Materials Chemistry and Physics 124 (2010) 1134–1138

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

An electrochemical study of the corrosion resistance of boride coating obtained by thermo-reactive diffusion

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ARTICLE INFO

Article history:
Received 11 May 2009
Received in revised form 7 August 2010
Accepted 14 August 2010

Keywords:
Boriding
TRD
Corrosion resistance
Tafel polarisation
EIS

ABSTRACT

The corrosion resistance of three special steels improved by thermo-reactive diffusion (TRD) was investigated. Samples prepared from the test materials were treated at graphite crucible bath where borax, boric acid and ferro-silicon were mixed. The coating process was done at 1220 K for 6 h. The corrosion resistance of the borided samples was evaluated by the Tafel polarisation and electrochemical impedance spectroscopy (EIS). The results show that the boronizing process can improve the corrosion resistance of the steels. Also, coating porosity with exposure time has been determined using the corrosion potential difference between substrate and coating, and polarisation resistance, R_p, which is obtained through EIS modelling using equivalent circuits.

1. Introduction

The use of hard coating to improve surface layer properties is a method for protecting substrate from environmental effects. The hard coatings have high hardness, low coefficient of friction, low porosity, high corrosion and adhesive wear resistance [1].

Using of hard coating to produce wear resistant surface layer that can increase the durability of the equipment is now well accepted [2–4]. Hard coating of nitride, carbide, boride and carbonitride of transition metal are extensively used to improve the wear resistance of ferrous materials [5,6]. Also, the wear, the micro-hardness and the micro-abrasive properties of nitride, carbide, boride and carbonitride coatings on the steel-substrate were studied [7–11].

Hard coatings have been produced by lots of coating techniques such as CVD, PVD and thermo-reactive diffusion (TRD). TRD is a method for coating steel with a hard, wear resistant layer of carbides, nitrides and boride. In this process, elements such as carbon, nitrogen and boron are surfaced into deposited layer to form a dense and metallurgically bonded carbide, nitride or boride coating at the substrate surface [12]. TRD process and its advantages over other deposition techniques have been extensively reviewed [13].

The coatings on the substrate improve the performance of cutting equipments which are used in industry. Because of higher hardness of boride layers, in the range of 1400–2100 HV [14], these layers are appropriate choices to increase the durability of cutting tools.

When cutting tools with boride coatings are used in corrosive environment such as sanitary and food industries, aggressive ions can attack the surface layer and corrosion occurs.

Providing coating layers have porosity, aggressive ions can penetrate through coating and subsequently corrode the metal's bare surface. The formation of oxide on the surface results in blunting the cutting tools and decreasing their durability. The corrosion resistance properties of hard coating especially boride coating are studied less frequently than mechanical properties.

However, boride layers on some steels were investigated by previous papers [15,16]. In these investigations, the corrosion resistance properties of hard coating have been studied only by current density-potential measurements. The use of electrochemical impedance spectroscopy method and modelling of their data are powerful methods for investigating corrosion resistance.

The aim of this study is to investigate the corrosion resistance of boride coating on three kinds of steels with variable manganese element by Tafel polarisation and electrochemical impedance spectroscopy (EIS). Furthermore, the porosity of this coating, formed by TRD process, is examined by data which is extracted from electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials

The three kinds of steels used in this investigation, were produced precisely according to their chemical composition for a special work. The chemical compo-

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doi:10.1016/j.matchemphys.2010.08.047

Table 1
Chemical composition of steels in wt%.

Steel label	C	Mn	P	S	Fe
S1	0.3	–	0.02	0.01	Balance
S2	0.3	0.5	0.02	0.01	Balance
S3	0.3	1	0.02	0.01	Balance

sitions of these steels are given in Table 1. These steel compositions have exactly been controlled so as to achieve the steel with minimum amount of impurity such as sulfur, phosphorus, etc. The test samples were cut from the above-mentioned steels in rectangular shape with 10 mm × 10 mm × 8 mm dimensions. These samples were polished using 1200-grid emery paper to obtain a good surface preparation. They were, then, cleaned ultrasonically in acetone and dried. All corrosion tests were carried out at constant temperature, 30 °C, with electrolyte 3% NaCl in equilibrium with the atmosphere.

2.2. Coating procedure

The boriding method used in this study is thermo-reactive diffusion (TRD). In this coating procedure, borax and boric acid are used as boron source and ferro-silicon as activator. This bath was continuously mixed in a graphite crucible to obtain a homogeneous bath. The condition of coating procedure that was carried out in this study is arranged in Table 2. All coating processes were done at 1220 K for 6 h. When the boriding process finished, borided samples were removed from the graphite crucible, cooled in air and rinsed by water to clean the surface for future examination.

2.3. Characterization

The samples selected for metallographical studies were sectioned from one side, mounted, ground up to 1200 grid emery paper and polished by 0.3 μm alumina suspension. Then, the samples were etched by 4% nital before metallographical examination.

Impedance spectroscopy measurements were carried out at the open circuit potential (E_{ocp}/V (SCE)), using a computer-controlled potentiostat PAR EG&G Model 273A and Frequency Response Detector 1025. In a conventional three-electrode assembly, a Pt foil auxiliary electrode and a saturated calomel reference electrode (SCE) were used. The AC frequency was extended from 1000 kHz to 100 mHz, with 5 mV peak-to-peak sine wave being the excitation signal. Tafel polarisation measurements were carried out by the same equipment used in the impedance measurements without the frequency response detector. Tafel polarisation curves were obtained using a sweep rate of 0.3 mV s^{-1}. All potentials were reported versus saturated calomel electrode.

3. Result and discussion

3.1. Composition and morphology of the boride coating

Boron atoms have relatively small size and high mobility, therefore, they can easily diffuse into ferrous alloys, forming FeB and Fe_2B intermetallic.

The X-ray diffraction patterns of the borided steels coated in the mentioned bath are given in Fig. 1. It can be seen that the layers are made up of Fe_2B, FeB, MnB and Mn_2B depending on the kind of steel. The layers were formed by the chemical combination of Fe or Mn atoms in the substrate with boron atoms dissolved in bath. Steel samples labeled as S2 and S3 have enough activity of manganese element to form MnB and Mn_2B respectively.

Fig. 2 shows an optical microscope cross-sectional view of the borided S1, S2 and S3 steels. The coating on the S1 steel reveals a saw-tooth and less compact morphology. However, the coating on the S2 and S3 steels disclose smooth and compact morphology.

Carbucicchio and Palombarini [17] showed the effect of alloying element on the growth mechanism of iron borides. The alloying elements can inhibit the growth kinetics of the layers. These elements can concentrate at the tip of the boride columns and this process results in decreasing the active borax flux in this zone, therefore, it reduces their columnarity.

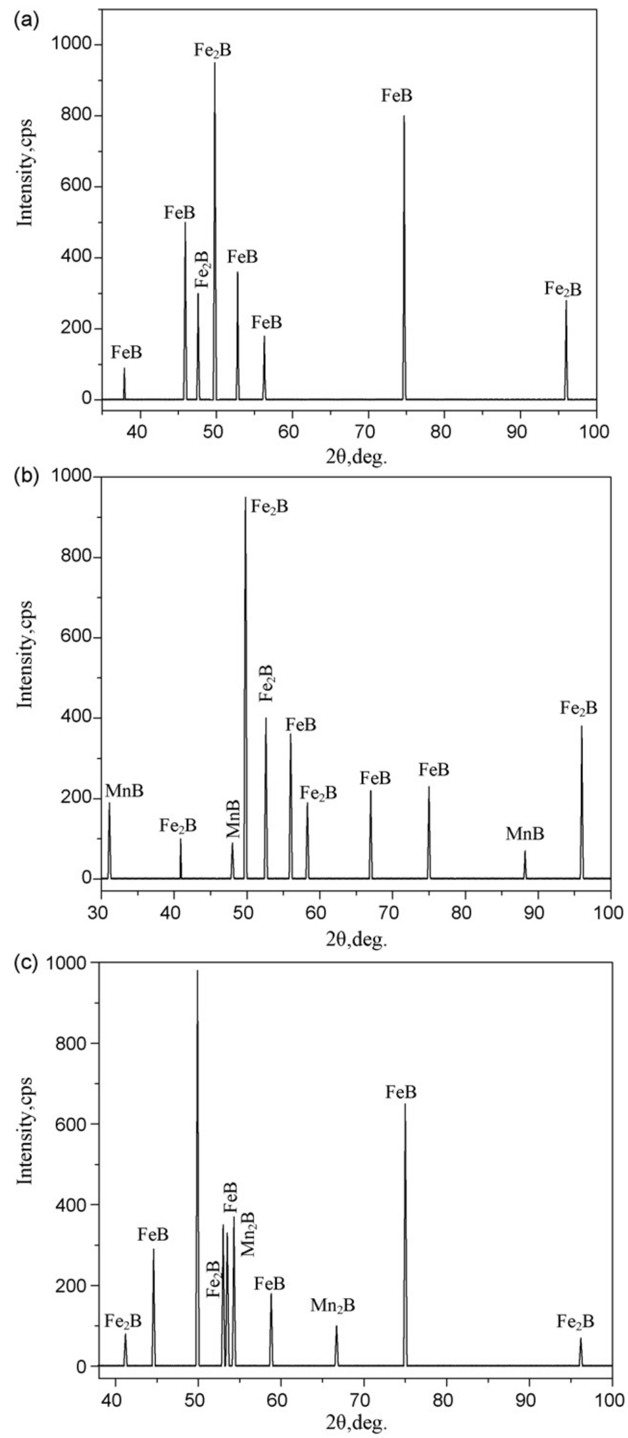

Fig. 1. X-ray diffraction patterns of the borided steels: (a) S1 steel, (b) S2 steel, and (c) S3 steel.

Table 2
Coating procedure condition applied to steel samples.

Percentage of bath compound (%)			Ratio of ferro-silicon to borax
Borax	Boric acid	Ferro-silicon	
65	14	21	0.3

3.2. Tafel linear polarisation studies of the layers

Due to their nature, boride layers produced by TRD process, usually have appropriate corrosion resistance [15]. The corrosion behaviour can be studied by short-time tests representing the exposure of a sample to a specific gaseous climate or a liquid