the pit bottom is mostly saturated by metal chloride [11]. Thus, the \( C_{M^+}^{sat} \) in Eq. (11) is taken from the weighted average concentration of the saturated metal chloride, \( C_{M^+}^{sat} \), of each element in the MG. Table 2 summarizes the relevant constants and parameters used for the model. Herein, notably, \( C_{M^+}^{sat} \) is taken from an equivalent binary MG with a nominal composition of Zr60Al20 without copper for ZCA. Then, for ZNA and ZCA MGs, the \( C_{ZNA}^{sat} \) and \( C_{ZCA}^{sat} \) are 3.38 M and 2.9 M, respectively. Based on Eq. (11), the calculated \( C_{H^+}^{ZNA} \) and \( C_{H^+}^{ZCA} \) for ZNA and ZCA MGs are 0.04 M and 0.18 M, respectively. The converted pH values are 1.3 and 0.8, respectively. For comparison, notably, the measured pH of solution in the occluded cells (in the form of pits or crevices) for several austenitic SS is known to range from 0.13 to 2.0 [44, 45]. This result indicated that the local acidity in the pits of two MGs is comparable to that of SS. According to the calculated pH, the acidity of the pit solution for Cu-bearing ZCA is greater than that for Ni-bearing ZNA MG, indicating that the pit solution is more aggressive for ZCA.

### 4.2. Differences in the pit growth kinetics

Our results indicated that the two investigated MGs, ZNA and ZCA, exhibit apparently different features either in the initial stage or in the steady stage of stable pitting growth. Fig. 16 shows the schematic graphs to describe the diffusion-controlled pit growth for two MGs. For comparison purposes, Table 3 summarizes remarkable differences in

\[ \text{M} \rightarrow \text{M}^{n+} + \text{e}^- \]

\[ \text{M}^{n+} + \text{H}_2 \text{O} \rightarrow \text{M(OH)}^{(n-1)+} + \text{H}^+ \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_M )</td>
<td>( 10^{-9} )</td>
<td>m²/s</td>
<td>[19]</td>
</tr>
<tr>
<td>( D_{iF} )</td>
<td>( 9.3 \times 10^{-9} )</td>
<td>m²/s</td>
<td>[19]</td>
</tr>
<tr>
<td>( C_{M^+}^{sat} )</td>
<td>2.85</td>
<td>mol/L</td>
<td>[47]</td>
</tr>
<tr>
<td>( C_{Al^{3+}}^{sat} )</td>
<td>3.11</td>
<td>mol/L</td>
<td>[41]</td>
</tr>
<tr>
<td>( C_{Ni^{2+}}^{sat} )</td>
<td>4.8</td>
<td>mol/L</td>
<td>[48]</td>
</tr>
</tbody>
</table>

\( D_j \): diffusion coefficient of species \( j \); \( C_{M^+}^{sat} \): saturated concentration of metal chloride.

Fig. 15. Schematic diagram of pit geometry based on Galvele’s localised acidification model.

Fig. 14. (a) Apparent resistance, \( R_{app} \) and (b) corresponding IR-drop versus several periods of potentiostatic polarisation for two MGs.

Electromigration within the pit is less predominant. For a 1-mm-deep pit, the potential drop caused by electromigration is approximately 67 mV [33]. This value is considerably less than that caused by the diffusion effect ( > 1 V). In this sense, in the local acidification model proposed by Galvele [19], only the diffusion equation is considered during the mass transfer, whereas the contributions from electromigration and liquid convection are neglected. Based on this model, the ion concentrations at the pit bottom are estimated for the ZNA and ZCA MGs.

The pit geometry during pit growth is assumed to be one-dimensional (Fig. 15). Two reactions, the anodic dissolution of the metal and the first-order hydrolysis of the metal cation, are considered at the pit bottom, namely,
the behaviour of stable pitting growth between two MGs.

First, in both cases, stable pitting rapidly reaches a diffusion-controlled growth state accompanied by the formation of a metal salt film at the pit bottom [26], as proven by a dramatic decrease in the current initially during potentiostatic polarisation (Fig. 3) and by an extensive plateau of the current density during potential backscanning (Fig. 11). Nevertheless, the salt film formed initially is less stable and can easily break down, leading to the accelerated localised dissolution and the formation of secondary pits. As indicated by the current transient events, the salt film formed on ZCA is considerably easier to be broken down and more difficult to be regenerated compared to that on ZNA. This result is supported by its higher values of \( \lambda \) and \( t_r/t_{ls} \). For the ZCA MG, the breakdown process of the salt film can last longer until the maturation of a deeper pit compared to the ZNA MG. The poor stability of the salt film for ZCA is probably related to the more aggressive pit solution, as discussed in Section 4.1. However, after the breakdown of the salt film, secondary pits of the two MGs are substantially comparable, with a radius of \( \sim 20 \mu m \).

Moreover, during the steady stage, differences in the dissolution current efficiencies between the two MGs are not significant, which is close to 1. This result indicated that the central event that occurs at the pit bottom is anodic dissolution. Because of selective dissolution, when the pit growth is sustained for a while, the pit volume and corresponding pit depth for ZCA is 1.4 folds greater than those for ZNA. In other words, the as-initiated pits in ZCA are more favourable to propagate at a higher growth rate. In addition, no significant differences in the diffusion-limited current density and apparent resistance inside the pit are observed between the two MGs.

Pickering and Frankenthal [42] have suggested that if the metal is under the pH and potential at the pit bottom, it is located in the active region of the Pourbaix diagram, and spontaneous dissolution is sustained. Based on the local acidification model, the pH of ZNA and ZCA are calculated as \( \sim 1.3 \) and \( \sim 0.8 \), respectively. The real potential \( E_{\text{real}} \) at the pit bottom is expressed as follows:

\[
E_{\text{real}} = E_{\text{app}} + \lambda \cdot R_{\text{ap}}
\]

where \( E_{\text{app}} \) is the externally applied potential, which is 1 V vs. SCE in this study. As the potential drop is calculated as 1.2 V as discussed in Section 3.6, the real potential at the pit bottom is roughly estimated as \( \sim 0.2 \) V vs. SCE in both MGs. In light of the Pourbaix diagram [46], the thermodynamic states of each element species in the MGs are generally estimated. For the ZNA MG, at a pH of 1.3 and \( E \) of \( \sim 0.2 \) V vs. SCE, all three constituent elements, Zr, Al and Ni, are present in the active dissolution state. In contrast, for the ZCA MG, at a pH of 0.8 and \( E \) of \( \sim 0.2 \) V vs. SCE, only two base metals Zr and Al are in the active dissolution state, while the Cu is under corrosion immunity. This result suggested that such intrinsic differences in the thermodynamic consideration between these two MGs are responsible for whether the selective dissolution occurs.

In brief, for the Cu-bearing ZCA MG, its more rapid rate of pit growth and more aggressive pit solution implied that pits are extremely favourable for stable growth. Hence, the ZCA MG exhibits an
apparently weaker pitting resistance compared to the ZNA MG, as directly highlighted by its considerably lower $E_{pc}$ and $E_{pc}$. In other words, in LTM-bearing Zr-based MGs, the dependence of the pitting resistance on the LTM species is intrinsically related to the significantly different pitting growth behaviours.

5. Conclusions

By virtue of artificial pit electrode approach, different growth behaviours of stable pits between two LTM-bearing Zr-based MGs, Zr$_{60}$Ni$_{25}$Al$_{15}$ and Zr$_{60}$Cu$_{25}$Al$_{15}$, respectively, exposed to a 0.6 M NaCl solution were revealed, as highlighted by the following aspects.

(i) By characterising the transient current events at the initial stage of stable pitting growth, the salt film formed on the Zr$_{60}$Cu$_{25}$Al$_{15}$ MG is broken down considerably easier than Zr$_{60}$Ni$_{25}$Al$_{15}$ as well as is more difficult to be regenerated. After the breakdown of the salt film, however, substantially comparable secondary pits are formed on both MGs.

(ii) Because of the occurrence of the selective dissolution of base-metal elements such as zirconium and aluminium, the pit growth rate of Zr$_{60}$Cu$_{25}$Al$_{15}$ MG is greater than that of Zr$_{60}$Ni$_{25}$Al$_{15}$ MG. No significant differences in the dissolution current efficiency, diffusion-limited current density, apparent resistance inside pits, and the corresponding potential drop are observed between the two MGs. The $i_{pk}$ values for the pit stability products of Zr$_{60}$Ni$_{25}$Al$_{15}$ and Zr$_{60}$Cu$_{25}$Al$_{15}$ MGs are 1.2 A/m$^2$ and 1.7 A/m$^2$, respectively. Combined with the local acidification model, the converted pH values at the pit bottom are 1.3 and 0.8, respectively, indicating that the Zr$_{60}$Cu$_{25}$Al$_{15}$ suffers a more aggressive pit growth.

(iii) Under the estimated pH and real potential at the pit bottom, all three constituent elements in Zr$_{60}$Ni$_{25}$Al$_{15}$ fall within the active dissolution state based on thermodynamic considerations. In contrast, for the Zr$_{60}$Cu$_{25}$Al$_{15}$ MG, only two base metals zirconium and aluminium are in the active dissolution state, while copper is under corrosion immunity. Such differences are responsible for whether selective dissolution occurs.

In summary, the stable pitting growth for Zr$_{60}$Cu$_{25}$Al$_{15}$ MG is considerably more favourable compared to Zr$_{60}$Ni$_{25}$Al$_{15}$ because of its more rapid growth rate and more aggressive pit solution. Such a difference in the kinetic behaviour also directly correlates to the indication of pitting potential ($E_{pc}$) in that the latter is considerably greater than the former (~485 mV). As a result, the effect of the LTM species in Zr-LTM-Al MGs on the pitting resistance is intrinsically related to their different pitting growth kinetics.

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