Low-temperature boriding of high-carbon steel

Xingliang He [a,1], Huaping Xiao [a,1], M. Fevzi Ozaydin [a], Karla Balzuweit [b], Hong Liang [a,*]

[a] *Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123, USA*
[b] *Department of Physics, Federal University of Minas Gerais, Belo Horizonte, Minas Gerais, Brazil*

ARTICLE INFO

ABSTRACT

Boriding has attracted great interests in improving mechanical performance of materials. The high processing temperature and the relatively thin boride layer, however, have limited its applications. Here we report a method to boronize high-carbon steels at a relatively low temperature (780 °C). Using the arc melting process, a thick (>400 μm) boronized coating is obtained. Two iron-boride phases (FeB and Fe_2B) coexist in the borided layer. The surface hardness of the steel is increased by ~57%, while the friction is reduced by ~17% and ~65% under steel-steel and steel-diamond contacts, respectively. In a 40,000 cycle wear test, the wear track on the steel surface becomes invisible after the boriding treatment. The low-temperature process developed in this study is applicable to other materials and is effective in making thick boride coatings with less energy consumption.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Boriding is a widely used thermo-chemical processing technique for surface modification [1,2].This process has been applied to a wide range of materials such as ferrous [3–6]/non-ferrous [7–11] alloys, and cermets [12–15] in order to improve their durability and mechanical performance. The boriding process entails diffusion of boron atoms into the lattice of a matrix material to form borided compounds. The diffusivity of boron atoms increases with temperature. A high temperature is essential for boronization because of two facts: 1) heat-induced formation of vacancies in the matrix and 2) activation of boron atoms to overcome the energy barrier for diffusion. Conventional boriding processes for ferrous were conducted at temperatures around ~1000 °C [16–23]. Such high temperature is one of the major sources in energy consumption in manufacturing. In addition, at an elevated temperature materials could deteriorate through several ways. Those include re-crystallization and phase transformation, reduction in dislocation density, precipitation or segregation of compositional elements, internal stresses elimination, and porosity [24,25]. In order to improve the boriding technology, a low-temperature process is always desirable.

For low-temperature boriding, activation energy for boron diffusion needs to be lowered [26,27]. This becomes particularly challenging for high-carbon steels (C %wt > 2%) [16–23]. This is because boron has relatively large atomic radius and small elemental affinity resulting low diffusivity in a carbon-rich matrix. Surface-modification methods developed to pre-treat materials for low-temperature diffusion

have been reported [28–35]. Such methods were based on mechanical processes and were suitable for non-ferrous metals or low-carbon (C %wt < 0.5%) steels. A non-mechanical pretreatment for low-temperature boriding has obvious advantages over above mentioned. In present study, arc melting is introduced as an alternative surface-modification technique for low-temperature boriding. This method generates significant amount of heat with an extremely high electric-field strength. It is capable to create a surface defect layer with the low activation energy in a short time. As a result, a high-carbon tool steel (CPM® S90V) is successfully boronized at a relatively low temperature (780 °C) with a thickness larger than 400 μm. The hard, slippery, and wear-resistant coating has potential to be used for high-carbon steels.

2. Experimental

2.1. Materials

A high-carbon steel (CPM® S90V) was used in this research. Its typical chemical composition is as the following: carbon, 2.30%wt; chromium, 14.00%wt; vanadium, 9.00%wt; molybdenum, 1.30%wt; manganese, 0.50%wt; silicon, 0.50%wt; and balance iron. Chemicals used for this research were purchased from Sigma-Aldrich: sodium tetraborate ($Na_2B_4O_7$), silicon carbide (SiC) nanopowder, ammonium chloride (NH_4Cl), sodium chloride (NaCl), phosphoric acid (H_3PO_4), and sulfuric acid (H_2SO_4).

2.2. Low-temperature boriding

The low-temperature boriding process is schematically shown in Fig. 1. The steel surface was pretreated using an arc-melting process.

---

* Corresponding author at: Department of Mechanical Engineering, TAMU, College Station, TX 7843-3123, USA. Tel.: +1 979 862 2623; fax: +1 979 845 3081.
E-mail address: hliang@tamu.edu (H. Liang).
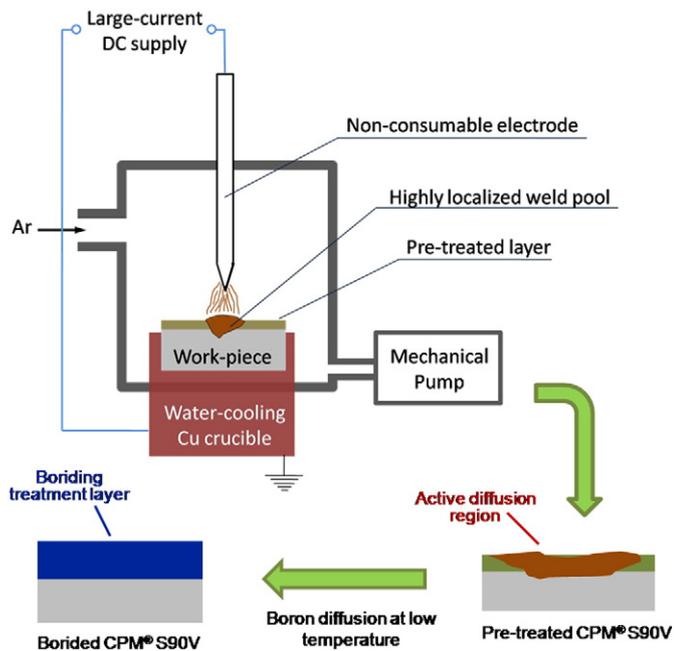[1] These authors contributed equally to this work.

Fig. 1. Schematic flowchart of low-temperature boriding process.

The work piece was placed in a water-cooling copper crucible (2 °C). The surface was treated in argon atmosphere by applying 90 A of current to a tungsten electrode for 5 s. Such pretreatment maintained the shape of the work piece while creating an active diffusion region on its surface. Small activation energy was needed for the diffusion of boron atoms in the defect layers, such as dislocation, void, and grain boundary. This led to the efficient boronization at low temperature (780 °C). Subsequently, the arc-melting pre-treated high-carbon steel (CPM® S90V) was boronized. The sample was placed in a ceramic crucible and was covered by boron-source powder. The powder contained 73%wt $Na_2B_4O_7$, 24%wt SiC, 1.5%wt NH_4Cl, and 1.5%wt NaCl. The $Na_2B_4O_7$ that could be melted at ~750 °C was used as the chemical source of boron. A slightly high temperature (780 °C) was adopted for low-temperature boriding using $Na_2B_4O_7$. The NH_4Cl and SiC were used as an activator and a carbo-thermally reducing agent, respectively. The NaCl was added into the boron-source powder as a diluting agent for the purpose of easy post cleaning. During boronization, the ceramic crucible was transferred to a resistance furnace that was preheated to 780 °C and was kept for 12 h. This was selected based on the consideration of the kinetics in the process. The borided thicknesses were ~60 μm, ~130 μm, ~400 μm, and ~420 μm, respectively after 2 h, 4 h, 12 h, and 24 h of treatment. The coating reached an optimal thickness after 12 h. The sample was then air-cooled, and the remaining powder was washed off in hot water. Experiments also showed that without arc-melting, the steel surface could not be borided at the same temperature.

2.3. Characterization

Specimens were cut and the cross section was polished using sand papers of grit sizes 800, 1200, and 2400. The final polish was with fumed silica suspension with a polishing cloth. The sample surface was then electrochemically etched in a solution of 50%vol H_3PO_4 and 50%vol H_2SO_4 under 5 V for 6 s. Samples were imaged using an optical microscope (Keyence VHX-600E) and a field emission scanning electron microscope (FESEM, FEI Quanta 3D FEG). Microstructures were characterized using a D8 advance X-ray diffractometer (XRD, Bruker).

The micro-hardness was measured on the cross-sectional area using Vicker's hardness tester (Macro TH720) under a load of 10 g. Tribological experiments were conducted using a reciprocal pin-on-disk

configured tribometer (CSM Instruments). Two pins were used: one was of synthetic diamond and the other of E52100 bearing ball. Each wear experiment was conducted for 40,000 cycles under an applied load of 3 N at a linear speed of 6.28 cm/s. The length of wear track was 3 mm for all tests. Surface profile before and after wear test was obtained using a profilometer (Veeco DEKTAK 150).

3. Results and discussion

3.1. Morphology and microstructure

The sample's cross-sectional area is examined through SEM images as shown in Fig. 2. Fig. 2a, a thick borided layer is observed high-carbon steel. The thickness of the layer is larger than 400 μm. Further study was conducted on this sample. Fig. 2b is the magnified area of "1" labeled in Fig. 2a. Here two distinguished regions are shown, the borided area, on the right of the dash line and the matrix, left. Several iron-boride phases have been reported [36–38]. This will be investigated using XRD to be discussed later. Fig. 2c is the magnified area corresponding to "2" labeled in Fig. 2a. This area is borided and there are three different morphology, corresponding different microstructures, light background, light grey spots, and dark grey spots. The light background is a solid solution of iron, chromium, and vanadium. The light and dark grey spots are two different secondary phases in the CPM® S90V resulted from the prior process. Fig. 2d shows the magnified SEM image of the borided layer (the circled area 3 in Fig. 2a). Comparing to the steel matrix (Fig. 2c), the light grey spots disappear in the borided layer (Fig. 2d), while the size of the dark grey spots becomes smaller. To confirm the nature of the microstructure, XRD analysis was conducted and results are shown in Fig. 3. Here the formation of iron borides is seen. The bottom black plot of Fig. 3a shows the XRD pattern of the as-received CPM® S90V sample. The matrix structures could be indexed by (110), (200), and (211) planes from a cubic Fe–Cr/Fe–V structure. In addition to the XRD patterns of the steel matrix, more peaks could be seen from the top red plot of Fig. 3a. Boriding the high-carbon steel leads to the formation of two iron-boride phases: FeB and Fe_2B. Each orientation plane is labeled in the figure, and these two phases coexist in the borided layer. The other metallic elements in steel, e.g., chrome, vanadium, and molybdenum, are used as agents for strengthening, anti-corrosion, oxidizing inhibition, and otherwise. They normally form metal carbides at the grain boundaries with excellent thermo-stability [39–46]. As a result, only iron and iron-boride phases are observed in the XRD pattern. In addition, a slight shift of the matrix XRD patterns in the borided layer is another difference found (Fig. 3b). All three characteristic XRD peaks shift their 2θ angles toward high values, meaning the narrowing of the inter-plane spacing. Boron atoms present in the boronized zone by occupying the interstitial sites. Once the boron enters Fe–Cr/Fe–V solid solutions, lattice mismatch in the borided layer could induce the shifts of the matrix XRD patterns. The arc-melting pre-treatment assists formation of a thick (>400 μm) coating at a relatively low temperature (780 °C). FeB and Fe_2B coexist in such boronized coating on the high-carbon steel surface.

3.2. Surface hardening and friction reduction

Low-temperature boriding is able to increase the hardness. The hardness of the as-received CPM® S90V sample is ~680 HV. Fig. 4a shows three indents across the borided surface. The darker area is the borided region, and the brighter area is the steel matrix nearby the borided surface. A visual difference in the size of the indents can be distinguished, indicating the greatly increased hardness from the bulk to the borided region. On the borided surface the measured hardness is ~1070 HV (indent # 1 in Fig. 4a), which is ~57% increase of the reference sample (~680 HV). At the indent nearby the steel matrix (indent # 2 in Fig. 4a), the hardness is 779 HV. This value is progressively reduced to 603 HV at the indent right out of the diffusion region (indent # 3 in