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Titanium, zirconium and vanadium conversion coatings (TZVCCs) on AZ91D magnesium alloy sheets

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Abstract

This paper reports the preparation, characterization, and corrosion resistance of an eco-friendly titanium/zirconium/vanadium-based conversion coating (TZVCC) on an AZ91D magnesium alloy sheet. The TZVCC microstructure and composition were investigated by SEM, EDS, and XPS. The corrosion behavior of treated and untreated magnesium alloy sheets was observed by potentiodynamic polarization and EIS. The coatings are found to be rapidly formed on the alloy exterior within 90 s and optimal conversion treatment time at 50 s. The primary components of the TZVCC were MgO, Mg(OH)2, V2O5, V2O3, MgF2, TiO2, ZrO2 and metal–organic complexation. The coating was also shown to markedly enhance the corrosion resistance performance of magnesium alloys.

1. Introduction

Magnesium alloys show remarkable potential for various transportation, aviation, aerospace, digital-3C, and biomedicine applications due to their high strength, light weight, low density, and strong biological compatibility [1–6]. Magnesium alloys are electrochemically active, however, and vulnerable to corrosion in natural environments with the service life of such alloys can be reduced substantially by material corrosion. Therefore, it is urgent to improve corrosion resistance performance and practicality.

Among the numerous surface modification methods available today, chemical conversion coatings are highly versatile corrosion inhibitor that can be easily applied and low in cost. As an intermediate layer, a conversion coating enhances not only the corrosion resistance of a given material but also can improve metal the adhesion to an overlaid paint layer. Traditionally, magnesium alloy conversion treatments have been prepared using hexavalent chromium compound solutions [7]. Hexavalent chromium (Cr (VI)) is poisonous and carcinogenic and produces environmentally hazardous waste products [8–10]. The use of Cr (VI) has been completely prohibited in Europe since 2017 which has created an urgent demand for novel chromate-free and ecological conversion treatment techniques [11]. Chromate-free treatments have been developed using several compounds such as phosphate [12], permanganate [13], molybdate [14], vanadate [15], zirconate [16] and combinations thereof [17]. However, there is currently no complete substitution available today due to the color-free and corrosion-prone nature of most chromate-free conversion coatings.

Previous researchers have successfully developed golden Ti/Zr/V conversion coatings (TZVCCs) composed of metal oxides (e.g., TiO2, ZrO2, V2O5 and Al2O3), metal fluorides (e.g., ZrF4 and AlF3), and metal organic complexation on 6063 aluminum alloy [18–20]. TZVCC formed on aluminum alloy 6063 shows excellent corrosion resistance and adhesion performance for epoxy coatings. In the present study, a similar TZVCC was prepared on AZ91D magnesium alloy and its morphology, composition, and corrosion resistance investigated by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), x-ray photoelectron spectroscopy (XPS), and electrochemical corrosion workshop analyses.
2. Experimental process

2.1. Coating preparation
The substrate metal used in this study was AZ91D magnesium alloy, the main compositional elements are listed in table 1. The specimens subjected to SEM and electrochemical testing were 20 × 20 × 2 mm in size and those for XPS were 10 × 10 × 2 mm. The sheets were ground mechanically and sequentially with 400- and 1000-grit waterproof SiC paper and then washed with distilled water. After degreasing samples in NaOH (40 g l⁻¹) and Na₂SiO₃ (40 g l⁻¹) alkaline solution at 25 °C for 2 min, they were washed with distilled water and immersed in a Ti/Zr/V-based aqueous solution composed of H₂TiF₆, H₂ZrF₆, NaVO₃, and tannic acid (TA; at 2, 0.8, 2, and 2 g l⁻¹, respectively) for treatments of 10, 30, 50, 70, and 90 s. The solution pH value and conversion temperature were controlled to 2.8 and 30 °C, respectively. The treated sheets were washed once more with distilled water and dried in a vacuum at 35 °C for 24 h.

2.2. Characterization methods
The morphology and composition of TZVCCs formed on treated sheets were investigated by SEM on a field emission Nova-nano SEM-230 scanning electron microscope with EDS (FEI Co., Hillsboro, OR, USA). The TZVCC layer thickness was measured using an optical film thickness meter (OPTM-A2, Otsuka Electronics Co., Ltd, Osaka, Japan). XPS was carried out on a Thermo K-Alpha instrument (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a standard Al-Kα x-ray source and a hemisphere electron energy analyzer in an extreme vacuum chamber, with 10⁻⁹ bar base pressure. All spectral binding energies were corrected per the reference standard binding energy of the C-1s peak at 284.6 eV.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization analyses were conducted on a CHI660D electrochemical workstation which had three electrodes: a working electrode, a saturated reference calomel electrode and platinum foil counter electrode. The electrolyte was a 3.5-wt% NaCl solution at room temperature. Specimens were first immersed in electrolyte for ~30 min to obtain a stable open circuit potential-time curve (OCPT). The EIS measurements were collected from 100 kHz to 0.01 Hz using a 5-mV amplitude sinusoidal voltage perturbation superimposed on a direct current potential set at the open circuit potential (OCP). The obtained impedance data was fitted using ZVIEW software and a corresponding equivalent circuit fitting diagram was accordingly established. Potentiodynamic polarization was performed at a scan rate of 1 mV s⁻¹ between −2.0 and −1.0 V in relation to the OCP. The electrochemical workstation software was used to collect Ecorr and Icorr and all specimens examined separately on the workstation.

3. Results

3.1. TZVCC characterizations
3.1.1. Optical images and coating thickness
Optical photos and coating thickness of specimens treated in the Ti/Zr/V-based solution for various conversion treatment times showed that specimen color gradually darkened from light-yellow to golden-yellow and ultimately to brown-yellow as the treatment time progressed from 10 s to 90 s (figure 1). A golden-yellow-color TZVCC was obtained at the 50 s time point. With further treatment beyond this point, the specimens became browner and their compactness began to degrade. The thickness was observed to gradually increase with increased treatment time, but beyond 50 s, this effect grew less pronounced.

3.1.2. SEM observations and EDS analysis
SEM images of the substrate and TZVCCs obtained at various treatment times showed that substrate surfaces without any treatment contained several granules, long grooves, and scratches caused by brittle particles fracturing and/or debris embedded in the substrate as it was processed (figure 2(a)) [21]. After 10 s of Ti/Zr/V-based solution treatment, the defects remaining in the substrate surface decreased significantly as a thin TZVCC layer developed on substrate surfaces (figure 2(b)). After a 30 s treatment, defects in the substrate surface were completely covered by a coating, which contained several typical micro-cracks (figure 2(c)).

After a 50 s treatment, the coating was uniform and cracks, caused by internal stress from the shrinkage during the drying process, were uniformly distributed on the substrate surface (figure 2(d)) [22]. Several white
granules were randomly dispersed on the coating surface, which were attributable to adsorption of organic complexes generated by aging of the conversion solution or to reactions between the substrate and surrounding conversion fluid. Optical images of longer treatment times showed that, with increased treatment time to 70 or 90 s, the coating became more coarse due to deeper cracks and more white surface particles, which also drove down the resulting corrosion resistance, as discussed below (figures 2(e) and (f)). In summary, the present SEM analysis revealed that the optimal conversion treatment time for TZVCC formed on this magnesium alloy was 50 s.

EDS spectra were used to analyze the elemental compositions of the white granules on the TZVCC surfaces (figure 3) and the white granules found to be composed of Mg, C, O, Ti, Zr, V, and F, from EDS analytical results. The Mg proportion was as high as 53.31 at.% in these samples, which probably originated from the substrate. The presence of the Ti, Zr, and V indicated that TZVCC played a role in the granule formation observed here while the C and O signals indicated metal-organic complexation and oxide and/or hydroxide in the granules.

3.1.3. XPS analysis
The elemental chemical states in 50-s TZVCC specimens were determined by XPS analyses, which showed that the TZVCC layer was mainly composed of Mg, O, C, Ti, Zr, V, and F (figure 4(a)). High-resolution Mg 2p, Ti 2p, Zr 3d, V 2p, F 1s, C 1s, and O 1s elemental XPS spectra are shown in figures 4(b)–(h), respectively. The Mg 2p spectrum was decomposed of three peaks located at 49.6, 49.7, and 50.0 eV, corresponding to Mg(OH)$_2$, MgO, and MgF$_2$, respectively (figure 3(b)) [23–25]. Two components with binding energies at ~457.7 and 458.2 eV were curve-fitted from the Ti 2p spectrum and corresponded to Ti-complexation compounds and TiO$_2$, respectively [26–28]. The Zr region in the XPS spectrum of Zr 3d was composed of two peaks at 181.5 and 183.8 eV, which were attributed to Zr-complexation compounds and ZrO$_2$, respectively [27–29]. The photoelectron peak of V 2p derived from two different V oxidation states, with the two peaks at 515.83 and 516.28 eV, assigned to V$_2$O$_3$ and V$_2$O$_5$, respectively [29–32]. The F 1s peak at 684.7 eV was attributed to MgF$_2$ [24, 26, 27]. The observed C 1s peak was divided into two peak components with 284.0 and 286.9 eV binding energies. The first peak at ~284.0 eV was caused by pollution during XPS measurement and the second can be ascribed to –C$\equiv$H$\equiv$ – [23, 24]. According to these XPS analyses, the coating was composed of MgO, Mg(OH)$_2$, MgF$_2$, V$_2$O$_5$, V$_2$O$_3$, TiO$_2$, ZrO$_2$, and the metal-organic complexes.

3.2. Corrosion resistance
3.2.1. Potentiodynamic polarization analysis
Potentiodynamic measurements were collected to evaluate the corrosion resistance of the substrate and TZVCCs, obtained after various conversion treatment times in a 3.5% NaCl solution at pH 6.8. The specimen polarization curves are shown in figure 5 and the corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) of different specimens, obtained by Tafel extrapolation [31], listed in table 2. The treatment generated significant changes in both anodic and cathodic responses, compared to untreated specimens, especially at over 30 s of treatment. The $E_{corr}$ values of TZVCC increased as conversion time extended from 10 to 50 s and decreased slightly from 50 to 90 s, with the $I_{corr}$ values showing opposing trends. The trends of $E_{corr}$ and $I_{corr}$ for the TZVCCs
Figure 2. SEM images of bare AZ91D magnesium alloy (a) and TZVCCs obtained with different conversion treatment times 10, 30, 50, 70, 90 s (b)–(f), respectively.

Figure 3. SEM-EDS results of white granules formed on TZVCC surfaces.
were closely related to coating morphology (figure 2). The $E_{\text{corr}}$ value of TZVCC obtained at 50 s was $-1.47$ V, which shifted to $\sim 130$ mV in the positive direction from that of the untreated AZ91D substrate at $E_{\text{corr}} = -1.60$ V. The $I_{\text{corr}}$ of the substrate was $23.58$ $\mu$A·cm$^{-2}$ while that of the 50 s TZVCC specimen was $2.45$ $\mu$A·cm$^{-2}$, i.e., about one order of magnitude lower. This significant decrease in $I_{\text{corr}}$ value suggested that the alloy’s corrosion resistance was markedly enhanced by TZVCC treatment.

Figure 4. XPS spectra of the TZVCC: overview XPS spectra (a); spectra of Mg 2p; Ti 2p; Zr 3d; V 2p; F 1s; C 1s and O 1s (b)–(h), respectively.)
3.2.2. EIS analysis

The corrosion resistance indicators of TZVCCs and AZ91D magnesium alloy sheets were further investigated via EIS. The corresponding Nyquist plots showed that the untreated AZ91D plot included a capacitive arc in the high-frequency region, which was created by metal dissolution in the corrosion process. There was also an inductive arc in the low-frequency region caused by weakening of the oxide film due to anodic dissolution of metals (figure 6) [33].

The equivalent circuit for the substrate and TZVCC/substrate was fitted according to the known characteristics of the corrosion process [34–36] using ZsimpWin software (figure 7(a)). Here, $R_s$ was the solution resistance, $Q$ the capacitance of the partial protective oxide/hydroxide layer formed on bare substrate in 3.5% NaCl solution, $R_t$ the resistance of charge transfer between the alloy surface and corrosive medium, $R_{WE}$ the diffusion or Warburg impedance, $R_c$ the resistance of the oxidation coating formed on the AZ91D

![Figure 5. Polarization curves of substrate and TZVCCs obtained with different conversion times, at 10, 30, 50, 70 and 90 s.](image1)

![Figure 6. Nyquist plots of bare AZ91D and with TZVCC from different conversion time, at 10, 30, 50, 70 and 90 s.](image2)

| Conversion Time | $I_{corr}$ (μA·cm$^{-2}$) | $E_{corr}$ (V) |
|-----------------|--------------------------|---------------|
| Substrate       |                          |               |
| 10s             | 23.58                    | −1.60         |
| 30s             | 23.76                    | −1.56         |
| 50s             | 13.69                    | −1.49         |
| 70s             | 2.45                     | −1.47         |
| 90s             | 3.04                     | −1.52         |
| 5.96            |                          | −1.53         |
magnesium alloy surface when exposed to air, and $L_1$ and $L_2$ the induction behavior at high and low-frequencies, respectively. The EIS spectra of TZVCC produced by various conversion times were also fitted by an equivalent circuit (figure 7(b)), where $R_c$ corresponded to conversion coating resistance while other parameters were denoted similarly as those used above.

The parameter values for untreated and treated specimens extracted from Nyquist plots are shown in table 3, where higher $R_c$ and $R_{ct}$ represent better corrosion resistance [37–39]. The $R_c$ and $R_{ct}$ values of all TZVCC specimens were much higher than those of untreated AZ91D alloy sheets. TZVCC produced by a 50 s treatment showed the highest $R_c$ and $R_{ct}$, which indicated that anodic dissolution was less likely in this sample substrate than others, with the TZVCC appearing to have prevented the corrosive medium from penetrating the substrate surface. The impedance value trend for different treatment times were in accord with the potentiodynamic measurements and SEM analytical results. Thus, TZVCC effectively inhibited anodic dissolution of the substrate, prevented corrosive material from entering the substrate surface, and altogether enhanced the alloy’s corrosion resistance.

### 4. Conclusion

A golden-yellow TZVCC layer was successfully applied on an AZ91D magnesium alloy sheet by a chemical conversion treatment using MgO, Mg(OH)$_2$, MgF$_2$, TiO$_2$, ZrO$_2$, V$_2$O$_5$, V$_2$O$_3$ and metal-organic complexation. SEM images showed that a conversion treatment time of 50 s produced a coating with a relatively uniform surface and thickness of $\sim$1.5 um. XPS analysis indicated that this 50-s TZVCC layers consists of Mg, C, O, Ti, Zr, V, and F. Electrochemical analyses including potentiodynamic and EIS measurements showed that the corrosion resistance of the AZ91D magnesium alloy improved considerably after this conversion treatment. The TZVCC reported here thus represented a promising conversion coating treatment for safe and effective magnesium alloy fabrication.

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