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The effect of boron-pack refreshment on the boriding of mild steel by the spark plasma sintering (SPS) process

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Abstract

Mild steel samples were borided with and without boron pack refreshment using the spark plasma sintering (SPS) process. Results show that the borided samples with boron pack refreshment developed a thicker boride layer compared to that without boron pack refreshment for the same boriding duration. When boriding duration is $t<120$ min, the boriding growth in the samples borided with boron pack refreshment followed a parabolic growth pattern. In contrast, the boride growth in samples processed without boron-pack refreshment deviates from parabolic at $t=60$ min. Computer simulation shows that the boron concentration change in the boriding media during the boriding process is an important factor affecting the composition and final thickness of the boride layer.

Keywords: Spark plasma sintering (SPS); Boriding; Growth kinetics; Non-steady-state diffusion; Microhardness

1. Introduction

Boriding is a thermochemical treatment technique used in various metal surface engineering processes [1–3], in which boron atoms diffuse into the surface of a workpiece to form borides with the base metal. Owing to the nature of the diffusion process, the boride layers formed show excellent adhesion to the base metal when compared to prevalent physical coating processes or various forms of advanced plating techniques. It offers a superior alternative to conventional surface hardening processes, such as carburizing, nitriding or carbonitriding [1,4,5], due to the superior hardness of borides (between 1500 and 2000 HV for ferrous borides). Besides its good wear resistance [2,6,7], the boride layer also has excellent corrosion and oxidation resistance, and a low coefficient of friction that greatly reduces the wear arising from adhesion, abrasion and surface fatigue [6].

The boriding process can be carried out in solid, liquid or gaseous medium [4,6,8–11]. Among these methods, only pack boriding has been widely used on a commercial basis. Yet the pack boriding process has the disadvantages of relatively high processing temperature (between 950 and 1100 °C) and long process duration (typically 4–15 h) for getting an effective boride layer thickness (~60 µm or more). Spark plasma sintering (SPS) boriding is introduced by Yu et al. to activate the pack boriding media as well as the workpiece with a high current discharge [4,12,13]. Previous studies [4,13] showed that SPS boriding technique significantly lowers activation energy for accomplishing the boriding operation.

Several investigations have been carried out on the boriding kinetics of various metallic materials [1,4,9,11,14–23]. The thickness of the boride layer is determined by a number of factors. It is determined by the applied boriding method as well as the temperature and the treatment duration. Other factors like pack thickness of the boriding mixture [8] and chemical composition of the substrate material [14] can also affect the thickness of the boride layer. Jain et al. [8] observed that, for boriding treatment carried out at 940 °C for 2 h, a boriding mixture pack thickness less than 10 mm will result in a thin boriding layer thickness of no more than 60 µm. Martini et al. reported that the starting boronizing potential of the boriding powder mixture also plays an important role on the phase composition and growth kinetics of

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the borided layer [15]. It is expected that the boron potential change during the boriding process is also an important factor affecting the final thickness of the boride layer. But in most reports on the boride layer growth kinetics, this factor is not taken into account. By assuming a non-changing surface and interface B-concentrations, the boride layer thickness is only the function of boriding temperature and boriding duration.

In this study, mild steel samples are borided by the SPS technique, and the effect of refreshing the boriding pack mixture after certain boriding duration on the boriding layer thickness is examined. Scanning electron microscopy (SEM) is used to characterize the microstructure of the boriding layer. X-ray diffractometry (XRD) is used to identify the phase composition of the boriding layer. A theoretical model is proposed to describe the phenomena, taking account of the depletion of the B-concentration of the boriding pack during the boriding process.

2. Experimental setup

Mild steel of grade AISI 1018, with a carbon content of 0.2%, was used in this study. The mild steel rods, with diameter of 10 mm and length of 5 mm, were ground, polished and cleaned with acetone before boriding. The boriding processes were carried out in the Sumitomo Coal Mining (SCM) SPS system (DR SINTER Model 1050) at a fixed temperature of 850 °C. The boriding medium contains B_4C as the boron source and SiC as the diluent. The effects of boriding durations and refreshment of boron pack on the boriding growth kinetics were investigated in this study.

The main parameter investigated in this study is the boriding duration. The boriding parameters for the samples are tabulated in Table 1. There were three sets of samples reserved for the boriding duration study. The first set (Set A) involved the once-through boriding of the mild steel for a full predetermined duration. The second set (Set B) of samples was borided for a total duration corresponding to the first set, except that the boriding was done with boron pack refreshment every 30 min. Other than the refreshing of the boron pack, all other conditions were kept constant. The third set (Set C) of the samples was first borided at 850 °C for 240 min, and then borided again with refreshed boriding media mixture at intervals of 30 and 60 min.

Table 1
Boriding parameters in this study

Total boriding duration	Temperature	Boriding duration		
		Set A	Set B	Set C
30 min	850 °C	30 min	–	–
60 min	850 °C	60 min	30 min × 2	–
90 min	850 °C	90 min	30 min × 3	–
120 min	850 °C	120 min	30 min × 4	–
150 min	850 °C	150 min	30 min × 5	–
180 min	850 °C	–	30 min × 6	–
240 min	850 °C	240 min	–	–
270 min	850 °C	–	–	240 min + 30 min
300 min	850 °C	–	–	240 min + 60 min

Table 2
Parameters for XRD analysis

Parameter	Setting
Anode	Cu
Generator voltage	40 kV
Tube current	30 mA
Alpha 1 & 2 wavelength	1.54056 Å, 1.54439 Å
Intensity ratio	0.5
Divergence slit	Fixed, 2
Receiving slit	0.2
2θ range	20.0000 to 90.0000
Scan step time (s)	2.00
Scan step size	0.040
Type of scan	Step
Monochromator used	Yes

After SPS boriding, the borided mild steel rods were sectioned, polished with Grade 4000 sandpaper and finally etched in 10% HNO_3 + 90% ethanol for 10 min to highlight the FeB and Fe_2B phases. The X-ray diffraction (Philips 7198W XRD) was used to identify the different phases contained in the sample. The parameters for XRD are given in Table 2. The scanning electron microscopy (SEM, JEOL JSM-5600LV, Japan) was employed to observe the morphology of the boriding layer. Since the boriding layer has a finger-like appearance, the definition of coating thickness is not obvious. A standard for the defining of the thickness of boriding layer was developed in a previous study [13], which considers both the height and the width of the boride fingers.

3. Results and discussion

Fig. 1 shows the morphology of the mild steel samples borided at 850 °C without boron pack refreshment (once-through boriding). Well-formed finger-like structures can be clearly observed from the SEM pictures. When the boriding duration is shorter than 90 min, boride layers with thin FeB layer on the top of Fe_2B layer can be found. The thickness of the Fe_2B phase is around three times that of the FeB phase. However, the FeB phase gradually vanishes with the further increase of the boriding duration, which is also confirmed by the XRD results [13]. The morphology of the borided samples with boron pack refreshment is shown in Fig. 2. The SEM pictures show that FeB phase is present in the boride layers even though the total boriding duration is as long as 150 min, indicating that different boriding processes were involved for the samples with and without boron pack refreshment.

The thickness of the boride layers vs. $t^{1/2}$ (t: total boriding duration) for the samples with and without boron pack refreshment is summarized in Fig. 3. The results in Figs. 1 and 3 indicate that, without boron pack refreshment, the total boriding growth (FeB + Fe_2B) does not satisfy parabolic growth after 60 min boriding duration. In a previous study, a mathematic model was developed to understand the abnormal growth phenomena [13] for the once-through borided samples. Those phenomena can be ascribed to the competition between two processes: the formation of the FeB phase and the phase transformation for FeB to Fe_2B phase at the boriding temperature. In