Surface & Coatings Technology 276 (2015) 239–247

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Preparation and characterization of colored Ti/Zr conversion coating on AZ91D magnesium alloy

Aihua Yi, Jun Du *, Jian Wang, Songling Mu, Guoge Zhang, Wenfang Li

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, PR China

ARTICLE INFO

Article history:
Received 29 January 2015
Revised 12 June 2015
Accepted in revised form 27 June 2015
Available online 4 July 2015

Keywords:
Magnesium alloys
Conversion coating
Colorization
Corrosion resistance

ABSTRACT

A golden-yellow Ti/Zr conversion coating on AZ91D substrate was successfully prepared in the solution containing titanium and zirconium ions with the addition of tannic acid. The growth process, microstructure, composition and corrosion resistance of this conversion coating were characterized by EDS, SEM, XRD, XPS, FTIR and electrochemical workstation. The application of H_2ZrF_6 and tannic acid was the key to the coating color. The coating possessed a double-layer structure, in which the inner layer was made up of $Mg(OH)_2$, MgO, TiO_2, ZrO_2, and MgF_2, and the outer layer was metal–organic complex. The π electronic chromophore in the metal–organic complex produced the conversion coating color. The coating was uniform and compact, leading to improved corrosion resistance and significantly reduced corrosion current density (from 93.72 $\mu A \cdot cm^{-2}$ to 1.047 $\mu A \cdot cm^{-2}$).

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Magnesium alloys are the lightest metallic structural materials (~1.8 g/cm^3) possessing outstanding properties such as high specific strength, high specific stiffness, good castability and machinability, and high damping capacity [1,2]. Therefore, magnesium alloys have wide applications in electronics, automotive and aerospace industries. Specially, the high specific strength and stiffness are the most desirable mechanical properties in the automotive and aerospace industries for the purpose of weight saving. The fuel consumption can be saved and consequently carbon dioxide emission is reduced [3]. However, magnesium and its alloys are electrochemically active due to the low standard potential of Mg ($E = -2.363$ V), and are susceptible to corrosion in various environments. The poor corrosion resistance severely limits the widespread application of magnesium alloys in a lot of critical industrial fields. Many attempts have been made to solve such problem of magnesium alloys [4]. Among the various surface modification techniques, chemical conversion treatment is the most widely applied method in metal finishing which not only improves corrosion resistance but also enhances the adhesion of painting to the underlying metals [5].

Chromate conversion coating (CCC) is one of the most widely applied chemical conversion coatings for corrosion protection of metallic alloys [6–8]. Hexavalent chromate Cr(VI) is highly toxic due to the carcinogenic effect and results in environmentally hazardous waste product. Therefore, Cr(VI) compounds will be completely forbidden by 2017 in the European Community according to the environmental laws of "Restriction of Hazardous Substances" (ROHS) [9]. Therefore, the development of chromate-free and environmentally friendly chemical conversion techniques has attracted wide attention in the past two decades [9,10]. Various chromate-free conversion coatings have been developed, such as phosphate/permanganate [11,12], vanadate [13], zirconia [14], molybdate [15,16], fluorozirconate [17], stannate [18,19], rear earth [20,21] and phytic acid [22,23] conversion coatings. Although significant progress has been achieved, it was pointed out recently that no chromate-free conversion coatings can match CCC up to date [9]. It is still challenging to develop chromate-free conversion coating with excellent performance.

Among the different chromate-free chemical conversion coatings, the hexafluoro-zirconic and/or hexafluoro-titanic based treatment (Ti and/or Zr coatings) is considered to be a promising candidate [24–29]. Ti/Zr conversion solutions are commercially available for aluminum alloy treatment [30–32]. AA 6014 can be successfully treated in the KGaA solution developed by Henkel AG & Co. [30], and AA6060 can be treated by commercial Gardobond X4707 solution [31] or Alodine 2840 solution [32]. However, until now the study of Ti/Zr conversion coating was mainly focused on aluminum alloys, little efforts were put on magnesium alloys [33].

The Ti/Zr-based treatments are considered to be a prospective and effective alternative to hazardous chromate-based methods. It is well known that chromate conversion coating is of light-brown color. It is easy to distinguish the treated metals from untreated ones on the production line. The coating is almost colorless for the Ti/Zr-based conversion treatments. Consequently, the application of Ti/Zr-based chemical conversion techniques was limited to a large extent.

* Corresponding author at: Department of Metallic Materials, School of Materials Science and Engineering, South China University of Technology, Wu Shan Road 381, Tian He District, Guangzhou 510640, PR China.
E-mail address: tandujun@sina.com (J. Du).

http://dx.doi.org/10.1016/j.surfcoat.2015.06.069
0257-8972/© 2015 Elsevier B.V. All rights reserved.

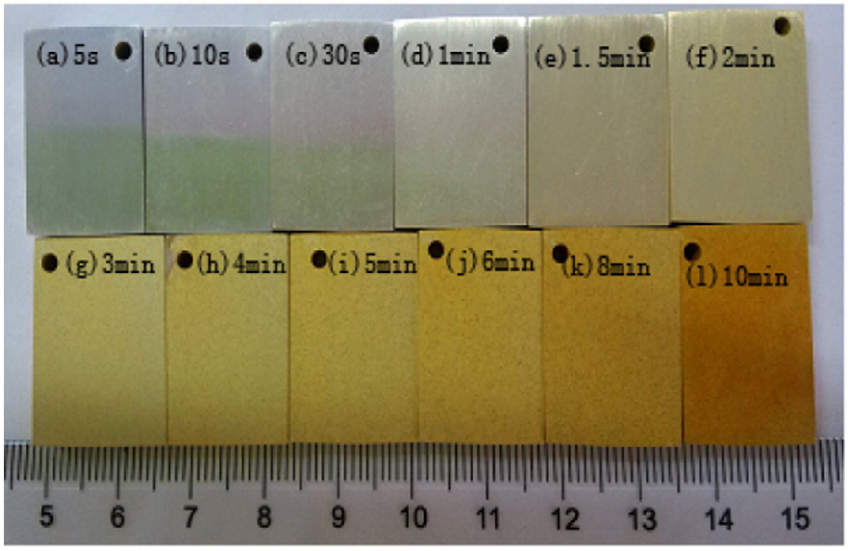

Fig. 1. Digital photos of the samples immersed in the solution for different conversion times of 5 s, 10 s, 30 s, 1 min, 1.5 min, 2 min, 3 min, 4 min, 5 min, 6 min, 8 min and 10 min.

In our previous study [34], a golden conversion coating mainly composed of $NaAlF_6$ was successfully prepared on 6063 aluminum alloys in the conversion solutions containing H_2TiF_6, H_2ZrF_6, NaF and tannic acid. However, no studies were reported on the colored Ti/Zr-based conversion coatings prepared on the substrate of magnesium alloys. In the present study, a colored Ti/Zr conversion coating was successfully developed on AZ91D substrate by adding tannic acid to the solutions containing H_2TiF_6 and H_2ZrF_6. The formation process of the colored Ti/Zr conversion coating was mainly studied. The composition and corrosion resistance of the coating were examined. The formation mechanism of the colored coatings was also investigated.

2. Experimental procedure

2.1. Preparation of the coatings

AZ91D, the most popular die-cast magnesium alloy, was used in the present study. The compositions of the alloy are: 8.8% Al, 0.85% Zn, 0.25% Mn and balanced with Mg. The contents of impurity elements are very low (≤0.05% Si, ≤0.002% Cu, ≤0.005% Ni and ≤0.005% Fe). The samples with a size of 30 × 30 × 5 mm^3 were electrical-sparkly machined from the AZ91D ingot. The samples were ground using abrasive paper with grit 2000. Then, the samples were degreased in the alkaline solution of NaOH (40 g/L) and Na_2SiO_3 (40 g/L) for 3 min at 30 °C, followed by washing with distilled water. The conversion solution was composed of 0.5 g/L H_2TiF_6, 1.5 g/L H_2ZrF_6 and 1.5 g/L tannic acid with the original pH value of 1.8–1.9. The pH value was adjusted to about 2.5 by adding a small amount of NaOH solution. The solution compositions and pH value were optimized based on our previous systematical experiments using orthogonal and single factor experiments. The conversion temperature was controlled in room temperature of 25–30 °C. The degreased samples were immersed in the conversion baths for different times from 5 s to 10 min. To study the colorization mechanism, three reference samples were prepared for an immersing time of 3 min in the solutions of H_2TiF_6 0.5 g/L and H_2ZrF_6 1.5 g/L (sample 1), H_2ZrF_6 1.5 g/L and tannic acid 1.5 g/L (sample 2), and H_2TiF_6 0.5 g/L and tannic acid 1.5 g/L (sample 3), respectively.

2.2. Coating characterization

The optical images of the samples were taken to observe the macromorphology of the coatings. Scanning Electron Microscopy (SEM) observations were performed with an acceleration voltage of 20 kV on an FEI Quanta 200 SEM machine equipped with an EDAX Genesis

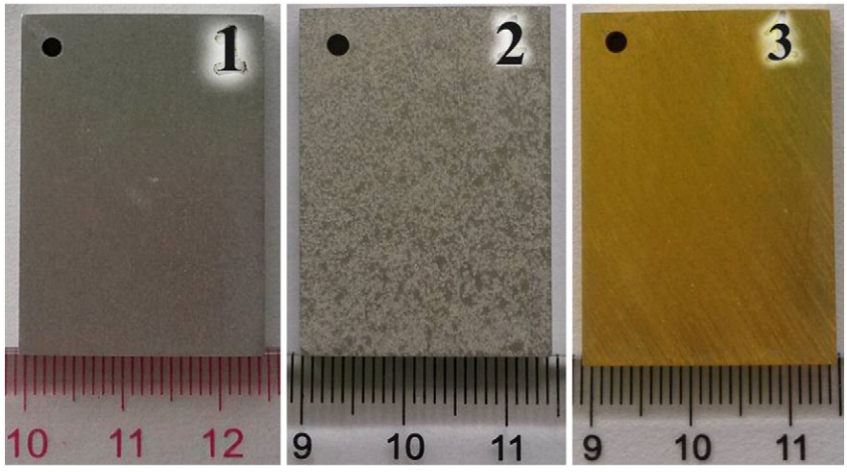

Fig. 2. Digital photos of the three reference samples prepared in different solutions (1: H_2TiF_6 0.5 g/L and H_2ZrF_6 1.5 g/L; 2: H_2ZrF_6 1.5 g/L and tannic acid 1.5 g/L; 3: H_2TiF_6 0.5 g/L and tannic acid 1.5 g/L).

Download English Version:

https://daneshyari.com/en/article/1656978

Download Persian Version:

https://daneshyari.com/article/1656978

Daneshyari.com