



# Formation of multi-component boronization by adding transition metal group VIB

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## ABSTRACT

Multi-component boron coatings of boron and transition metal group VIB (Cr, Mo, W) were studied on low carbon steel AISI 1018 by using simultaneous powder pack method of boronizing and metalizing at 950 °C. The coating morphology was observed and the coating thickness was measured. The microhardness across the depth of coating was also investigated. XRD phase identification revealed forming of Fe<sub>2</sub>B, Cr<sub>2</sub>B, and CrB on two-component diffusion of B–Cr; Fe<sub>2</sub>B and MoB on two-component diffusion of B–Mo, and Fe<sub>2</sub>B, FeB, W<sub>2</sub>B, and Fe<sub>7</sub>W<sub>6</sub> on two-component diffusion of B–W. XRD quantitative phase analysis was determined by using Rietveld Refinement. Moreover, Synchrotron Microfluorescence was used to identify the element distribution. Finally, the mechanism of formation of multi-component boronizing by adding transition metal group VIB was purposed responding to the coating formation and atomic size of the transition metals.

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## 1. Introduction

Multi-component boronizing is a thermo-chemical surface hardening process which involves boronizing and metalizing. By this process, boron and one or more metallic elements diffuse into the metal substrate and form boride phases and/or solid solution metallic boride layers. The boron-based coating can provide high wear resistance, corrosion resistance and high temperature oxidation resistance on metal substrates [1–4]. However, the specific properties of boron-based coating are still in need leading to the development of multi-component boronizing.

In multi-component boronizing, the complex boron phases (M–Fe–B; M = Al, Cr, Cu, Ni, etc) provide the increasing the microhardness, corrosion resistance, wear resistance and high temperature oxidation, compared to those of iron–boron phases in conventional boronizing. Many recent research works have reported these improved properties of borocopperizing, borochromizing, boronickeling borovanadizing and boroniobizing and boroaluminizing [5–11]. However, the study of multi-component boronizing based on the diffusion of boron and transition metals in groups in the periodic table has not been investigated yet. This present work devotes to the study of formation and characteristics

of multi-component boron-based coating when transition metal group VIB is added as the second element to the boron coating.

## 2. Experimental procedure

In this research work, low-carbon steel AISI 1018 was used as a substrate material. The chemical composition of AISI 1018 is 0.200% C, 0.720% Mn, 0.008% P, 0.008% S, 0.016% Si, 0.065% Al, and 98.98% Fe by weight. The steel samples with dimensions of 10 × 10 × 3 mm were ground to get smooth surface finish and then cleaned with acetone to remove dirt and grease. Three transition metals from group VIB (Cr, Mo, W) were used to add individually as the second element to form the multi-component boron-based coating. Thus, three multi-component systems of Cr–Fe–B, Mo–Fe–B and W–Fe–B were studied in this work. The simultaneous powder pack method of boronizing and metalizing was used, which consisted of powder mixtures of boron carbide, activator, and transition metal, and carried out at 950 °C for 4 h under an inert atmosphere. After the thermo-chemical treatment was completed, the specimens were mounted, ground and polished for observing the microstructure and coating thickness by optical microscope and measuring the microhardness across the coating depths by microhardness tester with load of 10 gf. The phase identification was investigated by XRD (with the 2θ scan range of 10–140°, the step size of 0.02° and 20 s time period per step) and the phase quantity and microstrain were analyzed by Rietveld Refinement Method. The Synchrotron Microfluorescence (with 200 nm beam

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size and 10–10.5 keV beam energy) was also used to detect the element distribution across the coating depths of multi-component boronized specimens.

### 3. Results and discussion

In this study, the single-component of Fe–B system was used as a comparative with the multi-component Cr–Fe–B, Mo–Fe–B and W–Fe–B systems. The needle-like or saw tooth structure was formed as a coating on low carbon steel for the single-component and multi-component specimens as shown in Fig. 1. In case of single-component system of Fe–B, deboronizing was observed as illustrated in Fig. 1(a). This occurrence led to the decrease of the coating thickness on the substrate and to the decrease of microhardness in the deboronized coating area. Without deboronizing, the Fe–B specimen is able to provide the coating thickness about 180  $\mu\text{m}$  at the heating process of 950  $^{\circ}\text{C}$  4 h (based on Universal Global Products, LLC. experimental data). The coating thickness, phases present, phase quantity, microstrain and microhardness of four systems (Fe–B, Cr–Fe–B, Mo–Fe–B, W–Fe–B) are summarized in Table 1.

To evaluate the microstrain of boride coating phases, NIST SRM 660  $\text{LaB}_6$  was used as a size-strain standard or instrument line position and profile shape standard, and compared with the observed XRD specimen spectrum. The analysis was processed by using Rietveld Refinement method. In theory, the lattice distortion from either interstitial or substitutional atoms can introduce the lattice strain or microstrain in the crystal structure. In case of single-component of Fe–B, boron atoms diffuse and fill the interstices of iron crystal lattice. Due to the difference of electronegativity of iron and boron, the intermetallic compounds of FeB and  $\text{Fe}_2\text{B}$  are formed. Although boron has a small atomic size of 0.460  $\text{\AA}$ , it is ordinary larger than the interstitial sites of  $\alpha$ -iron which is

about 0.360  $\text{\AA}$ . As a consequence, boron atoms introduce lattice strain on the iron structure, leading to microstrain on  $\text{Fe}_2\text{B}$  and FeB as calculated in Table 1. In multi-component systems, not only the interstitial diffusion of boron in iron, but also the substitutional diffusion of transition metals in iron occurs. The intermetallic boride compounds and the substitutional solid solution of transition metal-iron were detected. As the results from Table 1, when the atomic size of transition metals in group increases, the microstrain of boride phases and solid solution transition metal-iron phase in multi-component boronization has a trend of increase. This is due to the substitution of atoms in iron lattice with larger transition metal atoms, which introduces more lattice distortions and produces higher microstrain. Moreover, the microstrain of FeB phase in the single-component of Fe–B may be higher than expected because of deboronizing, which results to high imperfect crystal structure of FeB.

In the single-component of Fe–B deboronizing was observed. The coating was affected due to the loss of boron after forming the intermetallic compounds, resulting to the decrease of microhardness in deboronized coating area. However, adding the transition metal group VIB to the single-component of Fe–B was found to eliminate the deboronizing in the coating. Furthermore, the microhardness of multi-component boronization increases from top to bottom in group, which relates to the atomic size of transition metals in group as seen in Table 1. The valence electrons and electron configuration are used to explain the microhardness of the boride phases [11,12]. When the boride phases of iron and boron are formed, isolated boron atoms ( $2s^2sp^1$ ) may be converted into  $sp^3$ -configuration which is the most stable configuration. As well iron atoms ( $3d^64s^2$ ) tend to form stable  $d^5$ -configuration which results to a donor electron. Therefore, during the formation of boride phases of iron and boron, localized electrons occur and form the covalent bond between the  $sp^3$ - and  $d^5$ -configurations, which

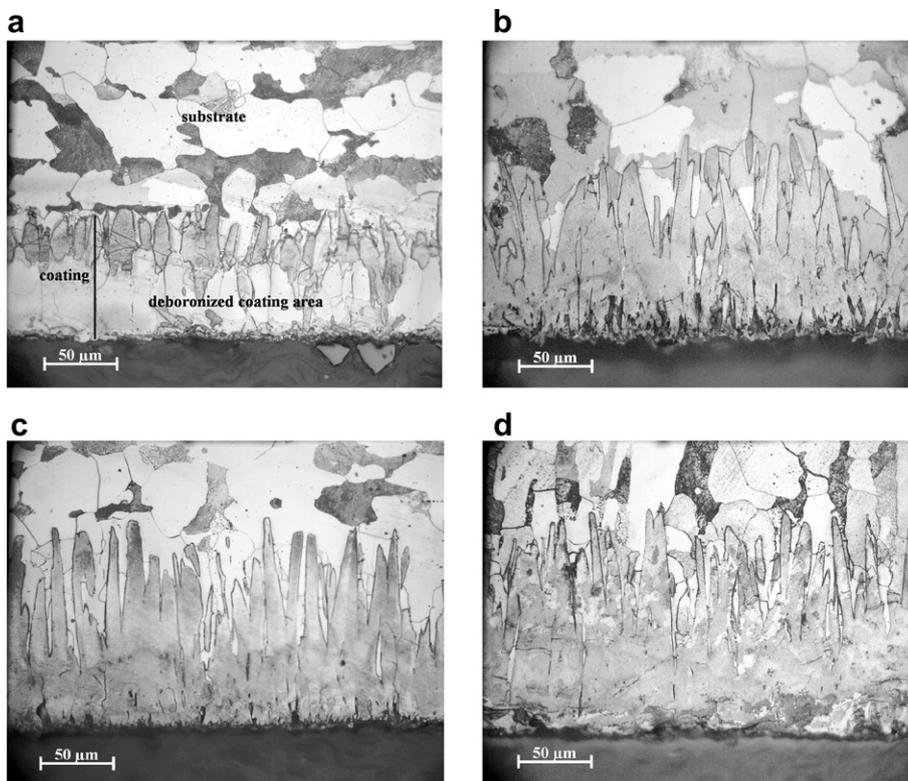


Fig. 1. Needle-like structures of (a) single-component Fe–B, (b) multi-component Cr–Fe–B, (c) multi-component Mo–Fe–B and (d) multi-component W–Fe–B.

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