Fabrication and Characterization of Multiscale Graded SMAT-MAO Composite Coating Formed on the Surface of 2024 Al Alloy

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Abstract. In order to improve the fatigue property of microarc oxidation (MAO) coated aluminum alloy, a new multiscale graded coating named SMAT-MAO graded coating, consisting of a bottom nanocrystalline layer covered by a top ceramic coating, was designed and fabricated on the surface of 2024 Al alloy by a duplex process with surface mechanical attrition treatment (SMAT) method prior to microarc oxidation process. Experimental results show that surface crystal size was refined to 52.8nm after SMAT for 15min. A 20μm thick nanocrystalline layer, with gradient changing crystal size from dozens of nm in the surface to 200~500nm deep into the substrate, was successfully obtained. The microarc oxidation ceramic coating with 5μm thickness grew by consuming part of the nanocrystalline layer. Since the local heat produced in the microarc discharge channels was not enough to lead to the growth of the substrate grain, the alloy substrate near to the coating/substrate interface still maintained a nano-grained size. Therefore SMAT-MAO coating, which consists of an outer ceramic coating and an inner nanocrystalline layer, was obtained.

1. Introduction
Microarc oxidation (MAO) technique is widely used to fabricate oxide ceramic coatings on Al [1-4], Mg [5], Ti [6, 7] and their alloys to enhance their corrosion- and wear-resistance properties, or to confer various other functional properties including anti-friction, thermal protection, optical and dielectric properties. However, the results that the MAO treated metal samples have a very low resistance to fatigue limited its applications [8-11].

The reduction of fatigue property can be ascribed to two possible factors: the one is micro defects in the coating, which result in an early fatigue crack initiation; the other one is tensile residual internal stress within the substrate adjacent to the coating, which not only leads an early fatigue crack initiation in the substrate, but also promotes the propagation of cracks. Thus, two ways can be considered to improve the fatigue property of MAO treated samples: Firstly, the structure defects of MAO coating, such as pre-existing cracks and micro pores, can be improved by adjusting experimental parameters. Furthermore, the tensile residual stress in the substrate can be offset by a cold-working pre-treatment. The combination of mechanical cold-working and microarc oxidation has been demonstrated to significantly improve the fatigue resistance compared to the results of MAO coating alone. Asquith

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et al. demonstrated that the loss in fatigue life can be recovered to a certain extent by the application of a suitable surface cold-working process prior to treatment [12]. In their study, shot-peening was employed as such a cold-working process and was demonstrated to recover fatigue life of MAO treated aluminum by approximately 85%.

Surface mechanical attrition treatment (SMAT) [13-19], producing a more severe cold-working compared with the conventional shot-peening, is a novel method which can not only introduce compressive residual stress into the surface layer, but also induce a grain refined gradient structure with nanometer to micro scale from the surface to the bulk substrate.

In our research, SMAT was used as the pretreated process of 2024 aluminum alloy, followed by the MAO treatment, in this way the specially modified graded structure (SMAT-MAO graded coating) with a refined grains bottom layer covered by a top conversion ceramic coating was fabricated. The composition, graded structure and morphologies of nanocrystalline layer and SMAT-MAO graded coating were investigated.

2. Experimental

2.1. Materials
The material used in the experiment is 2024 Al alloy with nominal composition 4.36% Cu, 1.49% Mg, 0.46% Mn, 0.25% Fe, 0.14% Si, 0.07% Zn, 0.01% Ti and balance Al. Tensile tests were conducted to ensure the mechanical properties of the alloy: yield strength 330 MPa, ultimate tensile strength 460 MPa and elongation 23%.

2.2. SMAT
The samples, 80 mm × 80 mm × 3 mm in dimensions, were ground with 400#, 800# and 1200# abrasive papers, ultrasonically washed with acetone and distilled water, and dried for SMAT. SMAT was performed in vacuum using a SNC-1 machine. A container of glass fiber reinforced plastic (GFRP) was placed in the steel chamber that was vibrated by a generator. ZrO2 balls with a diameter of 6mm, instead of steel balls used in the traditional SMAT, were placed at the bottom of GFRP container. This kind of set can effectively prevent the transfer of iron between shot and work-piece. The vibration frequency of the chamber is 50 Hz.

2.3. Coating preparation
The based electrolyte of alkaline silicate was prepared from the solution of Na2SiO3 (6.0 g/L), NaOH (1.2 g/L), (NaPO3)6 (35.0 g/L) and Na2WO4 (6.0 g/L) in distilled water. A 65 kW microarc oxidation device provides the voltage waveforms, and the main pulse parameters, such as pulse duration, voltage amplitude and duty cycle during both positive and negative biasing can be adjusted independently. The electrical parameters were fixed as follows: voltage 600 V, frequency 600 Hz, duty cycle 10.0%, and the treating time 10 min.

2.4. Characterization of nanocrystalline layer and graded coating
The microstructure of the sample surface treated by SMAT, MAO, and the combination of the two methods, was investigated by X-ray diffraction (XRD) with a Philips X’pert diffractometer using Cu Kα in the range of 30-100°, the measurements were performed with a continuous scanning mode at a rate of 4°/min with an incident angle of 4°. The surface and cross-section morphologies of the coatings were observed by a Hitachi S-4700 scanning electron microscopy (SEM). A Philips CM-12 transmission electron microscopy (TEM) was used to examine the microstructure of the nanocrystalline layer and the crystal sizes in different depth. To prepare TEM samples, 0.2 mm thick slices were cut from the different depth of surface layer. After mechanical grinding to 40-50 μm, 3 mm-diameter discs were punched from the thin foils, which were then ion-milled with a small incident angle till perforation from single side only.
3. Results and discussion

3.1. Structure design of graded coating
The structure design and fabrication process of SMAT-MAO graded coating are illustrated in Fig. 1. Firstly, the substrate alloy was processed by SMAT, resulting in the fabrication of a nanocrystalline layer on the surface, secondly, the nanocrystalline surface layer sample with a gradient distribution of crystal size was immersed in the electrolyte solution to be oxidized by spark discharge during MAO process, finally a SMAT-MAO graded coating with a nanocrystalline bottom layer covered by a top conversion ceramic coating was fabricated on the surface of 2024 Al alloy.

3.2. Microstructure of nanocrystalline layer
A surface layer with crystal size refined into nanometer level can be obtained on the surface of 2024 Al alloy after SMAT process. The XRD patterns of 2024 Al alloy samples before and after SMAT are shown in Fig. 2. It can be found that, compared with 2024 Al alloy, there is an evident broadening of the Bragg-diffraction peaks and a slight shift in the position of diffractions after SMAT. The Bragg-diffraction peak broadening in the surface layer may be attributed to grain refinement and the shift of the diffraction peaks is caused by the development of microstrain. During SMAT, a nanocrystalline surface layer forms due to large grain boundary misorientations, dislocation blocks and microbands [19]. Quantitative XRD measurements indicate that the average crystal size of treated surface layer was 52.8 nm after SMAT for 15 min.

![Figure 1. Structure design and fabrication process of SMAT-MAO graded coating formed on the surface of Al alloy](image)

![Figure 2 XRD patterns of 2024 aluminum alloy before and after SMAT](image)

a) substrate alloy; b) SMAT
Bright-field TEM images at different depth from the top surface of 2024 Al alloy after SMAT for 15 min are shown in Fig. 3a. It can be found that equiaxed shape grains of about dozens of nm are formed at the top surface of 2024 Al alloy after SMAT for 15 min. The crystal sizes at 10 μm and 20 μm depth from the sample surface increase to below 100 nm and several hundred nanometers, respectively, as shown in Fig. 3b and c. At about 30 μm depth from the top surface, the crystal size increases to a micron level.

![Figure 3. TEM micrographs of 2024 Al alloy after SMAT with ceramic balls: a) surface; b) 10μm, c) 20μm and d) 30μm from the top surface](image)

The hardness distribution along depth from the top surface of 2024 Al alloy after SMAT is shown in Fig. 4. It can be found that a maximum of hardness is at the top surface, and then the value decreased gradually along the depth. From the distribution of hardness, it can be concluded that the thickness of deformed layer caused by SMAT is less than 40 μm. By making a combination analysis of Fig. 3 and 4, it can be deduced that, after SMAT, about a 20 μm thick grain refined gradient structure layer, with a increasing from nanometer to micron meter scale grains along the surface to the bulk substrate was obtained at the surface of 2024 Al alloy sample.
3.3. Characterization of SMAT-MAO graded coating

After SMAT, the nanocrystalline layer was processed by MAO to obtain a SMAT-MAO graded coating. The results of the XRD analysis performed on MAO coated and SMAT-MAO coated samples are presented in Fig. 5. It can be found that $\gamma$-Al$_2$O$_3$ phase is the main composition of both simple MAO and SMAT-MAO graded coatings. Furthermore, no obvious difference can be distinguished from the XRD patterns between MAO and SMAT-MAO coated Al alloy samples.

![XRD patterns of coating: a) MAO coating; b) SMAT-MAO graded coating](image)

Fig. 6 illustrates the surface and cross section morphologies of MAO coated and SMAT-MAO coated 2024 Al alloys. It can be seen that more micro pores can be found at the surface of SMAT-MAO graded coating compared with that of simple MAO one (Fig. 6a and b). This phenomenon may be due to the specially refined grain surface of the alloy after SMAT pre-treatment. After SMAT, there are much more defect sites at the nanocrystalline surface layer, at which it is easier to induce discharge during the MAO process. Therefore, more discharge channels (micro pores at the surface) were formed at the surface of SMAT-MAO graded coating. The microarc oxidation ceramic coatings with...
5μm thickness grew by consuming part of the nanocrystalline layer, as shown in Fig. 6d. Furthermore, the similar coating thickness and good adhesion between coating and substrate can be observed for both kinds of coating, as shown in Fig. 6c and d.

In order to verify the gradient structure of SMAT-MAO graded coating, especially nanocrystalline layer under ceramic coating, TEM was employed to investigate the microstructure of 2024 Al alloy near the coating/substrate interface of SMAT-MAO graded coating, and the results were shown in Fig. 7. It can be found that a nanocrystalline structure characterized by equiaxed shape grains with crystal size bellow 100 nm can be observed in Fig. 7a. The corresponding selected area electron diffraction (SAED) pattern of A area in Fig. 7a, as shown in Fig. 7b, exhibits well-defined rings, illustrating the presence of fine grains with random orientation on the treated surface. Since the local heat produced in the microarc discharge channels was not enough to lead to the grain growth of the substrate, the alloy substrate near to the coating/substrate interface still maintained a nano-crystal size. Therefore SMAT-MAO graded coating, which consists of an outer ceramic coating and an inner nanocrystalline layer, was successfully fabricated on the surface of 2024 Al alloy.

Figure 6. Surface and cross-section morphologies of coated 2024 Al alloy:
Surface morphology of a) MAO coating; b) SMAT-MAO coating; Cross-section morphology of c) MAO coating; d) SMAT-MAO coating
Figure 7. TEM images of 2024 Al alloy near the coating/substrate interface of SMAT-MAO graded coating
a) Bright-field TEM image; b) Corresponding SAED of A area in a)

4. Conclusions
A 20μm thick nanocrystalline layer, with gradient changing crystal size from dozens of nm in the surface to several hundred nanometers deep into the substrate, was obtained by SMAT process. SMAT-MAO graded coating, which consists of an outer ceramic coating and an inner nanocrystalline layer, was formed on the surface of 2024 Al alloy by consuming part of the nanocrystalline layer during MAO process. Since the local heat produced in the microarc discharge channels was not enough to lead to the grain growth of the substrate, the alloy substrate near to the coating/substrate interface still maintained a nano-crystal size.

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