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Mixed rare earth metal conversion coatings on 2024 alloy and Al6061/SiC_p metal matrix composites①

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[Abstract] The processes of mixed rare earth metal (REM) conversion coatings on 2024 alloy and Al6061/SiC_p metal matrix composites (MMC) were introduced. The coatings were examined to be honeycomb-like feature by scanning electron microscope. X-ray diffraction analysis revealed that the coatings are amorphous structure. The results of X-ray photoelectron spectroscopy indicated that the mixed REM conversion coatings consist predominantly of Ce and O, the contents of other rare earth elements (such as La, Pr) are relatively low, the coatings are about 2 ~ 4 μm thickness with excellent adhesion and wearability. The results of mass loss test showed that the mixed REM conversion coatings produce corrosion resistant surface of 2024 alloy and Al6061/SiC_p.

[Key words] 2024 alloy; Al6061/SiC_p metal matrix composites; mixed rare earth metal; conversion coatings
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1 INTRODUCTION

For almost one century, chromate compounds (Cr^{6+}) have been used as very effective and inexpensive corrosion inhibitors for many alloys including aluminum, zinc and steel in a wide range of aqueous environments. However, the recent recognition that chromates are both highly toxic and carcinogenic has led to extensively worldwide research to develop effective alternative inhibitors.

Hinton and Arnott investigated the effectiveness of rare earth metal (REM) salts as corrosion inhibitors for aluminum alloys. They introduced new types of conversion coatings that were formed by immersion of aluminum alloys in a solution containing cerium chloride or other REM chlorides such as $LaCl_3$ and YCl_3. This chemical passivation process produced coatings that were more resistant to pitting than the naturally formed oxide film on the surface of aluminum alloys[1~4]. In 1990s, Mansfeld et al reported the Ce-Mo process for surface modification of aluminum alloys which involves immersion in boiling $Ce(NO_3)_3$ solution, anodic polarization in Na_2MoO_4 solution and immersion in boiling $CeCl_3$ solution. Significant improvements in the resistance to localized corrosion were obtained[5~8]. In the following years, Mansfeld et al developed the Ce-Mo process for high-copper aluminum such as 2024 and 7075 alloy by applying a copper removal electrochemical pretreatment step. Remarkable improvements in corrosion resistance were achieved[9,10]. LI et al studied the effects of REM conversion coatings on SCC behavior of LC4 (7075) alloy in 3.5% NaCl solution. The stress corrosion cracking of LC4 alloy was inhibited to some extent after the formation of REM conversion coating on the alloy surface[11,12]. The author has also made some progress in researching process and corrosion resistance of REM conversion coatings on 2024 alloy[13,14].

The rare earth compounds used for producing REM conversion coatings in current researches are mainly cerium chloride, cerium nitrate and cerium carbonate. However, the mixed rare earth compounds are much cheaper. In a research project devoted to reduce production costs, the processes of mixed REM conversion coatings on 2024 alloy and Al6061/SiC_p are developed in this paper. In addition, the corrosion resistance of the modified surfaces is investigated using mass loss test. The surface morphologies, microstructure and compositions of the coatings are investigated by employing scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2 EXPERIMENTAL

2.1 Materials

The major alloying elements of 2024 and 6061 alloys are listed in Table 1. The compositions and mechanical properties of Al6061/SiC_p are listed in Table 2. The major elements of mixed REM are listed in Table 3.

2.2 Surface modification process

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Table 1 Major alloying elements of 2024 and 6061 alloys (mass fraction, %)

Alloy	Cu	Mg	Mn	Fe	Si	Zn	Ni	Ti	Others	Al
2024	3.8 ~ 4.9	1.2 ~ 1.8	0.3 ~ 0.9	0.5	0.5	0.3	0.1	0.15	0.1	Bal.
6061	0.15 ~ 0.4	0.8 ~ 1.2	0.15	0.7	0.4 ~ 0.8	0.25	-	0.15	0.15	Bal.

Table 2 Contents and mechanical properties of Al6061 / SiC_p

Matrix	Reinforcer	Bending strength / MPa	Hardness / HV
6061	SiC particles (3.5 μm, 45 %)	600	200

Table 3 Major elements of mixed REM (mole fraction, %)

Ce	La	Pr
55	30	15

The 2024 alloy samples were first degreased and rinsed with hot distilled water. Then the samples were polished, rinsed with distilled water and pretreated in boiling water for 10 min. At last the samples were immersed in the solution containing mixed REM, rinsed with distilled water and dried with air. The Al6061 / SiC_p samples were first polished with 80#, 300#, 600# and 1 000# abrasive paper, dusted by cotton saturated with acetone and degreased in organic solvent. Then the samples were pretreated in boiling water for 10 min. At last the samples were immersed in the solution containing mixed REM, rinsed with distilled water and dried with air. The parameters of surface modification processes are described as Table 4.

Table 4 Parameters of surface modification

Item	2024 alloy	Al6061 / SiC_p
Mixed REM/ $(g \cdot L^{-1})$	5.0	5.0
H_2O_2/ $(g \cdot L^{-1})$	0.5	0.5
Modifier A/ %	0.02	0.02
Temperature/ ℃	25 ~ 30	30 ~ 35
Additive B/ %	-	0.002
pH	4.0 ~ 4.5	4.5 ~ 5.0
Time/ h	2	2

2.3 Experimental methods

The surface morphologies of the specimens were examined in a S570 scanning electron microscope (SEM).

The structure of mixed REM conversion coatings was analyzed with D_{max}-3B X-ray diffraction (XRD).

Surface analysis was performed by X-ray photoelectron spectroscopy, using a vacuum generator PHI 5700 ESCA. The X-ray source was unmonochromatized Al K_α radiation. The software packages MULTIPAK was used for the analysis of XPS data.

The thickness of the coatings was examined with an E110/ E110B vortex thickness detector. Eight spots were detected randomly to determine the range of the coating thickness.

The bending test was employed to evaluate the adhesion of the coatings on 2024 alloy. The sample was bent to a right angle with a bending radius of 1 cm. Adhesive tape test was used to evaluate the adhesion of the coatings on Al6061 / SiC_p. The surface of the sample was scratched vertically and horizontally to 100 squares with a gap of 1 mm. The depth of the scratch would match the thickness of the coating. Then the scratched surface was compressed with a piece of adhesive tape of 12 mm-width and the tape was dragged immediately after compressing. During the test, the score of adhesion would be defined to be 0 in course of 2024 alloy and Al6061 / SiC_p loosing all their coatings, while the score would be 100 if no coating escapes from 2024 alloy and Al6061 / SiC_p. Based on above standard, the adhesion of the coatings can be given suitable mark.

The wearability of the coatings was evaluated with falling grit test. 80 # SiC particles, used as abrasive, fall from a vertical pipe of 1 meter-long with a funnel at the top. The radius of the pipe is 5 mm. The falling volume of abrasive is (320 ±10) g/ min. The wearability is evaluated according to the time that the coating is eliminated.

The standard mass loss measurements were conducted with 25 mm × 50 mm × 1 mm sheet specimens to evaluate the corrosion resistance of the coatings. The constant immersion conditions were obtained by suspending the specimens on nylon threads in 100 mL of 3.5 % NaCl solution exposed to laboratory air. The immersion time and temperature satisfied the requirements of JB/ 6073 —92 Standard. The mass losses were determined after the removal of corrosion products.

3 RESULTS AND DISCUSSION

3.1 Surface morphologies of mixed REM conversion coatings

The micrographs shown in Fig.1 and Fig.2 reveal that the mixed REM conversion coatings are inhomogeneous and structurally complex.

In the photos with low resolving power (as shown in Fig.1(a) and Fig.2(a)), the mixed REM conversion coatings consist of different size of spherical particles, and larger particles are dotted with smaller ones. The smaller particles seem to be the initial stages of the larger particles. In the photos with high resolving power (as shown in Fig.1(b), (c) and Fig.2(b), (c)), the mixed REM conversion coatings

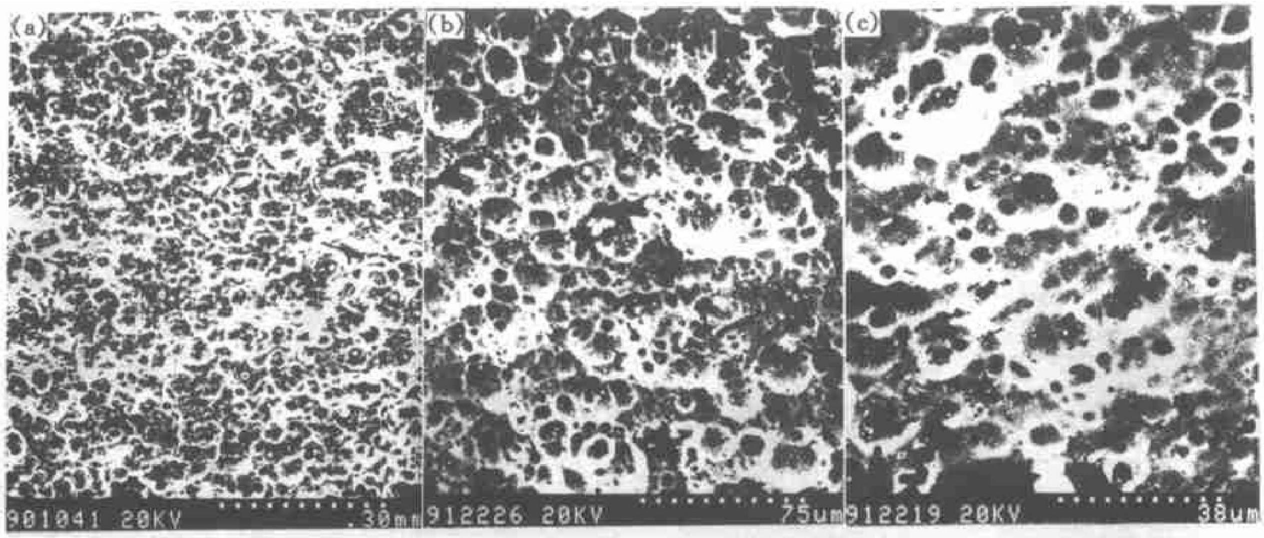

Fig.1 SEM photos of mixed REM conversion coatings on 2024 alloy

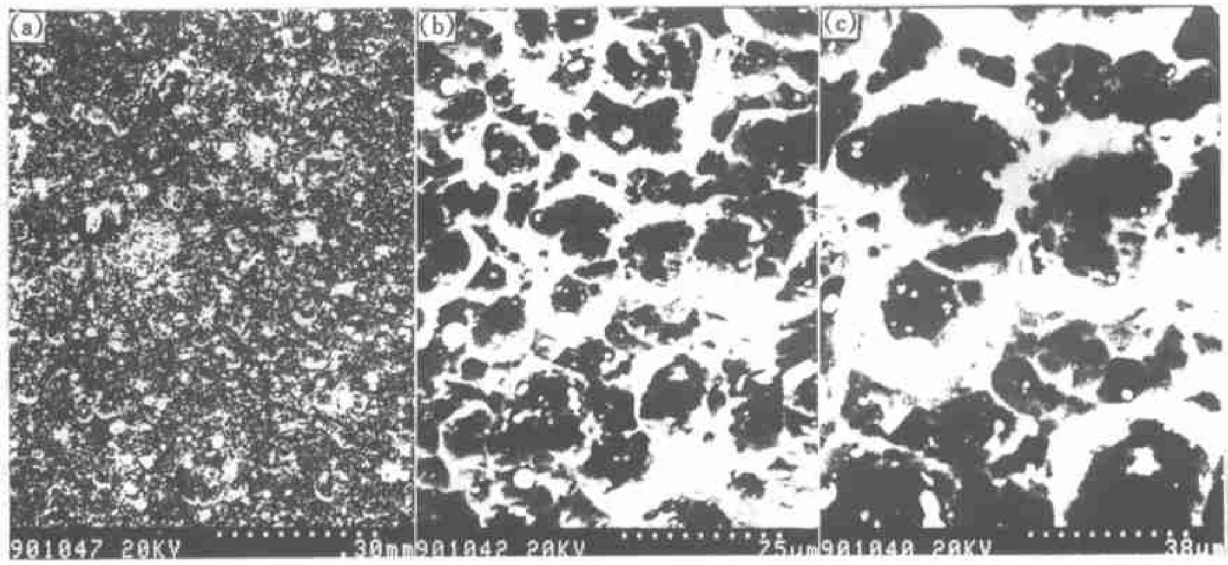

Fig.2 SEM photos of mixed REM conversion coatings on Al6061 / SiC_p

exhibit more complex structure. They consist of honeycomb-like background film of nonuniform thickness upon which smaller particles are attached.

The analysis above indicates that the mixed REM conversion coatings are probably formed initially by the deposition of smaller particles on the surface of 2024 alloy and Al6061 / SiC_p. The growth of smaller particles and the integration of larger particles (as a result of the growth of smaller ones) lead to the formation of the background film. When the background film forms, new smaller particles will deposit and grow again. In this way, the complex film spreads to cover the whole materials surface.

3.2 Microstructure of mixed REM conversion coatings

X-ray diffraction (XRD) spectra of the mixed REM conversion coatings on 2024 alloy and Al6061 / SiC_p MMC are shown in Fig.3. From Fig.3 it can be seen that the coatings are amorphous structure. This conclusion can be drawn from the facts that there is no sharp peak in XRD spectra, and only exist wide peaks in XRD spectra with the range of 20 ~ 40 degree of 2θ angle. The amorphous coating is isotropy and unsusceptible to form electrochemical cell in corrosion medium, thereby the corrosion of the materials was reduced effectively.

3.3 Surface analysis of mixed REM conversion coatings

Fig.4 is X-ray photoelectron spectra (XPS) of the mixed REM conversion coatings. The fact that O1s, Ce4d and Ce3d peaks are the main peaks in survey spectra (Fig.4) indicates that the mixed REM conversion coatings consist predominantly of Ce and O. The compositions of the mixed REM conversion coatings obtained from Fig.4 are listed in Table 5.

From Table 5 and Table 3 it can be observed that the ratio of other rare earth elements (such as La, Pr, etc) to O in the mixed REM conversion

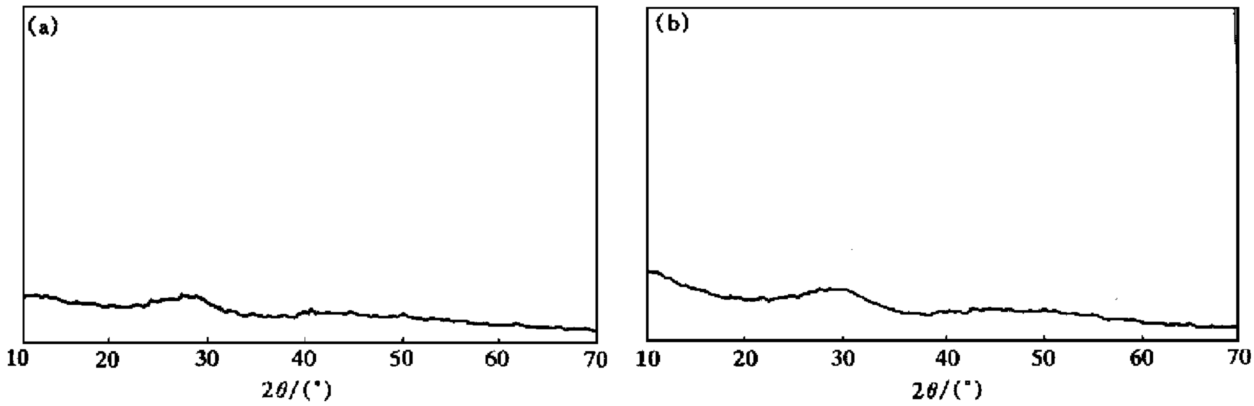

Fig.3 XRD spectra of mixed REM conversion coatings
(a) —On 2024 alloy; (b) —On Al6061/SiC_p

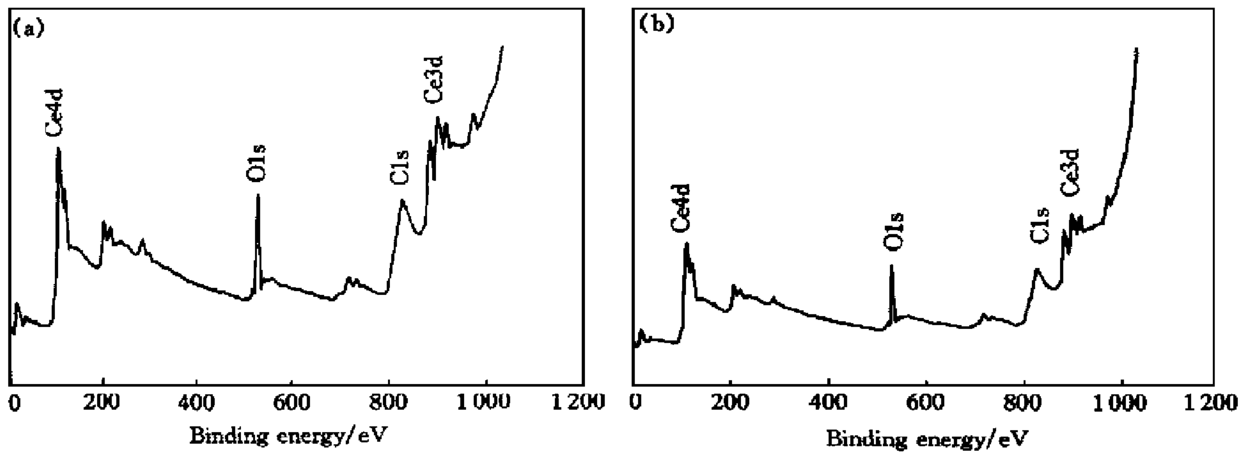

Fig.4 XPS analysis of mixed REM conversion coatings
(a) —On 2024 alloy; (b) —On Al6061/SiC_p

Table 5 Major elements of mixed REM conversion coatings (mole fraction, %)

Coating	O	Ce	La	Pr
Coating on 2024	71.9	24.2	3.2	0.7
Coating on Al6061/SiC_p	72.6	23.8	3.1	0.5

coatings is less than that in raw mixed REM. This indicates that other rare earth elements are more difficult to form REM conversion coatings than Ce.

3.4 Properties of mixed REM conversion coatings

3.4.1 Thickness, adhesion and wearability

The thickness, adhesion and wearability of the mixed REM conversion coatings on 2024 alloy and Al6061/SiC_p are listed in Table 6.

Table 6 Thickness, adhesion and wearability of mixed REM conversion coatings

Item	REM coating on 2024 alloy	REM coating on Al6061/SiC_p
Thickness/μm	2.0 ~ 2.9	2.5 ~ 3.2
Score of adhesion	10	10
Time of coating cleared out/s	40	38

The coatings are about 2 ~ 4 μm thickness with excellent adhesion and wearability.

3.4.2 Corrosion resistance

The corrosion rates of 2024 alloy and Al6061/SiC_p in 3.5% NaCl solution, measured by mass loss, are decreased by the presence of the mixed REM conversion coatings, as shown in Table 7. The decreases in the corrosion rate are more than a factor of ten. The effectiveness of mixed REM conversion coating on inhibiting corrosion for Al6061/SiC_p is less than that for 2024 alloy.

Table 7 Corrosion rate of 2024 alloy and Al6061/SiC_p coated or not ($\mu g \cdot m^{-2} \cdot s^{-1}$)

2024 alloy		Al6061/SiC_p	
Untreated	Coated	Untreated	Coated
7.5	0.6	13.4	0.9

4 CONCLUSIONS

1) Compared with the untreated samples, surface modification by the mixed rare earth metal conversion coatings can improve the corrosion resistance

of 2024 alloy and Al6061 / SiC_p. The thickness of the coatings is about 2 ~ 4 μm. The wearability of the coatings and adhesion between the coatings and the substrates are excellent.

2) The mixed REM conversion coatings exhibit honeycomb-like feature and they are amorphous structure. The coatings consist predominantly of Ce and O. The contents of other rare earth elements are relatively low. Other rare earth elements (La, Pr, etc) are more difficult to form REM conversion coatings than Ce.

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