

Preparation of Iron-Cobalt Alloy Ceramic Coating by Micro-arc Oxidation and its Application for Degradation of Rhodamine B

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Abstract. An iron-cobalt alloy ceramic coating grows on the surface of Q235 carbon steel in situ by the micro-arc oxidation technology; and the phase composition, elementary composition, surface morphology, surface roughness and thickness of the ceramic coating are analyzed by X-ray diffractometer, energy dispersive spectroscopy, scanning electron microscopes, handheld roughness meter and coating thickness gauge. The results show that the morphology of ceramic coating is irregular porous structures at the surface and the elements of electrolyte and Q235 carbon steel matrix exist in the ceramic coating as amorphous phase. And then, the degradation of the rhodamine B (RhB) by the ceramic coating in a H₂O₂ Fenton system was investigated. The degradation rate of the rhodamine B solution can reach 99%; and meanwhile, the degradation rate is not reduced along the increased using times.

Introduction

The micro-arc oxidation (MAO) technology is a new surface masking technique; it can grow a layer of ceramic oxidation coating on the surface of the metal in situ [1, 2]. Initially, this technology only applies to the surface of valve metal and achieves significant progress [3, 4]. However, research of MAO technology on steels was rarely reported because it was regarded as not feasible for many years [5, 6]. In recent years, our group successfully deposited ceramic coatings on steels by Micro-arc oxidation without any pretreatments and studied the anti-corrosion and anti-abrasion properties of such coatings [7, 8].

Fenton technology has lower H₂O₂ decomposing activation energy under the catalytic action of Fe²⁺; vast of intermediate state active species hydroxyl radical OH is generated during the reaction process, and then the organic substance is oxidized and decomposed [9-11]. The hydroxyl radical has higher redox potential so that the organic matters hard to biodegrade or chemical oxidation can be decomposed. In this text, the iron-cobalt alloy ceramic coating is directly prepared on the surface of Q235 carbon steel by the micro-arc oxidation technology; and Fenton system is formed together with H₂O₂ so as to degrade rhodamine B.

Experimental details

Materials. Q235 carbon steel for experiment (mass fraction %) comprises the components of 0.14-0.22 of carbon, 0.30-0.65 of manganese, 0.30 of silicon, 0.05 of sulphur, 0.045 of phosphorus and balance of iron.

Preparation of the coatings. The test blocks are orderly grinded by the waterproof abrasive paper and cleaned by the deionized water; and after being dried, the test blocks are subjected to micro-arc oxidation treatment in the electrolyte. The electrolyte is composed of sodium silicate, sodium hypophosphite and cobalt oxide powders; and the electrolyte is cooled by the cooling water during the experiment process. After the experiment, the sample is cleaned by the deionized water, and then the ceramic coating is dried.

Characterization. The microstructure of the ceramic coating is observed by the scanning electron microscope (SEM S-570, HITACHI); the elementary composition of the ceramic coating is analyzed

by the energy disperse spectroscopy (EDAX, Philips); the phase composition of the ceramic coating is analyzed by the D/maxr B automatic X-ray diffractometer (Cu target, Ka ray and RICOH). The roughness of the ceramic coating was detected by the roughness meter (TR200, Beijing times the peak of science and technology co., LTD, China); the thickness of the ceramic coating was measured by the coating thickness gauge (TT260, Beijing times the peak of science and technology co., LTD, China). The absorbance value of the solution is measured by the ultraviolet and visible spectrophotometer (UV762, Shanghai Precision and Scientific Instrument Corporation).

Degradation of Rhodamine B. 10 mL of 100 mg/L rhodamine B solution is arranged in the quartz cup reactor, and air is accessed in the reactor. 0.04 mL of the 30% H₂O₂ aqueous solution was added to the reaction solution at the beginning of the irradiation. The sample is soaked in the solution of the reactor; the absorbancy is measured by the spectrophotometer; the sample is radiated by 20 W ultraviolet lamp; the absorbance value is measured every 5 minutes; and after recording the data, the rhodamine B solution is returned to the reactor.

Results and discussion

Composition analysis of the coatings. When the peak emission current density is 15 A/cm², the power frequency is 2000 Hz and the oxidation time is 10 minutes, the XRD patterns of the ceramic coatings with and without cobalt oxide are shown in Fig. 1; the EDS patterns of the ceramic coatings with and without cobalt oxide are shown in Fig. 2.

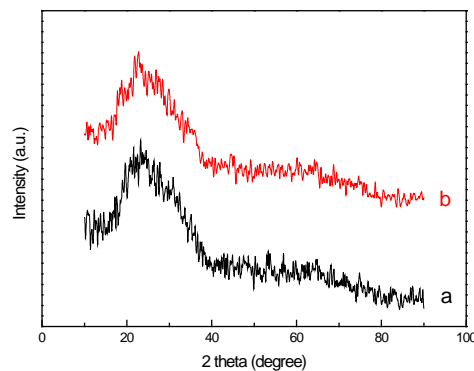


Fig.1 XRD pattern of ceramic coating; (a) without Co₂O₃; (b) with Co₂O₃

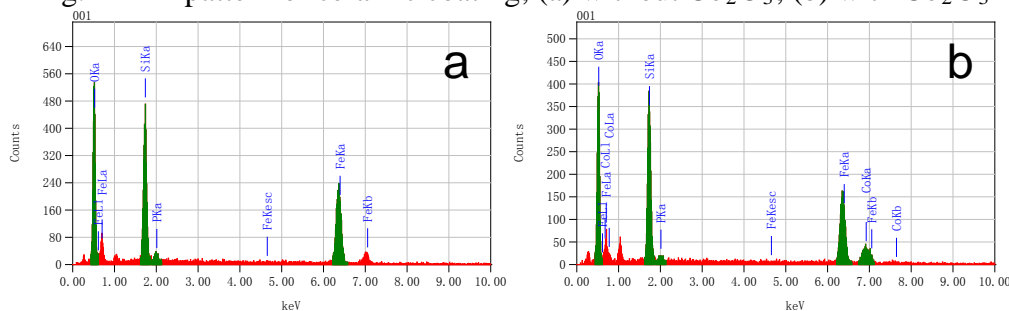


Fig.2 EDS pattern of ceramic coating; (a) without Co₂O₃; (b) with Co₂O₃

From Fig. 1, it can be noticed that both coatings obtained from solution with and without Co₂O₃ have nearly no crystalline phase. Fig. 2 displays that the two kinds of coatings comprise Fe, Si, O, little P elements; main alloy element Fe in Q235 carbon steel base appears in the ceramic coating; there is little other elements not detected in the ceramic coating. The component from the metal base and the electrolyte exists on the ceramic coating; and it shows that the elements in the electrolyte and the base takes part in the reaction during the micro-arc oxidation process, and the elements exist in the ceramic coatings. From Fig. 2 (b), it can be noticed that the coating obtained from solution with additives contain a large amount of Co element.

Surface morphologies and Roughness of the coatings. When the peak emission current density is 15 A/cm², the power frequency is 2000 Hz, the oxidation time is 10 minutes and the aqueous

solution is a mixture of three components ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and Co_2O_3), the surface morphology of the ceramic coating prepared by different Co_2O_3 dosage is as shown in Fig.3, the changing curve of the roughness is shown in Fig.4.

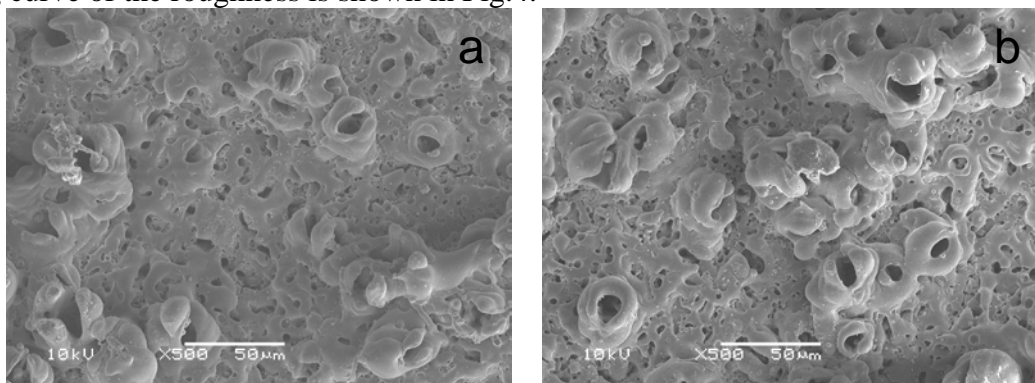


Fig.3 Surface morphologies of ceramic coating obtained with different Co_2O_3 dosage (a) 2.0 g/L Co_2O_3 ; (b) 5.0 g/L Co_2O_3

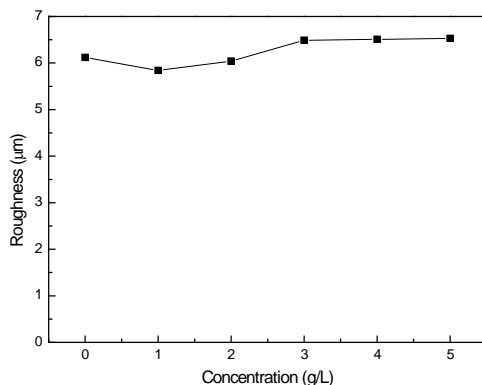


Fig.4 Effect of Co_2O_3 dosage on the roughness of the coatings

From Fig.3, it could be seen that the ceramic coating is typically characterized by the presence of dark circular pores and molten regions distributing all over the surface of the coating. These circular pores were the discharge residual channels in the discharge reaction and the molten regions were formed due to rapidly cooling effect of the electrolyte. From Fig.4, it could be seen that the ceramic coatings have high surface roughness, and the surface roughness is reaching $6.5 \mu\text{m}$. Fig.4 also could be found that the surface roughness of ceramic coating has nothing to do with Co_2O_3 dosage.

Thickness of the coatings. When the peak emission current density is 15 A/cm^2 , the power frequency is 2000 Hz, the oxidation time is 10 minutes and the aqueous solution is a mixture of three components ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and Co_2O_3), the thickness of ceramic coating prepared by different Co_2O_3 dosage is as shown in Fig.5.

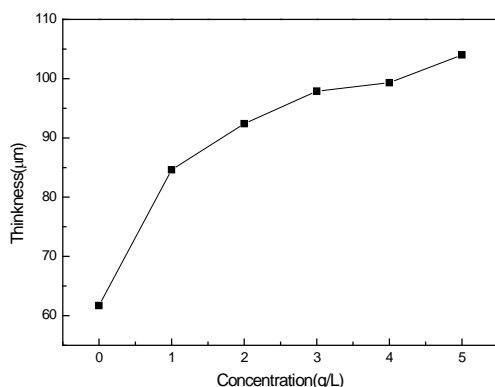


Fig.5 Effect of Co_2O_3 dosage on the thickness of the coatings

From Fig.5, it shows that the thickness of ceramic coating is gradually increased with the increase of Co_2O_3 dosage; it also shows that the thickness of ceramic coating well increases with the high Co_2O_3 dosage and it has a top thickness of more than $100\ \mu\text{m}$. This indicates that the additive has great effect on micro-arc oxidation; cobalt oxide participates in oxidation and affects the ceramic coating. The thickness of ceramic coating is always increasing with Co_2O_3 dosage; however, the oxidation reaction becomes unstable, so a maximum concentration of Co_2O_3 sets at $5.0\ \text{g/L}$.

Fenton reagent degradation of rhodamine B. The Fenton system is formed by the ceramic coating by micro-arc oxidation, and the H_2O_2 solution. Under the condition of UV-irradiation, $100\ \text{mg/L}$ of rhodamine B solution is degraded; and the obtained degradation curve is as shown in Fig.6. From Fig.6, it can be seen that the degradation rate of rhodamine B solution can reach 99% by Fenton reaction. It also finds that the Fenton reaction has an induced period of about 10 minutes, and after the induced period the Fenton reaction degrades rhodamine B more quickly. About 30 minutes, rhodamine B is not much left, most of it is degraded. After 30 minutes, rhodamine B residues are slowly degraded.

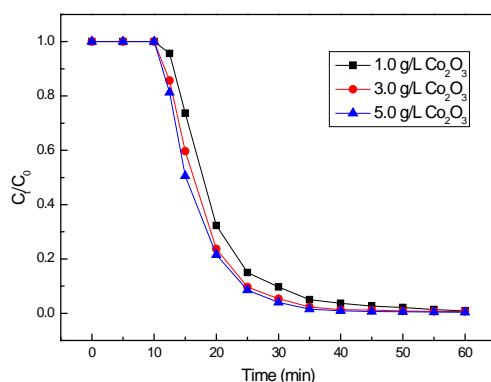


Fig.6 Effect of Co_2O_3 dosage on the degradation of RhB

Fig. 6 also shows the influence of Co_2O_3 dosage on the discoloration of rhodamine B. These experiments were also formed by the ceramic coating by micro-arc oxidation, and the H_2O_2 solution, under the condition of UV-irradiation, $100\ \text{mg/L}$ of rhodamine B solution was degraded. It is clear that a high concentration of Co_2O_3 dosage ($5.0\ \text{g/L}$) caused a shorter induction time and higher degradation rate and the discoloration of rhodamine B solution reached 75% when the reaction time is 20 minutes only.

Stability test of Fenton reagent. Fenton system is formed by ceramic coating and H_2O_2 solution; under the condition of UV-irradiation, $100\ \text{mg/L}$ rhodamine B is degraded; the rhodamine B is repeatedly degraded for five times by the ceramic coating to test that the efficiency of Fenton reagent degrading the organic pollutant is reduced along the increased using times; and the degradation efficiency is as shown in Fig.7.

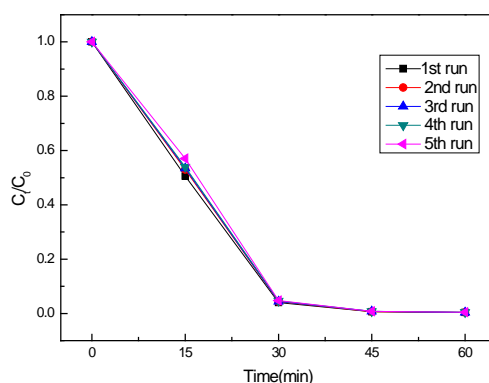


Fig.7 The stability of the coating for the degradation of RhB with cobalt oxide

As shown in Fig.7, the efficiencies of the Fenton reagent are not reduced along the using times. The curves of degradation are little variation from first use to fifth use, instead, in the early stages of degradation reaction slightly slower only. The stability can protect the environment and save source during actual use.

Summary

The morphologies of ceramic coatings are of irregular porous structure at the surface and the elements of electrolyte and Q235 carbon steel matrix joined micro-arc oxidation process. The ceramic coatings obtained with and without additives have no crystalline phase.

The degradation rate of rhodamine B solution can reach 99% by Fenton reaction which being composed of ceramic coating and H_2O_2 . Meanwhile, the degradation rate is increased with increasing Co_2O_3 dosage.

The Fenton reagent composed by ceramic coating and H_2O_2 has high photocatalytic stability, it still has excellent catalytic activity after five reaction cycles.

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