In situ growth of Mg-Al hydrotalcite film on AZ31 Mg alloy

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Abstract: An environmentally friendly method for in situ growth of Mg-Al hydrotalcite (HT) film on AZ31 magnesium alloy has been developed. The growth processes and corrosion resistance of the HT film were investigated. Then the HT film was surface modified by phytic acid solution to further improve the corrosion resistance. The film formation involves the dissolution of AZ31 substrate, adsorption of the ions from solution, nucleation of the precursor, followed by the dissolution of Al^{3+}, exchanging of OH^- by CO_3^{2-} and growth of the HT film. The HT film is very compact and acts as a barrier against Cl^- attack in the early stage of corrosion, and then the surface of the film is dissolved gradually. This dense HT film can provide effective protection to the AZ31 alloy. The HT film with surface modification by phytic acid presents a self-healing feature and exhibits better corrosion resistance.

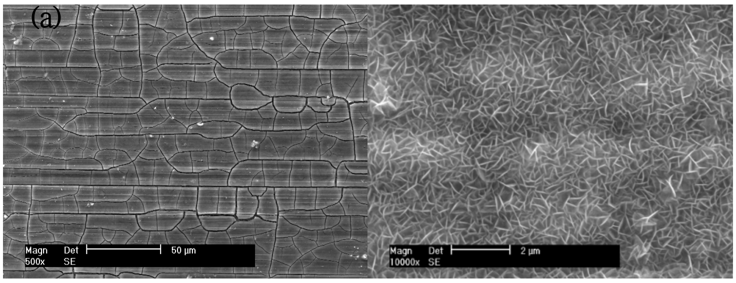
1. Introduction

Chemical conversion films are widely used to protect Mg alloys due to their low cost and simple preparation. However, the current conversion films are not satisfying in view of the poor corrosion resistance and environmental problem. Thus, it is necessary to develop a high corrosion-resistant and environmentally friendly conversion coating to protect Mg alloys.

Hydrotalcite compounds (HTs) possess a special layered structure and have already been developed as conversion coatings to protect metal Al and Zn [1]. Uan et al. [2] prepared a HT film on AZ91 Mg alloy in carbonic acid solution and can resistant salt spray test for 72 h. This result indicates that HTs are promising alternative coatings for improving the corrosion resistance of Mg alloys. However, the current technology is only available for the Mg alloys with high Al content because the elements of Mg and Al in the Mg-Al HT film originate from the dissolution of Mg substrate. In addition, the treatment time of at least 4 h is too long. Thus, this work aims at preparing a high corrosion resistance as well as environmentally friendly HT conversion film on AZ31 Mg alloy by in situ growth. Then the film formation and corrosion mechanism are clarified. Also, the HT film is surface modified by phytic acid to further improve the corrosion resistance.

2.Result & Discussion

The extra Al ions are added to the carbonic acid film formation solution by dissolving a pure Al panel in Na2CO3. A two-step method is used to in situ growth Mg-Al HT film on AZ31 Mg alloy. The Mg substrate is first immersed to the pretreatment solution to obtain a precursor film, and then the precursor film is immersed to the post pretreatment solution to obtain the HT film. Fig. 1 shows the SEM micrographs of the precursor film and HT film. The morphology of the precursor film (Fig. 1a) reveals a network structure due to the presence of many cracks. After post treatment, the morphology of the precursor film changes significantly. The dense and uniform blade -like flakes completely cover the surface of the Mg substrate (Fig. 1b). The HT film is very compact and smooth.




(b)

Fig. 1 SEM micrographs of the precursor film (a) and hydrotalcite film (b) Fig. 2 Optical morphology of AZ31 (a) and HT film (b) after immersion in 0.1 M NaCl for 6 h

Fig. 2 shows the optical morphologies of the AZ31 and HT film after 6 h immersion. Severe corrosion occurs on the bare Mg alloy (Fig. 2a). In contrast, no corrosion is visible on the HT film. It indicates that the HT film can provide good protection to the Mg substrate.

A possible mechanism of in situ growth of HT film on AZ31 alloy is proposed. Firstly, the AZ31 substrate is dissolved to give Mg^{2+}, meantime the enriched Mg^{2+} is combined with OH^- and CO_3^{2-} to form $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$. Then the further dissolution of the Al in the substrate and the transportation of Al^{3+}, OH^- and CO_3^{2-} from the solution to the substrate surface occur to form $Al_5(OH)_{13}(CO_3) \cdot 5H_2O$. Subsequently, the precursor film consisting of $Mg_2Al(OH)_7$ and $MgAl_2(OH)_8 \cdot xH_2O$ is formed. After that, the Al–rich compounds $Mg_2Al(OH)_7$ and $MgAl_2(OH)_8 \cdot xH_2O$ leach out Al^{3+} to form $Mg_6Al_2(OH)_{18} \cdot 4.5H_2O$. Finally, the OH^- in the interlayer of $Mg_6Al_2(OH)_{18} \cdot 4.5H_2O$ is exchanged by CO_3^{2-} to form $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$.

The possible corrosion mechanism of the HT film on the AZ31 alloy is that the film can act as a barrier against chloride attack because of the high affinity of CO_3^{2-} to the hydroxide sheets and protect the Mg alloy to a certain extent. However, HT is unstable in aqueous solutions, accompanying with the corrosion accelerating by the adsorbed Cl^- ions, partial of which is decomposed into $Mg_2CO_3(OH)_2 \cdot 3H_2O$, $Mg(OH)_2$ and $Al(OH)_3$. Then micro–cracks appear and corrosion occurs. These decomposed products associated with the corrosion products can inhibit the corrosion of the Mg alloy for a while during the long immersion.

Further, the HT film is surface modified by phytic acid solution. The surface modified HT film presents a self-healing feature and exhibits better corrosion resistance.

3.Conclusion

An environmentally friendly and high corrosion resistant Mg-Al HT film is in situ grown in AZ31 Mg alloy. The HT film is very compact and uniform and can provide good protection to the Mg substrate. The film formation mechanism and corrosion mechanism are proposed. After the HT film is surface modified by phytic acid, the film presents a self-healing feature after corrosion.

References

1. R.B. Leggat, W. Zhang, R.G. Buchheit, Corrosion 58 (2002) 322-328.
2. J.K. Lin, J.Y. Uan, Corros. Sci. 51 (2009) 1181-1188.