Microstructure and corrosion model of MAO coating on nano grained AA2024 pretreated by
ultrasonic cold forging technology

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Abstract: In order to study the effect of surface nano-structuring of aluminum alloy on the corrosion performance of MAO coating, ultrasonic cold forging technology (UCFT) was used as a pretreatment to produce a refined layer before a MAO coating was prepared on the surface of 2024 Al alloy (AA2024). The surface roughness was evaluated by atomic force microscope (AFM), and the average surface roughness value of the $5.00 \times 5.00 \mu\text{m}$ area of UCFT treated sample is 7.477 nm. The grain size of the modified layer were observed by transmission electron microscope (TEM). The result showed that UCFT can refine the grains. The microstructure and phase component of the coated samples were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The observations showed that the micro-pore size of the MAO coating on UCFT treated Al alloy is smaller than that of MAO coating on untreated alloy. The phases of the coated samples with and without UCFT remain the same. The hardness of the samples measured by the micro-hardness tester showed that the UCFT-MAO sample possesses the highest micro-hardness among all the samples. The potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were employed to characterize the corrosion rate and the electrochemical impedance in a 3.5% NaCl solution. For the PDP testing, the sweep rate was 5mV/s starting from -1.4 V to 0 V, while the EIS tests were carried out in the range of 0.01 Hz to 100 kHz with AC voltage amplitude of 10 mV. The PDP and EIS results show that the UCFT-MAO sample has the best corrosion resistance with the lowest corrosion current density, 0.412 A/cm^2 . The largest electrochemical impedance is attributed to UCFT pretreatment prior to MAO process on aluminum alloys. The corrosion model of MAO coated AA2024 pretreated by UCFT was proposed.

Keyword: Ultrasonic cold forging technology; Grain; Micro-arc oxidation; Corrosion model; AA2024; Microstructure

1. Introduction

Ultrasonic cold forging technology (UCFT) is a relatively novel technology to achieve nanostructured surface layer. UCFT technology uses the ultrasonic vibration energy to induce severe plastic deformation on metal surface, which not only can improve surface hardness significantly but also reduce surface roughness to 0.008-0.5 μm . Comparing with the most commonly studied grain refined method, surface mechanical attrition treatment (SMAT) [1-5], UCFT is easier to operate and is friendly to the environment. UCFT process highly promotes the general properties of engineering materials without any change in their chemical composition. This technique has been used in 316L stainless steel[6], tool steel SKD-61[7] and magnesium alloys[8] to improve the tribological and corrosion performance by forming a nano layer. By far, the majority of conducted studies on this process have been focused on preparation of nanocrystalline surface layers[3].

Microarc oxidation (MAO) is a surface modification technique. These types of coatings are distinguished from other coating techniques by their high productivity, economic justification, environmentally friendly, high hardness, appropriate corrosion resistance and excellent adhesion to metallic substrate[5]. Therefore, it is attracting increasing interests in producing ceramic coatings on light alloys in order to improve their corrosion resistance. MAO coatings have been successfully fabricated on the surface of Al [9-12], Mg [13-16], Ti [17-19] and their alloys.

M. Aliofkhazraei etc. has conducted a lot of contribution on the SMAT as a pretreatment prior to MAO process on magnesium and aluminum alloy [3-5, 20]. However, how the pretreatment of UCFT prior to MAO process influences the corrosion resistance of aluminum alloys is still unknown. In this study, in order to explore the role of UCFT on the corrosion resistance of MAO coatings, an attempt was made to use UCFT as a pretreatment prior to MAO treatment on AA2024. The Surface roughness value and the grain size of the AA2024 treated by UCFT were examined by atomic force microscope (AFM) and transmission electron microscope (TEM). The potentiodynamic polarization and electrochemical impedance spectroscopy tests were used to evaluate the corrosion behavior of modified AA2024. The effects of UCFT on the microstructure, phase composition, hardness and

electrochemical behavior were discussed.

2. Experimental

2.1 Materials

AA2024 slices with $60 \times 60 \times 3 \text{ mm}^3$ were prepared. The chemical composition of AA2024 is given in Table 1. Prior to the surface treatment, the samples were firstly ground by SiC sandpapers from 240# to 1200#, cleaned in ultrasonic cleaner in ethylalcohol for 10 min, and finally rinsed with deionized water and dried in the air.

Table 1 Chemical composition of AA2024 (wt.%)

Si (%)	Fe (%)	Mg (%)	Cr (%)	Al (%)
0.213	2.062	2.321	0.237	Bal

2.2 UCFT layer preparation

Ultrasonic cold forging technology was used as the pretreatment before MAO coatings were deposited on the surface of AA2024. UCFT uses ultrasonic vibratory energy as a source. A tungsten carbide ball is attached to the ultrasonic device and several tens of thousands of strikes per second from the ball strikes the surface of the sample, which may cause severe plastic deformation on the sample surface and induce a nanocrystal structure. The system has been demonstrated in the literatures [6, 7]. The parameters used in this study are shown in Table 2. The sample treated by UCFT was designated as UCFT sample.

Table 2 UCFT treatment parameters on AA2024

Frequency (kHz)	Amplitude (μm)	Load (N)	Spindle speed (r/min)	Freed rate (mm/rev)	Tip (tungsten carbide) diameter (mm)	Number of shots per mm^2
18.5	30	100	200	0.02	15	20000

2.3 MAO coating preparation

MAO coatings were processed using the HNMAO-20 equipment produced by Xi 'an HaoNing electronic technology co., LTD. In the MAO process, AA2024 sample was used as the anode while a stainless steel container with electrolyte inside was used as the cathode. An electrolyte prepared from 8 g/L Na_2SiO_3 , 2 g/L NaOH and 10 g/L $(\text{NaPO}_3)_6$ solution in distilled water was kept at room temperature during the entire coating procedure. The coatings were obtained under the applied voltage of 500 V for 30 min at working frequency of 50 Hz and at the duty ratio of 10%. The sample coated by MAO was designated as MAO sample, while the MAO coated sample on UCFT treated AA2024 was designated as UCFT-MAO sample.

2.4 Surface characterization

In order to investigate the microstructures of the UCFT treated layer, atomic force microscope (AFM, SPM-9500J3, Japan) and transmission electron microscope (TEM, JEM-2010, Japan) were used to observe the surface roughness and to estimate the grain sizes. To prepare TEM specimens, one 500 μm thick slice was cut from the UCFT modified sample. The top surface of the 500 μm thick slice was stuck to a glass and then hand grinding to the thickness of 50 μm . After that, 3 mm-diameter discs were punched from the thin foils, which were then thinned by the double spray instrument. Scanning electron microscope (SEM, XXS-550, Japan) was employed to observe surface and

cross-sectional morphologies of MAO coated samples. X-ray diffraction (XRD, Smart Lab, Japan) with Cu-K radiation was used to analyze the phase composition of the MAO coated samples at a scanning speed of 5°/min over a scan range of 20–80°, 2θ at glancing angles of 2°. The micro-hardness of the samples was measured under the load of 50 g for 10 s by HVS-1000. Five points were chosen on one sample and then average value and standard deviation had been calculated.

2.5 Corrosion resistance evaluation

Electrochemical corrosion instrument (IM6, Germany) was used to test potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The electrochemical measurements were carried out by the three electrode cells. A saturated calomel electrode (SCE) worked as the reference electrode and a platinum electrode worked as the counter electrode. The sample was used as working electrode with exposed area of 12.25 cm² to the NaCl solution. In the potentiodynamic polarization tests, the sweep rate was 5mV/s starting from -1.4 V to 0 V. The EIS tests were carried out in the range of 0.01 Hz to 100 kHz with AC voltage amplitude of 10 mV. The equivalent circuits were used to carry out the fitting of the experimental EIS data.

3. Results

3.1 UCFT treated surface characterization

3.1.1 Surface roughness

The AFM image showing the surface roughness of the UCFT-treated AA2024 is shown in Fig. 1. The surface roughness values of area A and area B are 4.834 nm and 9.425 nm, respectively. The average surface roughness value of the whole 5.00×5.00μm area is 7.477 nm, indicating that all surface area is quite smooth. The nano-level surface roughness value might be due to the plastic deformation due to UCFT strikes on the surface of AA2024.

Fig.1 Surface roughness of 2024Al treated by UCFT.

3.1.2 Grain size

In order to understand the influence of UCFT on the grain size of the modified layer, TEM was conducted on the surface of UCFT-treated AA2024. The TEM images with different magnification of the top surface were shown in Fig.2. It can be seen that from Fig. 2a that the grain size is not uniform and a number of subgrains were produced inside the big grains. The grain size of most of the grains is in several microns, but the smallest grain size can reach about 100 nm, which can be seen in Fig. 2b. The dislocations are also clearly found in Fig. 2b. These indicate that the grain has been refined because of the strikes of the vibration tip on the sample surface of AA2024.

Fig.2 TEM images of the top surface of UCFT-treated AA2024

3.2 SEM morphologies and phase composition of MAO coatings

Fig. 3 shows surface morphologies of the MAO and UCFT-MAO samples. It can be seen the typical micropores were formed during MAO process [21, 22]. The average pore size of the UCFT-MAO sample (Fig. 3(b)) is much smaller than that of MAO sample (Fig. 3(a)). This has similar trend to M. Aliofkhazraei's works[5]. The biggest pore size of the MAO sample without UCFT treatment can reach 10 μm, almost twice as that of UCFT-MAO sample. These results may due to the fact that UCFT decreased the surface roughness value and refined the grains. The smooth surface and refined grains may provide much more and smaller discharge channels for the MAO process. Fig.4 shows the cross-sectional morphology of the MAO coated sample. It can be seen that the thickness of the coating is about 5 μm.

Fig.3 Surface morphologies of MAO coatings on AA2024: (a)MAO and (b)UCFT-MAO

Fig.4 Cross-sectional SEM image of MAO coating on AA2024

Fig.5 shows the X-ray diffraction (XRD) patterns of MAO coated samples with and without UCFT treatment. As can be seen in this figure, the phases of the two coated samples remain the same. They are Al, Al_2O_3 , $\text{Al}_6\text{Si}_2\text{O}_{13}$, $\text{Al}(\text{PO}_3)_3$. The element of Al derives from the 2024 Al substrate. The generation of Al_2O_3 may contribute to the high temperature in the MAO process. The element of Si and P comes from the electrolyte, which shows the elements have been involved in the coating by oxidizing reaction[23]. The almost same phase compositions illustrate that the ultrasonic cold forging technology has almost no influence on the phase compositions. This is consistent with the SMAT as a pretreatment prior to MAO process in M. Aliofkhazraei's work[20].

Fig.5 XRD pattern of MAO coating and UCFT-MAO coating formed on AA2024

3.3 Hardness analysis

Fig.6 shows the micro-hardness of the samples surface under the load of 50 g for 10 s. It can be seen that the hardness of UCFT sample (105 HV) is a little higher than that of the untreated sample. While the hardness of the coated samples is much higher than that of the untreated samples. Between the two coated samples, the hardness of the UCFT-MAO sample is 136 HV, which is a little higher than that of MAO sample (129 HV). The higher hardness of the UCFT-MAO sample is due to the compact surface of the coating. These results manifest that UCFT does not improve the hardness much, while MAO technology contribute a lot to the improved hardness comparing uncoated samples.

Fig.6 Micro-hardness of the samples under the load of 50g for 10s

3.4 Electrochemical study

In order to evaluate the protection of the samples against corrosion, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were conducted on the samples of Untreated, UCFT, MAO coating and UCFT-MAO coating.

3.4.1 Potentiodynamic polarization

The potentiodynamic polarization tests carried out in NaCl solution are illustrated in Fig.7. The corrosion current density (I_{corr}) of the samples have been evaluated by Tafel extrapolation as summarized in Table 3. The corrosion current density is generally used as an important parameter to evaluate the kinetic of corrosion reactions[24]. As shown in the figure, all coated samples indicated improved corrosion resistance compared to the untreated sample. Similar trend has been confirmed in M. Aliofkhazraei's studies[3, 4]. This is due to the fact that they have both more noble potential (i.e., lower tendency to corrosion) and lower corrosion current density[25]. It is also clear that the I_{corr}

value of UCFT sample is $1.38 \mu\text{A}/\text{cm}^2$, which is lower than that of the untreated sample. This result means that the UCFT can decrease the corrosion reaction by reducing the surface roughness value and refining the grains. Comparing the two coated samples, the I_{corr} value of UCFT-MAO sample ($0.412 \mu\text{A}/\text{cm}^2$) is much lower than that of the MAO sample ($1.26 \mu\text{A}/\text{cm}^2$). This may contribute to the more compact coating induced by the smooth surface and refined grains produced by the ultrasonic cold forging technology prior to MAO treatment. The lowest I_{corr} value of UCFT-MAO sample means that the activity of the ion decreases and the corrosion resistance is improved.

Fig.7 Potentiodynamic polarization curves of the samples in 3.5% NaCl solution

Table 3 Corrosion current density of the samples in 3.5% NaCl solution

Sample	Untreated	UCFT	MAO	UCFT-MAO
$I_{\text{corr}}(\mu\text{A}/\text{cm}^2)$	2.57	1.38	1.26	0.412

3.4.2 Electrochemical impedance spectroscopy

The Bode plots of the samples in 3.5% NaCl solution are shown in Fig.8. It can be seen that the impedance at low frequency of the coated sample increased by at least one order compared with the

uncoated sample. While the impedance of the UCFT-MAO sample is the highest among all the samples, which means that the UCFT pretreatment and MAO process provide an effective barrier against NaCl solution.

In order to understand the resistance of different layer of the samples, the equivalent circuits were used to fit the impedance data [26, 27]. As shown in Fig.9, the R_s is the solution resistance, the R_{ct} and C_{dl} associate with the charge transfer process at the metal and electrolyte interface, the R_u and C_u represent the resistance of the layer treated by UCFT, the R_{mc}/C_{mc} is suggested the resistance of the MAO coating.

Fig.8 Bode diagram of the samples in 3.5% NaCl solution

Fig.9 Equivalent circuit for fitting impedance data of the samples: (a) Untreated, (b) UCFT, (c) MAO and (d) UCFT-MAO

Fitting parameters based on the equivalent circuits are listed in Table 4. The R_{ct} values of the samples are in the order of UCFT-MAO > MAO > UCFT > Untreated, indicating that UCFT and MAO technologies increased the charge transfer resistance of the samples. This may contribute to the fact that UCFT modified layer and MAO coating hindered the solution connecting with the samples. For two MAO coated samples, the R_{mc} value of MAO is less than that of UCFT-MAO samples. This may result from the fact that the smaller pores resisted the corrosion ions incorporating from the surface into the interior of MAO coating. Therefore, UCFT as a pretreatment prior to MAO process has an effective influence on the corrosion behavior of the AA2024.

Table 4 Fitting results of EIS plots of the samples in 3.5% NaCl solution

Sample	R_s ($k\Omega \cdot cm^2$)	C_{dl} (μF)	R_{ct} ($k\Omega \cdot cm^2$)	C_u (μF)	R_u ($k\Omega \cdot cm^2$)	C_{mc} (μF)	R_{mc} ($k\Omega \cdot cm^2$)
Untreated	0.72	423	7.09	--	--	--	--
UCFT	0.19	996	7.36	150	7.43	--	--
MAO	0.15	986	22.59	--	--	286	11.25
UCFT-MAO	0.39	322	32.22	324	24.12	185	22.59

3.5 Post-corrosion SEM morphologies

Fig.10 shows the SEM morphologies of the samples after corrosion in 3.5% NaCl solution. It can be seen that the corrosion damage level of the uncoated sample (Fig. 10a and Fig. 10b) is much higher than that of MAO coated samples. This might be because the solution contacted the metal directly whether the alloy is treated by UCFT or not for uncoated samples. Their surfaces are full of craters. However, the size of craters on UCFT samples is smaller than that of the untreated samples, indicating UCFT can improve the corrosion resistance of the sample through refining the grains of the AA2024, but not much. After MAO coatings were produced on AA2024, the samples were protected from corroding to a great extent. These can be seen from Fig. 10c and Fig. 10d. MAO and UCFT-MAO coating samples presented much better surface characteristics only with several craters and cracks. UCFT-MAO coating shows the lowest corrosion damage level, resulting from the combined contribution of UCFT pretreatment and MAO process.

Fig.10 Post-corrosion SEM images of the samples: (a) Untreated, (b) UCFT, (c) MAO and (d)

UCFT-MAO

4. Corrosion process model

Ultrasonic cold forging technology has been used on the surface of AA2024 in this study. The grain on the surface of AA2024 was refined by UCFT from several microns of the substrate to 100 nanometers although the level of refinement is not as obvious as the effects of UCFT on Magnesium alloy[8]. It is predicted that the grain size would be smallest on the top surface due to the most severe deformation resulting from the striking numbers during UCFT process. The surface roughness was improved and the mean value reached 7.477 nm. The hardness of the UCFT layer has been improved by over 30%. During the process of the UCFT, the aluminum alloy surface was exposed to the air and alumina was formed on the surface. Therefore, when the UCFT sample is immersed in the solution, the refined surface and the alumina would co-protect the sample from corroding.

In order to further improve the corrosion resistance, MAO coatings were successfully produced on the substrate of the aluminum alloys. It has been reported that MAO coatings possess a good corrosion resistance by many researchers [11, 28, 29]. The data of electrochemical tests has proved this point. MAO coating has been approved to have a more dominating role on the corrosion resistance 2024 Al alloy than UCFT layer.

UCFT is used as the pretreatment prior to MAO coating on AA2024. The refined grain on the surface of UCFT treated AA2024 provided more number of discharge channels for MAO coatings with small pore size. Therefore, the MAO coating becomes more compact and uniform. This resulted in the higher hardness of the UCFT-MAO sample than MAO sample. UCFT-MAO sample shows the lower corrosion current density and the higher electrochemical impedance due to the compact and uniform coating on the grain-refined layer treated by UCFT. The compact coating contributed to the better corrosion resistance largely. Furthermore, the underlying UCFT layer with refined grain below MAO coating is also beneficial to the corrosion resistance improvement of AA2024.

Fig. 11 shows a schematic diagram of the corrosion process of MAO coating on the AA2024 alloy pretreated by UCFT. Fig. 11a shows the initial stage of the UCFT-MAO coated sample, composing of MAO coating, UCFT layer and the AA2024 substrate. When the sample was immersed into the NaCl solution, the solution starts to enter the sample from the micropores on the top surface of the MAO coating, shown as Fig. 11b. With the ongoing reactions, the pores slowly enlarge. Therefore, the solution goes through the MAO coating and reaches the UCFT layer (Fig. 11c). The refined grain on the UCFT layer could slow down the corrosion of the sample to some extent. With the increase of the depth, the solution would penetrate the UCFT layer and reach the substrate (Fig. 11d). From this stage, the sample would start to deteriorate gradually. Generally the extent of corrosion damage of UCFT-MAO coated Al alloy in the NaCl solution depends on the size and the depth of the micropores on the MAO coating. MAO coating

would contribute the most to the corrosion protection. However, UCFT layer with refined grain also played a significant effect on the corrosion protection of Al alloy.

Fig. 11 A schematic diagram of the corrosion process of the MAO coating growing on the UCFT pretreated AA 2024

5. Conclusions

- (1) The surface roughness value was decreased to nano-level after UCFT treatment. The grain size of the UCFT-modified layer on 2024 Al was refined.
- (2) The pore size of MAO coating pretreated by UCFT is smaller and denser than that of the MAO coated sample without UCFT treatment. The micro-hardness of the UCFT sample has been enhanced compared with untreated sample. UCFT-MAO sample has the highest hardness among the samples.
- (3) The influence of UCFT on the corrosion behavior of MAO coated AA2024 is very significant.

The UCFT-MAO sample has the lowest corrosion current density and the highest impedance among all the samples. This may due to the combined contribution of UCFT pretreatment and MAO process.

(4) The corrosion process of the UCFT-MAO sample was discussed and its corrosion model was proposed.

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Table captions:

Table 1 Chemical composition of AA2024 (wt.%)

Table 2 UCFT treatment parameters on AA2024

Table 3 Corrosion current density of the samples in 3.5% NaCl solution

Table 4 Fitting results of EIS plots of the samples in 3.5% NaCl solution

Figure captions:

Fig.1 Surface roughness of 2024Al treated by UCFT.

Fig.2 TEM images of the top surface of UCFT-treated AA2024

Fig.3 Surface morphologies of MAO coatings on AA2024: (a)MAO and (b)UCFT-MAO

Fig.4 Cross-sectional SEM image of MAO coating on AA2024

Fig.5 XRD pattern of MAO coating and UCFT-MAO coating formed on AA2024

Fig.6 Micro-hardness of the samples under the load of 50g for 10s

Fig.7 Potentiodynamic polarization curves of the samples in 3.5% NaCl solution

Fig.8 Bode diagram of the samples in 3.5% NaCl solution

Fig.9 Equivalent circuit for fitting impedance data of the samples: (a) Untreated, (b) UCFT, (c) MAO and (d) UCFT-MAO

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