

Study of corrosion behavior of arc thermal sprayed Al-Mg alloy coating

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Abstract. In this study, Al-Mg alloy coatings were deposited on a C45 steel substrate using the electric arc spray technique. The corrosion behavior of the coating was studied by electrochemical measurements and salt spray tests. The electrochemical tests were performed in 3.5 wt.% NaCl solution. Polarization tests indicated that the corrosion potential of the coating was significantly more negative than that of the steel substrate after 240 hours of immersion. EIS measurements showed that after 24 hours of immersion, the total impedance increased with increasing the immersion time. This could be due to the sealing of the pores by corrosion products which hindered further penetration of the solution through the coating. Red rust spots did not appear on the surface of the coating after 1360 hours of salt spray test. The corrosion rate of the coating decreased with the increase in salt spray test time. After the salt spray test, the coating surface was pitted and in the cross section of the coating many long voids appeared. In addition, XRD analysis proved that the main corrosion product was Al(OH)₃. The results obtained indicated that arc thermal sprayed Al-Mg alloy coatings can reliably protect steel structures against corrosion in chloride-containing aqueous solutions.

Keywords: Al-Mg coating, electric arc spraying, corrosion, salt spray test

Classification numbers: 2.9.2, 2.9.4

1. INTRODUCTION

Most of the failures of steel structures are related to corrosion, especially the damage is more serious when the steel structure works in the marine environment. The cost of maintaining marine structures is very large. One of the effective anti-corrosion methods that have been used in recent years is the use of thermal spray coatings. The electric arc spray technique (TWAS) is one of the most commonly applied techniques in the field of corrosion protection as compared with other thermal spray techniques (flame spraying, plasma spraying, high-velocity oxy-fuel spraying, etc.). This technique has many advantages such as high performance, low-cost manufacturing, easy automation, and low-cost technology investment. TWAS is often used to deposit metallic coatings such as Al coating, Zn coating, alloy coatings, etc.

Al-Mg alloy thermal sprayed coatings have recently been used widely in various engineering applications due to their light-weight, good mechanical properties and high corrosion resistance. This coating has higher hardness, longer durability as compared to that of pure Al coating. Corrosion properties of Al-Mg alloy coating have been previously studied.

A higher concentration of Mg in Al-Mg coating reduced corrosion resistance of the coating [1, 2]. The Al-Mg coating was more resistant to corrosion and cavitation than Al coating in the actual marine environment, physical damages by external forces and corrosion damages occurred simultaneously in the combination [3 - 5]. After 1000 hours of exposure per ASTM B117, the Al-5 wt.% Mg coating had a lower corrosion current density than the coating of commercially pure Al (99.5 wt.%), high-purity Al (99.95 wt.%), AA5356 alloy, and AA4047 alloy [6]. The Al-Mg coating provided sacrificial protection to the steel substrate until 792 hours of exposure in the SAE J2334 solution (containing chloride and carbonate ions), while the Al-Zn coating provided protection for up to 120 hours. The corrosion rate of the Al-Mg coating was 15 times slower than that of the Al-Zn coating in SAE J2334 solution after 792 hours of exposure [7]. Currently, in Viet Nam, there has not been specific research on the arc thermal sprayed Al-Mg alloy coating.

In the present work, Al-Mg alloy coating was deposited on a C45 steel substrate using the electric arc spray technique. The corrosion behavior of the coating was studied using electrochemical measurements and salt spray tests. Furthermore, the microstructure and phase composition of the coating before and after the salt spray test were also investigated.

2. MATERIALS AND METHODS

2.1. Materials and preparation of samples

In this experiment, a C45 steel plate with the dimensions of 50 mm × 50 mm × 3 mm was selected as the substrate. Al-Mg alloy wire of 95 wt.% Al and 5 wt.% Mg provided by Metallisation Ltd. (West Midlands, UK) with a diameter of 2.0 mm was used as the feedstock wire. Before the spraying, the substrate specimens were cleaned with acetone and then grit blasted with corundum (grit size of ~ 1.2 mm). Grit blasting was performed at a blasting distance of 100 mm, blasting pressure of 8 bar and blasting angle of 90°. The Al-Mg alloy coating was deposited on the grit-blasted C45 steel substrate using OSU Hessler 300A (Germany) twin wire arc spraying equipment. The spraying parameters are shown in Table 1.

Table 1. Thermal spray parameters.

Parameters	Values
Arc Voltage, V	32
Current, A	150
Gas pressure, bar	4
Spraying distance, mm	200
Spraying angle, °	90

2.2. Analytical methods

The cross-sectional microstructure of the coatings was studied using a metallographic microscope (GX53 Olympus, Japan). The surface morphology of the coatings was investigated

by a scanning electron microscope JEOL JMS-6490 (Japan). The phase composition of the coatings was analysed by X-ray diffraction (X-RAY D5005/SIEMENS, Germany) at a temperature of 25 °C with Cu-K α radiation, 2 θ angle scanning from 10° to 90°. The porosity of the coating was determined according to the ASTM B276 standard, by using an image analysis software (Olympus Stream Basic).

The electrochemical tests were performed in a three-electrode cell using a platinum plate as counter electrode, a SCE as reference electrode and the Al-Mg coating sample as the working electrode on the VSP-300 multichannel potentiostat/galvanostat (Bio-Logic Science Instruments, France) equipment. Electrochemical impedance spectroscopy (EIS) tests were carried out at the open circuit potential (E_{ocp}). The frequency range varied from 10⁻² Hz to 10⁵ Hz with 7 points per decade, potential amplitude $\Delta E = 5$ mV. The polarization curves were obtained at a scan rate of 0.1667 mV/s and a scan range of -30 mV to 30 mV/SCE around the open circuit potential (E_{ocp}) according to the ASTM G95 standard. The corrosion potential (E_{corr}) was determined from the polarization curves by taking the value at the zero current point. This value was similar to that obtained by the intersection of Tafel lines [8]. Corrosion current density (I_{corr}) was extrapolated from the polarization resistance (R_p). At small potential scan, the polarization resistance (R_p) of a corroding electrode was defined from equation (1) as the slope of a potential versus current density plot at $i = 0$:

$$R_p = \left(\frac{\partial \Delta E}{\partial i} \right)_{i=0, dE/dt \rightarrow 0} \quad (1)$$

The corrosion current density (I_{corr}) was determined employing the Stern–Geary equation given by [8]:

$$I_{corr} = \frac{B}{R_p} = \frac{b_a b_c}{2.303(b_a + b_c)R_p} \quad (2)$$

where: b_a and b_c are anode and cathode Tafel coefficients and B is a constant.

The salt spray test was carried out according to the ASTM B117 standard using Q-FOG Cyclic Corrosion Tester CCT 600 (USA) with 5 wt.% NaCl solution for 1360 hours. During salt spray, the samples are measured in thickness over time using a thickness gauge Total Meter CM-8826FN (China). The corrosion rate was calculated using the following equation [9, 10]:

$$CR = \frac{(T_0 - T) \times 365 \times 24}{t} \quad (3)$$

where CR is the corrosion rate ($\mu\text{m}/\text{year}$), T_0 is the initial coating thickness (μm), T is the thickness of the coating after the salt spray test (μm), and t is the salt spray test time (hour).

3. RESULTS AND DISCUSSION

3.1. Microstructure analysis

The cross-sectional structure of the Al-Mg coating is shown in Figure 1. The result shows an average coating thickness of about 350 μm . This coating has the characteristic structure of a thermal spray coating consisting of layers and pores. During the spraying process, the molten metal droplets collide with each other, affecting the surface of the substrate material. They are deformed and connected along the contact surface, forming the layer structure of the coating.

When deformed metal elements are not closely linked together, the pores will be formed in the coating.

The porosity of Al-Mg coating was measured at ten different positions on the cross-sectional microstructure of the coating. The analysis results showed that the average porosity of the Al-Mg coating was about 11.8 ± 0.5 %.

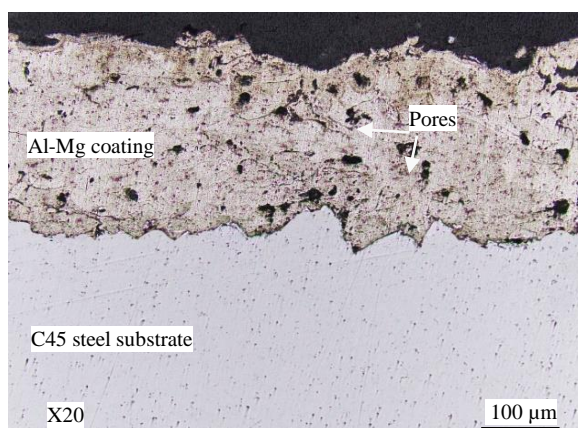


Figure 1. Cross-sectional structure of Al-Mg coating on C45 steel substrate.

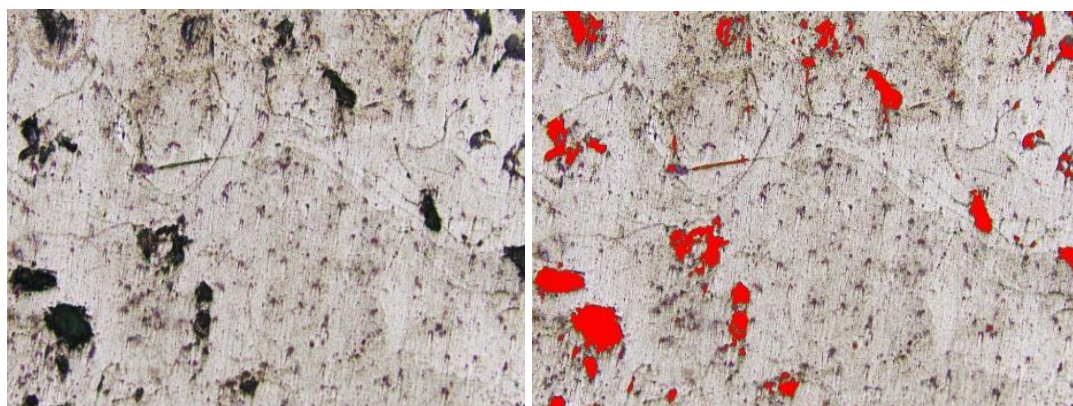


Figure 2. Cross-sectional structure of Al-5Mg coating using image analysis software.

3.2. Electrochemical measurement

The polarization curves of Al-Mg coating sample in 3.5 % NaCl solution at different immersion times are shown in Figure 3. The changes of corrosion potential and corrosion current density with time are shown in Figure 4 and Figure 5, respectively.

Figure 4 presents that at all times of immersion, the corrosion potential of the coating sample is much more negative than that of the C45 steel substrate (about -0.55V/SCE). This shows that after 240 hours of immersion in 3.5 wt.% NaCl solution, the coating still has good protection for the steel substrate.

The graph of corrosion current density variation in Figure 5 shows that at the beginning of immersion, the corrosion current density sharply increased from about $0.124 \mu\text{A}/\text{cm}^2$ (after 6 hours of immersion) to about $1.830 \mu\text{A}/\text{cm}^2$ (after 24 hours of immersion). This represents the

dissolution of the coating in 3.5 wt.% NaCl solution. Corrosion products are formed from the dissolution of the coating and have not yet diffused out of the coating, so they have prevented the contact of the coating with the solution. This reduced the corrosion current density of the coating to about $0.52 \mu\text{A}/\text{cm}^2$ after 168 hours of immersion. Then, the corrosion current density increased slightly after 240 hours of immersion. This indicated that corrosion products may have diffused into the solution or the corrosion solution has penetrated deep into the coating. The coating continues to be dissolved by the sacrificial anode mechanism.

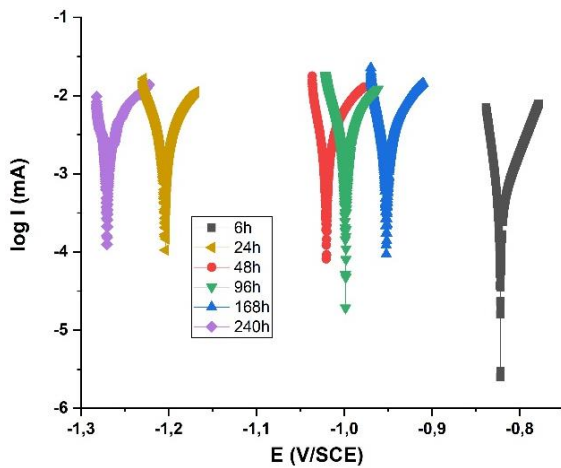


Figure 3. Polarization curves of Al-Mg coating at different immersion times in 3.5 wt.% NaCl solution.

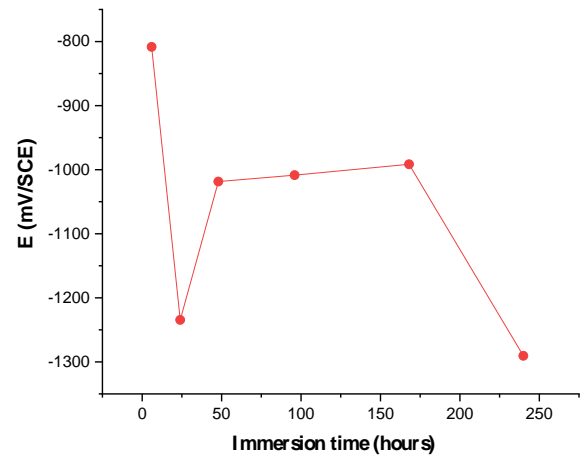


Figure 4. Variation of corrosion potential with time.

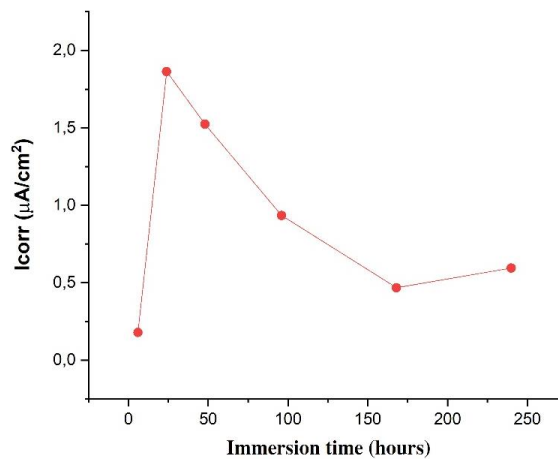


Figure 5. Variation of corrosion current density with time.

Figure 6 shows Nyquist plots and Bode plots of Al-Mg coating at different immersion times in 3.5 wt.% NaCl solution. In the Bode plots (Figure 6a), the magnitude of the impedance $|Z|$ is plotted as a function of frequency (f). Impedance at the low frequency region is related to the corrosion at the substrate/solution interface. Therefore, the low frequency part of the Bode plot can be used as an indicator of the coating performance [11].

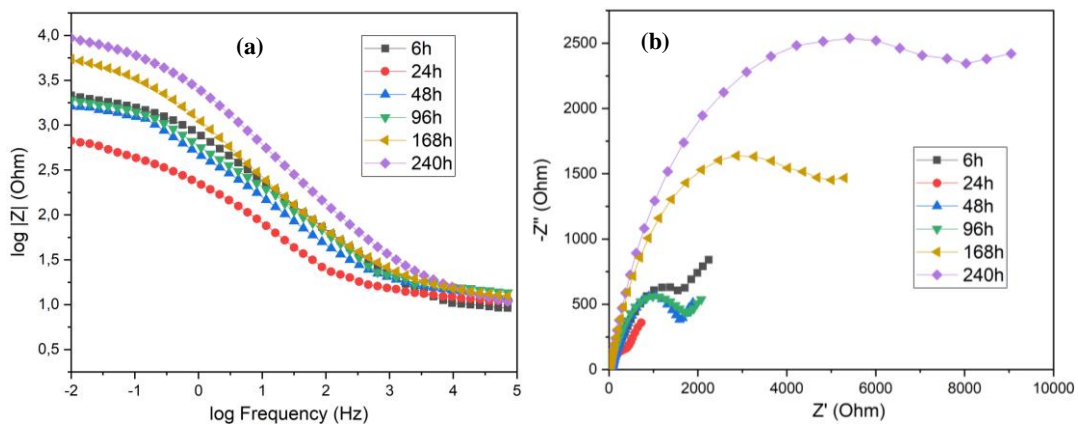


Figure 6. Bode plots (a) and Nyquist plots (b) of Al-Mg coating at different immersion times in 3.5 wt.% NaCl solution.

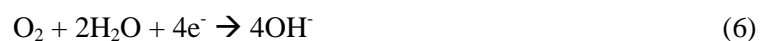
The results indicated that, at a low frequency, the impedance $|Z|$ of the coating decreased from about 2000Ω after 6 hours of immersion to about 1000Ω after 24 hours of immersion. This shows that the coating is corroded right in the first time of contact with the corrosive solution. After 24 hours of immersion, the low frequency impedance increases with the immersion time (from about 1000Ω after 24 hours of immersion to about 10000Ω after 240 hours of immersion). This indicates that the corrosion products have formed a passive film, which prevents corrosion in the coating. The Nyquist plots in Figure 6b show that, at all the time of immersion, there is a sign of the second semicircle but not clear. This shows that the corrosion processes inside the coating may have occurred but it is not significant compared with the process taking place on the coating surface in direct contact with the solution. The second semicircle can also be due to the deposition of corrosion products on the coating surface. Combined with the above polarization measurement results, it can be assumed that the Al-Mg coating sample still provides good protection for the steel substrate after 240 hours of immersion in 3.5 % NaCl solution.

Like other sacrificial anode materials, the cathodic protection mechanism of the Al-Mg coating is a self-dissolving mechanism based on the potential difference between the Al-Mg alloy and the C45 steel substrate. Al-Mg alloy coating acts as a sacrificial anode. When exposed to NaCl solution, the coating/steel system becomes an electrochemical cell in which the Al-Mg coating is always a corroded material due to the charge transfer occurring on the coating surface.

The reactions take place at the anode [12]:



In NaCl medium, the reaction takes place at the cathode:



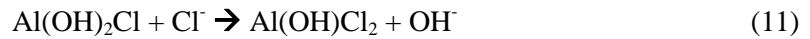
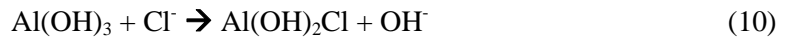
Accordingly, the formation of corrosion products can occur according to the following reactions:





The presence of chloride ion Cl^- in corrosive media often causes pitting corrosion of aluminum alloys. The chloride ions will compete for the cation vacancies and displace the oxygen in the oxide film to form metal chlorides, which leads to the deterioration of the oxide films and the onset of pitting.

The proposed aluminum chloride formation reactions are as follows [13]:



3.3. Salt spray resistance

After a salt spray test for 1360 hours with 5 % NaCl solution, the results of surface observation of Al-Mg coating are shown in Fig. 7. The result of observing the coating surface shows that the surface of the sample had no significant change and red rust spots did not appear on the surface of the sample after 1360 hours of salt spray test. These results indicated that the Al-Mg coating has excellent corrosion protection in chloride containing environments.



Figure 7. Surface change of Al-Mg coating sample during the salt spray test.

Table 2. Corrosion rates of samples after salt spray test.

Exposure time, hours	Average coating thickness, μm	Average corrosion rates, $\mu\text{m}/\text{year}$
0	358.12	--
96	353.67	221.74
240	350.50	205.86
480	345.94	186.33
720	341.89	171.55
1000	338.96	150.06
1360	333.82	143.77

Table 2 shows the corrosion rate of Al-Mg coating depending on the duration of tests. According to the test results, it was found that the corrosion rate of the coating decreased with the increase in salt spray test time. The corrosion rate drops from 221.74 $\mu\text{m}/\text{year}$ to 143.77 $\mu\text{m}/\text{year}$ with exposure from 96 to 1360 hours. This can be explained by the formation of corrosion products that prevent the corrosion solution from accessing the coating and slow down the dissolution of the Al-Mg coating.

The surface of the coating after 1360 hours of salt spray testing was pitted as shown in Fig. 8, indicating that the coating had been corroded when exposed to NaCl solution. The cross-sectional structure of the coating after 1360 hours of testing is shown in Figure 9. There is the appearance of many long voids inside the coating. Some areas at the border between the coating and the steel substrate have split. Thus, the solution has penetrated through the pores and micro-cracks deep inside the coating. Many areas in the coating are exposed to the corrosive solution and are dissolved, forming voids inside the coating.

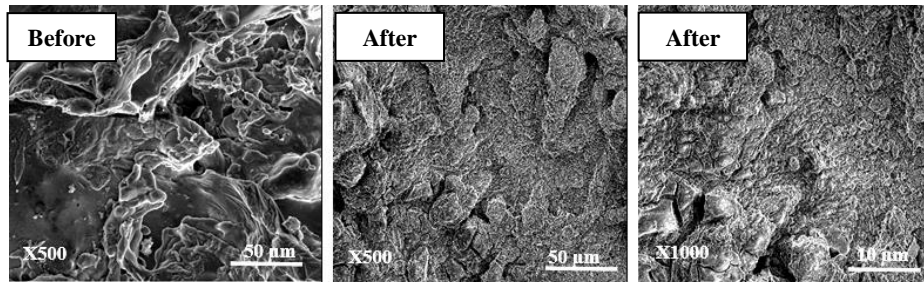


Figure 8. Surface morphology of Al-Mg coating before and after 1360 hours of salt spray test.

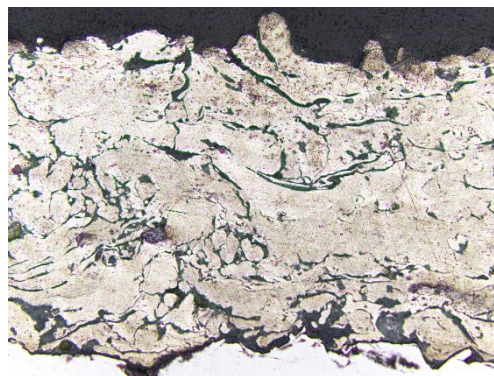


Figure 9. Cross-sectional structure of Al-Mg coating on C45 steel substrate after 1360 hours of salt spray test.

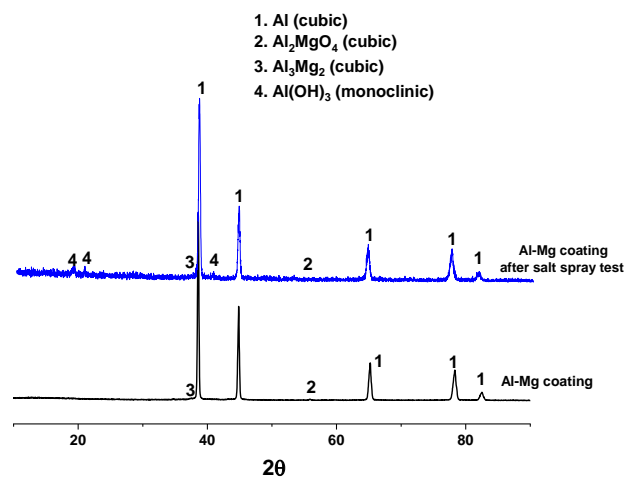


Figure 10. XRD pattern of the Al-Mg coating before and after 1360 hours of salt spray test.

Figure 10 presents the XRD pattern of Al-Mg coating sample before and after 1360 hours salt spray test. As shown in this figure, the coatings have phase composition with corresponding crystal structures as follows: Al (cubic), Al_2MgO_4 (cubic) and Al_3Mg_2 intermetallic phase. After 1360 hours of salt spray test, in addition to the above phase compositions, $\text{Al}(\text{OH})_3$ phase with monoclinic crystal structure was observed. However, there was no presence of corrosion products of Mg and chloride compounds. This is explained by the very small content of these compounds, which is difficult to detect by XRD method (their content is below the detection limit of the XRD equipment).

4. CONCLUSIONS

Al-Mg coatings were prepared by arc thermal sprayed technique on C45 steel substrate. The corrosion behavior of the coating was studied using electrochemical measurements and salt spray tests. The main findings of this research were as follows:

After 240 hours of immersion in 3.5 wt.% NaCl solution, the corrosion potential of the coating was significantly more negative than that of steel substrate. The total impedance increased with increasing the immersion time. The coating still had good protection for the steel substrate.

The surface of the coating sample had no significant change and red rust spots did not appear on the surface of the coating after 1360 hours of salt spray test. The corrosion rate of the coating decreased with an increase in salt spray test time. After the salt spray test, the coating surface was pitted and in the cross section of the coating many long voids appeared. In addition, XRD analysis proved that the main corrosion product was $\text{Al}(\text{OH})_3$.

The obtained results indicated that arc thermal sprayed Al-Mg alloy coatings can reliably protect steel structures against corrosion in chloride-containing aqueous solutions.

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CRedit authorship contribution statement. Ha Pham Thi: Writing-Review and Editing, Methodology, Formal analysis. Tuan Nguyen Van: Formal analysis, Supervision. Tuan Anh Nguyen: Formal analysis. Ly Pham Thi: Formal analysis, Investigation. Cuong Ly Quoc: Formal analysis. Thuy Dao Bich: Formal analysis. Quan Vo An: Formal analysis. Thanh Le Duc: Formal analysis.

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.

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