

Mechanical Behaviour of Non-Oxide Boride Type Ceramics Formed on The AISI 1040 Plain Carbon Steel

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A series experiments were performed to evaluate mechanical behavior of non-oxide boride type ceramics formed on the AISI 1040 plain carbon steel. Boronizing was performed in a slurry salt bath consisting of borax, boric acid, and ferro-silicon at 950°C for 2-6 h. The AISI 1040 steel used as substrate material was containing 0.4%C, 0.13%Si, 0.65%Mn, 0.02%P, 0.014%S. The presence of non-oxide boride type ceramics Fe₂B and FeB formed on the surface of steel was confirmed by metallographic technique and X-ray diffraction (XRD) analysis. The hardness of borides measured via Vickers indenter with a load of 2 N reached a microhardness of up to 1800 DPN. The hardness of unborided steel was 185 DPN. The fracture toughness of borides measured by means of Vickers indenter with a load of 10 N was about 2.30 MPa · m^{1/2}. The thickness of boride layers ranged from 72 µm to 145 µm. Boride layers have a columnar morphology.

Key words: Hardness, Borides, Plain carbon steels, Fracture toughness, Ceramics.

I. Introduction

Boronizing is, like nitriding and carburizing surface hardening processes, a thermal diffusion of boron into the surface layer of a workpiece by thermochemical treatment. In the boronizing process, boron atoms are introduced into the metal lattice at the surface of workpiece through thermal energy to form borides with atoms of the substrate. When boron atoms diffuse into the surface zone of a ferrous workpiece, a compound layer is formed that consists of either one iron boride (Fe₂B) or two iron borides (Fe₂B in the inner layer, FeB in the outer). Borides of the transition metals have high hardness values which may be advantageous for tribological applications. Tribologically interesting boride coatings are titanium diboride and iron boride. Iron boride coatings may be useful as brake materials because of their peculiar tribological property of giving very low wear and high friction at the same time. Thermal conductivity of borides are generally high, relative to many other ceramics. Also, thermal shock resistance of diborides is excellent, primarily due to their high thermal conductivity. It has well been known that boron reacts with many elements in the periodic table to form a wide variety of compounds. The strong covalent bonding of most borides is responsible for their high melting points, moduli and hardness values. Borides generally have high negative free energies of formation, which gives them excellent stability under many condi-

tions.¹⁻⁴ Actually borides are intermetallic compounds in which one element is boron and the other is a metal with compositions ranging from M₃B to MB₁₂; they are harder, chemically less reactive, and electrically more resistive than the constituent metallic elements are. They also have high melting points. Also, borides are non-oxide ceramics and could be very brittle.^{4,5} Borides are generally prepared by high temperature reactions. There are several methods which are used to make powders, in situ bodies or coating include;

a) Direct reaction of the elements by combustion synthesis, b) Reduction of the metal oxide and boron oxide with Al, Si, Mg, and/or B, c) Reaction of metal oxide or carbide with B₄C or BN, d) Deposition by fused-salt electrolysis, e) Deposition from the vapor phase.^{4,6} Hard boride layers can also be obtained by salt-bath and plasma boriding techniques. These layers are very hard and can afford very high wear and corrosion resistance to sliding surfaces.^{7,8} the boride layers exhibit strong bonds due to interlocking of columnar morphology with the base metal.⁹ As it is well-known, a Vickers hardness impression on the surface of a brittle ceramic is accompanied by a crack. Vickers or Knoop diamond pyramids utilized in hardness testing produce two types of crack pattern: radial-median and lateral. The first hypothesis that indentation cracking could give an indication of toughness was done by Palmqvist in 1957, while working exclusively on ceramics.^{10,11} Existing models of the fracture process are

based on oversimplistic elastic/plastic analyses and it may be written as follows: $K = X P/c_0^{3/2} = Kc$ where P is load, c_0 is the radial half crack length, and the parameter X represents the intensity of the residual driving force. For an ideal elastic/plastic case in which the indentation process can be represented by an expanding cavity model, the parameter X can approximately be expressed as $X \propto (E/H)^{1/2}$, where E and H are Young's modulus and hardness, respectively. In this study, we attempt to elucidate the some mechanical properties of borides for example, Fe_2B , FeB formed on the surface of AISI 1040 carbon steel. In order to determine morphological and structural characterization of borides formed on the surface of AISI 1040 carbon steel optical microscope and scanning electron microscope (SEM) were used. For hardness and layer thickness measurements of borides formed on the surface of AISI 1040 carbon steel Wilson Tukon Microhardness tester was utilized.

II. Experimental Procedures

1. Test materials

The test material used for this study was AISI 1040 plain carbon steel, essentially containing 0.4 wt.% C, 0.13 wt.% Si, 0.65 wt.% Mn, 0.02 wt.% P, and 0.014 wt.% S. The test piece of AISI 1040 plain carbon steel had a rectangular shape with a nominal dimensions of 5 mm × 4 mm × 3 mm. Vickers hardness values of untreated steel and borides formed on the steel substrate were 1.85 and 18 GPa, respectively.

2. Boronizing

Boronizing was performed in a salt bath consisting of borax, boric acid and ferro-silicon by conventional slurry method at 950°C and at atmospheric pressure for 2-6 h. The samples were processed in graphite crucible in an electrical resistance furnace, then quenched in air. Details of the experimental set-up are described elsewhere.¹²⁾

3. Hardness, fracture toughness and boride layer

The hardness of the unborided AISI 1040 plain carbon steel and borides formed on the surface of AISI 1040 plain carbon steel substrate were measured by means of Wilson Tukon Microhardness tester with a load of 2 N. In order to measure fracture toughness of borides formed on the surface of AISI 1040 plain carbon steel substrate Vickers indenter was utilized. The thickness of FeB and Fe_2B were measured by means of optical microscope attached to a digital thickness measuring instrument.

4. The characterization of borides

The morphology and types of borides formed on the surface of AISI 1040 plain carbon steel substrate were confirmed by means of classical metallographic technique. The presence of borides formed in borided layer was determined via x-ray diffraction (XRD) analysis.

A Phillips high-resolution diffractometer was utilized for x-ray diffraction (XRD) analysis of borides formed on AISI 1040 plain carbon steel surfaces. A $CuK\alpha$ radiation with a wavelength of 1.54056 Å was used over a 2θ range of 20° to 90°.

III. Results

1. Structure of borides

Optical and SEM examinations of cross-sections of borided AISI 1040 plain carbon steel showed a needle-shaped and/or columnar morphology to a depth of 145 μm and good bonding of the film to the substrate. Fig. 1a shows an optical cross-sectional view of borided AISI 1040 plain carbon steel substrate including microhardness marks. Fig. 1b shows a SEM cross-sectional view of borided AISI 1040 plain carbon steel. The FeB boride was located near the surface ranged in thickness from 5 to 10 μm. The second boride layer Fe_2B ranged in thickness from 72 to 145 μm. It had a needle-shaped structure.

2. Hardness, boride layer and fracture toughness

The hardness values of borides formed on the surface of AISI 1040 plain carbon steel were measured via Vickers microhardness tester under a load of 2 N. The Vickers hardness value of unborided steel substrate was about 1.85 GPa. Whereas, Vickers hardness value of borides formed on the steel substrate was about 18 GPa. As a

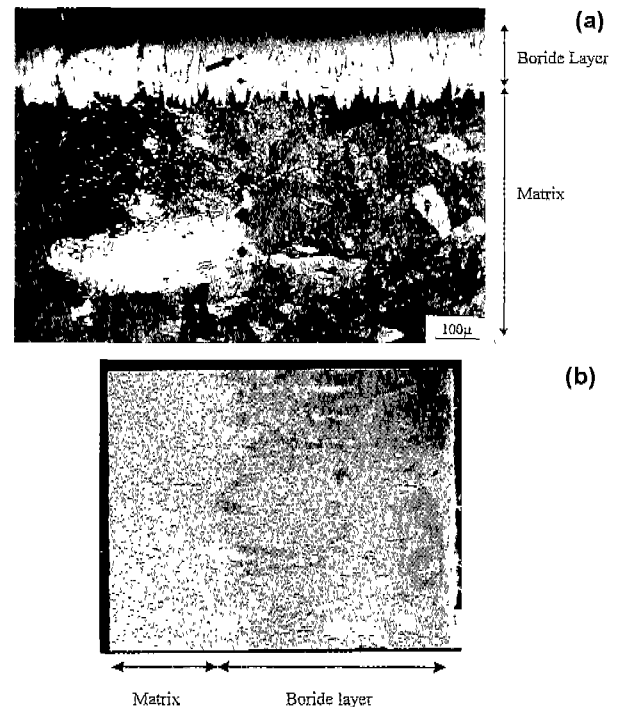


Fig. 1. (a) Optical micrograph of borided AISI 1040 plain carbon steel including microhardness marks indicated by arrow. (b) SEM cross-sectional view of borided AISI 1040 plain carbon steel.

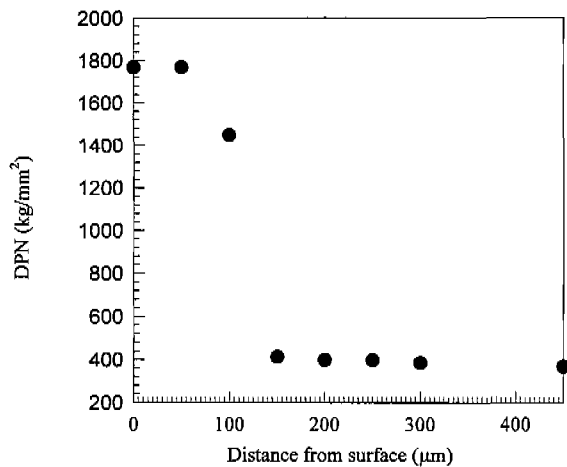


Fig. 2. The variation of hardness of borided AISI 1040 plain carbon steel as function distance from surface.

result, the hardness of borides are much higher than that of unborided substrate. These can be attributed to the presence of FeB and Fe₂B. In thermochemical boronizing treatments high hardness is attained directly through the formation of borides and does not require quenching. The hardness results are plotted the against distance from surface in Fig. 2.

As it can be seen in Fig. 2 hardness distribution diagram has three distinct regions, which are; (i) layer having borides, (ii) transition zone being below boride layer, where boron makes solid solution which has hardness less than that of borides and higher than that of original alloy, (iii) matrix, which are not affected by boron.

The prominent phases formed on the surface of AISI 1040 plain carbon steel substrate are FeB and Fe₂B (see Fig. 1). The FeB phase was located near the surface and ranged in thickness from 5 to 10 µm. The second Fe₂B

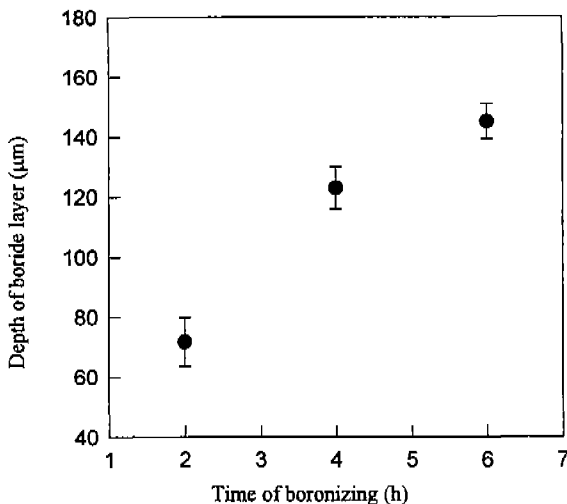


Fig. 3. Depth of borides formed on the surface of AISI 1040 plain carbon steel for different lengths of boronizing time.

Table 1. Depth of Boride Layers as Function of Boronizing Time

Time of boronizing (h)	Depth of boride layer (µm)
2	71.72 ± 8.10
4	122.75 ± 6.98
6	144.89 ± 5.84

Table 2. The Fracture Toughness of Borides Formed on the Surface of AISI 1040 Plain Carbon Steel as Function of Boronizing Time

Steel	Boronizing time (h)	Fracture toughness (MPa · m ^{1/2})
AISI 1040	4	2.30
	6	2.20

phase ranged in thickness from to 72 to 145 µm. As it is well-known, the thickness of borides depends strongly on chemical composition of substrate, boronizing time and process temperature. Fig. 3 shows the thickness of ceramic layer as a function of boronizing time.

As it can be seen in Fig. 3. there is nearly a parabolic relationship between boride layer thickness and boronizing time. Boride layer thickness values as a function of boronizing time are given in Table 1.

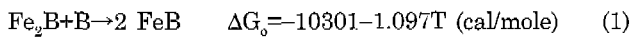
As it is well-known, the fracture toughness of borides formed on the surface of steel substrate depends strongly on alloying elements, steel substrate has, and boronizing time. It was observed that the longer boronizing time, the lower fracture toughness. It is likely that, this consequence of the presence of harder FeB phase. Since it is well-known that the the longer boronizing time results in the more FeB boride. However, it must be noted that the type of boride formed on the steel substrate is more than one. Each one, individually, has its own fracture toughness value, but it is unknown, what kind of interactions exist between different borides, and the influence of each one is hard to discern.

The fracture toughness of borides formed on surface of AISI 1040 plain carbon steel as a function of boronizing time are given in Table 2.

IV. Discussion

Optical microscope and SEM examinations of borides formed on the surface of AISI 1040 plain carbon steel revealed a needle-shaped morphology and good bonding of the layer to the substrate. The thickness of boride layer, doubtless, is closely related to the alloying element that base steel has and boronizing time. The diffusion coefficient of boron at 950°C is $1.82 \times 10^{-8} \text{ cm}^2 \cdot \text{sec}^{-1}$. for boride layer and $1.53 \times 10^{-7} \text{ cm}^2 \cdot \text{sec}^{-1}$ for diffusion zone respectively. As a result, the boron containing diffusion zone is extended several fold the depth of boride layer into steel substrate.¹³⁾ Previous thermochemical boronizing studies by Badini et al.¹⁴ also showed that firstly, boron diffu-

sion into the metal with a velocity slightly dependent on the lattice type: face or body centered (the respective diffusion coefficients as regarded in literature are $1.53 \times 10^{-7} \text{ cm}^2 \cdot \text{sec}^{-1}$ at 950°C and $1.45 \times 10^{-7} \text{ cm}^2 \cdot \text{sec}^{-1}$ at 900°C . The diffusivity of boron at 900°C is $9.25 \times 10^{-9} \text{ cm}^2 \cdot \text{sec}^{-1}$ for Fe_2B boride layer and $1.45 \times 10^{-7} \text{ cm}^2 \cdot \text{sec}^{-1}$ for Armco iron respectively.¹⁵⁾ On the contrary boron solubility in iron is very low and strongly dependent on irregularities in the crystal lattice and therefore also on the purity of the same metal. When a suitable boron concentration is reached at some points on the surface of the metal, Fe_2B crystal begin to nucleate. Boron is likely to react with Fe_2B at the B-FeB interface producing FeB. A scheme reaction might be as follow.¹⁶⁾



Depending on the boronizing time, the thickness of boride layers ranged from 72 to 145 μm . Previous studies by Bindal¹⁷⁾ and Pelleg *et al.*¹⁸⁾ showed that boronizing of carbon steels usually leads to formation of two boride phases FeB and Fe_2B . The FeB phase is adjacent to the upper surface and is about 5-10 μm thick. The Fe_2B phase located directly below the FeB, is much thicker than the FeB phase and consists of columnar grains (see Fig.1).

Also it is worth noting that, for the same coating, columnarity is lower at the FeB/ Fe_2B interface than at the Fe_2B /substrate interface.¹⁹⁾

The presence of FeB and Fe_2B are identified by optical microscopy, SEM and x-ray diffraction (XRD) analysis. The FeB boride is harder than Fe_2B is, since FeB is richer in B than Fe_2B is. Microhardness measurements are made from the surface to interior. Thus, the hardness of both the boride layer and matrix are compared. It was observed that hardness distribution diagram has three distinct regions, which are (i) layer having borides, (ii) the region below column, where boron makes solid solution which has less hardness than that of borides and higher than that of original alloy, (iii) matrix, which is not affected by boron (see Fig. 2). Previous studies by Brakman *et al.*²⁰⁾ showed that carbon does not dissolve significantly in FeB and Fe_2B . On boronizing, carbon is driven ahead of the boride layer and, together with boron, it forms boron-cementite, $\text{Fe}_3(\text{B},\text{C})$ as a separate layer between Fe_2B and the matrix. It was observed that the presence of carbon up to a content of 0.4 wt.% in steel brings about an increase in the hardness of the diffusion layer for both FeB-type and for Fe_2B -type phases. Since carbon is almost insoluble in these phases, but accumulates in the area adjacent to matrix in the form of carbides.²¹⁾ The hardness value of untreated substrate was 1.85 GPa. Whereas the hardness of borides layer ranged from 15 to 18 GPa. From these measurements, the hardness of non-oxide borides formed on the surface of AISI 1040 plain carbon steel was found to be much higher than that of the matrix (Fig. 2). These are the consequences of the presence of hard Fe_2B and FeB in the boride layer as deter-

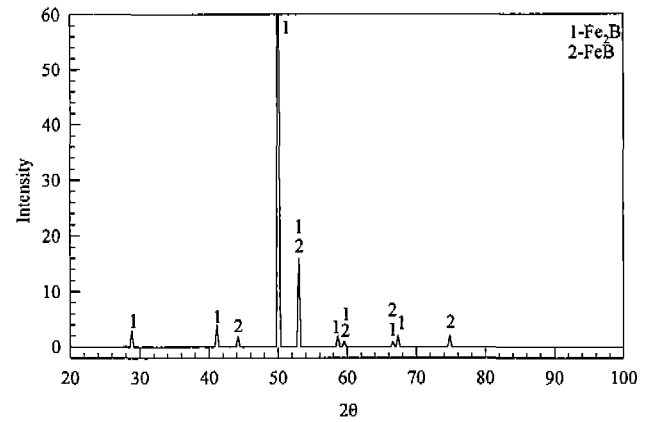


Fig. 4. X-ray diffraction patterns of borided AISI 1040 plain carbon steel.

mined by x-ray diffraction (XRD) analysis (Fig.4).

For fracture toughness measurements of borides formed on the surface of AISI 1040 plain carbon steel, the elastic modulus was simply assumed to be 289 GPa. It was also found that the longer boronizing time, the lower fracture toughness. The fracture toughness of borides formed on surface of AISI 1040 plain carbon steel as function of boronizing time was $2.30 \text{ MPa} \cdot \text{m}^{1/2}$ for 4 h and $2.20 \text{ MPa} \cdot \text{m}^{1/2}$ for 6 h, respectively. We believe that these are consequence of more presence of harder FeB.

V. Conclusions

The results obtained from present study can be summarized as follows;

a) Hardness of non-oxide boride type ceramics formed on the surface of borided AISI 1040 plain carbon steel are much higher than that of untreated steel substrates.

b) The hardness distribution diagram have three distinct regions; (i) a surface layer consisting of borides (i.e. Fe_2B , FeB), (ii) the region below boride layer, where boron makes solid solution, which has hardness less than that of borides and higher than that of original matrix, (iii) steel matrix, which is not affected by boron.

c) Optical and SEM examinations of non-oxide boride type ceramics formed on the surface of AISI 1040 plain carbon steel substrates revealed a needle-shaped and/or columnar morphology and good bonding of the film to the steel substrates.

d) Depending on holding time the layer thickness of non-oxide boride type ceramics ranged from 72 μm to 145 μm . There is nearly parabolic relationship between boride layer thickness and boronizing time, and the longer boronizing time results in the longer boride layer thickness.

e) The fracture toughness of non-oxide boride type ceramics formed on surface of AISI 1040 plain carbon steel as a function of boronizing time was $2.30 \text{ MPa} \cdot \text{m}^{1/2}$ for 4 h, and $2.20 \text{ MPa} \cdot \text{m}^{1/2}$ for 6 h, respectively. It is possible to claim that the longer boronizing time results in

the lower fracture toughness due to formation of harder FeB.

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