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Experimental study of corrosion rate supplied with an ab-initio elucidation of corrosion mechanism of biodegradable implants based on Ag-doped Zn alloys

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ABSTRACT

Biodegradable Zn-based alloys hold great promise for biomedical implant applications, with the Zn-Ag-Cu alloy being particularly intriguing due to the additional antibacterial and antimicrobial properties. Here, to enhance the mechanical properties of the Zn-4%Ag-1Cu alloy, equal-channel angular pressing (ECAP) is employed, which is found to induce strain and lattice distortions leading to a grain size decrease and corrosion rate enhancement. To understand key factors of the surface degradation behavior on atomistic level, the density-functional theory (DFT)-based method was employed. Specifically, the study investigated the corrosion mechanism of the Zn-Ag-Cu alloy's surface, providing valuable insights into the degradation behavior of Zn-Ag-Cu alloys. Both experiment and simulation reveal a higher corrosion resistance for the Zn-Ag-Cu alloys with higher Ag content that can be due to a homogeneous distribution of alloying induced stresses. The intermetallic component is shown to have the lowest degradation ability, which is important in terms of its contribution to dispersion hardening of the alloy. This work presents a comprehensive study shedding light on the corrosion rates of Zn-Ag-Cu alloys, which is useful for the development of biodegradable implants with improved structural and degradation characteristics.

1. Introduction

Corrosion properties play a crucial role in all structural materials, but they are of utmost importance in the case of bioresorbable alloys [1-4]. These materials provide an alternative to non-degradable materials in orthopedics to address the clinical challenges associated with stress protection and secondary surgery. It is crucial to consider the corrosion properties of these alloys to ensure they meet the required standards for medical applications. Currently, a significant focus in medicine is on the issue of damage to bones and soft tissues, which increases the demand for biocompatible materials that are non-toxic when exposed to the human body for long period of time [1-7]. The primary benefit of such materials is their capacity to dissolve in the body gradually, therefore avoiding the need for further surgical interventions. Among these biodegradable materials zinc-, iron- and magnesium-based are of significant interest [8–10], with zinc alloys being particularly notable. Zinc is recognized as a material having a nearly perfect corrosion rate among biodegradable alloys. Although the toxicity limit of zinc (100–150 mg/ d) is lower than that of magnesium (375–500 mg/d), this does not curb the use of zinc in biodegradable implants [1,11–13]. However, one drawback of pure zinc is its low tensile strength, which is lower than 50 MPa. To enhance its mechanical properties, severe plastic deformation and alloying are applied [14]. It is worth noting that the selection of alloying metals for biodegradable materials is restricted because some alloying elements may decrease corrosion resistance and deteriorate biocompatibility. Zinc alloys with silver and copper additions possess commendable antibacterial and antimicrobial properties, making then promising for urinary stent implants [15,16]. Silver ions effectively

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eliminate bacteria in the vicinity of the implant surface and copper is a crucial trace element vital for the growth of nerves, connective tissues and bones, besides its possessing exceptional antibacterial properties.

Grains refinement via severe plastic deformation (SPD) presents an alternate avenue for enhancing mechanical robustness of biodegradable alloys. Previously, objective research has demonstrated that the application of hot extrusion can significantly enhance the tensile strength of pure zinc, up to 110 MPa, while concurrently increasing plasticity to 14 % [17]. The use of severe plastic deformation by torsion in pure zinc with an equivalent deformation of 18 leads to a significant increase of its tensile strength up to 130 MPa and an increase of its ductility up to 40 % [18]. The microstructural refinement after high pressure torsion (HPT) leads to an increase of strength (σ_{02} increases from 70 MPa to 200 MPa, σ_B - increases from 90 MPa to 270 MPa) and ductility of pure zinc [19]. The application of SPD, in particular, Equal Channel Angular Pressing (ECAP) and alloying of zinc alloys, such as Zn-0.1 %Mg, allows to increase their tensile strength up to 380 MPa and their relative elongation up to 45.6 % [20]. By increasing the magnesium content to Zn-1 %Mg and using HPT, the strength of zinc alloys can be increased to \approx 470 MPa and their ductility to $\approx 7\%$ [21]. For the Zn-1.6 %Mg alloy using ECAP at 150 °C, after 12 passes, an ultimate strength of 423 MPa and a ductility of 5.2 % were achieved [22].

The research [23] indicates that there is an improvement in the strength characteristics of Zn-1 %Cu-1 %Ag and Zn-1 %Cu-0.5 %Ag zinc alloys as a result of hot extrusion. The tensile strength increases to \sim 295 MPa, while ductility decreases to 36 % for Zn-1 %Cu-1 %Ag and to 26 % for Zn-1Cu-0.5Ag. Further analysis of the mechanical and corrosion features of Zn-Ag alloys with varying silver content revealed that hot extrusion leads to a decline in grain size in these alloys. High silver content of 7 % results in a noteworthy rise of tensile strength up to 236 MPa and ultimate strength up to 287 MPa. This effect is due to the grain refinement and high proportion of AgZn3 fine particles intrinsic to the extrusion process. Negligible corrosion acceleration was shown by the Zn-Ag alloys in degradation tests. The analysis of degradation products revealed the presences of ZnO and Zn(OH)2 on the surfaces of the degraded specimens. The specimens featuring high silver content of 5 %-7 % present reduced micro galvanic corrosion as a consequence of the increased volume fraction of AgZn3 particles that act as anode sites.

Corrosion resistance is usually evaluated experimentally using mass loss and corrosion rate methods. However, those methods are integral and does not allow to identify the nature of factors lead to the change of the degradation rate. It is known that during corrosion new chemical bonds are formed, which significantly changes the structure and symmetry of the lattice. DFT-based approach proves to be an effective tool for prediction the structure and characteristics of materials due to its prevalent consistency with experimental outcomes. The DFT-based method permits the estimation of deviation from an ideal crystal lattice state and to evaluate the deformation of the crystal lattice and the distortion of its symmetrical structure at the atomic level, resulting from several factors, including alloy atom insertion, external impacts and others. This opens up new possibilities for designing materials based on high symmetry estimates of crystal lattice deviation.

DFT-based methods have been previously employed to study degradation and mechanical performance of alloys [24–26] to scrutinize 2D materials [27–29] and their amalgamation [30–32]. The studies utilize DFT to examine the responses of gas sensors to different organic substances, specifically investigating the reactions of gas sensors based on ZnO to volatile organic compounds [33] and exploring a range of graphene-based sensors [34–36]. DFT-based calculations have also been used to study the reaction properties of metals, including the adsorption of various substances on their surfaces and the resulting processes. For instance, the corrosion of steels in concrete due to chlorine ions, with the nature of the oxide film dissolution clarified has been examined through DFT calculations [30]. Chlorine decreases the bond length between oxygen and iron at the surface, and it likewise contributes to the loss of charges of iron atoms, thereby enhancing their interactions with water

Table 1		
Chemical com	position of a	lloys.

Alloy	Chemical elements composition, %			
	Zn	Ag	Cu	Other
Zn-1 %Ag-1 % Cu Zn-4 %Ag-1 % Cu	95.93 ± 0.11 92.68 ± 0.12	$\begin{array}{c} 1.05 \pm \\ 0.1 \\ 4.08 \pm \\ 0.1 \end{array}$	$\begin{array}{l} 0.758 \pm \\ 0.04 \\ 1.06 \pm 0.05 \end{array}$	$egin{array}{c} 1.08 \pm \\ 0.08 \ 1.18 \pm \\ 0.08 \end{array}$

molecules and promoting corrosion processes. In [37], the impact of small molecules on the surface of arsenene, as well as procedures for safeguarding the material from corrosion have been analyzed. Protection against corrosion, such as corrosion inhibition have been actively studied with the aid of DFT. For instance, quinazoline derivatives have been investigated to protect mild steel from hydrochloric acid [38]. Additionally, the efficacy of Tramadol as a safe inhibitor for the prevention of corrosion in aluminum from hydrochloric acid has been assessed in [39]. This is one of numerous examples demonstrating that DFT calculations play a pivotal role in corrosion studies, offering precise insights into electronic structure changes and reactivity, enabling the development of effective corrosion inhibitors. They bridge the gap between corrosion inhibition efficiency and molecular orbital energy, shedding the light on inhibitory mechanisms via precise examination of lattice distortions and symmetry, leading to a better understanding of how these factors alter the charge distribution within the lattice.

This study examines zinc alloys containing 1 % and 4 % of silver, both in their initial state and after SPD [40–43]. All alloys from the same Zn-Ag-Cu system exhibited high tensile strength values of 348 MPa and good ductility up to 30 %. The study focuses on their corrosion properties, particularly, the oxygen adsorption properties and chemical reactions at the surface. The aspects of asymmetry of zinc crystal lattice due to silver atoms and its impact to the surface degradation is studied. A comparison of experimental data on the corrosion resistance of Zn-Ag-Cu alloys and the Zn₃Ag intermetallic phase with the results obtained via DFT modeling allow to access both integral corrosion characteristics and atomic mechanisms associated with lattice strains. Thus allowing to design zinc-based alloys with tailorable biodegradations properties.

2. Materials and methods

2.1. Experimental details

The studied materials were zinc alloys of the Zn_xAgCu system with different silver contents of x = 1 % and x = 4 %, more details in [40]. The chemical composition was measured using an ARL Optim'X X-ray fluorescence spectrometer. X-ray diffraction patterns were recorded in the continuous scanning mode at a speed of 1°/min within the scattering angle of 20 from 10° to 150° on Cu radiation generated at a voltage of 40 kV and a current of 40 mA. More details can be found in [40]. The results can be found in Table 1. All specimens underwent analysis after homogenisation annealing. Prior to certification preparation a specimen of the necessary dimensions and shape was carved using an ARTA-120 CNC electrical discharge machine. Microsections were then generated from the acquired specimens on waterproof sanding paper of diverse grit sizes with a continual transition from rough P100 to finer P4000 abrasive. Before progressing to the next abrasive number, metal dust from the section was meticulously eliminated and the grinding direction was shifted by 90°. The microstructure of the alloy was studied using the JEOL JSM-6490LV and FEI Thermo Scientific Q250 scanning electron microscopes (SEM) at an accelerating voltage of 25 kV and SEM Tescan energy dispersive analysis was carried out using the Aztec program at an accelerating voltage of 20 kV.

The gravimetric method following ASTM G1-03-E [44] was used to investigate corrosion resistance. Immersion tests were performed in Ringer's solution at 38 °C, containing NaCl (8.6 g/L), KCl (0.3 g/L),



Fig. 1. Unit cell (a) and $6 \times 6 \times 4$ supercell (b) of Zn.

CaCl₂ (0.25 g/L), and saline solution pH = 7. Samples were removed every 48 h during the 35-day study, cleaned and weighed using an A&D GR-123 analytical balance providing measurement accuracy of 0.001 g. Before measuring the samples mass, the corrosion products were removed from the samples by washing them in an ultrasonic bath model BAKU BK-9050. The bath was operated at 50 W power for 2 min with a washing solution containing 200 g of CrO₃ and 1000 ml of water (as per GOST 9.907-2007). Distilled water was used after that for additional purification to determine the exact weight loss of samples studied. At least three samples were taken for each condition. The corrosion rate (CR) in mm/year was calculated according to the ASTM G1 03-E standard as follows:

$$CR = \frac{K(M_0 - M_1)}{S\rho\tau},\tag{1}$$

where K = 8.76*104, h is the coefficient for the transition from measuring the weight indicator of the corrosion rate per 1 h to the depth indicator per 1 year (24 h × 360 = 8760 h); *S* is the sample surface area, cm²; M₀ – initial mass, g; M₁ – mass after immersion, g; τ is the holding time, h; ρ – metal density, g/cm³. The mass loss in % was calculated as follows:

$$ML = \frac{(M_0 - M_1)}{M_0}.100\%,$$
(2)

where M_o is the initial mass, g; M₁ is the mass after immersion, g.

2.2. Simulation details

Spin-polarized DFT-based calculations were carried out using the



Fig. 2. Top and side views of Zn(100) (a), Zn(110) (b) and Zn(111) (c) slab models.

Table 2

Surface parameters of Zn slab models.

Surface plane	Surface area, Å ²	<i>E_{surface}</i> , eV/Å
(100)	219.90	0.0698
(110)	458.74	0.0826
(111)	450.15	0.0839



Fig. 3. Top and side views of Ag-doped Zn-1%Ag (a) and Zn-4%Ag (b) slab models.

Vienna Ab Initio Simulation Package (VASP) [45]. The generalized gradient approximation parameterized by Perdew–Burke–Ernzerhof exchange–correlation functional were used [46]. All structure's models were built using VESTA software [47]. The most stable electronic state for all considered structures was found by geometry optimization. The periodic boundary conditions were used. Cutoff energy value of 520 eV was used. Energy and force convergence tolerances were 1×10^{-4} eV/ atom and 0.001 eV/Å, respectively. The Brullouin-zone integrations were sampled with a 30 × 30 × 20 centered *k*-point mesh for bulk Zn. For sampling the Brillouin zone, k-points mesh was employed, where the number of *k*-points (NK) was selected so that NK × L equal to ~30–40 Å, where L is the lattice constant [48]. The optimized Zn unitcell structure (Fig. 1a) belongs to the space group of P63/mmc and has lattice parameters *a* = 2.610 Å, *b* = 2.610 Å and *c* = 4.869 Å.

The Zn unitcell structure was expanded to 6x6x4 supercell (Fig. 1b) to create Zn slab models. Three slab models Zn (100), Zn (110), and Zn (111) were used as shown in Fig. 2a–c. The Brullouin-zone integrations for slab models were sampled with a $1 \times 1 \times 1$ centered k-point mesh. All slab models have 6 atomic layers and a vacuum size of 20 Å to avoid interactions with the periodic layer. The upper layers of atoms were free to move and the lower two layers were fixed to simulate bulk.

Surface energy E_{surf} was calculated as follows:

$$E_{surf} = \frac{E_{slab} - \frac{N}{n} E_{bulk}}{2A},\tag{3}$$

where E_{slab} is the energy of the slab, E_{bulk} is the energy of the unit cell, A is the surface area, n is the number of atoms in the unit cell, and N is the number of atoms in the slab model.

The data obtained during the calculation is presented in Table 2. According to Table 2 it can be concluded that the (100) surface is the most energetically favorable one for adsorption processes as it possesses the lowest E_{surf} of 0.0698 eV/Å² among considered surfaces. In order to simulate the Zn-xAg-1 %Cu alloy, the model of the Zn (100) slab doped by Ag atoms was created. For x = 1 % (see Fig. 3a) and x = 4 % (see Fig. 3b), 3 Ag and 12 Ag atoms, respectively, were added into the Zn



Fig. 4. Top and side views of Zn₃Ag(100) (a), Zn₃Ag(110) (b) and Zn₃Ag (111) (c) slab models.

Table 3

Surface parameters of Zn₃Ag slab models.

Surface plane	Surface area, Å $^{\rm 2}$	$E_{\rm surf,}~{\rm eV/\AA}$
(100)	200.628	0.1071
(110)	231.270	0.0951
(111)	214.240	0.0970

lattice. Ag atoms were distributed randomly across the grid. Cu additions were not considered in slab models as per experimental data there is no Cu phase on the surface except for (Ag,Cu)Zn₄, which is observed at higher magnification at grain boundaries with a volume fraction of less than 1 %. The tolerances for convergence of force and energy, as well as cutoff energy value, remain the same as for pure Zn. For doped Zn, the upper layers of atoms were free to move and the lower two layers were fixed to simulate bulk.

According to experimental results, the presence of Zn₃Ag intermetallic phase on the Zn-x%Ag-1 %Cu alloy surface is found. Therefore, this intermetallic compound and its structure and adsorption behavior was also considered. It should be noted, that the intermetallic compound has covalent bonds and the adsorption process on the surface of such materials is challenging. It is not feasible to anticipate a significant contribution to the corrosion process from the intermetallic counterpart. The intermetallic compound adopts a hexagonal lattice with space group symmetry P63/mmc and lattice parameters a = 5.484 Å, b = 5.484 Å, and c = 4.600 Å. To determine the surface energy of elemental Zn₃Ag phase, a 6x6x7 *k*-point mesh was employed. Zn₃Ag(100), Zn₃Ag(110), and Zn₃A (111) slab models with a vacuum size of 20 Å were created (Fig. 4a–c). The tolerances for convergence of force and energy, as well as cutoff energy value, remain the same as for pure Zn. For doped Zn, the upper layers of atoms were free to move and the lower two layers were fixed to simulate bulk.

The data obtained during the calculation of the surface energy for Zn₃Ag is presented in Table 3. Based on the data obtained, it can be concluded that the Zn₃Ag(110) surface is the energetically favourable one for adsorption processes due to its low surface energy $E_{\text{surf}} = 0.0951 \text{ eV} / \text{Å}^2$ among considered surfaces.

The corrosion process is considered as the interaction of abovementioned Zn-based alloys surfaces with the oxygen molecule (O_2) as an adsorbate. It should also be noted that due to the complexity of the considered DFT model, as it is already includes many factors such as Ag concentration, surface plane and orientation of the adsorbat, etc, the specific media was not taken into account [26,49,50]. The O_2 not only lead to a fast degradation of metals in air but also exist in human blood and is a strong oxidizing agent, thus, its presence preliminary contributes to the corrosion of implants located inside the body [42]. The adsorption energy E_{ads} of O_2 on the surface was calculated as follows:

$$E_{ads} = E_{total} - E_{slab} - E_{adsorbate},\tag{4}$$

where E_{total} is the total energy of the system with the adsorbate, E_{slab} is the energy of the isolated slab, and $E_{\text{adsorbate}}$ is the energy of the isolated O₂ molecule.



Fig. 5. Microstructure of the Zn-4%Ag-Cu alloy in the as-cast state (a) and after ECAP (b). The EDS patterns of the Zn-4%Ag-Cu alloy for the element distribution in the initial state (c).



Fig. 6. Microstructure of the Zn-1%Ag-Cu alloy in the as-cast state (a) and after ECAP (b).



Fig. 7. The X-ray diffraction patterns of the Zn-4%Ag-Cu (a) and Zn-1%Ag-Cu (b) alloys.

3. Results

3.1. Microstructure

It is found that the Zn-4 %Ag-Cu alloy has an original eutectic structure containing dark Zn grains and twins. A ternary eutectic is observed in the volume and at the edges of the studied sample (Fig. 5a). The presence of ternary eutectic in the studied system was observed earlier in [51], where the patterns in SEM images correspond to the ones observed here. The eutectic volume fraction amounts to 20 ± 0.5 %. After undergoing Equal Channel Angle Pressing (ECAP), the structure undergoes noticeable transformation. Dynamic recrystallization occurred during deformation results in a banded structure containing two types of precipitates with the size ranging from 90 nm to 690 nm and an average width of 1.3 µm (Fig. 5b). Treatment with ECAP at

150 °C leads to an increase of the Zn-4 %Ag-Cu precipitates size. The precipitation of AgZn₃ particles and growth of the dislocation density is evidenced by SEM imaging. The ternary particle volume percentage is measured to be 21 \pm 0.5 % [40].

The EDS patterns of the Zn-4 %Ag-Cu alloy for the element distribution in the initial state are shown in Fig. 5c. The color distribution analysis of the EDS plot indicates that intermetallic particles primarily consist of a combination of zinc and silver, with a discernible presence of silver within the solid solution. Furthermore, an examination of the internal structure of these particles reveals a fair homogeneity in terms of chemical composition. It should be noted, that the EDS data for the element distribution of the Zn-4 %Ag-Cu alloy in the ECAP state are not available due to small size of particles formed after the ECAP.

The Zn-1 %Ag-Cu zinc alloy exhibits a polyhedral microstructure comprising of coarse grains with the average size of 326 \pm 31 μm and of

Table 4

Surface images of Zn-Ag-Cu alloy samples in different initial states after corrosion tests for 40 days.

	2 nd day	7 th day	11 th day 16 th day	21 st day	25 th day	30 th day	35 th day	40 th day
Zn-1%Ag- 1%Cu cast structure								
Zn-1%Ag- 1%Cu ECAP	٢	Û		0		0	0	0
Zn-4%Ag- 1%Cu cast structure	×D			S				
Zn-4%Ag- 1%Cu ECAP		A.						



Fig. 8. (a) Corrosion rate of Zn-1 %Ag-Cu as cast alloy (green line) and after ECAP (yellow line), Zn-4 %Ag-Cu as cast alloy (red line) and after ECAP (blue line) for samples during immersion in Ringer's solution for a period of 1–40 days. (b) CR of Zn-1 %Ag-Cu as cast alloy (green bar) and after ECAP (yellow bar), Zn-4 %Ag-Cu as cast alloy (red bar) and after ECAP (blue bar) calculated according to Eq. (1), in mm per year. The test was performed in Ringer's solution.

structural twins. The initial hexagonal phase and the ternary intermetallic phase of zinc, silver and copper contain α -Zn. The SEM imaging at high magnifications allow to reveal presence of the Zn-4 %Ag-Cu particles having a typical dense hexagonal crystal structure similar to the one of the Zn matrix [40,52]. However, its volume fraction is less than 1 %, as illustrated in Fig. 6a. Fig. 6b displays that the alloy experiences marked grain refinement following the ECAP treatment. The mean grain size is 3 \pm 0.5 μ m, and particle release occurs along the grain boundaries, as demonstrated in Fig. 6a,b. The volume fraction of the second phase experiences a significant increase to 1.8 \pm 0.4 %.

According to the X-ray analysis (Fig. 7a,b), the application of ECAP processing at 150 °C leads to an increase of the presence of Zn-4 %Ag-Cu precipitates, the formation of additional AgZn₃ particles and a rise of the dislocation density. Moreover, the presence of two distinct precipitates after ECAP treatment at 150 °C is observed. It is noteworthy that the crystal lattices of all three phases, Zn, Zn-4 %Ag-Cu, and AgZn₃, appear to be distorted. These findings addressed in [35], allow to determine different chemical composition of observed precipitates that can affect the corrosion dynamics of the alloy.

3.2. Corrosion behavior

Table 4 displays the structure changes of the considered Zn-Ag-Cu alloys in Ringer's solution during 40 days. An increase of the corroded surface area with time is clearly visible. The effect of the solution on the samples and the progression of the corrosion are in line with the mass loss test of the samples presented in Fig. 8a.

The investigation of the corrosion resistance revealed no significant impact of ECAP on the alloy's degradation rate (Fig. 8b). It is found that the studied Zn-Ag-Cu alloy in a coarse-grained state showed heightened localized corrosion activity and corrosion predominantly occurred along the grain boundaries. The corrosion progress graph demonstrates that intensive corrosion in the Zn-Ag-Cu alloy in a coarse-grained state takes place in the first few days. However, as samples remain exposed in the Ringer solution for an extended period, the rate of corrosion gradually declines. It is expected that the main reason for the is that after the atoms at the grain boundary are already undergone a chemical reaction further corrosion requires overcoming a greater potential barrier due to position of resting atoms in the undistorted lattice. Consequently, the mass loss process is significantly slower, as demonstrated in the graphs in Fig. 8a. The higher loss of mass and lack of saturation plateau on the CR dependency for post ECAP sample Zn-4 %Ag-1 %Cu may be attributed to



Fig. 9. SEM images of the microstructure of the Zn-1 %Ag-1 %Cu alloys – cast alloy (a,b) and after the ECAP (c,d) and the microstructure of the Zn-4 %Ag-1 %Cu alloys – cast alloy (e,f) and after the ECAP (g,h) after 23 days of aggressive solution exposure.



Fig. 10. Top and side views the O_2 molecule on the surface of pure Zn(100) (a), Zn-1%Ag(100) (b), Zn-4%Ag(100) (c) and $Zn_3Ag(110)$ (d).

the growth of the ternary Zn-4 %Ag-Cu phase and the AgZn₃ phase at the boundaries, which result in micro-galvanic corrosion. Indeed, a previous study suggests that AgZn₃ particles resulting from the alloy decomposition process act as the degradation site for any oxide film covering the surface of Zn-Ag alloys [16]. This idea is supported by the significant presence of intermetallic particles in the post ECAP Zn-4 %Ag-1 %Cu, as depicted in Fig. 5. The proposed finding is supported by the surface of the UFG sample Zn-4 %Ag-1 %Cu, which turns black after 35 days of incubation in Ridger's solution. This could be attributed to the loss of surface smoothness caused by the precipitation of small particles.

The reduction potential Zn is -0.76 V and the reduction potential of Ag is +0.8. With a large potential difference, galvanic corrosion is more likely to occur. The ratio of the area of the anode and cathode metal has a huge influence. As long as the cathode surface area is very small compared to the anodic surface area, no change in corrosion behavior is observed. As the volume of the alloying element increases, the corrosion rate increases. After the ECAP, the Zn-1 %Ag-Cu alloy has particles with an average size of 470 ± 20 nm and a volume fraction of 0.8. In the case of the Zn-4 %Ag-Cu alloy, the particles size is larger and the volume fraction is 20 times higher after the ECAP, which can explain the difference in corrosion rate (Fig. 4b) of Zn-4Ag-Cu and Zn-Ag-Cu after the ECAP. In addition, according to the X-ray diffraction pattern (Fig. 7a), the Zn-4 %Ag-Cu alloy an increased integral intensity of the diffuse background is observed, indicating an increased concentration of defects in the Zn-4Ag-Cu alloy compare to the Zn-1 %Ag-Cu alloy (Fig. 7b).

Data depicted in Fig. 8 indicating that the presence of silver accelerates the corrosion, while the impact of the alloy composition is less prominent. Notably, the corrosion rate is higher for a cast alloy containing 1 % silver compared to the alloy with 4 % silver in a similar condition. This relationship also holds for the post-deformation condition. Silver has a mixed effect as a non-active metal, an increase in its amount can promote the passivation of the structure, while an increase in its content leads to the formation of intermetallic phases. These phases can alter the dynamics of corrosion due to the above-outlined effect. To gain insight into the role of silver to the corrosion process of the studied Zn-4 %Ag-1 %Cu further objective analysis is needed. This analysis is performed using DFT-based simulations and the detailed explanation is provided in the subsequent section.

SEM images in Fig. 9 show the surface characteristics of specimens from both Zn-1 %Ag-Cu and Zn-4 %Ag-Cu alloys after the ECAP following exposure to an aggressive solution for 23 days. In the 4 %Ag-Cu pitting phenomena are more pronounced. Additionally, in SEM images at higher magnifications, a clearer pitting effect at the boundaries is

Table 5 O₂ adsorbtion on Zn (100), Zn-1%Ag(100), Zn-4%Ag(100), and Zn₃Ag(110).

Zn alloy	E _{ads} , eV	O_2 bond length, Å	Distance from O_2 to the surface, Å
Pure Zn	-5.778	1.387	2.001
Zn-1 %Ag	-3.457	1.389	1.985
Zn-4 %Ag	-3.113	1.485	1.930
Zn ₃ Ag	-1.480	1.53	1.970

observed. In the cast state, local pitting is observed, while in the samples after the ECAP, pitting occurs uniformly over the entire area. In addition, in SEM images at higher magnification, more pronounced pitting effect at the boundaries of both Zn-1 %Ag-Cu and Zn-4 %Ag-Cu alloys is observed.

3.3. Simulation results

Various geometric positions of oxygen molecules on pure Zn(100), Zn-1 %Ag(100), and Zn-4 %Ag(100) and the intermetallic Zn₃Ag(110) phases were considered. The lowest-energy configuration of O₂ on the Zn(100) ($E_{ads} = -5.778 \text{ eV}$), Zn-1 %Ag (100) ($E_{ads} = -3.457 \text{ eV}$), Zn-4 %Ag(100) ($E_{ads} = -3.113$ eV) and Zn₃Ag(110) ($E_{ads} = -1.480$ eV) surfaces is shown in Fig. 10a-d, respectively. In all cases O2 locates parallel to the surface plane. In all considered cases, there is a strong elongation of the O₂ bonds (Table 5), which indicates comparably strong interaction of the molecule and the surface, on the other hand, the dissociation of the molecule does not occur. Notably, among the considered structures pure Zn(100) surface possesses the lowest adsorption energy of O2, while an increase of Ag content leads to a decrease of E_{ads} of O_2 (Table 5). In all cases, the distance from the molecule to the surface is approximately the same and vary from 1.93 Å to 2.0 Å. In the case of O₂ adsorption on the Zn-4 %Ag(100) surface, the O2 bond length has increased significantly compared to that in the case of O_2 adsorption on the Zn-1 %Ag(100) surface or Zn(100) surface. This may be due to the curvature of the surface that occurs due to Ag adatoms in the Zn lattice and related lattice distortions and electrostatic landscape symmetry. At the same time the E_{ads} remains quite high, which may be due to the large content of Ag atoms that is a noble material and reacts poorly with adsorbents. The highest E_{ads} of O_2 is found for the Zn₃Ag(110) surface, which may be because of covalent nature of bonds in intermetallic Zn_3Ag that hampered adsorption of molecular O_2 . Moreover, the high content of Ag atoms in Zn₃Ag may also hinder the O₂ adsorption.



Fig. 11. Distortions in Zn-1%Ag (a) and Zn-4%Ag lattices (b), represented as the difference of the bond length without and with Ag atoms in the lattice. Length differences are presented in Å. The top layer of the slab model was removed for viewer's clarity. Radial distribution function for pure Zn, Zn-1%Ag and Zn-4%Ag lattices (c).

From the above-described data, it is proposed that the Ag additions in the Zn lattice does not accelerate corrosion processes, while slightly improves the corrosion properties of Zn alloys. In addition, the separate Zn₃Ag phase has fairly good corrosion properties due to presence of covalent bonding.

3.4. Corrosion mechanism

In order to investigate the factors that affect the corrosion rate of the material, it is necessary to examine the change in lattice symmetry that results from the introduction of different types of atoms. The substitution of Ag atoms into the Zn lattice leads to its symmetry breaking, causing lattice distortion and generation of internal stress. The lattice distortion is illustrated through the example of Zn alloy containing 1 % of Ag (Fig. 11a). It is seen that the length of the Zn-Ag bond is amplified due to Ag adatom. This elongation results in subsequent contraction of Zn-Zn bonds (see bonds Zn116-Zn174, Zn128-Zn198, Zn95-Zn93 in Fig. 11a) located in the vicinity of Ag adatoms. Concurrently, the bonds of Zn atoms (Zn116-Zn128, Zn127-Zn128, etc.) located at the vertices of the hexagon surrounding the central Ag atom are expanded. In particular, the bond length of Zn45-Zn104 increases significantly (+0.17738 Å), which can be attributed to the location of this bond on the vertices of two hexagons with a central Ag atom. For the zinc alloy containing 4 % of Ag, the nature of lattice distortions arise is similar. Meanwhile, as the high number of Ag atoms in the lattice are located, the region of stress and consequent lattice distortion is considerably large (Fig. 11b). These distortions arise from the overlap of electron clouds of Ag and Zn atoms and due to the difference in their electronegativity (1.65 eV-0.5 for Zn, 1.93 eV-0.5 for Ag). To deeper consider the lattice distortion in Agcontaining Zn alloy, a graph of the radial distribution function was plotted (Fig. 11c). As it can be seen, the radial distribution density for the Zn-4 %Ag is the lowest, indicating strong lattice distortion. Internal stresses related to the asymmetry of the electrostatic field created by metal ions and generalized electrons yield localization areas in the lattice that promote more facile atom adsorption due to the reduced electrostatic barrier. This is in line with the experimental data showed highest corrosion rate increase following severe plastic deformation (Fig. 8), which leads to a loss of lattice symmetry. The enhanced alteration of lattice symmetry in this case could be the reason for the accelerated material degradation rate.

From the experimental point of view, raising the Ag content resulted in a rise of the volume fraction of the eutectic mixture and a reduction in grain size in the alloys. The Zn alloy was found to be capable of recrystallization at room temperature, facilitating a substantial amount of cold deformation without failure. These findings demonstrate a significantly more refined microstructure with a high abundance of grain boundaries, which are recognized high-speed pathways for element diffusion [53,54], thus hastening the diffusion of solute atoms and the subsequent precipitation of secondary phases at room temperature. As the atomic packing density within boundaries is lower than that in a crystal, grain boundaries are linked to additional volume availability associated with GBs' crystallography, thereby leading to significant interactions with dissolved atoms.

Based on the DFT and experimental results presented in this work, it can be inferred that introducing of Ag atoms into the Zn lattice leads to intensification of its corrosion processes. Surprisingly, it actually improves corrosion properties. This effect can be attributed to the chemical properties of Ag, which reacts poorly with adsorbents because of its high "nobility". It is worth noting that the Zn₃Ag intermetallic phase exhibits higher corrosion resistance than alloyed Zn, possibly due to covalent bonding in it. Strong nature of covalent bond is much lower affected by absorption atoms allowing to retain high symmetry of crystal lattice in their presence. Consequently, it is proposed that defects such as grain boundaries, resulting from Zn casting with Ag alloys, are the primary cause of corrosion.

4. Conclusion

The research findings can be concisely stated as follows:

- Elevating the Ag proportion in zinc alloys leads to a finer microstructure exhibiting higher eutectic mixture volume fraction and smaller grain size, aided by room temperature recrystallization in Zn alloys.
- Furthermore, the incorporation of silver atoms into the lattice bolsters corrosion resistance by virtue of silver's chemical peculiarity, which encompasses its low susceptibility to adsorbents and potential covalent bonding in the Zn₃Ag intermetallic phase.
- Increasing the silver content to 4 % does not cause a significant alteration in the degradation of the zinc alloy, indicating that non-equilibrium grain boundaries play a dominant role in the process due to their enhanced ability to change lattice symmetry.
- The combination of experimental and simulation approaches enables a comprehensive physical comprehension of the studied processes, which is necessary for the production of alloys with desirable properties.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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