

The Effect of Boronizing on the Magnetization Behaviour of Low Carbon Microalloyed Steels

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The change of saturation magnetization in boronized low carbon microalloyed steels was investigated as a function of boronizing time. Specimens were boronized in an electrical resistance furnace for times ranging from 3 to 9 h at 1123 K. The metallurgical and magnetic properties of the specimens were investigated using optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). A boride layer with saw-tooth morphology consisting of FeB and Fe₂B was observed on the surface, its thickness ranged from 63 μm to 140 μm depending on the boronizing time. XRD confirmed the presence of Fe₂B and FeB on the surface. The saturation magnetization decreased with increasing boronizing time. This decrease was attributed to the increased thickness of the FeB and Fe₂B phases. Cracks were observed at the FeB/Fe₂B interfaces of the samples. The number of interfacial cracks increased with increasing boronizing time.

Key Words : boronizing, iron boride, saturation magnetization, x-ray diffraction, coatings

1. Introduction

Low-carbon microalloyed steels are widely used in mechanical engineering, particularly in pressure vessels and pipelines transporting oil and natural gas due to their high strength, good toughness and weldability [1]. The improved mechanical properties of these steels are due to small additions of Nb, Ti and V which form carbonitrides in the steel. For example, introducing very small amounts of Nb into a low carbon steel results in Nb(CN) precipitation and significant grain refinement [2-7]. The mechanical properties of these materials may also be further improved by surface modification treatments such as hardening or coating [8].

Boronizing (or boriding) is a thermochemical surface modification and hardening treatment similar to carburization, which enriches the steel surface with boron, where B atoms diffuse into the surface of the material at high temperatures [8-11]. Borides are formed at the surface the type of boride formed depends greatly on the substrate as well as the boronizing source, temperature and time.

Magnetization is an important parameter for steels and under a magnetic field, the behavior of these materials can

vary greatly depending on their particular characteristics. It has been shown that the change in magnetic parameters of irradiated steel depends on various conditions: specimen preparation, irradiation conditions, residual stress and microstructural differences [12, 13]. The effect of these parameters on saturation magnetization is the subject of controversy [14]. A possible cause is the strong interaction between the domain walls of small precipitates, which have a spontaneous magnetization different from that of the matrix. Vaccari [15] showed that the substitution of Co for Fe in Fe-based amorphous alloys improves the saturation magnetization ($B_s = 1.8$ T). In addition, Weglinski and Kaczmar [16] reported an increase in saturation magnetization from 1.6 to 1.78 T after the addition of 0.8 wt % P to powder metallurgically processed Fe. Gopalan *et al.* [17] observed a high saturation magnetization of 1.9 T in melt spun Fe-P alloy ribbons after magnetic annealing at 673 K. In rapidly quenched Fe-Si alloys, Varga *et al.* [18] noted a saturation magnetization value of 0.6 T for nanocrystalline Fe₆₇Si₃₃ ribbons.

Previous work thus indicates that alloying elements have a significant effect on the magnetization behaviour of steels. It is therefore necessary to further examine the effects of alloying elements and impurities on the magnetization behaviour of steels. In this study the effect of the boronizing time on the saturation magnetization of low carbon

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Table 1. Chemical composition (wt %) of low carbon microalloyed steel.

C	Si	Mn	P	Mo	Mg	Cr	Al	Nb	Fe
0.044	0.353	1.345	0.011	0.023	0.010	0.010	0.030	0.030	Bal.

microalloyed steels is investigated.

2. Experimental Method

The chemical compositions of the test materials are listed in Table 1. The samples were cut into dimensions of $2 \times 2 \times 15 \text{ mm}^3$, ground with 180, 320 and 400-grit SiC abrasive papers, and finally cleaned with acetone to remove grease and dirt. The finished samples were packed in a commercial Ekabor-II boron source with an approximate chemical composition of 90% SiC, 5% B₄C and 5% KBF in an alumina crucible of 60 mm diameter and 70 mm height. The samples were then boronized in an electrical resistance furnace for durations of 3, 5 and 9 h at 1123 K. After boronization the samples were removed from the furnace and cooled in air.

Both unboronized and boronized cross-sectional samples were mounted in epoxy, ground with 180, 320, 600 and 1000 grit SiC abrasive papers, and polished with 6 μm diamond paste for microstructural and microhardness studies. The unboronized specimens were etched with 2% Nital to reveal the ferrite grain boundaries for optical microscopy (OM).

X-ray characterization of the borides on the surface of the boronized steels was performed by a Rigaku D-MAX 2200 X-ray diffractometer (XRD) on additional unmounted specimens. Cu-K α radiation of 0.15418 nm wavelength was used with a 2θ range of 20° to 90° .

The borided cross-sectional specimens were coated with gold for scanning electron microscopy (SEM). Microstructural and morphological details were then observed using a JEOL-5600LV scanning electron microscope. The thicknesses of the boride layers were also measured from the SEM micrographs. The thickness of the boride layer was taken as the distance between the coating surface and the root of the boride layer.

The magnetization of the steel specimens was measured using a Cryogenic Q-3398 vibrating sample magnetometer (VSM) at the Inonu University [19]. The measurements of magnetic hysteresis loops were performed at 295 K with applied magnetic fields of up to $\pm 0.95 \text{ T}$.

3. Results and Discussion

An optical micrograph of the steel before the boronizing treatment is given in Fig. 1. The microstructure of the steel consists mostly of fine ferrite grains (bright contrast), with very few pearlite grains (dark contrast). Fig. 2 shows the

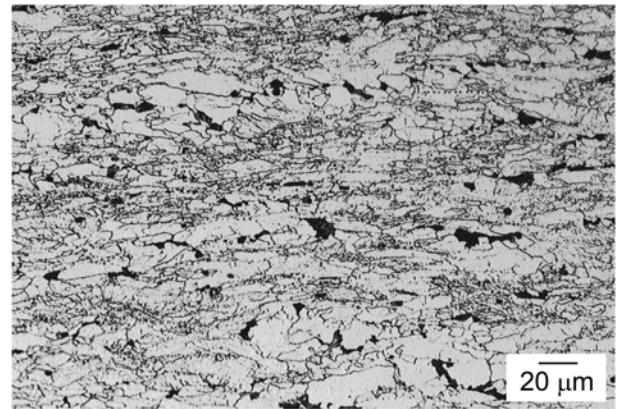


Fig. 1. Optical micrograph of the substrate prior to boronization.

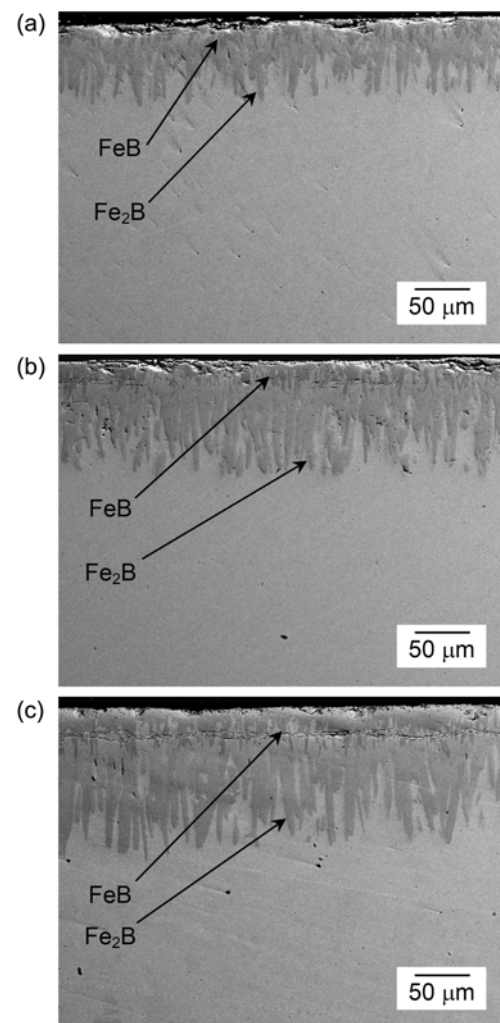


Fig. 2. SEM of the cross-sections of boronized low carbon microalloyed steels at 1123 K for (a) 3 h, (b) 5 h, (c) 9 h.

cross-sectional SEM micrographs of the boronized low carbon microalloyed steels. The figure illustrates that a well adhered boride layer with saw-tooth morphology is formed

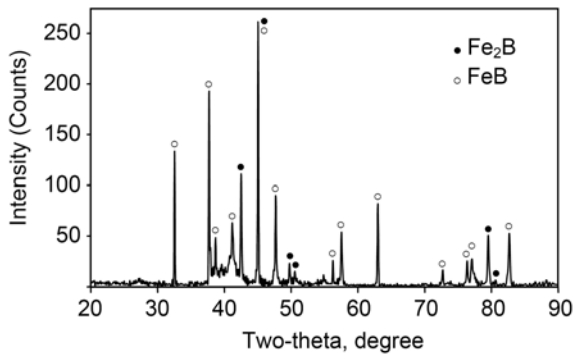


Fig. 3. XRD pattern for the steel sample boronized at 1123 K for 9 h.

on all borided samples. The boride layer is composed of two distinct phases that can be distinguished by their contrast difference. In many iron-based alloys the boride layer consists of both FeB and Fe₂B, where FeB forms on the outer surface and Fe₂B forms adjacent to the core. The outer dark region was determined to be FeB and the inner lighter region was found to be Fe₂B by XRD (Fig. 3). Previous studies have shown that the characteristics of this boride layer depends on the physical state of the boride source used, the boronizing temperature, treatment time, stress and properties of the boronized material [20-22]. It was found that the duration of the boronizing process affects the thickness of the boride layer (Fig. 2). The thickness of the boride layer increases from 63 μm to 140 μm for 3 h and 9 h boronizing time, respectively.

All of the specimens show some degree of cracking at the interface between the FeB and Fe₂B. This cracking increases with increasing boronizing time, and cracks begin to follow a path parallel to, and 25 μm beneath, the surface. The cracking at the interface is caused by the differences in the coefficient of thermal expansion (CTE) between the two layers [23, 24]. Microcracks were occasionally observed in the FeB layer (Fig. 2a), these are caused by the mismatch between the thermal expansion coefficients of FeB ($2.3 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$) and Fe₂B ($7.85 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$). Cracks initially develop within the FeB phase. Despite being very hard, the FeB layer is very brittle and has a substantially different coefficient of thermal expansion. During the cooling phase after boronizing, high tensile stresses develop in the FeB phase while compressive stresses form in the Fe₂B; hence, borided steels with high amounts of FeB develop extensive cracks at the interface between the FeB and Fe₂B. It is likely that the continuous nature of the FeB layer is what causes the microcracking to occur at the specific depth in the sample borided for 9 h.

The typical hysteresis loops as a function of boronizing time are shown in Fig. 4. The saturation magnetization and initial permeability of the boronized low carbon microalloyed steels decreases with boronizing time. The satura-

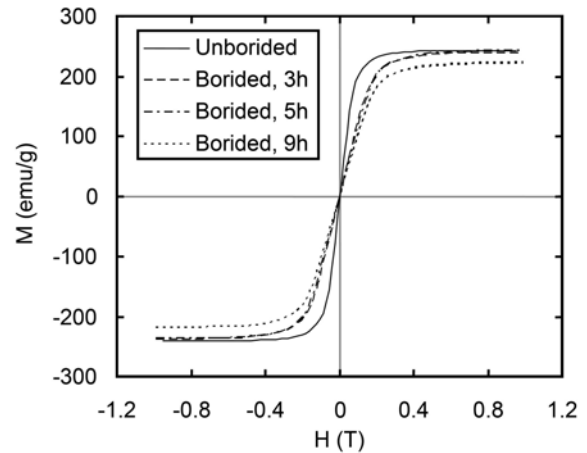


Fig. 4. The typical hysteresis loops as a function of boronizing time of low carbon microalloyed steels.

tion magnetization decreases from 243 emu/g to 223 emu/g for the unborided steel and 9h-borided steel, respectively. The most significant decrease in saturation occurs in the 9h-borided steel. In previous literature it has been pointed out that the saturation magnetization is known to be insensitive to structure in the sense that it does not depend on the details of the fine structure, such as strain, lattice imperfection and/or small amounts of impurities [15, 25]. Therefore, the decrease of saturation magnetization in boronized low carbon microalloyed steels can be explained by the increase of boride layer thickness. Iron borides FeB and Fe₂B were formed at the surface of the steel through the diffusion of B into the steel during boronization. Longer boronizing times result in more FeB and Fe₂B formation and hence thicker layers [26]. However, increasing boronizing time also results in cracking between the FeB and Fe₂B layers due to the thermal expansion mismatch [23, 24, 27], as can be seen in Fig. 2.

The magnetic saturation depends on the type and amount of ferromagnetic components in the alloy (unfilled d levels in the case of Fe). Since B is diamagnetic, the magnetization in FeB and Fe₂B is lower than that of Fe [28, 29] and there is a decrease in magnetization with increasing boronizing times (Fig. 3). The Fe atoms at or near the surface possess enhanced moments compared to the Fe atoms in the bulk. Therefore, the saturation magnetization decreases as more and more FeB and Fe₂B phases are introduced with increasing boronizing time. In a low alloy steel, Park *et al.* [13] showed that the increase of saturation magnetization is due to Fe atoms being separated from Fe₃C carbide after neutron irradiation. In this study the decrease in saturation magnetization is attributed to the formation of the FeB and Fe₂B phases.

While the magnetization of paramagnetic steels -such as AISI 316L- can be increased considerably by boronizing treatments [30], it is clear that short-time boronizing treat-

ments (up to 5h) have little effect on the magnetization of ferromagnetic steels. The greatest decrease in saturation magnetization was observed in the 9-h boronized specimen, in which an 8% decrease was detected.

4. Conclusions

The effect of boronizing time on the microstructure and magnetic properties of low carbon microalloyed steels were investigated. The main results are as follows:

1. According to XRD analysis and SEM micrographs, the boride layers of the steels were composed of FeB and Fe₂B phases. Borides formed on the substrates had a saw-tooth morphology and higher boronizing times resulted in an increase in layer thickness, from 63 μm to 140 μm.

2. The saturation magnetization of the steels decreased with boronizing time, this was attributed to the increased thickness of the FeB and Fe₂B phases.

3. The cracks observed at the FeB/Fe₂B interface were caused by a thermal expansion mismatch between the two layers during cooling.

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