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A Study of SiC/Borax Liquid Boride Layer on AISI H13 Hot Work Tool Steel

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Abstract— In this present work, the mechanical property and microstructure of liquid boride formed on AISI H13 steel substrate were studied. Liquid boriding treatment was carried out in a mixture of 30% SiC + 70% borax decahidrat ($Na_2B_4O_7.10H_2O$) at 900-920 °C hold time 6 hours. After permeating by the SiC/Borax mixture, the microstructure of the boride layer includes both the FeB and Fe2B phases. The HRC scale determines the hardness of the boron permeate layer. After SiC/Borax boriding is then quenched and tempered, the hardness is twice that of the untreated H13 steel matrix. Consequently, the study has suggested an appropriate heat treatment process to enhance the mechanical properties of AISI H13 steel to meet up the requirements: annealing steel at 870 °C for 1.5 hours and 720 °C for 2 hours, cooling in air, then boriding at 900 oC and keep heating for 6 hours, quenched at 1050 °C for 25 minutes, and finally tempered at 650 °C for 2 hours.

Keywords— Boriding, H13 steel, Boride layer, Boriding mixture, quenched and tempered

INTRODUCTION

Nowadays, wear resistance issues on tool steels increase dramatically as complex, high temperature and high load applications are more required in industries. Therefore, surface treatment to improve the wear resistance of the tool steel is often mentioned. The boriding or boronizing process improves mechanical properties such as hardness, wear resistance, abrasion, and surface corrosion resistance of ferrous and non-ferrous materials, due to the formation of boride layers. The boride layer has special advantages over conventional hard layers, such as nitrided or carburized layers [1-3]. In Ibrahim Gunes [4] study, the author uses various B_2O_3 paste mixture to plasma paste borided on AISI 8620 steel by DC plasma system. Analysis of X-ray diffraction of boride layers on 8620 steel surface showed FeB and Fe_2B phases. According to Haili Yang [5], Boronizing of silicon steel is performed by electrodeposition in $KCl-NaCl-NaF-Na_2B_4O_7 \cdot 10H_2O$ molten salts with different amounts of borax. The result showed that the thickness of the boride layer reached maximum values and smallest values of surface roughness at 0.05 mol borax. I. Uslu [6] investigated some properties of borides formed on the AISI 1040 and AISI P20 steel substrates.

The hardness of borides was about 1500 HVN. Borides formed on the 1040 steel are FeB and Fe_2B, while borides formed on the P20 steel are MnB, CrB, FeB, and Fe_2B. SEM microstructure revealed that boride formed on the 1040 steel has columnar morphology and the P20 steel has columnar and dense structure. I. Campos-Silva [7] studied the kinetics of the FeB/Fe_2B layers and diffusion zone at the surface of AISI 316 steels exposed to the powderpack boriding process. G. Kartal [8] employed an ultra-fast boriding technique to grow hard boride layers on low carbon steel substrates. XRD results revealed two principal boride phases: FeB and Fe_2B. The mechanical characterization of the borided surfaces has confirmed hardness values as high 19 GPa at where FeB phase is present.

The AISI H13 hot work tool steel is well suited for surface treatments such as nitriding and boriding. In industrial applications, H13 steel is the most commonly used among hot work die steels. Boriding has been put into this steel to extend the service life of parts such as dies for hot forming, which need to display high wear resistance [9-11]. Ali Günen [12] used the powder-pack method to boride B_4C and $NaBF_4$ powder on the H13 steel. It is found that the borided H13 steel displayed up to 33.5 times higher corrosion resistance than untreated H13 steel. This suggests potential use of borided H13 steel as an alternative to the more costly martensitic and duplex stainless steel grades. In George K. Kariofillis' research [13], boriding was done by pack cementation, showed a better corrosion behavior in H_2SO_4 and H_3PO_4 environments for short exposure periods when compared to H13 steel, therefore, H13 hot work tool steel after boriding has better corrosion resistance than substrate steel. Yossapong Boonplook's work [14] found that the thickness of the boride coating on hot work tool steels H13 by using a packed boriding process increases with increasing boriding temperature was borided. The results of K. Genel's study [15] showed that the boride layer hardness was 1650 - 2000 HV, and its morphology has a smooth and compact morphology. In addition, the kinetics of boriding shows a parabolic relationship between layer thickness and process time.

Author Wu Xiao-Chun [16] researched the transformation of phase constitutions of boride layer, showed that boronizing treatment of H13 steel improves thermal fatigue behavior due to its excellent thermal stability and high strength. A similar result was reported by A. P. Krelling [17], solid boriding of two boriding agents thermochemical treatment was carried out on AISI H13 steel, the thickness of the borided layer was higher for samples borided with Ekabor powder than those borided with the mixture. Besides, the formation of the layers was carried out by the powder pack boriding process at 1273 K with 8 h of treatment by N. López-Perrusquia [18]. The results obtained by both techniques show that the fracture toughness of the boride layer can be expressed, high delamination is obtained around the Rockwell-C indentation prints that denote poor adhesion between the coating and substrate interface. Sukru Taktak [19] investigated mechanical properties of borides formed in a slurry salt bath consisting of borax, boric acid, and ferrosilicon on AISI H13 hot work tool. Microstructure showed that the boride layer was a ragged morphology.

MATERIALS AND METHODS

AISI H13 hot work tool steel with $20 \times 50 \times 25$ mm is the substrate. Before boriding, the surfaces of all samples are ground on 2000 grits sand paper and cleaned with acetone to remove grease, rinsed with water, and then dried with a hot air blaster. This surface preparation removes all dirtiness that can prevent boron diffusion through the surface.

Figure 1. Coal furnace

Boriding mixture is sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$), also known as "borax" powder, and SiC powder with a ratio of 30% SiC + 70% borax. Laboratory equipment include resistance furnace, ram furnace, graphite container and coal furnace (Figure 1). The samples for microscopic observation were grinded, polished, and impregnated with HCl and HNO_3. The morphology of borides formed on the H13 steel substrate was confirmed by optical microscopy. The hardness of sample was measured on Rockwell machines.

Experimental procedures

Annealing: Preheat the furnace to 870 °C, arrange the SiC/Borax sample in the container for charcoal to fill the sample, cover the lid and seal the container with clay. Put the sample container in the furnace when it reaches 870 °C, keep the heat for 1.5 hours.

Reduce container temperature to 720 °C and keep heat for 2 hours (Figure 2 and Figure 3). Turn off the furnace and wait for the furnace to reach about 300 - 400 °C, take out the sample container to cool in the air.
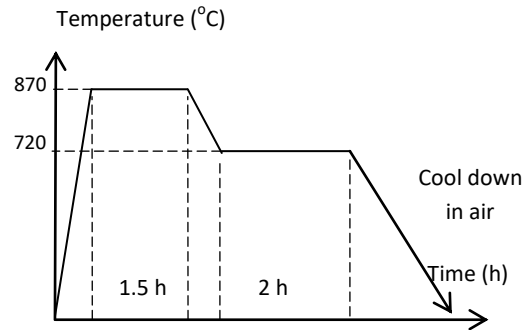

Figure 2. H13 steel annealing scheme [9, 20-22]

Figure 3. H13 steel samples after annealing

Boriding treatments were performed in an furnace between 900 °C and 920 °C temperature with a 50 °C intervals for holding time of 6 h (Figure 4 and Figure 5).
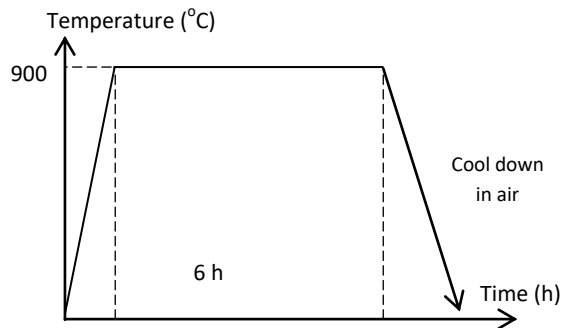

Figure 4. Boriding treatment scheme [23]

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┌─────────────────────────────────────────┐
│  Mix 30% SiC + 70% Borax in the container │
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│   Turn on the furnace to reach about 500 ᵒC │
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│  Put the container (SiC + Borax) into the furnace │
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│  After the mixture flows out, put the sample in the │
│  container and turn on the furnace to 900 - 920 ᵒC │
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│   Keep the heat of the container for 6 hours │
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│  Turn off the furnace and take out the container to │
│  cool down │
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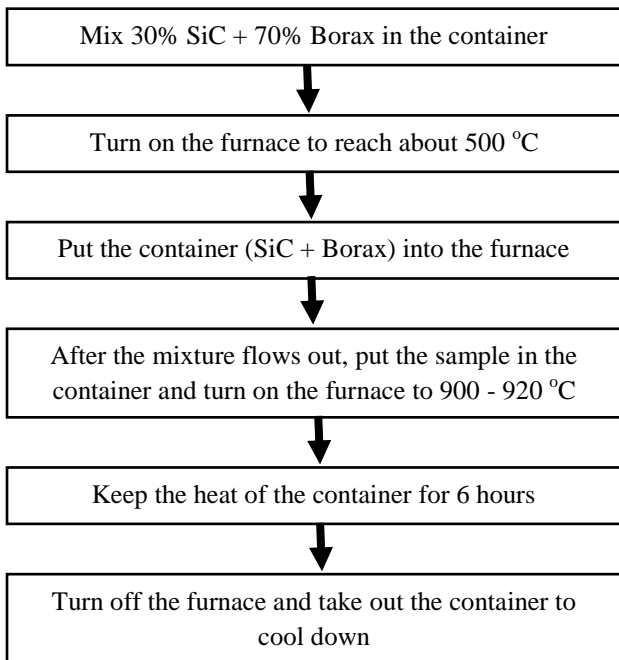
Figure 5. Flow chart of preparing of 30% SiC + 70% borax powder on the samples steel for boriding.

Quenched and Tempered: Some samples which borided with (SiC + Borax) powder were then quenched and tempered. They were heated at 1050 ᵒC for 25 min, after that they were cooled down in oil. The tempering was carried out at 650 ᵒC for 2 h, then turn off the furnace, and took out the sample container to cool down.

RESULTS AND DISCUSSION

A. The microstructure of untreated H13 steel and annealed H13 sample
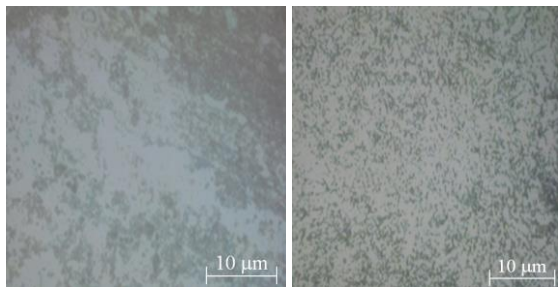
a) Untreated H13 steel   b) Annealed H13 steel

Figure 6. The microstructure of untreated H13 steel and annealed H13 steel sample

(Ferrite matrix: White, Carbide: Dark)

Figure 6 shows the microstructure of untreated H13 steel sample and annealed H13 steel sample. It can be seen that the microstructure of untreated sample distinguishes the Ferrite matrix structure and spherical carbide dispersed in ferrite matrix. The microstructure of H13 steel depends mainly on the chemical composition (alloying elements, impurities) and the heat treatment. The appropriate ratio of three basic alloying elements, Cr, Mo and V, combined with the appropriate % C content to form Mo_6C, VC and Cr_7C_3 carbides.

The sizes of these carbides depend on their constituent elements. Mo and V carbides tend to be larger and often concentrated in clusters, while Cr and Fe carbides are usually finer and less concentrated.

After annealing, the grain size is more homogeneous and more evenly dispersed. Since H13 steel is the Hypo-eutectoid steel, when annealed at temperatures over 727 ᵒC, its microstructure has austenitic phase and ferrite phase. As the temperature continues to increase, there will be the dissipation of ferrite phase into austenite phase.

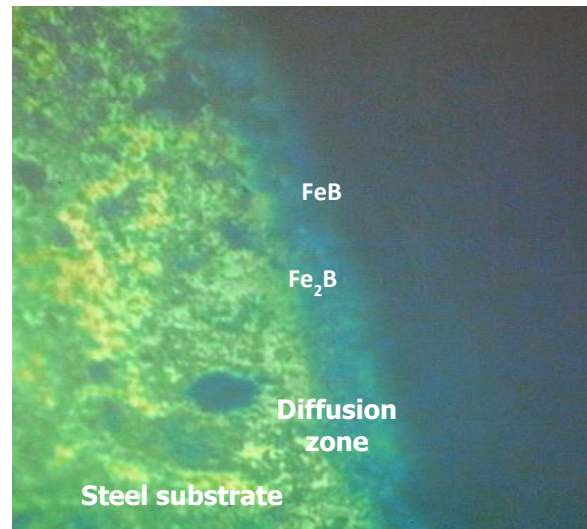### B. Microstructure of borided H13 steel sample

Figure 7. Microstructure of H13 steel after boriding treatment (400X magnification)

Figure 7 exhibits the microstructure of borided H13 steel sample. It can be seen that the SiC/Borax boride layer has exellent bonding with the H13 steel substrate with a steady thickness. After boriding, the microstructure has FeB phase in the upper part, the middle layer is Fe_2B phase and the inner layer is the substrate. Research by I. Uslu [6], George K. Kariofillis [13], and A. P. Krelling [17] showed that the boride layer can form Fe_2B monophase or (FeB + Fe_2B) double-phase on steel substrate surface. In boriding conditions for a long time, it often forms a double-phase. In the case of forming a double-phase, the upper part of the layer is the FeB phase, middle part is the Fe_2B phase, bottom part is diffusion zone, then H13 substrate.

According to Fe-B diagram (Figure 8), boride layer microstructure in H13 steel can be form Fe2B monophase or (FeB + Fe_2B) double-phase. The Fe_2B layer is obtained from the single phase layer, while the double-phase layer consists of the outer layer of the FeB phase and the inner layer is the Fe_2B phase, resulting in the shape of the boride layer having a needle-shaped structures which help to improve mechanical adhesion to the substrate. Because the FeB phase is thinner than the Fe_2B phase, the Fe_2B phase structure is more desirable than the FeB phase in the borided process. It is also observed that Fe_2B produces the lower layer subject to high compressive stress, while FeB produces the upper layer subject to high tensile stress.

Therefore, in borided process, it is necessary to avoid the overlap of Fe_2B and FeB phases, causing surface cracking of the double-phase (FeB + Fe_2B) layer. The formation of cracks leads to cracking and even separation of the double-phase under mechanical action (impact strength) or heat. To limit this problem, the annealing process can reduce the appearance of the FeB phase in boriding. Mechanism of the borided process consists of two steps:
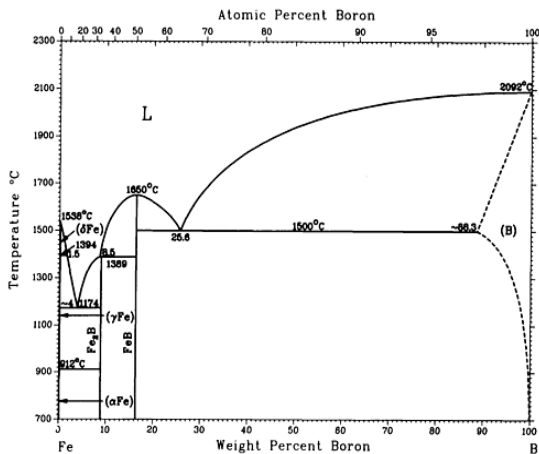

Figure 8. Fe-B phase diagram [24]

1. The first stage takes place the reaction between the element Bor and the elements in the surface. Particles are formed as a function of borided temperature and time leading to the development of the boride layer. The Fe_2B layer is pre-formed and develops into a thin layer at the defects of the metal surface, macroscopic defects (surface roughness, scratches...) and microscopic defects (grain boundaries, network deviation...). If the Bor activator is in excess, Bor-rich phases such as FeB will form and develop on the Fe_2B phase.
2. The second reaction is a controls diffusion process, the boride layer thickness is formed according to a time parabolic law: X = KT (1). Where X is the thickness of boride layer (mm); K is a temperature dependent constant; T is the borided time according to a given temperature (s). In the case of a metallic material, the Bor atoms tend to diffuse into the lattice and form clumps - the body-centered cubic of Fe_2B to reach the maximum integer quantity in this direction.

For liquid boriding process, the controlling of atomic boron concentration in the surface of the part is relatively difficult. Because during the boriding process, the boron concentration in the molten salt bath will decrease gradually. The borided mixture is evaporated, therefore, it is necessary to control and add the appropriate borided absorbent or change the borided temperature and borided time. The liquid boriding layer is formed quickly, however, the layer is not uniform, the borided sample often stick with the absorbent.

C. Microstructure of quenched and tempered H13 steel sample

Figure 9 presents the microstructure of quenched and tempered H13 steel sample. The microstructure includes the martensitic base and the carbides of the alloying elements distributed in it. In this steel, the three elements Cr, Mo, V are the elements that make the carbides. For H13 steel, the elements Cr, Mo, V create a relatively large amount of carbides (about 12%). It can be observed that compared to the borided sample, quenched and tempered H13 steel sample has a smaller particle size which is finer and more evenly distributed. The reason is that after quenched, the sample was tempered at 650 ^{o}C. During the tempered process, when the temperature reaches 400 ^{o}C, Ferrite and Cementite appear. In this stage, the Cementile starts to be granular and Ferrite also changes to form polygonal granular Ferrite. When the temperature continues to increase, there is a phenomenon of agglutination and spherical formation of Cementite molecules, forming a sphere shape. At the temperature of 500-650 ^{o}C, a mixture of Ferrite and Cementite in granular form was formed or Sorbite tempered is formed. At that time, the seeds are formed, fine and uniform, with good synthetic mechanical properties. A similar result was reported by A. P. Krelling [17], solid boriding treatment is carried out on AISI H13 steel with two boriding agents (commercial powder Ekabor 1-V2 and a mixture of 73.26% of borax, 24.06% of SiC, 1.22% of NH_4Cl, and 1.46% of NaCl). The thickness of the boride layer for samples borided with Ekabor powder is higher than for samples borided with other mixture. Compared to the quenched and tempered samples, the borided samples have a higher rate of crack appearance, which facilitates flaking and reduces grooves formed by abrasion.
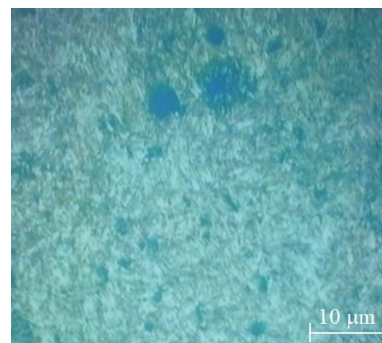

Figure 9. Microstructure of quenched and tempered H13 steel sample

D. Hardness of H13 steel

TABLE I
HARDNESS OF H13 STELL (HRC) WITH DIFFERENT CONDITION

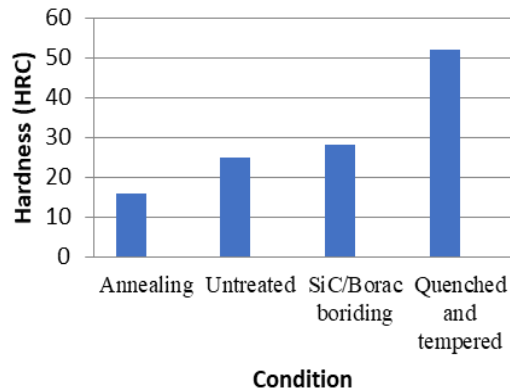| Hardness	Annealing	Untreated	SiC/Borax boriding	Quenched and tempered
Average (HRC)	16	25	28	52

Figure 10. The hardness of annealed H13 steel, untreated sample, SiC/Borax boriding, and quenched and tempered H13 steel sample

Figure 10 shows the hardness of annealed H13 steel, untreated sample, SiC/Borax boriding, and quenched and tempered H13 steel sample. It can be seen that the hardness of the samples is 16, 25, 28, and 52 HRC, corresponding to the annealed H13 steel, untreated sample, SiC/Borax boriding, and quenched and tempered H13 steel sample. Compared with untreated H13 steel, the hardness of the annealed sample decreases rapidly by about 9 HRC. The hardness of SiC/Borax borided sample is 28 HRC, higher than that of untreated H13 steel.

The quenched and tempered H13 steel sample's hardness has enhanced remarkably (52 HRC), twice higher than the substrate. Due to boriding, the boride elements diffuse into the austenitic matrix to form a hard boride layer on the H13 steel surface. After quenched and tempered, the results showed that the hardness was much higher than that of H13 steel. Therefore, it can be concluded that boriding allows for further heat treatment without losing the properties of the boriding layer. Boride layers give a much higher mechanical property than the initial state steel. In N. López-Perrusquia' work [18], Borides is a hard material with a hardness value ranging from 1800-2100 HV. These values are almost impossible to achieve with other conventional thermochemical treatments. AISI H13 steel has a value of 1500 HV which depends on the high growth anisotropy of the layers, the presence of residual stress, and the processing time and temperature. In addition, the hardness values depend on the chemical composition of the base material.

In chromium-based low-alloy steels, Cr tends to dissolve into the boride layers, and combines with boron to form CrB-type compounds, improving the surface hardness of the steel. In the study of Ali Günen [12], the surface of AISI H13 steel is borided by a powder mixture of B_4C and $NaBF_4$. The boride layers are compact and crack-free under all borided conditions. Depending on the coating parameters, the coating thickness and hardness found ranges from 5.81 to 102.46 µm, and 1635 - 1915 HV. The results of K. Genel's [15] show that the morphology of the boride layer is smooth and firm, and its hardness is found to be in the range of 1650 - 2000 HV.

CONCLUSION

For H13 steel, a suitable heat treatment process has been found to increase the mechanical properties of the mold to meet the working requirements: annealing steel at 870 ºC for 1.5 hours and 720 ºC for 2 hours, cooling in air, then boriding at 900 ºC and keep heating for 6 hours, quenched at 1050 ºC for 25 minutes, and finally tempered at 650 ºC for 2 hours.

Hardness of boriding layer is higher than the hardness of the H13 steel; hardening and tempering steel sample's hardness is twice higher than the hardness of H13 steel. Therefore, it can be concluded that boriding allows for further heat treatment without losing the properties of the boriding layer. Boride layers give a much higher mechanical property than the initial state steel.

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28