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Identification of Delamination Failure of Boride Layer on Common Cr-Based Steels

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Adhesion is an important aspect in the reliability of coated components. With low-adhesion of interfaces, different crack paths may develop depending on the local stress field at the interface and the fracture toughness of the coating, substrate, and interface. In the current study, an attempt has been made to identify the delamination failure of coated Cr-based steels by boronizing. For this reason, two commonly used steels (AISI H13, AISI 304) are considered. The steels contain 5.3 and 18.3 wt.% Cr, respectively. Boriding treatment is carried out in a slurry salt bath consisting of borax, boric acid, and ferrosilicon at a temperature range of 800-950 °C for 3, 5, and 7 h. The general properties of the boron coating are obtained by mechanical and metallographic characterization tests. For identification of coating layer failure, some fracture toughness tests and the Daimler-Benz Rockwell-C adhesion test are used.

Keywords adhesion, boriding, delamination failure, fracture toughness, stainless steel, tool steel

1. Introduction

Adhesion is an important aspect for the reliability of coated components. Adhesion testing is often based on the application of mechanical loads. In the case of low adhesion of interfaces, different crack paths may develop depending on the local stress field at the interface and the fracture toughness of the coating, substrate, and interface. The crack path can follow the interface or can be parallel to the average interface within either substrate or coating, where combinations of adhesive and cohesive failure have also been observed (Ref 1). Often tensile or compressive mechanical loads are applied to the interface to promote delamination.

Austenitic stainless steels and hot work tool steels have high chromium content and are commonly used engineering materials. Austenitic stainless steels cannot be hardened to any great extent by conventional heat treatments, and they are used mainly in corrosion-resistant applications. They are, however, occasionally used in tribological applications, such as determining wear due to poor surface hardness and low load bearing capacity. Great efforts have been made to improve its surface properties (Ref 2). Hot work tool steels are tool materials that are used almost exclusively on extrusion dies as well as for tools for hot pressing of copper alloys and steel forging. They are characterized by high strength and ductility, good tempering resistance, and moderate cost (Ref 3). These are also well suited and established for surface treatments such as nitriding and boronizing. The steels are used in a quenched and tempered condition at a hardness range of 450-500 HV.

One surface treatment is boriding, which is technically well developed and widely used in industry to produce an extremely hard and wear-resistant surface layer on metallic substrates. Borided steel components display excellent performance in several tribological applications in mechanical engineering and automotive industries. Borided steels exhibit high hardness (about 2000 HV), high wear resistance, and improved corrosion resistance (Ref 4-7). Boron atoms can dissolve in iron interstitially and can also react with it to form FeB and Fe_2B intermetallic compounds. Depending on the potentials of medium and chemical composition of base materials, a single or duplex layer may be formed. During boriding of ferrous alloys, generally, a boron compound layer develops that consists of a surface-adjacent FeB sublayer on top of a Fe_2B sublayer (Ref 8). In fact, for practical applications, the formation of a monophase (Fe_2B) with saw-tooth morphology is more desirable than a dual-phase layer composed of FeB and Fe_2B (Ref 4, 9). Although the boron-rich FeB phase is harder, it is more brittle than the iron sub-boride, Fe_2B phase. Furthermore, crack formation is often observed at the FeB/Fe_2B interface of a dual-phase layer, as FeB and Fe_2B phases exhibit substantially different coefficients of thermal expansion. These cracks often lead to flaking and spalling when a mechanical load is applied (Ref 10, 11).

Much research has been carried out on the tribological behavior and in particular on the wear resistance of borided steels of very different composition. Less attention has been focused on failure of the boride layer and relationship between fracture toughness and adhesion. The main objective of this study was to investigate failure of boride layers on the surface of AISI H13 hot work tool steel and AISI 304 stainless steel. Boriding is realized by a molten salt bath technique. For this reason, four different temperatures (800, 850, 900, and 950 °C) and three different durations (3, 5, and 7 h) are selected for boriding. General properties of the boron coating are obtained by mechanical and metallographic characterization tests. For identification of the failure of the coating layer, some fracture toughness tests and The Daimler-Benz Rockwell-C adhesion test are used. Examination of the failure was carried out using scanning electron microscopy (SEM).

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Table 1 Chemical composition of test materials

	Chemical composition, wt.%								
Steel	C	Cr	Ni	Si	Mn	Mo	V	S	P
AISI H13	0.4	5.3	…	1	0.3	1.4	1	0.005	0.025
AISI 304	0.04	18.3	8.7	1	2	…	…	0.03	0.045

2. Experimental Procedures

Chemical compositions of the studied steels are given in Table 1. The test samples had dimensions of ∅ 20 × 6 mm. Before boriding treatment, specimens were ground with emery paper up to 1200 mesh and polished. Boriding was carried out using a slurry salt bath consisting of borax (60 wt.%) and boric acid (20 wt.%) as boron sources and ferrosilicon (20 wt.%) as activator. Boriding treatments were performed in an electrical resistance furnace between 800 and 950 °C at intervals of 50 °C and with holding times of 3, 5, and 7 h. Test materials to be borided were immersed in the slurry salt bath in stainless steel containers. After the boriding heat treatment, test materials were removed from the bath and quenched in air.

Fracture toughnesses of the boride layers were assessed by micro-Vickers indentation using a Vickers microhardness tester (Shimadzu HMV-2, Tokyo, Japan) on polished cross sections. Loads of 25 and 50 g were used to measure the hardness of the boride layers, and a load of 200 g was used to measure the fracture toughness. The microhardness indenter technique was used for the calculation of fracture toughness. The equation used for calculating fracture toughness was $K_c = 0.028(E/H_v)^{1/2} \cdot (P/c^{3/2})$, where E and H_v are the Young's modulus and hardness of the boride layer, P is the applied load, and c is the radial half-crack length (Ref 12). The crack length was measured by an optical microscope (400×) attached to the microhardness test equipment.

The Daimler-Benz Rockwell-C adhesion test (Ref 13) was used to assess the adhesion of the boride layers. The well-known Rockwell-C indentation test is prescribed by the VDI 3198 norm as a destructive quality test for coated compounds. A load of 1471 N was applied to cause coating damage adjacent to the boundary of the indentation. Three indentations were conducted for each specimen. SEM was used to evaluate the test.

3. Results and Discussion

3.1 Metallographic Studies and Hardness Tests

Figure 1 shows SEM views of AISI H13 and 304 steels borided at 950 °C for 5 h. SEM-BEI cross-sectional observations of borides formed on the surface of H 13 steel reveal saw-tooth morphology. However, the saw-tooth nature of the boride layer was less prominent when compared with borides formed on the surface of plain carbon steel (Ref 4). A flat boride morphology appeared on the surface of the 304 stainless steel because diffusion was more restricted due to presence of a high content of alloying elements (Cr, Ni). When the chromium content of steel was increased, the boride layer formed on the steel was thinner and the interface between the boride layer and matrix became more smooth (Ref 14). Microstructure

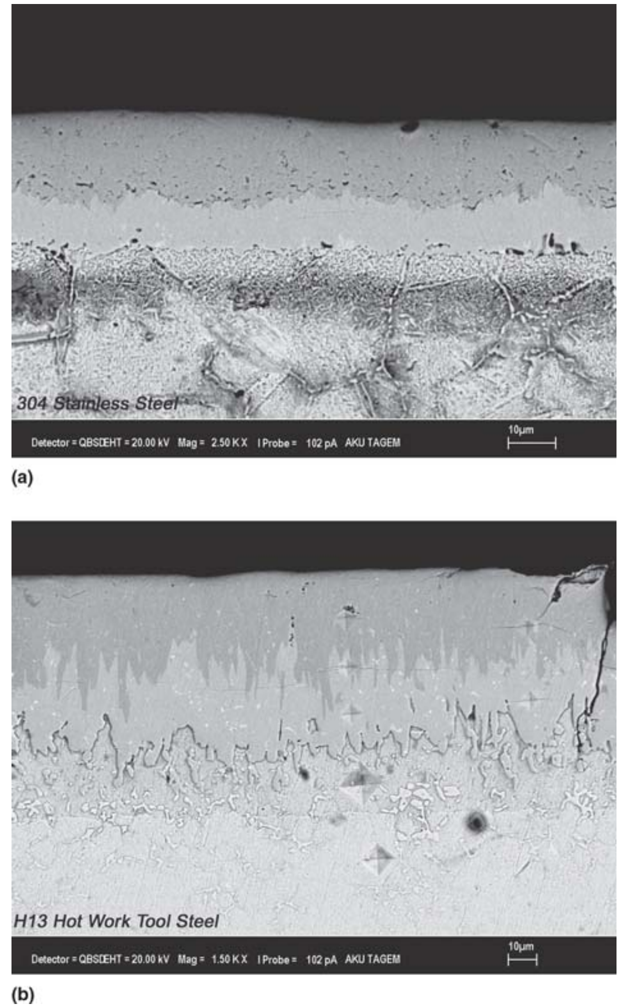


Fig. 1 SEM-BE image of microstructure of AISI H13 hot work tool and AISI 304 austenitic stainless steels borided at 950 °C for 5 h

and mechanical properties of borided hot work tool steel and stainless steel depended strongly on chemical composition, process temperature, and boriding time.

The thickness and average hardness of boride layers on the borided H13 and 304 steels at various temperatures for holding time of 5 h are given in Table 2. Table 2 suggests that both thickness and hardness increase with increasing the boriding temperature. It was observed that boride layer thickness reduced with increasing the amount of alloying element. The coating thickness was influenced by alloying elements in the metal substrate (especially by chromium), which can modify the active boron diffusivity by entering the iron boride lattice (Ref 15). In addition, Carbucicchio et al. (Ref 16) reported that with increasing content of the third alloying element in the alloys, both the depth of FeB-base region and the FeB/Fe_2B ratio increase in the case of Cr-containing alloys. Chromium tends to concentrate within the coating layers.

Hardness measurements showed that the hardness of borides is much higher than that of base steels. In the boride layers formed on H13 and 304, the average microhardness values of ~1967 and ~2150 HV were obtained, respectively. The differences in the hardness of boride layers of both steels may be explained as the consequence of the presence of more

Table 2 Thickness and average hardness of boride layers on the borided H13 and 304 steels at various temperatures for holding time of 5 h

Boriding temperature, °C	Boride layer thickness, µm		Average hardness of boride layer, Hv	
	AISI H13	AISI 304	AISI H13	AISI 304
800	10	6	1550	1660
850	18	14	1725	1805
900	32	23	1885	1945
950	53	33	1967	2150

chromium and nickel borides in the coating layer of stainless steel. Furthermore, Badini et al. (Ref 17) have reported that chromium increased the hardness of the boride layer. In thermochemical boriding treatments, high hardness is attained directly through formation of borides during boriding and does not require quenching.

3.2 Fracture Toughness Tests

Indentation fracture toughness tests are performed for the samples borided at 900 and 950 °C for 5 and 7 h. Other samples do not have the necessary thickness for the fracture toughness measurement. To calculate the fracture toughness, the elastic modulus of boride layer must be known. Bindal and Ucisik estimated the value of elastic modulus approximately as 280 GPa (Ref 12). The Vickers indentation mark with a crack for AISI 304 stainless steel is shown in Fig. 2. The flat morphology of both FeB-rich and Fe_2B-rich layers and the crack propagated along the interface between the FeB-Fe_2B interfaces should be noted. The fracture toughness of boride layers formed on the H13 tool steel and 304 stainless steel ranged between 4.46 and 3.12 and between 4.08 and 2.45 $MPa \cdot m^{1/2}$, respectively (Table 3). These results reveal that the fracture toughness of boride layers decreases with increasing treatment time and temperature. The fracture toughness values of boride layers on the H13 and 304 steels decrease by 12 and 5% when boriding time is increased 40% at 900 °C, respectively. Increasing the temperature causes a reduction in fracture toughness value. For example, the toughness value of stainless steel decreased 55% when the temperature increased from 900 to 950 °C for 7 h of boriding. The reduction is 25% for hot work tool steel. This indicates that boriding time and temperature have a considerable effect on the reduction of fracture toughness of boride layers.

It was recognized that the fracture toughness values of borides formed on the surface of H13 and 304 steels depended strongly on the alloying elements, boriding time, and temperature. Boride layer of stainless steel resulted in lower fracture toughness values when compared with that of hot work tool steel. This case can be accompanied by high Cr and Ni boride content in the stainless steel. Bindal and Ucisik (Ref 18) reported that Cr has a negative effect on the fracture toughness of borides formed on the chromium-based low alloy steel substrates. However, it must be noted that more than one type of boride formed on the tool and stainless steels. Each one individually had its own fracture toughness value, but what kinds of interaction existed between the different borides were unknown, and the influence of each was hard to distinguish. It was also found that fracture toughness decreased with increasing treatment time and temperature due to the increase of hard and brittle borides, such as iron and chromium borides, in the coating layer. This case was also reported by other workers (Ref 10, 19). It was also concluded that an increase of hardness in the boride layers resulted in a decrease of fracture toughness.

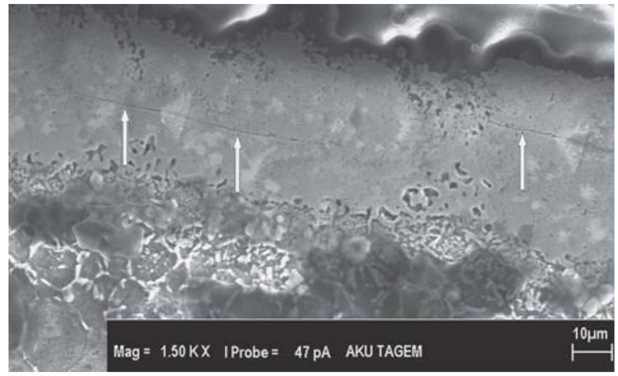


Fig. 2 Vickers indentation mark with a crack for AISI 304 stainless steel borided at 950 °C for 7 h

Table 3 Fracture toughness variation of borides formed on the surface of AISI H13 and 304 steels as a function of boriding time and temperatures

Boriding temperature, °C	Boriding time, h	K_c ($MPa \cdot m^{1/2}$)	
		AISI H13	AISI 304
900	5	4.46	4.08
	7	3.96	3.89
950	5	3.54	2.67
	7	3.12	2.45

3.3 Adhesion Tests

A standard Rockwell-C hardness tester was used in this study. The principle of this method is given in the literature (Ref 20). Damage to the coatings was compared with the adhesion strength quality maps HF1-HF6. In general, the adhesion strength quality maps HF1-HF4 define sufficient adhesion, whereas HF5 and HF6 represent insufficient adhesion (Ref 13-20). A conical diamond indenter penetrated into the surface of a coated compound, thus inducing massive plastic deformation to the substrate and fracture of the coating. As in every indentation test, the 1/10th rule must be accomplished, and therefore the overall specimen thickness must be at least 10 times greater than the indentation depth. The type and the volume of the coating failure zone exhibit first the film adhesion and, second, its brittleness. The coated specimen may be adequately evaluated by means of conventional optical microscopy. However, the specific quality-control method becomes significantly more effective when SEM and spectroscopy are used. The contact geometry, in combination with the intense load transfer, induces extreme shear stresses at the interface. Well-adhering coatings manage to withstand these shear stresses and prevent extended delamination circumferentially to the imprint. On the other hand, extended delamination at the vicinity of the imprint indicates a poor interfacial adhesion.

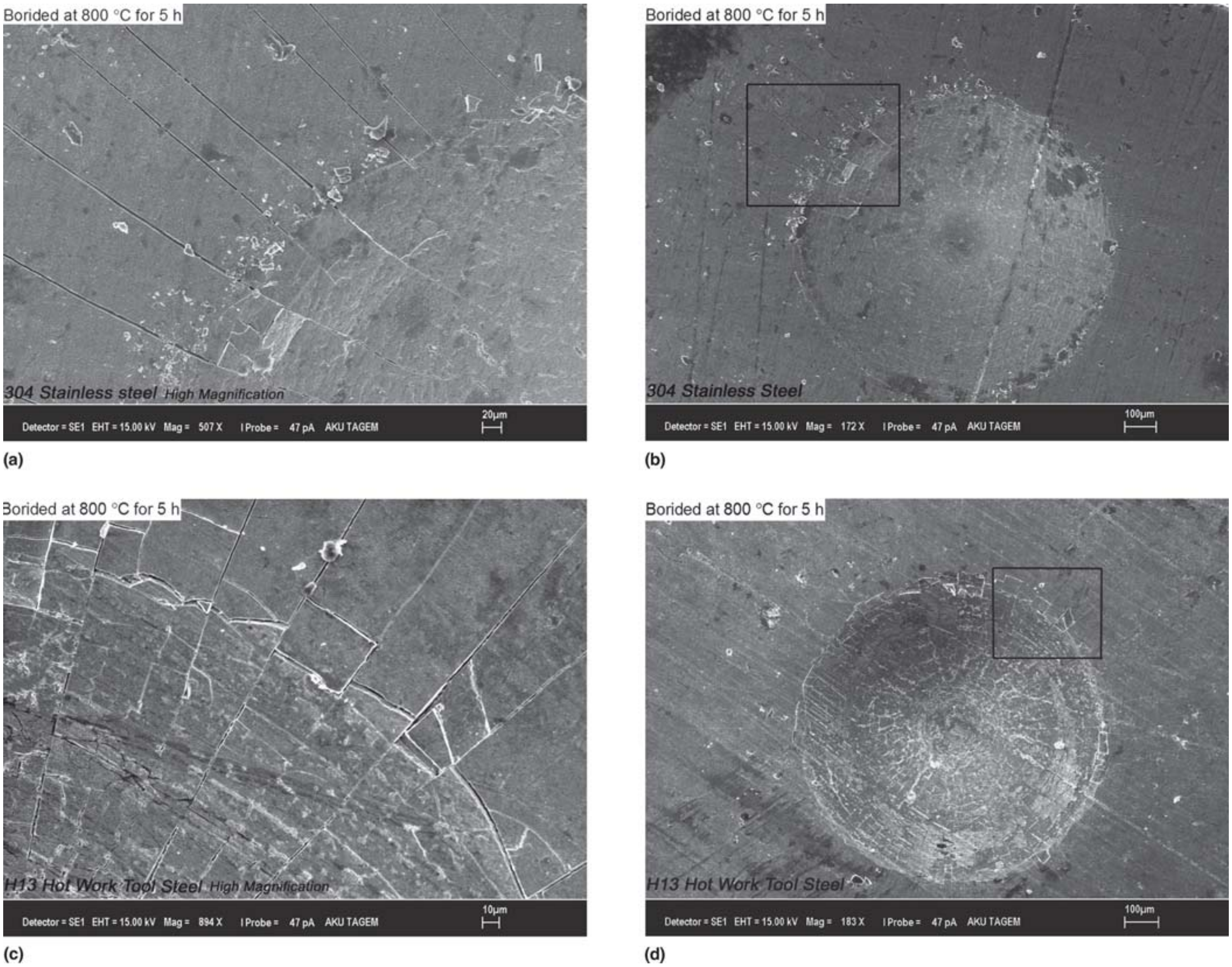


Fig. 3 SEM micrographs of VDI adhesion test on AISI H13 and 304 steels borided at 800 °C for 5 h; general appearance of crater and magnified area in the rectangle in figure showing radial cracks at the side of crater

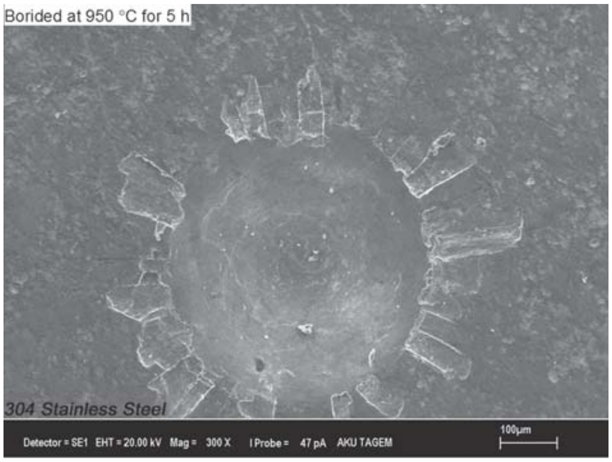
Furthermore, radial cracks and poor delamination indicate a coating that is both strongly adherent and brittle. Figure 3 and 4 show the indentation craters for samples H13 and 304 borided at 800 and 950 °C for 5 h. SEM micrographs in Fig. 3 indicate that there are radial cracks at the perimeter of indentation craters without flaking and that adhesion of boride layers on H13 and 304 steels borided at low temperature (800 °C) is sufficient. The adhesion strength quality of these boride coatings is related to HF1 and HF2. However, delamination or flaking at the perimeter of indentation craters is found for the boride coatings on H13 and 304 steels borided at high temperature (950 °C; Fig. 4), and adhesion of these boride layers is insufficient. The adhesion strength quality of these boride coatings is related to HF5 and HF6.

The Daimler-Benz Rockwell-C adhesion test results show that adhesion of boride layers on H13 and 304 steels decreases with increasing in boriding temperature. This case supports the increase of the depth of FeB-based layer. FeB phases were highly prone to cracking and scaling when mechanical strain was applied, due to tensile residual stresses (Ref 4, 10, 11). Indentation induces compressive stresses immediately under the indent but tensile stresses at the lip of the indentation. The subsequently induced damage or cracking has been referred to as a relative measure of the coating-substrate interfacial toughness (Ref 21). Adhesion test results are in agreement with the fracture toughness results.

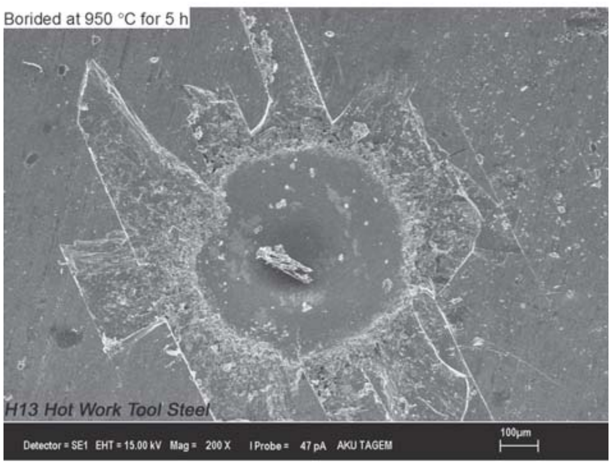
4. Conclusions

Several conclusions can be drawn:

- Fracture toughness of boride layers decreased with the increase in hardness and ratio of brittle FeB phase
- Adhesion of boride layers decreased with the increase in boriding time and temperature due to the increase of the depth of hard and brittle FeB-based layer.
- The Daimler-Benz Rockwell-C adhesion test can be used properly to identify the delamination failure characteristics of boride-coated Cr-based steels. It is a destructive technique, but its low cost and ease of use may be considered as advantages.



(a)



(b)

Fig. 4 SEM micrographs of VDI adhesion test on AISI H13 and 304 steels borided at 950 °C for 5 h

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