

Article

The Preparation and Properties of the Brown Film by Micro-arc Oxidized on In-Situ TiB₂/7050Al Matrix Composites

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Received: 11 June 2020; Accepted: 26 June 2020; Published: 29 June 2020



Abstract: The brown or grayish-white color films were prepared by the micro-arc oxidation (MAO) method on in-situ TiB₂/7050Al composites using these alkaline electrolytes with/without KMnO₄ as an additive. The microstructure, elemental composition, chemical state and corrosion behavior have been investigated by the microstructure characterizations and electrochemistry measurements on the MAO films comparatively. The results indicated that a brown film was obtained via adding KMnO₄ into the alkaline electrolyte. The coloration mechanism of the brown color can be ascribed to the existence of MnO inside the film. Furthermore, the initiation of corrosion to the Al composite was intensively hindered by the brown MAO film. Compared with the Al substrate and grayish-white film, the brown MAO film exhibited the elevated corrosion potential and reduced corrosion current. Therefore, the brown film has presented an optimized corrosion resistance for the composite.

Keywords: Al matrix composites; micro-arc oxidation; surface modification; corrosion resistance

1. Introduction

Recently, Al matrix composites (AMCs) are extensively developed and exhibited some superior properties, including high specific strength [1–6], good ductility [7,8], superior fatigue limit [9] and elevated modulus [2,10,11]. As a result, the composites have been widely applied in the automotives, ships, spaceflights and other fields [12–14] as a category of novel structural materials. However, the corrosion resistance and color unity of AMCs often fails to satisfy the design and application demands, which limits their further practices. The surface treatment is always applied to enhance the corrosion resistance for long-term service, wear resistance, decoration and hardness for Al-based materials. Herein, the surface appearance treatment of AMCs has drawn intensive interests, because the color has played a crucial part both in the decorative properties and functional applications (i.e., medical identification/optical absorption/spacecraft application [15]).

Generally, an increasing number of colorful films on several metallic materials by the micro-arc oxidation (MAO) treatment have been created [16–18]. For Al alloys, Li et al. [19] prepared a black MAO film on the LY12 Al alloy derived from the silicate electrolyte embracing NH₄VO₃. Hwang and

Shin [20] obtained a sort of black film by adding Na_2WO_4 into the phosphate electrolyte. Wang and Nie [21] invented a new blue plasma electrolytic oxidation film on wrought 2024 Al alloy. Regarding Mg alloys, Yang et al. [22] produced Sn-doped MAO films showing the yellow color in the sodium stannate (Na_2SnO_3) electrolyte system. Wang et al. [23] fabricated MAO films with the different colors (i.e., black, white and gray) on AZ91D Mg alloy. Adding the titania sol into the polyphosphate electrolyte, a blue MAO layer with good corrosion resistance was obtained in the Mg-Li alloy [24]. For Ti alloys, Han et al. [25] reported a black MAO film on the TC4 alloy or pure Ti in the alkaline silicate solution. Jiang et al. [26] obtained a novel yellow ceramic film with good thermal stability via the MAO treatment on Ti alloys.

However, there are few reports on the coloration of the MAO films of AMCs. Indeed, the study on a variety of colored ceramic films is of critical meaning for the actual application of the AMCs. In the paper, the brown films were produced on in-situ TiB_2 /7050Al composites by the MAO treatment adopting the alkaline electrolyte aided by KMnO_4 addition. A systematic investigation has been carried out to study the effects of electrolytes on the formation mechanisms of the microstructure/phase composition in the MAO films and their corrosion resistances thereby. Lastly, the compositions of oxide films were detected by grazing incidence X-ray diffractometer (GIXRD) and X-ray photoelectron spectroscopy (XPS) to reveal their coloration mechanisms.

2. Materials and Methods

2.1. Fabrication of Composites

Firstly, the as-cast 5 wt % TiB_2 /7050Al composites ingot were prepared using the mixing salt reaction [27]. Subsequently, the as-cast ingot was homogenized. Lately, the as-homogenized ingot was hot extruded at an extrusion ratio of 7.8:1 of 420 °C to produce the as-extruded bar. Then, the as-extruded bar was solution treated (477 °C/70 min) and quenched into the cold water. At last, the artificial aging was implemented at 120 °C for 20 h. Samples (dimensions: 30 mm × 30 mm × 5 mm) were cut from the above composite bar, and the plane normal to the extrusion direction (ED) was used for investigation. We named it as the normal direction-transverse direction (ND-TD) plane. The chemical composition of the composite (identified by the inductively coupled plasma method) is 2.24 wt % Mg, 6.30 wt % Zn, 2.20 wt % Cu, 0.13 wt % Zr, 0.023 wt % Fe, 0.044 wt % Si, 3.35 wt % Ti and 1.46 wt % B and Al balance. Prior to the MAO treatment, the sample was abraded using 320#, 800#, 1200# and 2500# SiC sandpapers successively. Then, the abraded sample was rinsed using acetone and deionized water. Afterwards, the prepared sample was blown dry to use.

2.2. The MAO Treatment on Composites

To perform the MAO experiment, an AC power unit was adopted with a stainless steel electrolyzer cooled by the circulating water. The stainless steel and the composite samples acted as the cathode and anode, respectively. The alkaline electrolyte was prepared using the deionized water, which included 9 g/L Na_2SiO_3 , 4 g/L NaOH and 2 g/L EDTA-2Na, and 5 g/L KMnO_4 as an additive. The pH of the alkaline electrolyte was 13, and the addition of KMnO_4 merely changed the pH value. In the MAO treatment, the controlled electrolyte temperature was at ≤ 30 °C. There were 50% (+) and 50% (−) in the duty cycle at the working frequency of 1000 Hz. For the constant current mode, the current density was adopted at 7.5 A/dm². Each MAO treatment was conducted for 15 min. After the treatment, the specimen was rinsed in the deionized water and dried subsequently.

2.3. Film Characterization

The MIRA 3 scanning electron microscope (SEM, MIRA 3, TESCAN, Czech Republic) equipped with the electron dispersive spectroscopy (EDS) was used to characterize the film morphologies. Before the SEM observation, a gold layer was evaporated onto the MAO treated sample due to the poor conductivity of the film. Simultaneously, the sample microstructure can be characterized using the

electron backscattered diffraction (EBSD, MIRA 3, TESCAN, Czech Republic) technique. The EBSD results were analyzed using HKL Channel 5 software. In an EBSD map, the misorientation between 2° and 15° was considered as low angle grain boundaries (LAGBs, green lines), and that larger than 15° was as high angle grain boundaries (HAGBs, black lines).

The phase compositions of MAO films were determined using the GIXRD (D8 ADVANCE Da Vinci, Bruker, Germany) using a Cu K α source, and the scans proceeded from 20° to 80° (in 2θ). Using XPS (ESCALAB 250XI, Thermo Fisher Scientific, Waltham, MA, USA) with a monochromatic Al K α source (1486.6 eV), the chemical compositions of the films were obtained. In related to the C 1s peak (284.8 eV) from hydrocarbons adsorbed on the sample surface, binding energies were adjusted in the XPS test. The ED400 gauge with eddy current was adopted to measure film thickness. This instrument was widely applied for testing the MAO film thickness [28–30]. In each sample, at least 10 measurements were taken at different places to achieve an average film thickness.

For pore size and porosity in the MAO film, they were analyzed using the ImageJ software (Version 1.4.3.67). At first, the photoshop software was applied to convert an SEM micrograph of the MAO film (Figure 1a) into a black and white image. In detail, the areas containing pores are converted to black, and the areas without pores are converted to white (Figure 1b). Then, the ImageJ was employed to calculate the proportion and size of the black region, which embody the porosity and pore diameter of the film, accordingly.

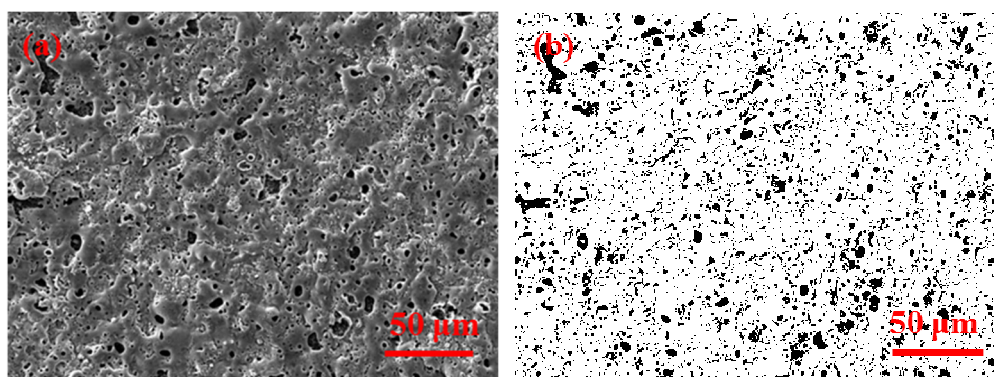


Figure 1. Pore features of the micro-arc oxidation film measurement: (a) unprocessed and (b) converted scanning electron microscope images.

2.4. Electrochemistry Experiments

Utilizing a CHI660C electrochemical workstation (Huachen, Shanghai, China), the electrochemistry tests of both the bare composite and MAO-coated composite were performed. In a standard three electrode system, a 3.5 wt % NaCl solution was served in the electrochemical test at ambient temperature ($25 \pm 2^\circ\text{C}$). The system consists of a saturated calomel electrode (the reference electrode), a Pt electrode (the counter electrode) and the sample (the working electrode) with a 1 cm^2 exposed region to the NaCl solution. The test was performed by a single factor variable method. The samples were soaked in a NaCl solution for 3600 s to attain stable open circuit potential (OCP) before testing. In electrochemical impedance spectroscopy (EIS, CHI660C, Huachen, Shanghai, China) test, the scanned frequency was selected from 10^5 to 0.1 Hz with an AC amplitude (10 mV) perturbation on the OCP. The ZsimpWin software (Version 1.0) was used to simulate and model of the experimental result. In the polarization curve measurement, a scan speed of 0.5 mV/s and a potential range from -1.0 to -0.3 V were adopted referring to the OCP value. In addition, the corrosion current (i_{corr}) was obtained by Tafel curve extrapolation, the polarization resistance (R_p) of the sample can be expressed by Stern Gary's equation (Equation (1)) [31,32]:

$$R_p = \beta_a \times \beta_c / [2.303 i_{\text{corr}} (\beta_a + \beta_c)] \quad (1)$$

where β_a and β_c indicate the anodic and cathodic polarization slopes of the sample, respectively.

3. Results and Discussions

3.1. Morphological Characterizations

Figure 2 exhibited the typical morphology for the in-situ TiB_2 /7050Al composite normal to the extrusion direction (ED). It is known that the grains are equiaxed in the ND-TD plane. Many TiB_2 particles are clustering at the grain boundaries to form the particle clusters (Figure 2a,b). At the same time, the rest TiB_2 particles are randomly dispersing into the grains (Supported by Figure 2c).

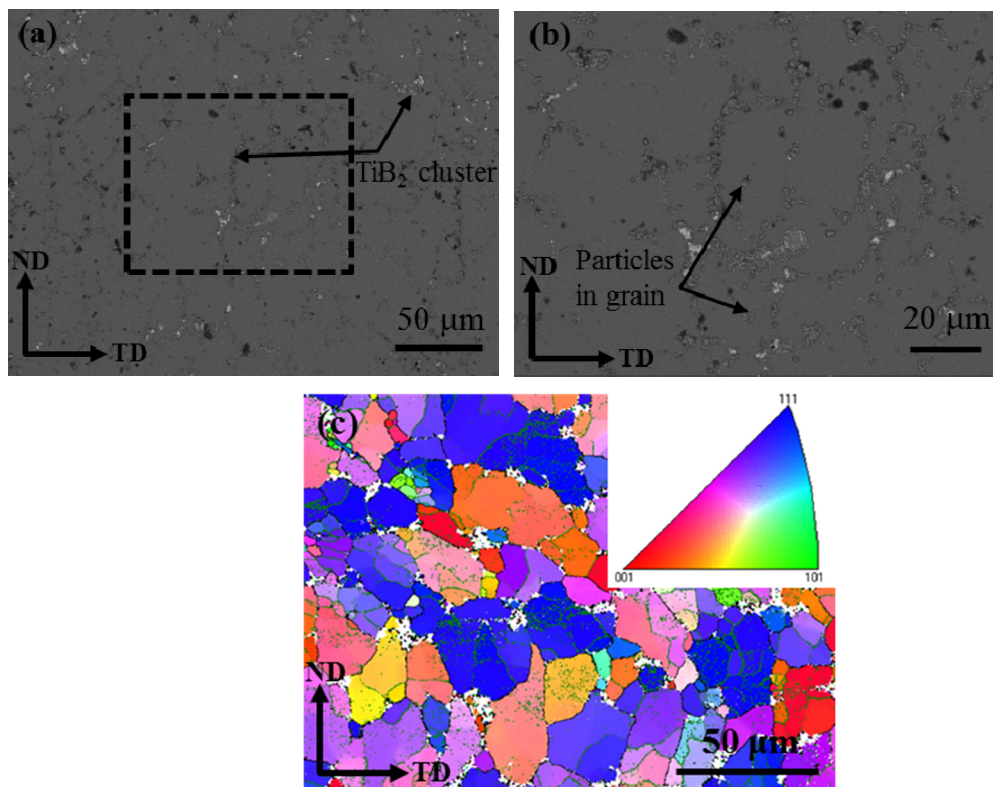


Figure 2. The TiB_2 /7050Al composite microstructure: (a) a back scattered electron micrograph, (b) an enlargement from the area of (a) and (c) the electron backscattered diffraction map.

3.2. Voltage–Time Response

The voltage–time ($U-t$) curve is often used to discuss the growth behavior of the film during the MAO process. Huang [33] and Sun [34] applied the $U-t$ curves to discuss the MAO film created on Al and Ti alloys focusing on their growth mechanisms, respectively. Figure 3 shows the typical $U-t$ responses for the electrolytes with/without of KMnO_4 addition during the MAO of the TiB_2 /7050Al composite. Our previous study [29] indicated that the $U-t$ curve was obviously able to be divided into a four-stage character to create the MAO film for the TiB_2 /Al composite. In stage I, the voltage rose rapidly with time, which corresponded with the insulating film formation before the micro-arc discharge. Meanwhile, a lot of bubbles have emerged on the surface of the sample. In stage II, the voltage is almost unchanged, and a plateau appears. Meanwhile, the sample is surrounded by tiny bubbles and a faint light. In stage III, the voltage increased rapidly again and the buzzing sound was heard obviously. Correspondingly, lots of micro arcs appear on the surface of the sample. In stage IV, the voltage was basically stable at a higher value. Simultaneously, the color of the micro arc also changed from white to yellow, and the size of micro arcs had become bigger. Herein, the TiB_2 particles exhibited the hindering effect to the film growth at the second stage with the lower voltage, and the Raman test showed that TiB_2 was oxidized to TiO_2 gradually at this stage. Observably, the $U-t$

curve for the $\text{TiB}_2/7050\text{Al}$ composite shows the four-stage MAO process in the electrolytes without KMnO_4 as well (Figure 3a), which indicated a similar film formation mechanism hereby. Although, the second stage is shorter than the former report [29], it might be due to a different electrolyte used in this MAO experiment.

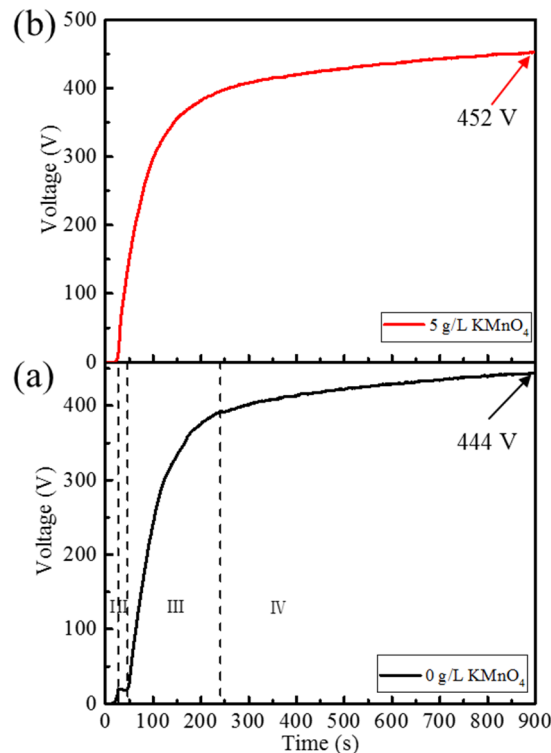


Figure 3. Dependences of voltage on oxidation time for the electrolytes (a) with and (b) without KMnO_4 addition during the micro-arc oxidation process.

However, when KMnO_4 was added into the electrolyte, the second stage was rarely seen in the $U-t$ curve (Figure 3b). This indicates that the addition of KMnO_4 accelerated the transformation process of TiB_2 to diminish its hindering effect. This point was evidenced by the fact that the participation of KMnO_4 into the solution causes the increasing overall voltage. Such an enhancement can promote film growth, as confirmed by the measurement of the film thickness (Table 1).

Table 1. The average thickness, porosity and average pore size of different samples based on scanning electron microscope images.

Film Color	Average Thickness (μm)	Average Pore Size (μm)	Porosity
Grayish-white film	9.51 ± 0.34	1.11 ± 0.36	4.23%
Brown film	10.95 ± 0.56	3.23 ± 1.74	1.79%

3.3. Microstructure Analysis on the Films

Figure 4a exhibited a macro photo that revealed that the MAO film had presented the grayish-white color in the alkaline electrolyte. Microscopically, this MAO film exhibits the typical surface morphology disclosing the crater-like features, or full of pores on the film surface [35–38] (Figure 4c). During the MAO process, the oxides were melted and ejected from the discharging channels. Surrounded by the cold liquid, these oxides were quickly solidified. As a result, the pores were generated and shown on the film surface [21,39–41]. The average pore diameter was $1.11 \mu\text{m}$, and the porosity for the film was 4.23% (Table 1).

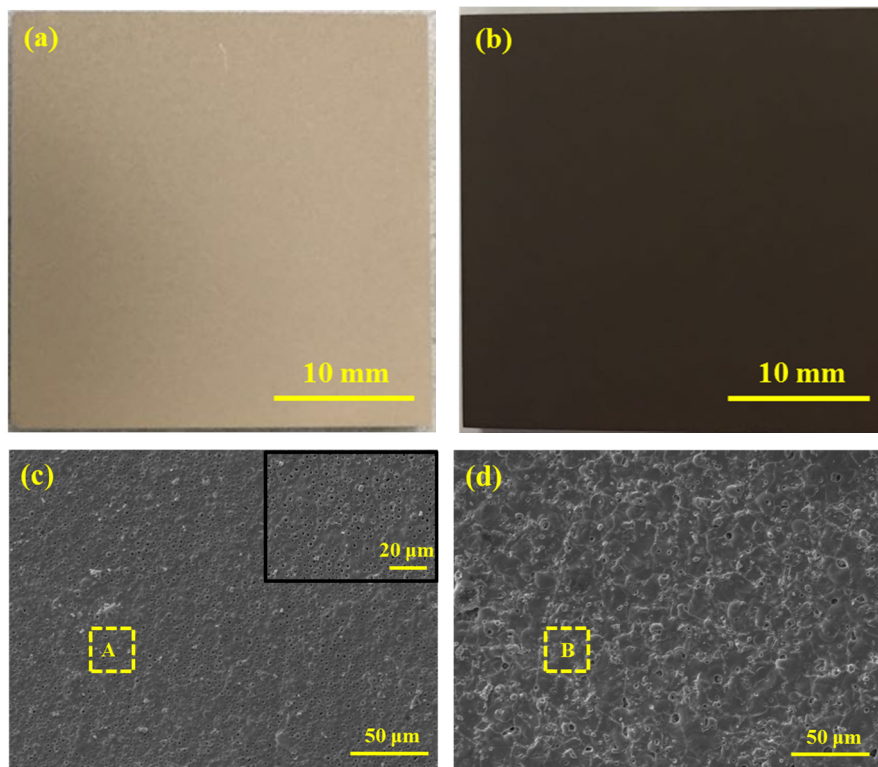


Figure 4. Micro-arc oxidation films from alkaline electrolytes. (a,c) Macro pictures and with the addition of KMnO_4 (b,d) scanning electron microscope images.

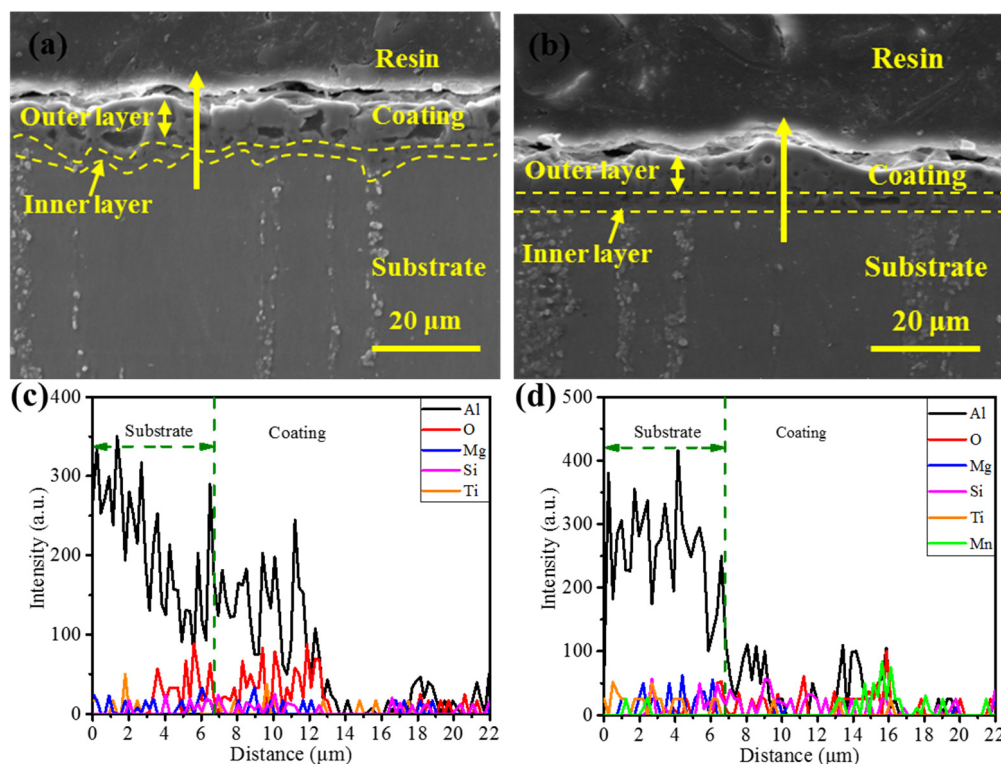
When KMnO_4 was mixed in the electrolyte, the MAO film showed a brown color (Figure 4b). Meanwhile, when MnO_4^- was added to the solution, the solution appearance transformed from purplish red to dark green. This is mainly because MnO_4^- is easily reduced to MnO_4^{2-} in an alkaline solution. In the whole MAO process, MnO_4^{2-} mainly participates in the reaction. The negatively charged colloids created on the sample surface are formed as MnO_4^- is added into the electrolyte. During the MAO process, these colloids are forced into the discharge channel under the influence of applied electric field [42]. Nevertheless, the brown film (Figure 4d) was similar to the surface morphologies of the grayish-white film. In detail, the pores were larger, although the overall porosity was smaller in the brown MAO film (Table 1). Furthermore, the growth rate of the film should be promoted owing to the existence of MnO_4^{2-} ions [42]. Therefore, the brown MAO film was 15% thicker than the grayish-white film.

The compositions for grayish-white and brown films were derived from the EDS analyses on the typical areas A (Figure 4c) and B (Figure 4d), respectively. The grayish-white film contained the typical elements (i.e., Al, Si, O, Mg and Ti). Notably, when KMnO_4 was added into the alkaline electrolyte, the Mn element was present in the brown film, and the content of Si increased to a higher extent as well (Table 2). It demonstrated that MnO_4^{2-} from the electrolyte engaged in the film formation during the MAO treatment, which should cause the film change from the grayish-white to the brown color. Simultaneously, due to the addition of MnO_4^- , more SiO_3^{2-} ions participated in the MAO reaction as well. In the above two films, Al was derived from the matrix, and Mn and Si were both from the electrolyte. Besides, Cu and Zn elements were not detected in either MAO films. This is mainly because only valve metals (i.e., Al, Mg, Ti and Zr) can be directly incorporated to the MAO film on the surface, while the non-valve metals (Cu and Zn) are anodically dissolved into the electrolyte.

Table 2. Electron dispersive spectroscopy results of micro-arc oxidation films (atomic percentage).

Film Color	Region	Al	O	Si	Mg	Ti	Mn
Grayish-white	A	35.9	57.6	3.9	0.7	1.9	0.0
Brown	B	29.0	47.9	12.1	0.8	0.5	9.7

The cross-sectional (CS) morphologies of MAO films and the EDS line scans of grayish-white and brown films are presented in Figure 5. Clearly, there were no obvious boundaries between the films and matrices from Figure 5a,b. Compared to the grayish-white film, the brown film had the denser CS morphology with less micro-pores. In addition, Si was distributed throughout the whole grayish-white (Figure 5c) and brown films (Figure 5d). For the brown film, Mn was primarily scattered in the outer layer (Figure 5d).

**Figure 5.** Cross-sectional morphologies of micro-arc oxidation films and EDS line scans: (a,c) alkaline electrolyte without KMnO_4 and (b,d) adding KMnO_4 .

3.4. GIXRD Analysis on the Films

The GIXRD spectra for both grayish-white and brown MAO films were exhibited in Figure 6. All Al peaks originated from the substrate were clearly identified in both films. The $\gamma\text{-Al}_2\text{O}_3$ crystal phase was detected for both films, indicating the $\gamma\text{-Al}_2\text{O}_3$ was the main crystalline phase for the MAO film.

Representative crystalline phase $\gamma\text{-Al}_2\text{O}_3$ has always existed in the MAO films of Al-based materials [43–46]. Notably, the amorphous peak ($20^\circ\text{--}30^\circ$) in the film was obvious, indicating that there was a certain amount of amorphous phase in the film. However, when KMnO_4 was added into the alkaline electrolyte, MnO was detected for the brown film at the positions of 35.0° , 40.6° , 58.7° , 70.2° and 73.8° . It matches the MnO standard spectrum (JCPDS No. 07-0230) [47]. Meanwhile, the relative intensities of $\gamma\text{-Al}_2\text{O}_3$ reduced, which was related to the reduction of Al content (Table 2). Thus, it demonstrated that KMnO_4 benefited by generating MnO in the MAO film to show the brown color.

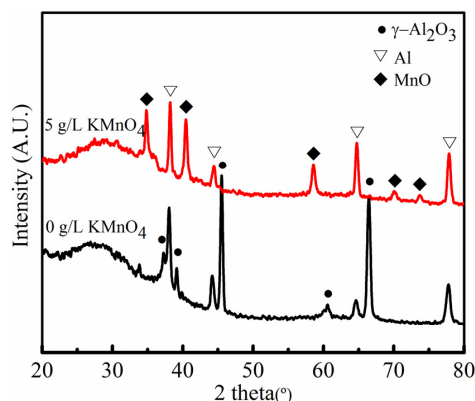


Figure 6. Grazing incidence X-ray diffractometer patterns of both grayish-white and brown micro-arc oxidation films with/without KMnO_4 .

3.5. XPS Analysis on the Films

For the purposes of a deeper understanding for the composition information of the brown MAO films, the XPS characterization was carried out to analyze the chemical compositions of MAO films formed in the electrolytes with/without KMnO_4 addition. Furthermore, the datum analyses of XPS peaks were performed using XPSPEAK41 software.

The XPS spectra (Figure 7a) and the peaks for Mn 2p (Figure 7b) and Si 2p (Figure 7c,d) of the MAO films with/without KMnO_4 addition are exhibited. Normally, the C element is from the outward pollution. Notably, a large amount of the Mn element in the MAO film with KMnO_4 addition was detected (Table 3). The Mn 2p peaks at 642.48 and 654.38 eV can be indexed into the Mn 2p_{1/2} and Mn 2p_{3/2}, with a spin energy separation of 11.7 ± 0.2 eV. This should indicate the existence of MnO [48], leading to the conclusion that most MnO_4^{2-} was reduced to MnO during the MAO process.

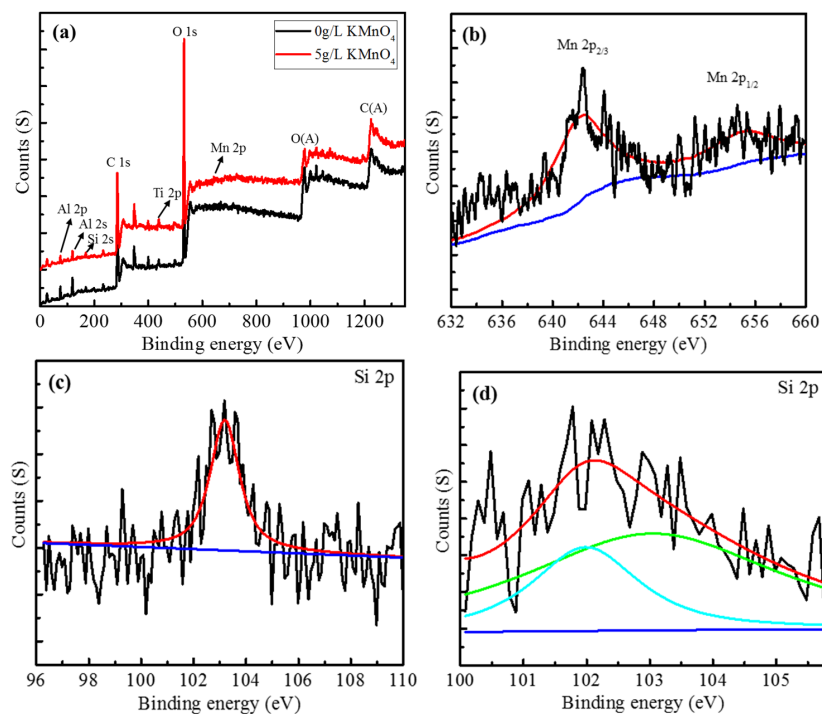


Figure 7. (a) X-ray photoelectron spectroscopy patterns of micro-arc oxidation films (added with/without KMnO_4), (b) Mn 2p spectrum (film added with KMnO_4) and (c,d) Si 2p spectrum (film added without/with KMnO_4).

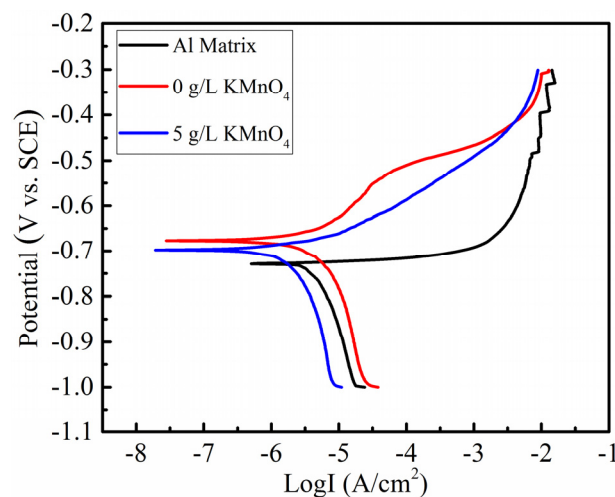
Table 3. Corrosion parameters obtained from the polarization curves analysis.

Films	E_{corr} (V)	i_{corr} (A·cm ⁻²)	R_p (kΩ·cm ²)	Corrosion Rate (mm/y)
Al composite	−0.729	1.119×10^{-4}	0.476	2.581
0 g/L KMnO ₄	−0.677	6.162×10^{-6}	6.937	0.142
5 g/L KMnO ₄	−0.698	2.452×10^{-6}	10.93	0.057

The XPS spectra of Si 2p in the layers are shown in Figure 7c,d. For Si 2p in the MAO film without KMnO₄, only one composition (103.2 eV for SiO₂) was from the spectrum. Regarding Si 2p in the MAO film with KMnO₄ addition, two components (i.e., 101.88 eV for Si/103.2 eV for SiO₂ [22]) are derived from the spectrum, suggesting that the inclusion of KMnO₄ in the solution should have a certain impact on the conformation of Si element in the MAO film as well.

3.6. Analysis on Potentiodynamic Polarization

In the 3.5 wt % NaCl solution, the potentiodynamic polarization curves of the composite, the MAO films without and with KMnO₄ were obtained (Figure 8). Thereafter, Table 3 exhibits the corresponding results analyzing the data on Figure 8. Through the MAO process, the film shows a more positive the corrosion potential (E_{corr}). Notably, the more positive E_{corr} has signified a reduced occurring trend for corrosion [49]. Therefore, the MAO films prevent the corrosion medium from contacting the substrate, making the substrate less susceptible to corrosion. In addition, the corrosion current densities (i_{corr}) can be assessed via the Tafel extrapolation method. It is seen that the i_{corr} of the sample was greatly reduced (approximately two orders of magnitude) through the MAO treatment. Comparably, the brown MAO film had the lowest i_{corr} (2.452×10^{-6} A·cm⁻²) value among the three samples (Table 3). The smaller i_{corr} should correspond to the superior corrosion resistance for the sample [49–53]. The decrease in current density indicates that the MAO films formed on the surface limited the corrosive ions penetration and reduced the transmission of the ions in the metal-electrolyte interface. All these factors can increase the corrosion resistance of the substrate.

**Figure 8.** Potentiodynamic polarization curves of the Al composite, micro-arc oxidation films with/without KMnO₄.

Compared with the Al composite, the R_p value of the MAO treated sample (without KMnO₄ addition) increased significantly (Table 3). Moreover, the R_p of the MAO treated sample (with KMnO₄ addition) was further increased by about two orders of magnitude. At the same time, the corrosion rate of the sample was significantly reduced after the MAO treatment. Furthermore, when KMnO₄ was added into the electrolyte, the corrosion rate of the film was about two orders of magnitude lower than

the substrate (Table 3). As a consequence, the brown MAO film should have the optimum corrosion resistance in this work.

3.7. Electrochemical Impedance Spectroscopy Tests

Figure 9 shows the results for the electrochemical impedance spectroscopy (EIS) measurements conducted in the 3.5 wt % NaCl solution, which can be used to evaluate the corrosion property of the films. Clearly, the Al composite, the grayish-white film and the brown film had different corrosion mechanisms, accordingly (Figure 9). For the Al composite, only a smaller capacitive arc appeared in Figure 9a. Normally, it is considered that the appearance of the capacitive arc is closely related to the surface oxide film. After the MAO treatment, there were two larger capacitive reactance arcs in the impedances of the film (Figure 9a). This was complied with the film structure made up of a dense inner layer and a porous outer layer (CS morphologies in Figure 5). Typically, the impedance of the outer porous layer is related with the capacitive reactance arc at high frequency, and the inner compact layer has corresponded to the capacitive reactance arc at lower frequency [54,55]. These microstructural and electrochemical features can primarily affect the corrosion resistance of the film [31].

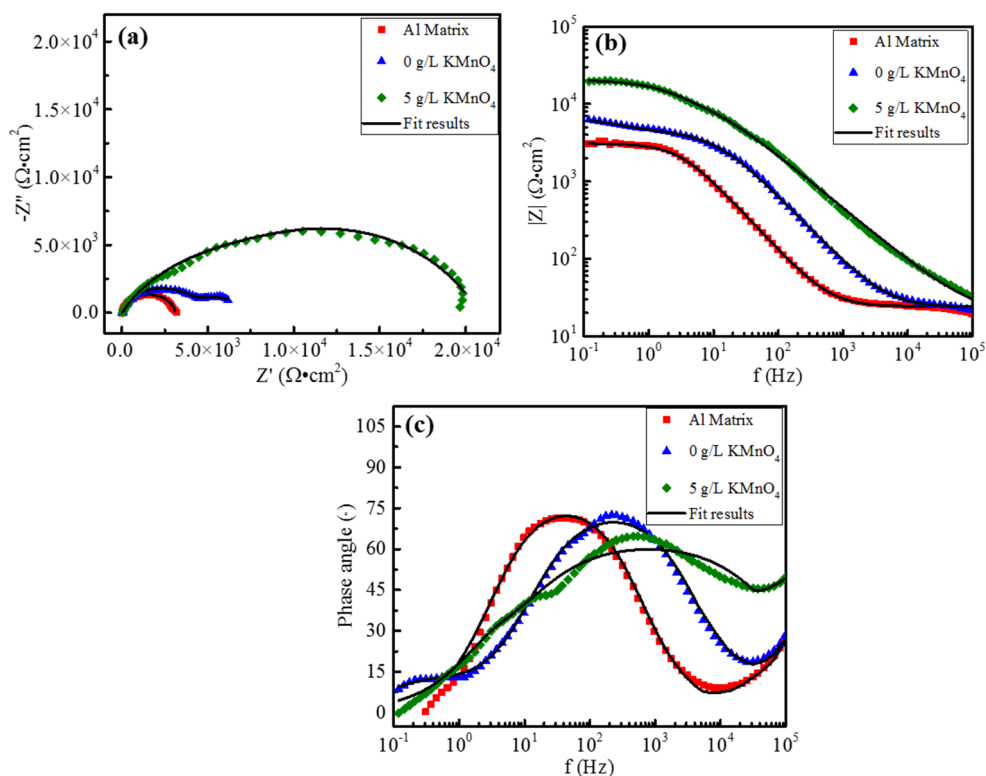


Figure 9. Electrochemical curves of the substrate, micro-arc oxidation films with/without KMnO₄: (a) Nyquist curves, (b) Bode curves and (c) phase curves.

The same regularity can be also obtained from the Bode plots (Figure 9b). Generally speaking, the value of $|Z|$ at a low frequency indicates the corrosion resistance of the material [56]. After the MAO process, the $|Z|$ value of the film at the same frequency increased obviously. In particular, the $|Z|$ value of the brown film at low frequency is an order of magnitude greater than the substrate. The brown film exhibited the highest impedance value, which agreed with the result of the polarization curves. In Figure 9c, the EIS of the substrate displayed a one-time constant, which means that the corrosion process of the substrate was controlled by an interface charge transfer [57]. However, EIS of the films displays two-time constants representing the double layer. The time constant at high frequency was associated with the outer layer, and the time constant at low frequency was related with the inner layer.

Figure 10 shows the equivalent circuit (EC), which is used to fit EIS data to quantify the corrosion behaviors of samples. In Figure 10, the uncompensated electrolyte resistance is labeled as R_s ; the corrosion resistance and CPE (constant phase-angle element) between the alloy and corrosive media are represented as R_c and CPE_c , respectively; the outer porous layer CPE and outer porous layer resistance are shown as CPE_o and R_o , respectively, and the inner porous layer CPE and inner porous layer resistance are nominated as CPE_i and R_i , respectively. Then, the following equation has defined the impedance of CPE [38,58,59]:

$$Z_{CPE} = 1/[T(j\omega)^n] \quad (2)$$

where T is the admittance constant; j is the imaginary unit; ω is the angular frequency ($\omega = 2\pi f$) and n is exponent number of the CPE ($0 < n < 1$), which shows the surface characteristics of heterogeneity/roughness [59,60]. This situation ($n = 0$) means a pure resistance of CPE, and the situation ($n = 1$) reflects it as a pure capacitor.

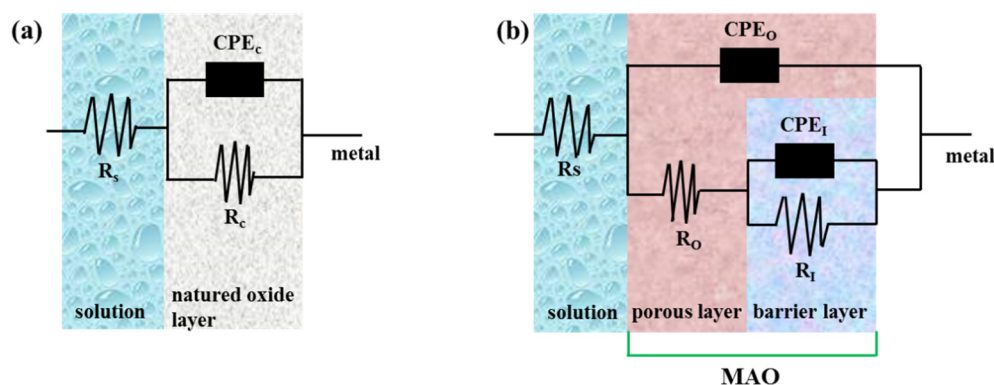


Figure 10. Equivalent circuit models of the simulated experimental impedance values: (a) Al matrix and (b) film with/without $KMnO_4$.

Table 4 shows the obtained values for electrical elements via fitting the EIS values into the EC models. Clearly, the film created by the MAO treatment can obviously enhance the corrosion resistance of the composite. For the MAO film, the inner layer shows the higher resistance over the outer layer confirming the barrier effect of the inner layer. Similar findings are also reported by Masoud et al. [38]. In detail, the inner layer resistance of the brown film was significantly higher over the grayish-white film (approximately an order of magnitude). Thus, the more difficult charge transfer can induce the improved corrosion resistance. Additionally, the brown film had significantly higher impedance than the others (Figure 9b), suggesting that the brown film had better corrosion resistance. This was consistent with the analysis on the Tafel curves.

Table 4. Electrochemical parameters obtained from the electrochemical impedance spectroscopy test.

Circuit Diagram	Al Composite	Parameter	Grayish-White Film	Brown Film
	(a)		(b)	(b)
R_s ($\Omega \cdot \text{cm}^2$)	24.11	R_s	23.62	17.53
CPE_c ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	2.21×10^{-5}	CPE_o	2.901×10^{-4}	1.094×10^{-5}
n_c	0.9114	n_o	0.7119	1
R_c ($\Omega \cdot \text{cm}^2$)	3.091×10^3	R_o	2.926×10^3	4.497×10^3
CPE_i ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	—	—	5.76×10^{-6}	4.785×10^{-6}
n_i	—	—	0.8661	0.7018
R_i ($\Omega \cdot \text{cm}^2$)	—	—	4.355×10^3	1.627×10^4

To further understanding the corrosion behavior, the surface morphologies (Figure 11) and EDS results (Table 5) of samples after the polarization test were characterized. It can be see that the pitting corrosion mainly occurred on the composite surface (Figure 11a–b). In contrast with the corrosion state of the 7050Al composite, the corrosion of MAO treated samples was rather slight. Only a small piece

of corrosion occurred on the grayish-white film (Figure 11c). Especially, the surface morphology of the brown MAO film shows hardly any change after the corrosion test (Figure 11d).

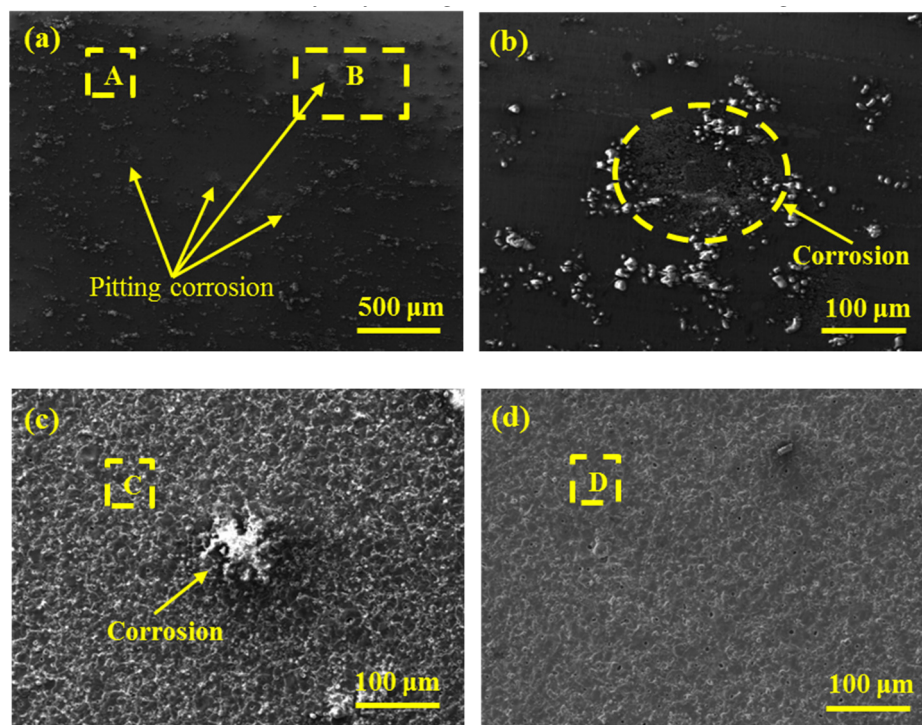


Figure 11. Corrosion morphologies for micro-arc oxidation films after polarization experiments. (a) Al composite, (b) an enlargement of the region B, (c) film without KMnO_4 and (d) film with KMnO_4 .

Table 5. Electron dispersive spectroscopy results values of samples by potentiodynamic experiments (atomic percentage).

Films	Region	Al	O	Si	Mg	Ti	Mn	Cl
Al matrix	A	56.8	37.9	0.1	1.0	3.4	0.1	0.7
0 g/L KMnO_4	C	35.3	57.7	3.7	1.0	2.1	0.0	0.2
5 g/L KMnO_4	D	31.4	42.0	11.7	1.0	0.6	13.3	0.0

In addition, the Al composite has the highest Cl^- content (0.67 at.%; Table 5). The Cl element was not detected on the brown film after the test, which means the MAO film could strongly enhance the corrosion resistance. Convincingly, the occurrence of corrosion for the Al composite was intensively inhibited by the brown MAO film. Therefore, the brown MAO film could exhibit superior corrosion resistance. Generally, the results observed from Figure 11 and Table 5 were consistent with the results from polarization curves and EIS analyses.

3.8. Coloration Mechanism

When MnO_4^- was added to the MAO electrolyte, MnO_4^- was easily reduced to MnO_4^{2-} in an alkaline solution (Equation (3)). In fact, MnO_4^{2-} (not MnO_4^-) was involved in the MAO process. In this process, the film color should gradually turn to brown, in which the final average power of the spark discharge to create a quantity of colored oxides on the film surface can be accounted for this phenomenon [61]. During the MAO process, MnO_4^{2-} should shift to the anode driven by the electric field force, and then is reduced to MnO , as shown in Equation (4).





As the MAO proceeds, more MnO should deposit at the outer layer of the discharges, and mix with other materials, such as alumina and silica. At last, the film has exhibited a brown color.

4. Conclusions

The oxide films on in-situ TiB₂/7050Al composites were produced using the MAO method in the alkaline solution. Notably, a brown MAO film produced by an alkaline solution with the KMnO₄ additive exhibited the superior surface quality. The GIXRD and XPS analyses indicated that the MnO phase should be the main factor to make the brown film. The results of electrochemical experiments of MAO films demonstrated that the brown film improved corrosion resistance. Generally, our work could provide the cognate value to the in-depth study of MAO brown film on the Al matrix composite to the practical application. In addition, the prepared film could be used in the fields requiring corrosion and decoration, i.e., mobile phone shells, notebook shells, sport goods and so on.

Author Contributions: Conceptualization, C.X., J.H., and M.W.; methodology, J.H., and M.W.; validation, J.T., S.W., L.C. and M.W.; investigation, C.X., J.H., and M.W.; resources, J.T. and S.W.; data curation, C.X., L.C. and D.C.; writing—original draft preparation, C.X.; writing—review and editing, J.H., and M.W.; supervision, J.H., and M.W.; project administration, J.H., and M.W.; funding acquisition, H.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (Grant No. 2018YFB1106302), the National Natural Science Foundation of China (No. 51821001), and the Anhui Province Engineering Research Center of Aluminum Matrix Composites (Grant No. 2017WAMC002).

Conflicts of Interest: The authors declare no conflict of interest.

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