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The Analysis and Fabrication of a Novel Tin-Nickel mixed Salt Electrolytic Coloring Processing and The Performance of Colored Films for Al-12.7Si-0.7Mg Alloy in Acidic and Alkali Corrosive Environments

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KEYWORDS : Al-12.7Si-0.7Mg alloy, Tin-nickel mixed salt, Electrolytic coloring, Performance, Corrosion resistance

We present for the first time the analysis and fabrication of a novel Tin-Nickel mixed salt electrolytic coloring processing and the performance of colored films for Al-12.7Si-0.7Mg alloy. Furthermore, this compound was further evaluated in acidic and alkali corrosion tests, showing that the corrosion resistance of colored sample was higher than those of untreated samples. Al-12.7Si-0.7Mg is a novel compound containing high silicon aluminum alloy extrusion profile which presents excellent mechanical properties as well as broad market prospects. Nevertheless, this kind of material is urgent in need of surface treatment technology. The orthogonal design and single factor tests were applied to optimize for electrolytic coloring technological conditions. By controlling operation conditions, the uniform electrolytic coloring films with different color were obtained. Analysis of microstructure showed that tin particles had been deposited in the colored film. The colored films, about 10 μm thick, were uniform, dense and firmly attached to the substrate. After the colored samples were maintained at 400 °C for 1h, or quenched from 300 °C to room temperature, the coloring films did not change, demonstrating excellent thermostability and thermal shock resistance. Acid and alkali corrosion tests and potentiodynamic polarization showed that corrosion resistance of colored sample was much better than those of untreated samples. After 240 h neutral salt spray test, protection ratings and appearance ratings of colored films were Grade 9.

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1. Introduction

High silicon content aluminium alloys have been used widely as structural materials for automobiles, ships and airplanes due to their excellent properties, such as low density, high strength, small linear expansion coefficient, good dimensional stability, castability and machinability.¹⁻⁴

Mg bearing wrought Al-Si alloys have been indigenously-developed in China, with typical composition of Al-12.7Si-0.7Mg.^{5,6}

Compared with the famous 6063 aluminium alloy, the novel alloy possesses better yield strength and similar extensibility. Nevertheless, surface treatment techniques are urgently needed for these alloys with excellent mechanical properties and promising market potential.

Industrial processes for aluminium alloy surface treatment are chemical oxidation, anodic oxidation, electrolytic coloring and electrophoretic painting, of which anodic oxidation is the most widespread. Two contrary processes are involved in anodic oxidation of Al alloys. Firstly Al dissolves from the alloy and subsequently

Al₂O₃ is generated on the alloy's surface, forming a micron-size film of Al₂O₃ which promotes hardness and corrosion resistance of the aluminum alloy.⁷⁻¹² After Al-12.7Si-0.7Mg was treated by anodic oxidation, silicon granules were exposed and could not be covered by Al₂O₃ film. Granular silicon will cause crystal boundary corrosion and structure defects on the surface. For high silicon content aluminum alloys, further surface treatment is necessary after anodic oxidation.

Electrolytic coloring is usually applied after anodic oxidation which has resulted in porous Al₂O₃ film. By carrying out alternating current (AC) electrolysis on anodized Al alloys in metallic salt solutions, metals, metal oxides or metallic compounds will be electrolytically deposited on the porous surface. Different electrodeposited coatings scatter lights and show various colors. Dominant constituents for electrolytes are tin salt,^{13,14} nickel salt.¹⁵⁻¹⁸ Sometimes, ferrous salt,¹⁹ copper salt²⁰ and silver salt²¹ are also used. Nickel salt electrolyte is stable, but sensitive to the interference of impurity ions. Tin salt electrolytes have certain advantages such as lack of sensitivity to the impurity of ions. Furthermore, hydrolysis and oxidation easily lead to the short of use cycle. Therefore, a highly effective, environmentally friendly, safe, nontoxic electrolytic coloring process suitable for large-area fabrication is needed.

To the best of our knowledge, tin-nickel mixed salt was used for the first time as an electrolyte as well as the investigation of a new electrolytic coloring process for Al-12.7Si-0.7Mg. The obtained colored films are homogenous, dense and firmly attached to the matrix. Furthermore, the colored film presents excellent corrosion resistance properties, thermal stability as well as heat shock resistance.

2. Experimental

2.1 Materials and pre-treatment

The base materials used was Al-12.7Si-0.7Mg alloy with dimensions of 32 mm×30 mm×3.8 mm, whose chemical composition was listed in Table 1. All chemical reagents employed in this work were of analytical purity. Deionized water was used as solvent.

Table 1 Chemical composition of Al-12.7Si-0.7Mg alloy

Element	Si	Mg	Fe	Cu	Ni	Ti	Al
Content / (wt%)	12.7	0.7	0.3	1.5	0.3	0.3	Bal.

Pretreatment, which can remove impurities, oil stain and natural oxide film on Al-Si alloy surface, has a remarkable influence on the colored film in morphology, thickness, hue and chromaticness. The pre-treatment of Al-12.7Si-0.7Mg samples includes mechanical polishing, deoil, caustic wash, acidic wash and bright dipping. Bright dipping is also called desmutting.²² Al-12.7Si-0.7Mg alloy exhibits hypereutectic microstructure, and contains uniformly distributed silicon particles with diameters circa 3 μm in the eutectic matrix. After having washed the compound with NaOH solution, aluminum oxides and aluminum metal were removed from the surface, leaving

un corroded Si particles exposed which form a dark grey loose cover. The silicon loose cover has to be eliminated by bright dipping process.

2.2 Anodic oxidation and electrolytic coloring

Anodic oxidation is the key step for the electrolytic coloring of Al-12.7Si-0.7Mg alloy as quality of the anodized surface is directly influenced on the effect of electrolytic coloring. Usually, cellular Al₂O₃ film with thickness of several to hundreds of microns is formed on Al alloy surface after anodic oxidation.⁸ When applied to electrolytic coloring, Sn metal granules are deposited in micro-caves of the cellular film. Processing parameters for anodic oxidation were 150-190 g·L⁻¹ of H₂SO₄, 13-20 °C, 18-30 min, 1.0 A·dm⁻² of current density and 30 r·min⁻¹ of stirring rate.

The composition of electrolyte has a remarkable effect on the properties of coloring films. The addition of nickel sulfate increased the stability of stannous sulfate in the electrolyte, meanwhile hydrolysis and oxidation reactions decreased significantly. Antioxidant was also used to prevent Sn²⁺ from hydrolyzing. The formula composition of electrolytic coloring solution were 5 g·L⁻¹ of SnSO₄, 10 g·L⁻¹ of H₂SO₄, 25 g·L⁻¹ of NiSO₄, 7 g·L⁻¹ of tartaric acid and 5 g·L⁻¹ of antioxidant.

Five principal factors of the experiment such as coloring voltage, coloring temperature, anodic oxidation temperature, anodic oxidation time and the concentration of H₂SO₄, were investigated by orthogonal tests of five factors and five levels.

Optimal electrolytic coloring condition was worked out by comprehensively assessing uniformity, shade and corrosion resistance of color films, according to GB/T12967.6-2008 and JIS H 8681-1:1999. On the basis of optimal electrolytic coloring condition, effects of coloring time, coloring voltage, coloring temperature and the concentration of SnSO₄ were investigated by single factor tests. Figure 1 shows schematic illustration of technological process of anodic oxidation and electrolytic coloring of Al-12.7Si-0.7Mg alloy.

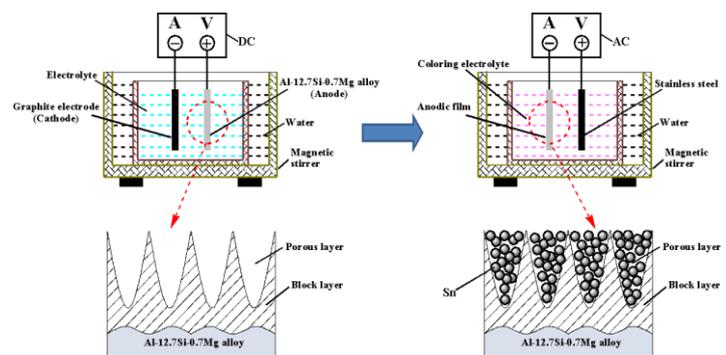


Fig. 1 Schematic illustration of anodic oxidation and electrolytic coloring of Al-12.7Si-0.7Mg alloy

3 Results and discussion

3.1 Determination of electrolytic coloring processing conditions

Effects of each factor of electrolytic coloring processing conditions on comprehensive index for colored films were illustrated in Figure 2. As presented in Figure 2 (a), the coloring voltage was applied from 8 V to 24 V. Considering the uniformity, shade and corrosion resistance of the coloring film, the ideal coloring voltage applied was found to be 16 V. Therefore, the optimal conditions of electrolytic coloring processing were as follows: 170 g·L⁻¹ of H₂SO₄, 26 °C of oxidation temperature and coloring temperature, 24 min of oxidation time and 16 V of coloring voltage.

The effects of coloring time, coloring voltage, coloring temperature and the concentration of SnSO₄ on properties of colored films were investigated by single factor tests in this work. The color of the electrolytic coloring film becomes darker with time. No change on sample surface was observed within 1 min. The longer the electrolytic time, the darker the color, the thicker the coating, the better the uniformity as well as high corrosion resistances. Excessive electrolyzing could decrease uniformity and corrosion resistance of the colored film. Over the range from 3 to 7 min, the film's color changed from light to dark in which Sn²⁺ can readily be hydrolyzed or be oxidized.

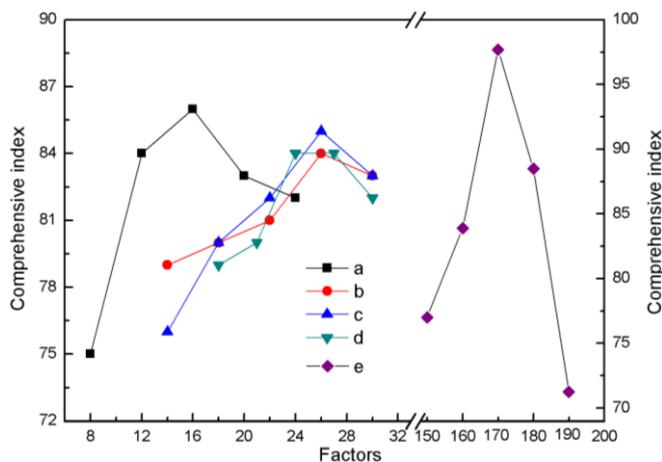


Fig. 2 Effect of electrolytic coloring condition on comprehensive index of colored film. Factors were consist of a: coloring voltage (V); b: coloring temperature (°C); c: anodic oxidation temperature (°C); d: anodic oxidation time (min); e: the concentration of H₂SO₄ (g·L⁻¹). Comprehensive index was investigated by assessing uniformity, shade and corrosion resistance of coloring films, according to GB/T12967.6-2008 and JIS H 8681-1:1999.

The ideal concentration range for stannous sulfate was 2-8 g·L⁻¹. Temperature was related with metal deposition rates and hydrolysis degrees of Sn²⁺. The effects of temperature on colored films were tested over the range from 14 to 30 °C. Below 15 °C, metal deposition rates were slow and the resulted films were thin and uneven. Above 26 °C, hydrolysis of Sn²⁺ was observed which made the electrolyte denature, and the performance of the films became poor. Consequently, suitable temperature range was 20-26 °C. When AC voltage was lower than 8 V, no metal tin was deposited on sample

surface. As the voltage rose up, the film became thicker, darker and more uniformity. When AC voltage was higher than 24 V, hydrogen evolution reaction became vigorous, making the coatings loose and uneven. So the AC voltages among 12-24 V were appropriate.

The optimal experimental conditions of electrolytic coloring were as follows: 170 g·L⁻¹ of H₂SO₄, 24 min of oxidation time, 26 °C of oxidation temperature, 3-7 min of coloring time, 20-26 °C of coloring temperature, 2-8 g·L⁻¹ of SnSO₄ and 12-24 V of coloring voltage. By controlling the process parameters, firmly bonded films with different colors could be fabricated.

3.2 Microstructure of electrolytic coloring film

Figure 3 shows SEM images of anodization film (a) and electrolytic coloring film (b). Anodization film is composed of porous layer and block layer. The outer porous layer presents cellular structure with pseudo hexagonal prisms. These pseudo hexagonal prisms constitute numerous nano-channels, whose bottom is the inner block layer.²³⁻²⁵ White particles in the Figure 3 (a) are silicon granules which are evenly distributed. Silicon granules improve mechanical and casting properties of aluminum alloys, while, the continuity of the anodization film and corrosion resistance of aluminum alloys are greatly weakened. During electrolyzing, reduced tin atoms were deposited in nanochannels of anodization film, which gradually make the surface smooth. EDS analysis of point A (in Figure 3 (a)) and point B (in Figure 3 (b)) indicated that anodization film contained O, Al, Si and S for Figure 3 (a) and the colored film contained O, Al, Si, S and Sn for Figure 3 (b). XRF was also applied to analyze anodization film and colored film, which verified the existence of tin in the colored film, which is in agreement with the EDS analysis results. XRF demonstrated that the longer the electrolyzing time, the higher the metal tin deposited in colored film.

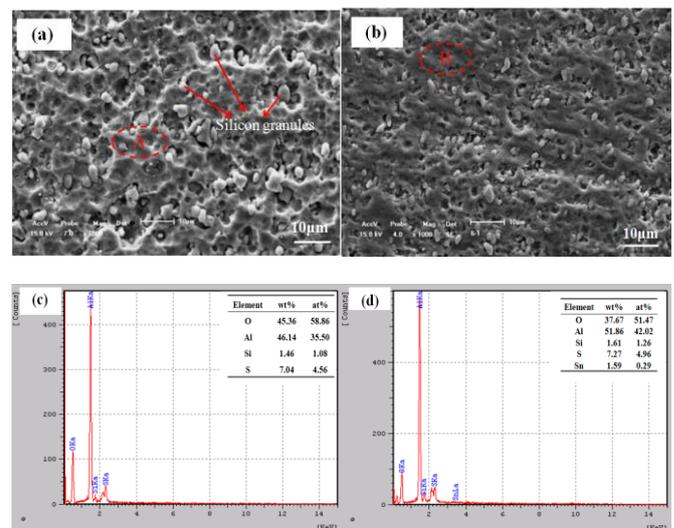


Fig. 3 SEM micrographs and the corresponding EDS analysis of the surface of the different samples (a-Anodization sample, b-Electrolytic coloring sample, c-EDS spectrum of the anodic film (A), d-EDS spectrum of the coloring film (B)).

Figure 4 illustrates the SEM images of cross section of a colored sample. The upper loose section was adhesive used to fix the sample. The light-colored bottom was the alloy matrix. The middle section marked in red was the colored film with thickness of 10 μm . Cross section SEM images revealed that there was no independent tin coating, for tin atoms when they were deposited in nanochannels of anodization coating.

Figure 5 shows the XRD pattern of Al-12.7Si-0.7Mg Alloy surface, which had been anodized and electrolyzed in sequence. In agreement with EDS and XRF analysis, XRD pattern showed that the colored film contained tin and silicon. The fact that no peaks of Al_2O_3 were observed implied that the film oxide of Al_2O_3 was noncrystalline.

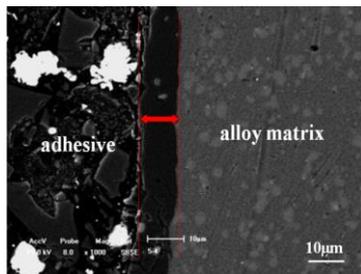


Fig. 4 The SEM cross-sectional photomicrograph of electrolytic coloring sample.

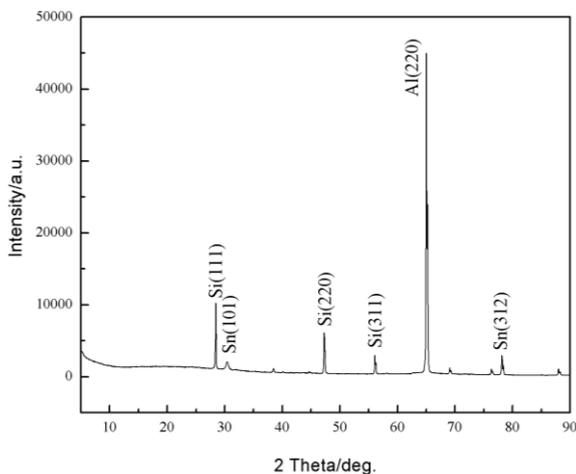


Fig. 5 XRD pattern of the electrolytic coloring sample

3.3 Performance of colored films

In chemical soaking tests, various samples were dipped in 0.1 $\text{mol}\cdot\text{L}^{-1}$ HCl solution, 0.1 $\text{mol}\cdot\text{L}^{-1}$ NaOH solution and 5% NaCl solution, respectively, for 24 h. In both acidic and alkaline media, the average corrosion rates of colored sample were less than those of untreated sample, as shown in Table 2. Almost no weight loss was detected for both untreated and colored samples after soaking in 5% NaCl solution. Neutral salt spray test was conducted for 240 h continuously, and the results are also listed in Table 2. According to Appendix B of GB/T 6461-2002, protection grade of anodized film

was 6, and that of colored film was 9, close to the highest grade 10.

Table 2 Average corrosion rates of colored and untreated samples

Sample	Average corrosion rate / ($\text{g}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$)		
	Acid corrosion ⁱ	Alkali corrosion ⁱⁱ	NSS ⁱⁱⁱ
Untreated sample	2.1501	1.9257	0.0149
Colored sample	1.7822	1.3413	0.0108

Note: i- Soaked in pH=1 HCl solution for 24 h, ii- Soaked in pH=12 NaOH solution for 24 h, iii- Hanged in NSS tester for 240 h.

The potentiodynamic polarization curve is a helpful tool for characterization of corrosion protection. In a typical polarization curve, a higher corrosion potential (E_{corr}) and polarization resistance (R_p), a lower corrosion current density (I_{corr}) and corrosion rate (V_{corr}) corresponds to a lower corrosion rate and a better corrosion resistance.^{26,27} Figure 6 showed the polarization curves of untreated sample, anodizing sample and electrolytic coloring sample measured in 3.5 wt% NaCl solution after immersion for 30 min. The corrosion current density, corrosion potential and corrosion rate were presented in Table 3. In this work, the corrosion potential of untreated sample, anodizing sample and electrolytic coloring sample was circa -1.104 V, -0.702 V and -0.334 V, respectively. Additionally, the corrosion current density of electrolytic coloring sample was 8.90×10^{-8} $\text{A}\cdot\text{cm}^{-2}$, only about one fourth of that was attributed to the anodizing sample (3.37×10^{-7} $\text{A}\cdot\text{cm}^{-2}$) and about 125-fold decrease from the original value was related to the untreated sample (1.12×10^{-5} $\text{A}\cdot\text{cm}^{-2}$). The R_p value of coloring sample was higher than that of untreated sample. Compared with other two specimens, electrolytic coloring sample exhibited excellent corrosion resistance, due to its higher E_{corr} and R_p , lower I_{corr} and V_{corr} .

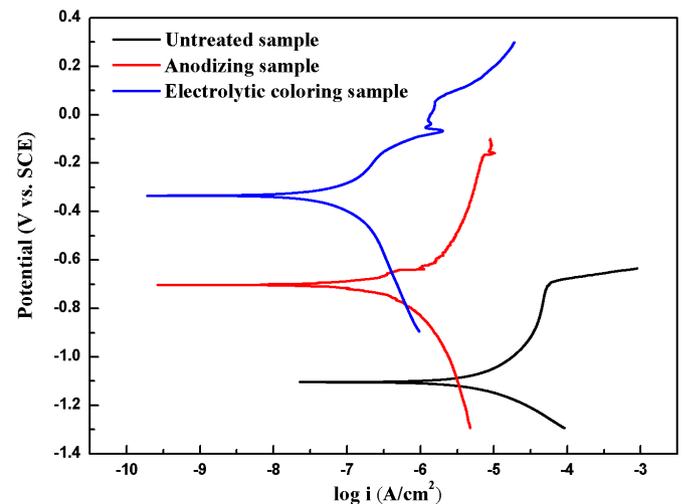


Fig. 6 Polarization curves of untreated sample, anodizing sample and electrolytic coloring sample in 3.5 wt% NaCl solution at room temperature (a-untreated sample, b-anodizing sample, c-electrolytic coloring sample).

Table 3 Corrosion potential, corrosion current, corrosion rate of different samples.

Sample	E_{corr} (V vs. SCE)	I_{corr} (A·cm ⁻²)	V_{corr} (mm·a ⁻¹)	R_p (kΩ·cm ⁻²)
Untreated sample	-1.104	1.12×10 ⁻⁵	0.131	3.9
Anodizing sample	-0.702	3.37×10 ⁻⁷	3.96×10 ⁻³	94.2
Electrolytic coloring sample	-0.334	8.90×10 ⁻⁸	1.05×10 ⁻³	611.5

Colored samples were put into a muffle and kept at 100 °C, 200°C, 300 °C, 400 °C and 500 °C, respectively, for 1 h. After cooling to room temperature in air, their surface films were inspected. Treated at 300 °C and below, the colored films did not change at all. For the 400 °C treated sample, its color became lighter, but there were no bubbles or cracks on the film. The film was severely damaged after treatment at 500 °C.

A thermal shock test was also carried out in which the colored samples were kept in a muffle at 200 °C, 300 °C and 400 °C, respectively, for 1 h. Then, the colored samples were immediately dipped in room temperature water. No crack, bubble or peeling appeared on the colored film for samples heated below 300 °C or 300°C as shown in Figure 7. However, there were cracks on the sample surface when it was treated at 400 °C.

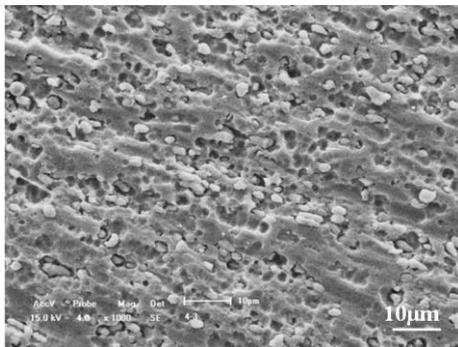


Fig.7 SEM image of the electrolytic coloring sample after thermal shock test at 300 °C

4 Conclusions

For Al-12.7Si-0.7Mg alloy, the optimal experimental conditions of electrolytic coloring were 170 g·L⁻¹ of H₂SO₄, 24 min of oxidation time, 26 °C of oxidation temperature, 3-7 min of coloring time, 20-26 °C of coloring temperature, 2-8 g·L⁻¹ of SnSO₄ and 12-24 V of coloring voltage. By controlling the operation conditions, the uniform electrolytic coloring films with different color were obtained. Analysis of microstructure (SEM/EDS, XRF, XRD) showed that tin particles had been deposited in the colored film. The colored films, were circa 10 μm thick, were uniform, dense and firmly attached to the substrate. Compared with anodized film, tin colored film possessed better corrosion resistance. After 240 h neutral salt spray test, protection ratings and appearance ratings of colored films were

Grade 9. Also colored film showed high thermal stability and heat shock resistance.

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