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Diffusion Boronizing of H11 Hot Work Tool Steel

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The H11 hot work tool steel was boronized at various processing parameters, austenitized, quenched, and tempered to a core hardness of 47-48 HRC. Microstructure, phase constitution, and microhardness of boronized layers were investigated. Effect of boronized region on the bulk properties was determined by the Charpy impact test. Structure of boronized regions is formed by the compound layers and diffusion inter-layer. The compound layers consisted of only $(Fe,Cr)_2B$ phase, but in the case of longer processing time, they contained also of the (Fe,Cr)B-phase. The inter-layer contained enhanced portion of carbides, formed due to carbon diffusion from the boride compounds toward the substrate. Microhardness of boronized layers exceeded considerably 2000 HV 0.1. However, boronizing led to a substantial lowering of the Charpy impact toughness of the material.

Keywords boronizing, Charpy impact strength, fracture behavior, hot work tool steel, microstructure

1. Introduction

Besides the widely used and popular techniques of carburising and nitriding, boronizing also plays an important role in the scale of thermo-chemical treatments. As a product of boronizing, thin, very hard, wear-resistant and corrosion-resistant compound layers on the surface are formed. Boronized layers have much higher hardness than those formed due to the nitriding or carburizing. The frequently achieved hardness value exceeds 1500 HV 0.1, but in some cases, especially in boronizing of tool steels, the limit of 2000 HV 0.1 can also be achieved. Owing to the diffusion of boron into the steel substrate, boronized layers exhibit a good adhesion, generally much better than the layers prepared by various physical vapor deposition methods. One of the most important problems of boronizing is the choice of optimal temperature with respect to subsequent quenching and tempering procedure. Boronizing is mostly carried out in various powder mixtures in hermetically sealed containers, which makes it difficult or impossible to quench the material directly from the processing temperature. Boronized specimens or components must then be cooled down slowly to a room temperature, removed from the containers, and heated again up to the austenitizing temperature which increases the risk of grain coarsening, or, in some cases, also the risk of failure of boronized layers. In addition, many materials have the optimal austenitizing temperature higher than that of boronizing which imposes strong limitations in their processing.

Boronizing of tool steels is an object of scientific interest over many years due to the effort to develop and optimize the surface techniques of these materials. The application of boronizing is mostly aimed to reduce the friction coefficient of sliding couple tool/worked material and to improve the wear resistance. The thickness of compound layers consisting of FeB- and/or Fe_2B-boride can reach up to 60-100 µm (Ref 1, 2). Owing to the high alloying of tool steels, other elements also can easily form the borides in the layers, especially Cr, if the alloy contains sufficiently high amount of chromium (Ref 3). Phase constitution of boronized layers changes from the free substrate to the layer/base material interface as the boron content decreases in the same direction. The free surface side of boronized layer is often formed by the FeB phase, and its content decreases in favor of the increase of Fe_2B amount (Ref 4). Close to the base material also, complex borides like $(Fe,Cr)_2B$ or (Fe,Cr)B for the chromium ledeburitic tool steels can be formed (Ref 3, 4). Hardness of boronized layers can measure over 2000 HV 0.1 for Cr-ledeburitic steels as well as for high speed steels (Ref 4, 5).

It is well known that besides the positive effects of thermo-chemical treatment upon very important mechanical properties like hardness and/or wear resistance, undesirable effects like embrittlement also can take place in some cases. For example, a lowering of the three-point bending strength, as a measure for resistance against crack initiation, for various nitrided PM ledeburitic steels was reported recently (Ref 6, 7). This is associated with a surface region having an increased hardness and low fracture toughness, which does not undergo plastic deformation during the fracture propagation, and also with limited fracture toughness of core material (Ref 7). Also for hot work steel of a H13-type, the lowering of resistance against crack initiation, measured by absorbed Charpy impact energy, was found due to the nitriding, although this material has much higher fracture toughness than the ledeburitic steels.

For the boronized layers also, such an effect can be expected. However, neither are the practical experiences of embrittlement of the material due to boronizing known nor has the exact quantification of the effect of boronized layer upon the fracture behavior been published yet. The aim of this article

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is thus to describe the structure and properties of boronized layers formed on the surface of H11 hot work steel and to relate them to the embrittlement of the material.

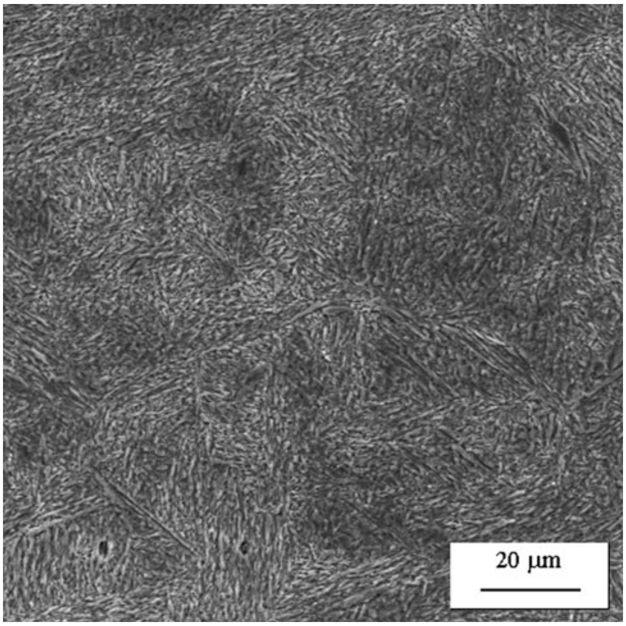

Fig. 1 The microstructure of the bulk material

2. Experimental

The hot work steel of H11-type (THYROTHERM 2343 EFS) with the composition 0.37% C, 1% Si, 5.3% Cr, 1.3% Mo, 0.3% V, and Fe bal. chemical composition has been used for experimental investigations. Round-shaped plate specimens, intended for the structural investigations and microhardness measurements, of 20 mm in diameter and 5 mm in thickness were fine ground to a surface roughness of R_a = 0.3-0.4 μm. Besides the specimens for microstructural evaluation, the samples for the Charpy impact testing according to the NADCA 202-97 standard were also prepared.

Both types of specimens were cleaned, degreased, and boronized using the Durborid® powder mixture in hermetically sealed containers at a temperature of 1030 °C for 30, 45, 75, and 150 min. After boronizing, the containers with specimens were furnace cooled down slowly to a room temperature, and then the specimens were removed and subjected to standard vacuum heat treatment. This procedure consisted of austenitizing at 1020 °C for 30 min, nitrogen gas quenching (pressure of 6 bar), and triple tempering—each tempering cycle for 2 h. The first tempering temperature was 570 °C, the second one 610 °C, and the third one 550 °C. After each tempering cycle, the samples were cooled down slowly to a room temperature. Resulting core hardness of the steel was 47-48 HRC.

The light and scanning electron microscopy after a deep etching were used for the microstructural evaluation. Scanning electron microscopy was used also for the fractography. For the

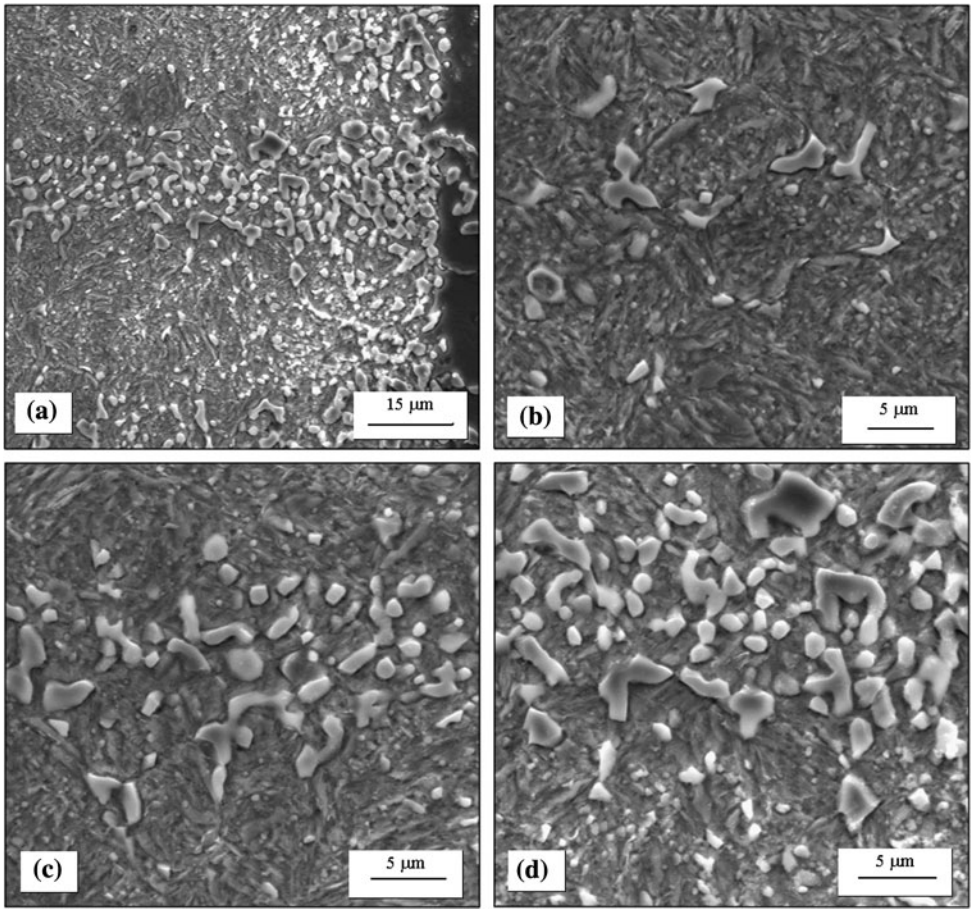

Fig. 2 The microstructure of the material close to boronized layer. (a) Overview and (b-d) detailed SEM micrographs

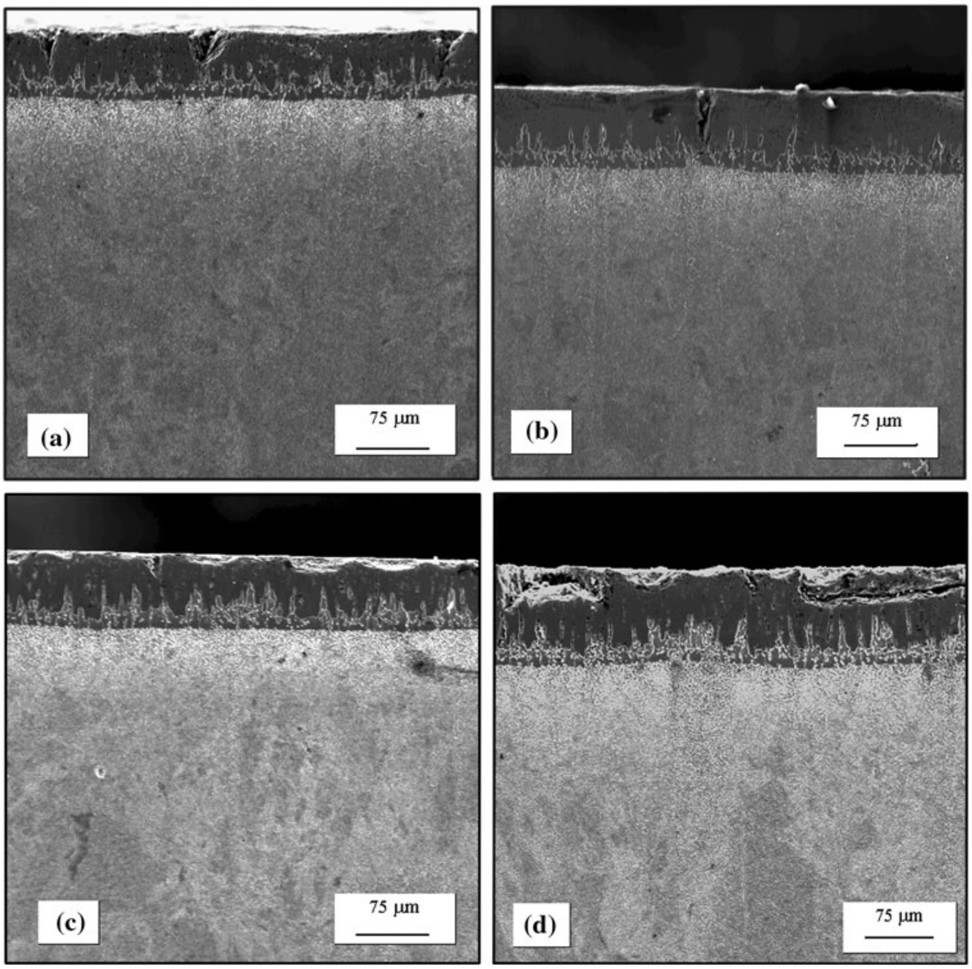

Fig. 3 Boronized layers on the H11-steel surface formed at 1030 °C for (a) 30 min, (b) 45 min, (c) 75 min, and (d) 150 min

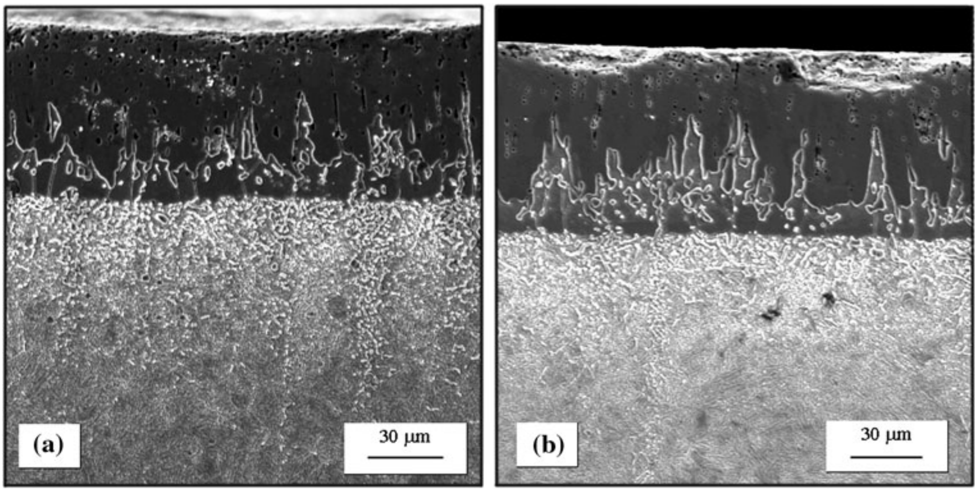

Fig. 4 Boronized layers formed at 1030 °C for (a) 30 min and (b) 75 min

EDS mapping and point chemical analysis, the EDS-detector was used whereas the acceleration voltage of the SEM was lowered to 7 kV. For the EDS-analysis of boronized layer and carbides below this layer, 20 measurements were made, and the mean values and standard deviations were calculated. Microhardnesses of boronized layer, transient region, and core material were measured with a Hanemann indenter placed in a Zeiss Neophot 21 light microscope, at a load of 100 g (HV 0.1). The x-ray patterns of the boride layers were recorded using a Phillips PW 1710 device with Fe-monochromatic radiation. Data were recorded in the range 27-120° of the 2 theta angle. Charpy impact testing was carried out on an instrumented machine with a maximal impact force of 300 J. Five specimens processed by each heat treatment were examined, and the average value of absorbed impact energy was then calculated.

3. Results and Discussion

Microstructure of the substrate material, Fig. 1, consists of fine tempered martensite. The martensite has a needle-like morphology. Martensitic needles are uniformly distributed throughout the material, with neither the presence of undissolved carbides nor that of the pro-eutectoidal phases at the grain boundaries. These facts confirm that the heat treatment after the boronizing was performed in an appropriate way.

In the close vicinity of the boronized layers, undissolved carbides can be found, Fig. 2. SEM micrograph, Fig. 2(a), demonstrates how the density of carbide particles increases from the core material to the bottom of compound boronized layer. More detailed micrograph shows that in the distance relatively far below the surface, only few randomly distributed carbide particles can be found, Fig. 2(b). In the direction to the boronized layer, the size and the number of particles increase rapidly, Fig. 2(c) and (d). This indicates that their nature would be connected with the carbon diffusion from the boronized layer toward the bulk material. It is known that the carbon is almost completely insoluble in borides. Therefore, it diffuses from the surface into the core material, and one can expect the formation of an intermediate region containing more carbides below the boronized layers. Similar phenomenon was documented also by Campos et al. (Ref 8) for boronized M2-type high speed steel. Based on these observations, one can assume that the carbon redistribution in the region, affected by boronizing, which is associated with increased amount of

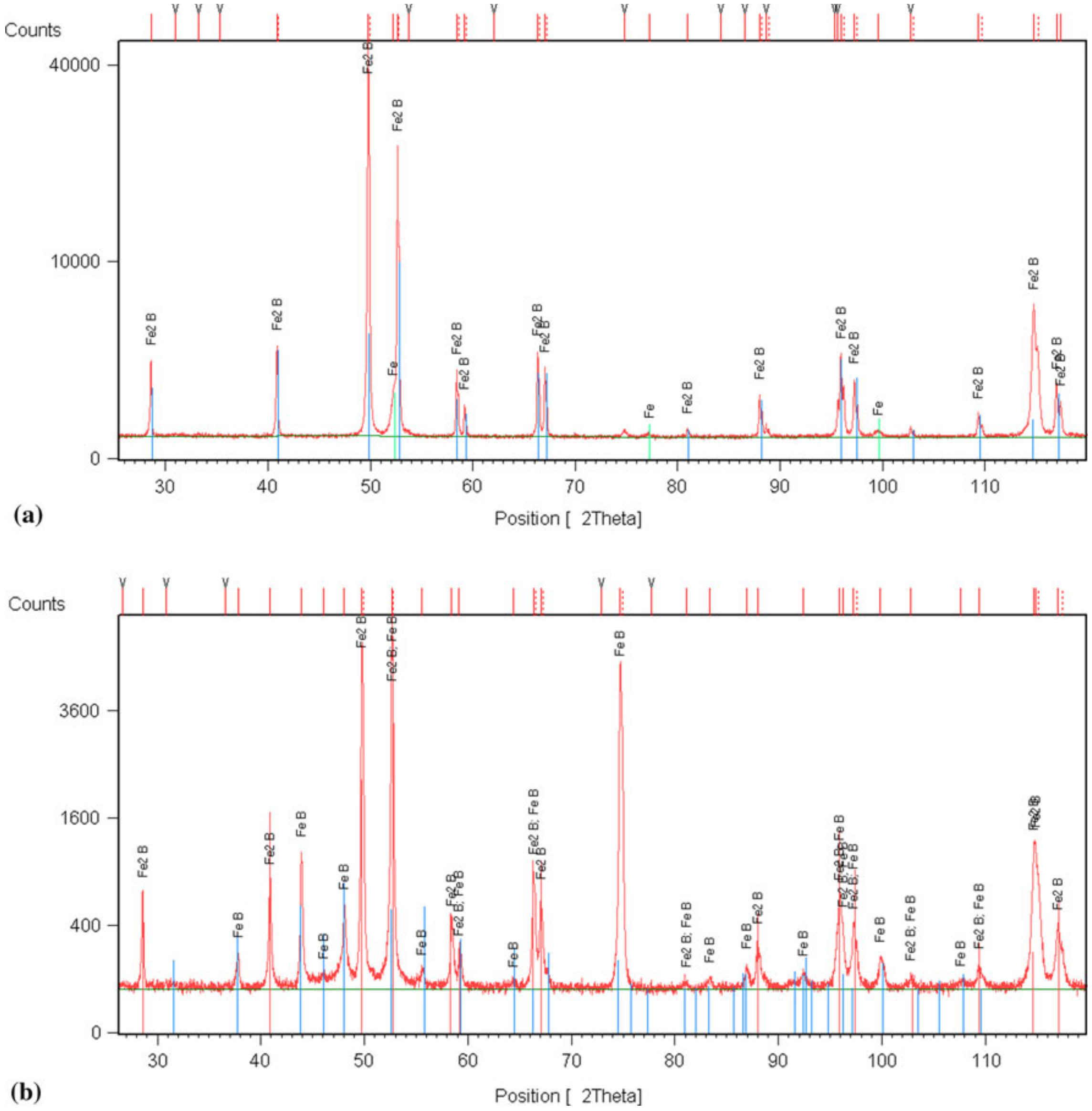

Fig. 5 The x-ray patterns from boronized layer formed at (a) 1030 °C for 75 min and (b) 1030 °C for 150 min

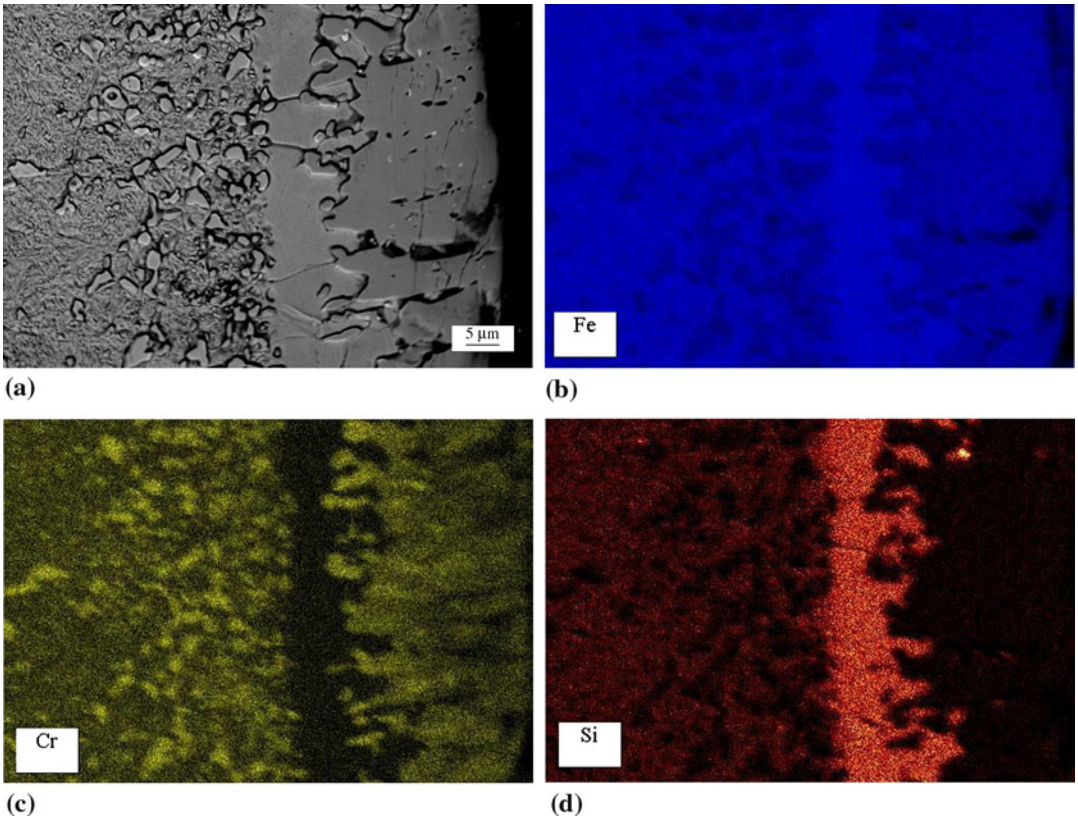

Fig. 6 EDS maps of boronized layer formed at 1030 °C for 75 min and intermediate region in the substrate. (a) Electron image, (b) iron, (c) chromium, and (d) silicon

Table 1 Results of EDS measurements of compound layer and carbides in the intermediate region

Element content, wt.%	Cr	Si	Mn	V	Mo
Compound layer	6.25 ± 0.63	Tracks	…	0.47 ± 0.06	…
Carbides	7.25 ± 1.08	Tracks	0.5 ± 0.2	0.68 ± 0.2	3.61 ± 0.81

Table 2 Mechanical properties of boronized layers and bulk material

	Microhardness HV 0.1			
Boronizing	FeB	Fe_2B	Diffusion region	Charpy impact energy absorbed, J
1030 °C/30 min	…	1483	416	…
1030 °C/45 min	…	1473	406	…
1030 °C/75 min	…	2221	638	17.8
1030 °C/150 min	2325	1686	560	12.4

carbides in the close region below the layers, is a systematic phenomenon for tool steels with higher alloying level.

Boronized layers formed at 1030 °C for 30, 45, and 75 min are all of only one phase, Fig. 3(a)-(c). The layer formed at the same temperature but for a processing time of 150 min contains clearly visible two phases, Fig. 3(d). As clearly seen from this micrograph, the boronized layer formed when processed for 150 min is cracked at the interface between the two boron phases. The crack propagated longitudinally to the surface. The cracking would be explained by the fact that when, e.g., both Fe_2B and FeB phases are formed, a stress discontinuity at their interface can lead to the cracking, mainly in the region of the FeB phase. The monophase layers are homogeneous in the absence of macrocracking, Fig. 4.

Monophase boronized regions can be divided into two basic parts, Fig. 4. The first one, close to the surface, is the compound layer, containing a lot of thin pores mostly in near-surface area. As detected by x-ray analysis, Fig. 5(a), the compound layer contains only the Fe_2B phase for the samples processed for 75 min On the other hand, the x-ray patterns confirmed without doubt that the material boronized for 150 min contained also the FeB phase on the surface, Fig. 5(b). The boundary between the compound layer and the diffusion region exhibits a typical sawtooth morphology. This is rather surprising in the first sight since the sawtooth morphology of interface is typical mainly for the growth of layers on low-alloyed tool steels. However, the H11 tool steel contains 7.9 wt.% of alloying elements and thus cannot be considered as the low-alloyed steel. The sawtooth morphology of interface was neither detected in boronizing of the steel with 0.5% C and 8.85% Cr nor in boron saturation of M2 high-speed steel (Ref 8-10). In addition, there are no relevant data on the boronizing of hot work tool steels of similar chemistry as the H11 material. Further investigations are thus necessary to determine the chemistry of the steel, which initiates the formation of the sawtooth morphology of the compound layer.

Below the compound layer, there is the diffusion region. Diffusion region contains some carbides also because carbon is not soluble in borides, and during the boronizing, it diffuses into the core material as discussed above.

Figure 6 shows the results of the EDS mapping of the boronized layer, formed at 1030 °C for 75 min, and the substrate material in its vicinity. The EDS maps of iron, Fig. 6(b), and the main alloying elements demonstrate that the boronized compound layer is enriched mainly by chromium, Fig. 6(c). On the other hand, no boride-forming element silicon diffuses from the compound layer below it to the diffusion region, Fig. 6(d). The intermediate region with enhanced density of carbide particles also contains more chromium mainly in the carbides, and less silicon.

Point EDS-analysis, Table 1, reveals that the chromium and, to a limited extent, also vanadium are accumulated in the compound layer in amounts slightly higher than those in the actual alloy composition. The chromium content of around 6.25 wt.% is in very good agreement with the Dybkov's observations valid for pure Fe-10%Cr alloy (Ref 11). Therefore, the compound layer can be characterized as $(Fe,Cr)_2B$—boride, with a small addition of other elements.

The carbides in the intermediate region contain also an increased amount of chromium, vanadium, and molybdenum. Nevertheless, iron is still the dominant element in the carbides so that we assume that they are characteristic of alloyed cementite $(Fe, Cr, Mo, V)_3C$. This hypothesis, however, requires further investigations for validation.

Hardness measurements of boronized layers are summarized in Table 2. If only Fe_2B compound is formed, and the processing time was short, then it had the average microhardness of 1473-1483 HV 0.1. Diffusion region was considerably softer—its microhardness was 638 HV 0.1. If the processing time was longer (75 min), then the hardness of boronized layer increased to 2221 HV 0.1. Such a high value indicates that at least tracks of FeB phase could be formed—however, neither the x-ray diffraction nor the structural investigations confirmed the same. For the specimens processed for 150 min also, the FeB compound was evidently formed, and its average value of microhardness exceeded 2300 HV 0.1. In this case, the microhardness of Fe_2B layer reached only up to 1700 HV 0.1.

The material after heat treatment without boronized layer had the Charpy impact strength of more than 300 J. The presence of boronized layer on the surface lowers the Charpy impact strength dramatically, and the lowering is more evident as the thickness of boronized layer increases. The impact strength of layers formed for short-time processing has not been measured yet; however one cannot expect any significant improvement. Various authors (Ref 9, 10, 12) have found that the fracture toughness of boronized layers is very poor—it ranged between 2.1 and 4.8 $MPa.m^{1/2}$ for some ledeburitic steels and other high-alloyed steels. Boronized layers have thus several times worse resistance against propagation of brittle cracks than the steel substrate (although, in addition, the fracture toughness of high-alloyed and heat-treated tool steels is not good), and any sub-microscopical defects can easily act as fracture nuclei.

Figure 7 shows the fracture surface of the material without boronized layer on the surface. The surface clearly exhibits evident ductile morphology with some secondary cracks and deep dimples, Fig. 7(a). The detailed micrograph, Fig. 7(b), demonstrates that the propagation of the fracture is associated with an evident plastic deformation. This is a natural explanation for the high values of the absorbed Charpy impact energy and good impact strength of the material.

The situation in the case of boronized material differs clearly from that of the non-boronized. Figure 8 shows the results of fractographic analysis of Charpy specimens boronized at 1030 °C for 150 min The fracture is initiated at the tensile side of the specimens (a), probably due to the cracking of boronized layer, and propagated downward the material through diffusion interlayer (b). Cracking of the boronized layer is evidently supported by its morphology i.e., columnar character of the microstructure contributes to the brittle character of failure. The interlayer exhibits clearly transcrystalline cleavage character of the fracture, i.e., only minimum energy is absorbed by plastic deformation. Further propagation of the fracture, also in the core material (c), is also realized mostly via transcrystalline cleavage. In fact, an increased amount of carbides found in the vicinity of boronized layer probably makes the material less capable to withstand against the crack propagation. The explanation of dramatic embrittlement of the bulk material due to the boronizing, compared to non-boronized steel, is then complex—all the parts of affected region contribute to the total embrittlement in a specific manner: compound layer due to the brittleness itself, diffusion,

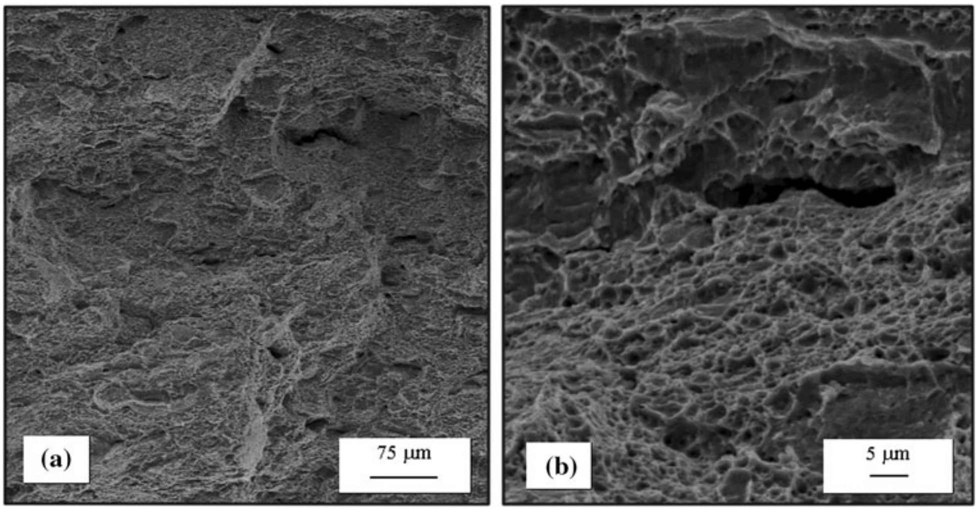

Fig. 7 SEM micrographs of the fracture surface of the specimen without boronized layer. (a) Overview and (b) detail

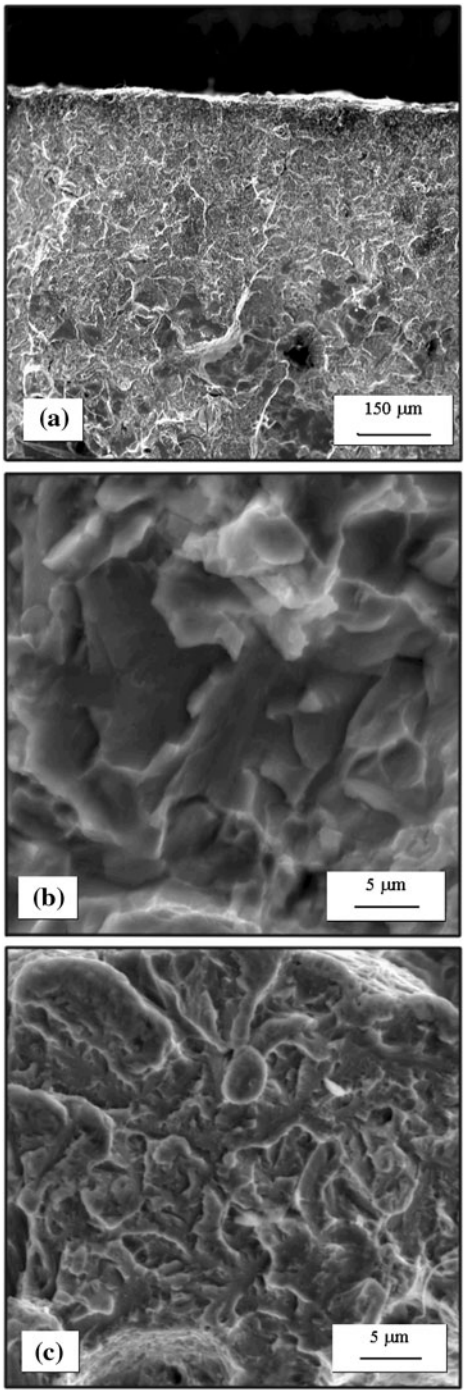

Fig. 8 The results of fractographic analysis of Charpy specimen boronized at 1030 °C for 150 min. (a) Overview, (b) diffusion region, and (c) substrate

and intermediate region by the enhanced amount of hard carbides.

4. Conclusions

The main goal of this experimental effort is to develop the optimal boronized layer with a good adhesion on the substrate, sufficiently high hardness, good resistance against cracking, and with as minimally as possible negative influence on the bulk properties.

(1) All the developed layers have a thickness exceeding 50 μm. No cracks or inhomogeneities on the layer/substrate interface were found in the case of monophase layers. If the layer consisted of two phases, then longitudinal cracks on the boundary of these phases were detected.
(2) The boronized layers have a sawtooth morphology, surprisingly at the first sight, because this morphology is typical rather for plain carbon and low-alloyed steels.
(3) Boronizing leads to extensive carbon redistribution in the affected region which is associated with formation of intermediate region with considerably increased density of carbide particles.
(4) Boronized layer formed for 150 min consisted of FeB and Fe_2B phases. The layers produced for shorter processing time were formed only from Fe_2B phase. In all the cases, the borides are alloyed, mainly with chromium.
(5) The layers formed for 150 min had microhardnesses of 2325 HV 0.1 and 1700 HV 0.1 for FeB and for Fe_2B, respectively. The layers formed for 30, 45, and 75 min had microhardnesses of about 1500 HV 0.1, excepting the surface of the layer produced for the time of 75 min. The last one was significantly harder.
(6) The presence of boronized layers on the surface lowered the Charpy impact energy of the bulk material in order of magnitude. It seems that there is only limited possibility to reduce the embrittlement of the material due to the boronizing to an acceptable level. The use of boronizing for dynamically loaded hot work tools is therefore only hardly possible.

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