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Formation and structure of composite coating of HDA and micro-plasma oxidation on A3 steel ①

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Abstract: Composite coatings were obtained on A3 steel by hot dipping aluminum(HDA) at 720 ℃ for 6 min and micro-plasma oxidation(MPO) in alkali electrolyte. The surface morphology, element distribution and interface structure of composite coatings were studied by means of XRD, SEM and EDS. The results show that the composite coatings obtained through HDA/MPO on A3 steel consist of four layers. From the surface to the substrate, the layer is loose Al_2O_3 ceramic, compact Al_2O_3 ceramic, Al and FeAl intermetallic compound layer in turn. The adhesions among all the layers are strengthened because the ceramic layer formed at the Al surface originally, FeAl intermetallic compound layer and substrate are combined in metallurgical form through mutual diffusion during HDA process. Initial experiment results disclose that the anti-corrosion performance and wear resistance of composite coating are obviously improved through HDA/MPO treatment.

Key words: hot dipping aluminum; micro-plasma oxidation; composite coating; ceramic coating

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1 INTRODUCTION

With the development of industry technology, better performances of material surface are asked for. Because of its limitations, an individual surface treatment technology can't meet the excessive demands under high speed, heavy load, high temperature and seriously corrosive conditions alone. Composite surface treatment combining two or more than two kinds of surface treatment technologies in proper order with proper methods to prepare composite coating can put the advantages of different treatments together, so every performance of material is improved and service life of parts is prolonged. Composite treatment is an important developing direction of modern surface engineering fields[1].

Hot dipping aluminum (HDA) can improve the anti-corrosion and heat-resisting performances of steel and iron, so it was used more and more widely. It was paid more attentions recent years and developed quickly[2-7]. But because of its limitations, individual HDA coating can't meet the needs of serious service environment. It is corroded in acid and alkaline conditions, its hardness is low, its wear resistance is low, and its heat resistance remains to be improved further.

Micro-plasma oxidation (MPO) is a kind of surface treatment technology developed based on anodic oxidation[8,9]. Differed from usual anodic oxidation, MPO applies higher working voltage, so the working field changes from Faraday field for usual anodic oxidation to high-voltage discharge field, micro-plasma arc discharge takes place on samples' surface, and surface ceramic layer is formed. During this oxidation process, chemical oxidation, electrochemical oxidation and micro-plasma oxidation take place at the same time. In high-voltage discharge field thin section is punctured firstly to produce arc discharge, while the final oxidation layer on samples' surface is even. MPO has high energy density, the temperature in micro-arc zone can reach several thousands degree[10], and it can melt metal and metal oxides in this zone, so dense α-Al_2O_3 ceramic layer with corundum structure is formed. This layer has excellent physical, chemical, electrical and mechanical performances. Except for high strength, high wear resistance and high corrosion resistance that belong to usual structure ceramics, this layer possesses

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such advantages as good bonding between the layer and the substrate, small dimension changes, good entire tenacity, and high insulation resistance. MPO technology has wide apply prospect in many fields as war, mechanics, aviation, aerospace, auto and textile industry. At present this technology is in study and develops, and it is used to treat aluminum, titanium, zirconium, niobium and their alloys.

In this article, composite coating is prepared on steel surface through treating HDA layer with MPO technology. The surface morphology, element distribution, interface structure, anti-corrosion performance and wear resistance of composite coatings are studied.

2 EXPERIMENTAL

2.1 HDA

A3 steel was made into samples with the size of 10 mm×10 mm×14 mm. Solvent HDA method was applied with technological process as the following: degreasing(10 - 30 min)→water rinsing→activating in acid (HCl 20%(mass fraction), room temperature)→water rinsing→promoting (promotion flux 7%-9%(mass fraction), 70 - 80 ℃)→drying(200 - 300 ℃)→HDA.

HDA was done in pure aluminum at 720 ℃ for 6 min, and the hoisting speed was 800 mm/min.

2.2 MPO

MPO was done using self-made 30 kW frequency conversion type MPO power supply. Alkaline solution was applied, and its composition is 10 g/L Na_2SiO_3 and 2 g/L NaOH. The current density was 5 A/cm^2, and the frequency was 50 Hz. The temperature of solution was maintained below 30 ℃ through circulating water cooling.

2.3 Measuring and testing

Surface morphology was observed by means of KYKY-2800 SEM, and element distribution at the interface of composite coating was analyzed through EDS. XRD was conducted on D/Max-rB type instrument with Cu target, 40 kW, 120 mA and graphite monochromator. Micro-hardness was measured by means of NEOP-200 micro-hardnessmeter.

Friction and wear testing was conducted on MM-200 type wear and tear tester, and the part mate was YG6 hard alloy block with the size of d45 mm×10 mm and hardness of HRC 70-73. The testing lasted for 8 h at the load of 40 N and turning speeds of 200 r/min. Wear mass loss was used to show wear resistance. The wear mass loss of samples was measured on lightening analytical balance with the precision of 0.1 mg. Each kind of samples was tested parallelly for three times, and their arithmetic mean was calculated. The anti-corrosion performance of the composite coating was measured through immersion mass loss method in 5%NaCl solution at (30±1) ℃.

3 RESULTS AND DISCUSSION

3.1 Surface morphology and forming mechanism of composite coating

SEM surface micrographs of HDA/MPO composite coatings are shown in Fig. 1 (Fig. 1(b) is the enlargement of Fig. 1(a)). Trace of the solidifying of melt substance can be seen on the surface, and the pellets with different sizes combine with each other to be integrated. Small gas holes exist among some pellets, and the morphology of these gas holes is similar to that of solidifying of magma from volcanic eruption. These gas holes are discharge gas holes formed during MPO process. When samples are put into electrolyte, initially, small air bubble produces on their surface, the surface turns dark and oxide layer is formed on aluminum. Although this stage belongs to usual anodic oxidation because of low current and low volt-

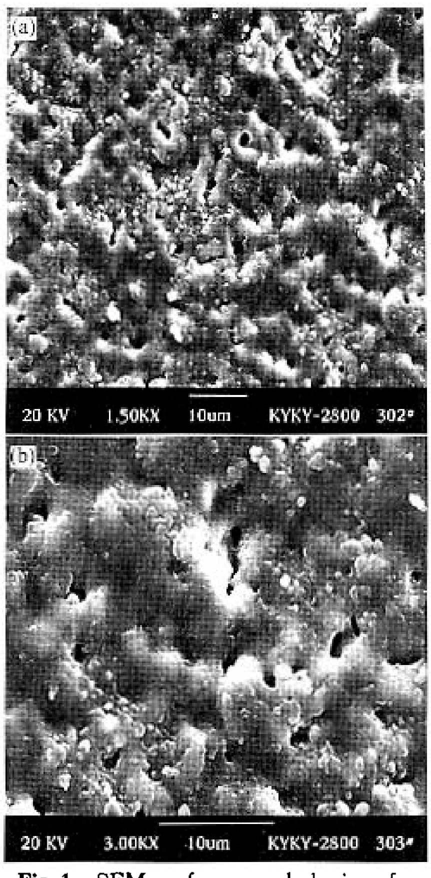

Fig. 1 SEM surface morphologies of HDA-MPO composite coatings

age, it is very important for the formation of MPO layer. The oxide layer will stop growing without a dense layer formed at this stage, and a dense oxide layer is ensured only by proper electrolyte making-up and conditions. If a large number of gas bubbles produce at this stage, the oxide layer is loose even doesn't form, thus it stops growing. The growing of oxide layer takes place at the same time with the dissolution of aluminum during usual anodic oxidation. Only when the rate of the former is higher than that of the latter, can the oxide layer become thicker. It is same for MPO at its initial stage. When the growing rate of oxide layer is controlled to be higher than the dissolve rate of aluminum, oxide layer forms, then the electric resistance increases, which leads the voltage to increase, thus, thinner part of oxide layer is punctured. At these parts the temperature reaches several thousands degree to melt aluminum, so trace of solidifying can be seen on the surface of samples. New oxide layer forms at the thinner parts where the layer is punctured. When it's thick enough, other thinner parts are punctured, and in this way, the whole oxide layer gets thicker. During this process, jumping and swimming of many micro-arcs can be seen on the samples' surface to leave discharge gas hole there.

3.2 XRD analysis of composite coating

XRD patterns of composite coating at different depth from its surface are shown in Fig. 2. It can be seen from the XRD pattern of the composite coating's surface in Fig. 2(a) that there are mainly α-Al_2O_3 phase and γ-Al_2O_3 phase, and the quantitative XRD analysis discloses that the content of α-Al_2O_3 phase is lower than that of γ-Al_2O_3 phase. While at the depth of 20 μm from surface, the content of α-Al_2O_3 phase is higher than that of γ-Al_2O_3 phase (as shown in Fig. 2(b)). This illustrates that the phase distribution in MPO layer on the surface of HDA is the same as that in MPO layer on the surface of aluminum alloy[11]. XRD pattern of composite coating at depth of 40 μm from the surface is shown in Fig. 2(c), and it can be seen that Al (111) diffraction peaks appear mainly and some diffraction peaks of $FeAl_3$ appear, which is the same as the results got from un-oxidized HDA coating. This indicates that the whole aluminum coating does not turn ceramic coating after MPO treatment. Furthermore experiments disclose that under the same MPO conditions (electrolyte, time, current density and voltage), the oxide layer formed on HDA coating is obviously thinner than that on aluminum or aluminum alloy. The possible reason is that, unlike aluminum and aluminum alloy, iron that diffuses into aluminum during HDA can't be oxidized during MPO process and hinders the increase of oxidation voltage, and it becomes discharge path where the coating is always in the state of being punctured with spark. Because of this reason, the oxide layer doesn't turn thicker any longer after a certain time.

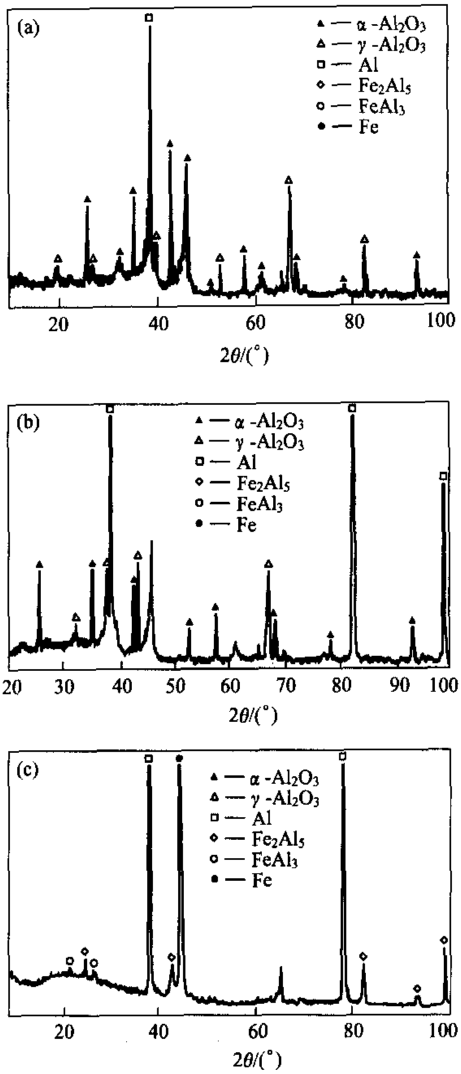

Fig. 2 XRD patterns of composite coating
(a)—Surface; (b)—20 μm from surface; (c)—40 μm from surface

3.3 Interface structure and element distribution of composite coating

SEM micrographs of the cross section of the composite coating (without corrosion) are shown in Fig. 3, and the corresponding element distributions are shown in Fig. 4. It can be found that the composite coating consists of three layers. The outer layer is about 30 μm thick, containing 50% Al and 50%O(mass fraction), which conforms to the chemical formula of Al_2O_3, as disclosed by

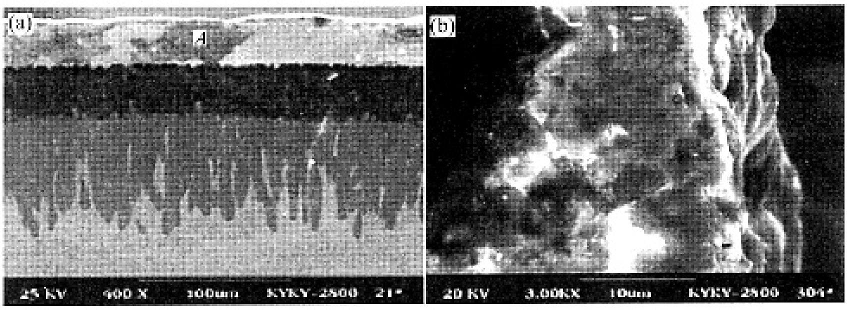

Fig. 3 SEM micrographs of cross section of HDA/MAO composite coating

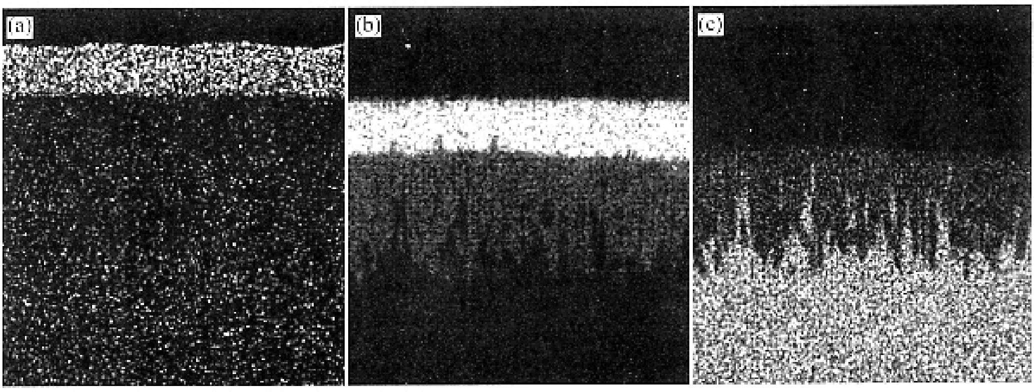

Fig. 4 Element distribution of section interface of composite coating
(a)—O element; (b)—Al element; (c)—Fe element

EDS results. The element distribution of O is shown in Fig. 4(a). Combined with XRD results, the outer layer can be judged to be Al_2O_3 layer. From the SEM micrograph in Fig. 3(b) that is the amplifying of part *A* in Fig. 3(a), it can be seen that the outer layer consists of loose layer and dense layer. The element distribution is shown in Fig. 4(b) for the coating at the depth of 30 μm - 60 μm (dark part in Fig. 3(a)) from the outer layer. Aluminum is found to be the main composition at this layer. Combined the saw tooth-like part in Fig. 3(a) with aluminum distribution in Fig. 4(b) and iron distribution in Fig. 4(c) together, this inner layer is found to be contain iron and aluminum element, which means that this layer is Fe and intermetallic layer of Al formed during HDA process. To sum up, the composite coating composes of four layers, which are outer loose ceramic layer, dense ceramic layer, aluminum layer and intermetallic layer of Fe and Al in turn.

3.4 Initial analysis of composite coating's performances

Mass loss results of composite coating are shown in Fig. 5. It can be seen that the mass loss of HDA coating decreases obviously after MPO treatment, that means its wear resistance is increased. After a certain time during the testing, mass loss increases quickly, which is due to the exposition of the middle aluminum layer. So, the whole aluminum coating needs to be turned into ceramic layer to further improve the wear resistance of composite coating.

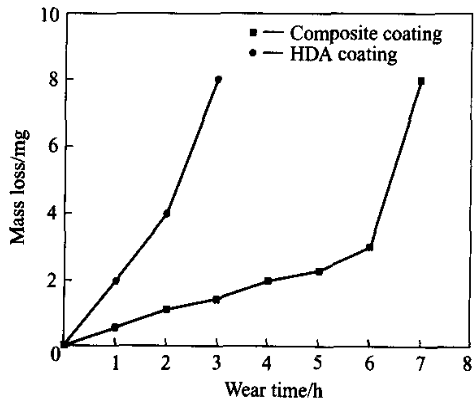

Fig. 5 Curve of mass loss of coatings

The composite coating was immersed in 5% NaCl solution for 360 h, then was weighed. The results indicate that its mass loss speed is 0.6mg/(m^2 · h), while in the same testing the mass loss speed of HDA coating is 5.8mg/(m^2 · h). It can be concluded that the corrosion resistance is increased after MPO treatment.

4 CONCLUSIONS

1) After HAD and MPO treatment of steel, composite coating forms. It consists of Al_2O_3 layer, aluminum layer, Fe layer and intermetallic layer of Al from the surface to the substrate.

2) HDA coating's wear resistance and corrosion resistance are improved obviously after MPO treatment.

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