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Improving the corrosion resistance of LY12 aluminum alloy via a novel Mo–Zr–Ti composite conversion coating

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Abstract

To improve the corrosion resistance of LY12 aluminum alloy, a novel Mo–Zr–Ti composite conversion coating on its surface was prepared. The surface morphology, elements distribution, phase compositions and the corrosion resistance were systematically determined, and the relation between them were established. The results indicate that the optimal conversion temperature and conversion time are 40 °C and 15 min, respectively. The surface morphology of the composite coating under the best conversion condition is continuous and dense. The major elements are Mo, Zr, Ti, Al, O and F, and their distribution between the inner and outer coating are distinction. The phase compositions mainly consist of MoO\textsubscript{3}, Mo\textsubscript{2}O\textsubscript{5}, TiO\textsubscript{2}, ZrO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, AlF\textsubscript{3}, 3H\textsubscript{2}O, Na\textsubscript{3}AlF\textsubscript{6} and ZrF\textsubscript{4}, and the nucleation and growth mechanisms are proposed. Additionally, the composite coating can significantly reduce the \(I_{corr}\) and increase the film resistance \(R_f\) in the temperature range from 0 to 60 °C through electrochemical test, and its activation energy \(E_a\) increases from 25.7 to 34.5 kJ • mol\(^{-1}\). Compared with Al matrix, the average corrosion rate of the composite coating is reduced by 65% to 85% in the full immersion test. Therefore, the composite conversion coating greatly improves the corrosion resistance of Al matrix.

1. Introduction

Aluminum alloy is widely used in household appliances, automobile, navigation, aerospace and other fields due to the advantages of high specific strength, good electrical conductivity, easy processing and low price \cite{1–3}. Normally, an inartificial coating will be easily formed on the aluminum alloy surface that imparts a certain level of protection under natural environment \cite{4, 5}. However, because of its undesirable characteristics of thin, loose, porous and uneven, it usually breaks down in some specific areas under conditions of corrosive anions, oxidants and sustained high temperature. Then various forms of corrosion are produced, such as pitting corrosion, intergranular corrosion, galvanic corrosion, crevice corrosion, stress corrosion and so on, thereby altering its service performance \cite{6, 7}. Therefore, it is urgent to determine an appropriate method to improve the corrosion resistance of aluminum alloy.

Conversion coating process is one of the effective methods to enhance the corrosion resistance due to its simple operation, wide application range and low cost \cite{8}. Currently, the conventional conversion coating process of aluminum alloy on the market is chromate conversion coating process \cite{9}. However, Cr\textsuperscript{6+} is highly toxic, carcinogenic and bioaccumulative, leading to great damage and serious threat to the environment and human health \cite{10, 11}. Consequently, researchers have extensively focused on chromium free conversion alternative process, and a series of achievements have been made in recent decades \cite{12, 13}. According to the relevant studies, the common chromium free conversion coating processes are as follows: permanganate conversion coating process \cite{14, 15}, rare earth salt conversion coating process \cite{16, 17}, organic salt conversion...
Table 1. Chemical composition of LY12 aluminum alloy (wt.%).

| Element | Cu | Mg | Mn | Fe | Si | Zn | Ti | Ni | Other | Al |
|---------|----|----|----|----|----|----|----|----|-------|----|
| Content/% | 4.64 | 1.59 | 0.59 | 0.42 | 0.32 | 0.18 | 0.1 | 0.05 | 0.15 | Bal. |

coating process [18, 19], Ti-Zr based conversion coating process [20, 21], molybdenum conversion coating process [22, 23], etc.

Through the comparison of the above chromium free conversion coating process, it is found that each conversion coating process has its own defects. The process of permanganate conversion coating is extremely complex and uncontrollable, which limits its application. The performance of purely rare earth salt conversion coating cannot achieve the industrial application level, and even the reagent cost and high preparation temperature also restrict its use [24]. The application of organic conversion coating is limited due to its soft surface and easy to cause scratches, even though it has fairly corrosion resistance [25]. Ti-Zr based conversion coating is the focus research in recent years, nevertheless its corrosion resistance, self-healing and adhesion are far from those of Cr$_6^+$ coatings, thereby affecting its industrial application [3]. Mo and Cr belong to the same family and have similar chemical properties [26]. Moreover, Mo has low toxicity and is even an essential trace element for human body. Consequently, as an environmental friendly Mo based composite conversion coating process is the most promising process to replace conventional chromate conversion coating process.

In this work, we explored a new type of Mo–Zr–Ti composite conversion coating, and the influences relevant to conversion parameters such as conversion temperature (CTE) and conversion time (CTI) on the corrosion resistance were systematically investigated. The nucleation and growth mechanisms of the composite conversion coating were proposed, and the corresponding relationships between the morphology, elements distribution, phase compositions and corrosion resistance were discussed. So as to provide the important theoretical and technical support for the use of aluminum alloy.

2. Experimental details

2.1. Materials and preparation of Mo–Ti-Zr conversion coating

Commercially available LY12 aluminum alloy was used as the matrix, and its chemical composition was shown in table 1. After the mixed alkaline washing and acid degreasing treatment, the matrix was immersed in conversion solution to form coating. The conversion treatment solution was composed of Na$_2$MoO$_4$·2H$_2$O: 2 g l$^{-1}$, H$_2$ZrF$_6$: 2.0 ml l$^{-1}$, H$_3$TiF$_6$: 1.0 ml l$^{-1}$, and (NaPO$_3$)$_3$: 0.4 g l$^{-1}$. The pH value of the solution was 5.0. The CTE was 20, 30, 40, 50 and 60 °C, and the CTI was set as 0.5, 1, 5, 10, 15 and 20 min at each CTE. The influences of the CTE and CTI on the corrosion resistance were studied through copper sulfate dropping corrosion (CSD) test coupled with neutral salt spray (NSS) test.

2.2. Morphology and composition analysis

The surface morphology with the optimal CTE at different CTI have been observed under S-3400N scanning electron microscope (SEM). The samples were coated with gold to preclude the charging effect, and the operating potential of the field emission source was 15 kV. The chemical composition, distribution and valence state of the elements and the types of the compounds at different formation stages were qualitatively analyzed by the x-ray photoelectron spectroscopy (XPS) with a monochromated Al K$_\alpha$ source (1486.6 eV), and the spectra are corrected by C 1s with the binding energy of 284.8 eV.

2.3. Copper sulfate dropping corrosion test (CSD)

The corrosion resistance of the Mo–Zr–Ti composite conversion coating was examined by a copper sulfate dropping corrosion test, and the time it took for the droplets to change from sky blue to light red was recorded. The longer the dripping time was, the better the corrosion resistance was. The drip solution was composed of HCl: 13 ml l$^{-1}$, CuSO$_4$·5H$_2$O: 41 g l$^{-1}$, and NaCl: 35 g l$^{-1}$.

2.4. Neutral salt spray test (NSS)

The neutral salt spray (NSS) test was operated in accordance with ASTM B117-2009. The salt spray corrosion solution was 5.0 wt.% NaCl solution, and the pH value was about 6.5 to 7.2. The test temperature was 35 ± 2 °C with the salt spray settlement of 2 ml/(cm$^2$·h). In addition, the salt spray resistance time was determined by the appearance of rust accounting for 5% of the whole panel area, which could directly reflect corrosion resistance.
2.5. Electrochemical test
Electrochemical test was performed using a CHI660D electrochemical workstation. The samples to be tested were pre-immersed in a 3.5 wt.% NaCl solution under various test temperature (0, 15, 30, 45 and 60 °C) for 15 min to achieve the constant open circuit potential. The exposed area of corrosion samples was 1 cm². The potentiodynamic polarization curves were acquired from −2.0 to +0.5 V with a scan rate of 0.01 V/s, so as to obtain the self-corrosion potential (E_{corr}) and the self-corrosion current density (i_{corr}). The EIS spectra were recorded over a frequency range from 10⁵ to 10⁻² Hz with an amplitude of 0.005 V sinusoidal AC voltage.

2.6. Full immersion test
The samples to be tested were immersed in 3.5 wt.% NaCl solution at five temperatures (0, 15, 30, 45 and 60 °C), and the immersing time was 168 h. For each temperature, three samples were taken. The loose corrosion products on the surface were removed, then weighed, and the average corrosion rate was calculated lastly.

3. Results and discussion

3.1. Effect of conversion solution parameters
As two of the most important conversion solution parameters, CTE and CTI closely correlate with the nucleation and growth of the conversion coating, and consequently affect the corrosion resistance. Figures 1(a) and (b) illustrate the coupling effects of CTE and CTI on dripping time and salt spray resistance time, respectively. The results of CSD and NSS tests both show that the CTE and CTI of the red region with the best corrosion resistance are about 40 °C and 15 min, separately.

As the CTE is lower than 40 °C, the ion activity of conversion solution is lower, which result in the decrease of coating-forming deposition reaction rate on the surface. At this moment, the growth of the conversion coating is slow, and the incomplete conversion coating cannot protect the matrix well. However, as the CTE exceeds 40 °C, the ion activity of conversion solution is improved substantially, and resulting in the higher deposition rate and internal stress. As a result, the formed conversion coating will be destructed with prolonging the CTI instead, and its corrosion resistance becomes poor.

Additionally, the cathode reaction is strengthened with a massive release of hydrogen under the high CTE. The resulting gas flow of hydrogen hinders the formation of conversion coating, which also leads to the deterioration of coating quality and the decrease of corrosion resistance.

3.2. Morphology and composition analysis
3.2.1. Morphology of Mo–Zr–Ti conversion coating
Figure 2 displays the micro morphology evolution with prolonging the CTI under the optimal CTE of 40 °C. Obviously, in the first 10 min, the conversion coating is in the growth stage, and the coating-forming deposition reaction is not sufficient. Hence, there are different degrees of gaps on the surface, appearing the typical type of 'dry river bed', as shown in figures 2(a)–(d). With the increase of the CTI, the gap width decreases due to the two-dimensional growth. After 10 min, the gaps gradually disappear, and even those almost vanish at 15 min, as shown in figure 2(e). However, because of the high internal stress introduced during the growth process, the generated conversion coating without gaps is partially destroyed and peeled to produce new rhombic cracks, as...
shown in figure 2(f). Normally, corrosion ions are easy to adsorb and accumulate at the gaps or cracks, and corrosion occurs preferentially. Therefore, the conversion coating with the CTI of 15 min is relatively flat without crackles and has good corrosion resistance, whereas those generated by the other CTI all incomplete, leading to the decrease in corrosion resistance. In a word, the low corrosion resistance is attributed to the incomplete conversion coating. To be specific, it is owing to incomplete growth for shorter CTI and the formation of cracks for longer CTI. The micro morphology analysis can fairly sustain the results of CSD and NSS tests.

3.2.2. Composition of Mo–Zr–Ti conversion coating

XPS was utilized to characterize the detailed variations information relevant to chemical compositions, valence states and types of compounds on the conversion coating surface, and the total spectra of the Mo–Zr–Ti conversion coating with the CTI of 0.5, 5 and 15 min are shown in figure 3. As illustrated in figure 3, the conversion coating is mainly composed of Mo, Zr, Ti, Al, F and O elements. However, H element was not detected during the test, it is impossible to exclude the possibility that the conversion coating contains other substances containing H.

To further explicate the different types of compounds on the surface, the detailed peaks of Al 2p, O 1s, F 1s, Mo 3d, Ti 2p, and Zr 3d spectra and appropriate fitting peaks are shown in figures 4(a)–(f), respectively. The peaks in the Al 2p spectra (figure 4(a)) can be curve-fitted to three fitting peaks, components with binding energies at about 74.20, 75.30 and 76.90 eV. Corresponding to the standard database, they belong to Na3AlF6, Al2O3 and AlF3∙3H2O, respectively. The fitting results of O 1s spectra (figure 4(b)) exhibit two peaks at about 530.50 and 531.50 eV. The binding energy of 530.50 eV is assigned to MoO3, TiO2, ZrO2, and the other peak corresponds to Al2O3. The details of F 1s peaks (figure 4(c)) reveal two peaks with binding energies at about 684.5 and 685.5 eV, which are assigned to ZrF4 and Na3AlF6, separately.

The peaks of Mo 3d spectra (figure 4(d)) can be fitted into four peaks, including the peaks at 232.6 and 235.6 eV being attributed to MoO3, and the peaks at 231.2 and 234.5 eV being attributed to Mo2O5, respectively. The split peaks of Ti 2p (figure 4(e)) include two fitted peaks at 464.2 and 458.3 eV both belonging to TiO2. The two peaks (figure 4(f)) of Zr 3d at 182.5 and 185.1 eV are ascribed to ZrO2 and ZrF4. As discussed above, the compounds in the conversion coating are mainly a series of oxides and fluorides. The main oxides are MoO3, Mo2O5, TiO2, ZrO2, Al2O3, and the primary fluorides are AlF3∙3H2O, Na3AlF6, ZrF4.

Figure 5 displays the atomic percentage with the CTI of 0.5, 5 and 15 min, which were calculated by the XPS results. The coating grows continuously with the extension of CTI, and thus the coating generating process should be consistent with the X axis. In other words, the elements distribution with the short CTI of 0.5 min represent the composition characteristics of the inner coating, and whereas that with the long CTI of 15 min demonstrate the outer coating. As seen from figure 5, the atomic percentage of Al declines rapidly during the
coating-forming process, but the tendency of the remaining elements are opposite. The reason for such phenomenon is that the O, F and conversion atoms such as Mo, Zr, Ti atoms adsorb and form coating on the Al matrix surface, resulting in the decrease of the Al atoms. Evidently, in the early stage of deposition, the inner coating contains high content of Mo atoms, followed by Zr atoms, and then Ti atoms. With the extension of CTI, the content of Mo atoms continues to increase rapidly, but that of Ti atoms rises slightly. In contrast, the content of Zr atoms decreases greatly.

Figure 3. XPS total spectra of Mo–Zr–Ti conversion coatings with different CTI: (a) 0.5 min, (b) 5 min, and (c) 15 min.

Figure 4. The detailed XPS spectra of (a) Al 2p, (b) F 1s, (c) O 1s, (d) Mo 3d, (e) Ti 2p, and (f) Zr 3d.
Figure 5. Surficial atom percentages of Mo- Zr-Ti conversion coating at different CTI.

Figure 6. The schematic diagrams of the nucleation and growth process.
3.3. Formation mechanism of Mo–Zr–Ti conversion coating
A model of the nucleation and growth mechanisms are proposed, as shown in figure 6. LY12 aluminum alloy contains Mg2Si and Al2CuMg intermetallic compounds [27, 28], the chemical potential of which are different from Al-rich matrix. Because of the difference in chemical potential between the intermetallic compounds and Al-rich matrix, intermetallic compounds are used as the micro cathode, while the Al-rich matrix is used as the micro anode. As a result, the hydrogen evolution reaction can be found in the intermetallic compound region, and the dissolution evolution reaction can occur in the Al-rich matrix, as shown in figure 6(a).

MoO42−, ZrF62−, Al3+ and TiF62− are adsorbed on the surface of alloy and react with H+ and OH−, resulting in the nucleation of metal oxides on the surface of the intermetallic compound region, as shown in figure 6(b). After nucleation, metal oxides deposit continuously in each nucleation center, and the conversion coating grows. However, owing to the limitation of deposition rate and short CTI, the edges of the conversion coating between different nucleation centers are not connected, and thus resulting in many gaps. With the extension of the CTI, the gaps width become smaller and smaller until the gaps disappear, as shown in figures 6(c) and (d). In addition, the elements distribution is quite complicated during the nucleation and growth process, the inner coating is rich in Mo, Zr and Ti elements, and the outer coating has a large content of Mo and Ti. The difference of the elements distribution is mainly attributed to the change of converted ions concentration in the conversion solution, and then affecting its adsorption rate with respect to dynamics aspect. With the further extension of the CTI, cracks are formed on the surface due to the high growth internal stress and stress release, as shown in figure 6(e).

3.4. Electrochemical analysis
3.4.1. Polarization curve
The corrosion behaviors of Al matrix and the optimal conversion coating (CTE: 40 °C and CTI: 15 min) were demonstrated by potentiodynamic polarization curves in a neutral 3.5 wt.% NaCl solution under different test temperatures (0, 15, 30, 45 and 60 °C), as shown in figures 7(a) and (b) respectively. Most notably, potentiodynamic polarization curves at 0 °C have a wide passivation area, indicating that it is in passivation state between a wide range of corrosion potential. It can be well known that icorr is one of the most important kinetic parameters to estimate the corrosion resistance, and a higher value of icorr means poor corrosion resistance.

As described in figure 8(a), the icorr of Al matrix is higher than that of the composite conversion coating at each test temperature, which show that the conversion coating can effectively protect the Al matrix in the temperature range from 0 to 60 °C. Furthermore, the icorr of Al matrix and the composite conversion coating both rise with the increase of test temperature. Hence, high test temperature can accelerate the corrosion rate. It is mainly attributed to the increased activity of aggressive ions, then positively adsorb on the surface, and thus accelerating the corrosion. Ec0rr is a thermodynamic parameter of corrosion, which is only used as a reference. The various trend is similar to that of icorr, and its rise is closely related to the increase of the test temperatures.

Activation energy (Ea) values for the Al matrix and the composite conversion coating in 3.5 wt.% NaCl solution under different test temperatures were calculated from the Arrhenius equation.

\[
\ln (i_{corr}) = B - \frac{(E_a)}{RT}
\]  

where B is a constant which depends on the metal type, and R is the universal gas constant. The plot of \(\ln (i_{corr})\) versus reciprocal of absolute temperature \((1/T)\) gives a straight line whose slope \(= -E_a/R\), from which the activation energy values for the corrosion process were calculated. The Arrhenius plots for the Al matrix and
Mo–Zr–Ti conversion coating in 3.5 wt.% NaCl solution under different test temperatures are shown in figure 9. The $E_a$ value represents the energy barrier for the occurrence of corrosion reaction. The $E_a$ of the Al matrix is $25.7 \text{ kJ} \cdot \text{mol}^{-1}$, and that of Mo–Zr–Ti conversion coating is $34.5 \text{ kJ} \cdot \text{mol}^{-1}$, which implies that the corrosion is thermodynamically more favored with the Al matrix.

3.4.2. AC impedance
For completeness, figure 10 shows the EIS results with the same test temperature as the polarization curves. The Nyquist diagrams compose of real part, imaginary part and a single semicircle arc. In general, the semicircle arc represents the charge transfer process in the electrode system, and its radius is the measurement of the corrosion resistance.

In order to enable an accurate analysis of the impedance diagram, the EIS equivalent circuit reported in figure 11(a) is used; $R_s$ is the solution resistance; $R_{coat}$ is the coating resistance, in parallel with a constant-phase element (CPE$_{coat}$); $R_{ct}$ is the charge transfer resistance on the metal surface, in parallel with a constant-phase element (CPE$_{dl}$). In general, CPE is used to describe the existence of surface defects, and thus it is not discussed in this paper.

The fitting value of $R_s$, $R_{coat}$ and $R_{ct}$ are exhibited in figures 11(b)–(d) separately. Thereinto, $R_{coat}$ is used as the corrosion resistance parameter of the conversion coating itself. The larger value of $R_{ct}$ indicates the good corrosion resistance. As illustrated in figure 11(b), the $R_{coat}$ of the composite conversion coating is higher than that of the Al matrix at each test temperature, suggesting a favorable corrosion resistance of composite conversion coating. The variation of $R_{ct}$ is consistent with that of $R_{coat}$ which show that the introduction of conversion coating can significantly reduce the charge transfer on the metal surface. To sum up, both the higher

![Figure 8](image_url)

**Figure 8.** (a) Self-corrosion current density (b) self-corrosion potential under different test temperatures.

![Figure 9](image_url)

**Figure 9.** Plots of $\ln(j_{corr})$ versus $\frac{1}{T}$ for the Al matrix and Mo–Zr–Ti composite conversion coating in 3.5 wt.% NaCl solution under different test temperatures.
and $R_{ct}$ for chemical conversion treated specimen make it isn’t easy for the corrosive ions in electrolyte to get across the conversion coating. Therefore, the EIS results demonstrate the corrosion reaction resistance from the perspective of electron transfer, which supplements the results of polarization curves.

### 3.5. Full immersion corrosion test

The full immersion test can simulate the real service condition to a certain extent, and figure 12 shows the average corrosion rates of the matrix and the composite conversion coating in 3.5 wt.% NaCl solution for 168 h at different immersion temperatures. It can be clearly seen that the average corrosion rate of whether matrix or conversion coating both accelerate with the increase of immersing temperature, which are consistent with the electrochemical results. It can be mainly attributed to the introduction of Cl$^{-1}$ ion, and it is more likely to attack the surface at higher temperature, resulting in surface corrosion damage. Moreover, the average corrosion rate
of conversion coating is obviously lower than that of the Al matrix at each immersing temperature. Compared with the Al matrix, the average corrosion rate of the conversion coating is reduced by 65% to 85%.

4. Conclusion

(1) The conversion temperature and conversion time have a great influence on the construction of Mo-Ti-Zr conversion coating. The optimal temperature and time are 40°C and 15 min, respectively. The conversion time is insufficient or too long that both can cause the decrease of corrosion resistance.

(2) The compositions of Mo–Zr–Ti conversion coating are mainly composed of Mo, Ti, Zr, Al and O elements. The inner coating mainly contains Mo, Zr and Ti elements, and the outer coating mainly contains Mo and Ti elements. The phase compositions of the conversion coating consist of MoO₃, Mo₂O₅, TiO₂, ZrO₂ and Al₂O₃, as well as AlF₃•3H₂O, Na₃AlF₆ and ZrF₄.

(3) Mo–Zr–Ti conversion coating can significantly improve the corrosion resistance of the Al matrix. The corrosion kinetic of Al matrix and conversion coating both follow Arrhenius law, and the corrosion resistance decrease with the increase of the test temperature. The various trend of full immersion test is consistent with the electrochemical test, and the decrease range of average corrosion rate relevant to conversion coating is from 65% to 85% than that of the Al matrix.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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