BORIDING OF STEELS IN FUSED MEDIA

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The saturating medium usually used in electrolytic boriding is fused borax. The saturating ability of borax can be increased considerably by various additions. With the addition of 50-60% \( \text{B}_2\text{O}_3 \) [1] or 30% \( \text{Na}_2\text{SiO}_3 \) the saturation rate increases 25-30%. Further increase of the \( \text{Na}_2\text{SiO}_3 \) concentration (over 40%) does not increase the depth of the diffusion layer but leads to the formation of new borosilicided diffusion layers. The activity of the electrolyte can also be increased 15-20% by small additions (10-15%) of sodium fluoride and potassium ferrocyanide [1]. The accelerating effect of additions of \( \text{B}_2\text{O}_3 \), \( \text{Na}_2\text{SiO}_3 \), and \( \text{NaF} \) on electrolytic boriding results from the mechanism described in detail in [2]; the effect of potassium ferrocyanide is probably due to its deoxidizing effect. To increase the fluidity of the bath it has been recommended that 10-25% NaCl be added [3]. The concentration of sodium chloride should not exceed 15% because it reduces the depth of the boride case [1]. Electrolytic boriding can also be conducted in other baths based on borax. For boriding molybdenum a melt consisting of 33% HBO\(_2\) and 67% NaF was used [4]. This melt can also be used for boriding steels.

Liquid (without electrolysis) boriding is conducted in fused borax with boron carbide [5]. The maximum depth of the layer is obtained in a melt consisting of about 50% \( \text{B}_4\text{C} \) and 50% \( \text{Na}_2\text{B}_4\text{O}_7 \). The melt is very viscous, however, and the process is not very workable. To increase the fluidity and reduce the cost of the process, melts with smaller amounts of boron carbide (30-40% \( \text{B}_4\text{C} \)) are used. The fluidity of the melt can also be increased (without reducing the depth of the diffusion layer) by adding 10-15% NaCl.

The rate at which the boride case is formed in liquid boriding is far lower than in electrolytic boriding. However, the simplicity of liquid boriding makes it a more attractive process for commercial use. We made an investigation of cheaper and more easily available deoxidizers for boriding, including the following: calcium-silicon (KaCu I), ferrosilicon (Cu90, Cu75), silicon, ferromanganese (Mn5), and also SiC, the closest of covalent carbides to the structure of boron carbide. We determined the optimal compositions of the baths at a processing temperature of 950-1000°C; 1) 85-90% \( \text{Na}_2\text{B}_4\text{O}_7 \) +10-15% KaCu I; 2) 90% \( \text{Na}_2\text{B}_4\text{O}_7 \) +10% Cu90; 3) 85-90% \( \text{Na}_2\text{B}_4\text{O}_7 \) +10-15% Si; 4) 80% \( \text{Na}_2\text{B}_4\text{O}_7 \) +20% Mn5; 5) 65% \( \text{Na}_2\text{B}_4\text{O}_7 \) +35% SiC.

The particle size of the deoxidizers should be as follows: KaCu I, 1.0-1.4 mm; Cu90, 0.06-0.1 mm; Si, 0.06-0.1 mm; Mn5, 1.0-1.4 mm.

The depths of the boridic layers obtained in different melts at 1000°C for 6 h are given in Table 1. The saturating ability of the melts can be greatly increased by adding boric anhydride (85% \( \text{B}_2\text{O}_3 \) +15% \( \text{Na}_2\text{O} \)) or small amount (5-8%) of sodium fluoride and potassium ferrocyanide. With the addition of 5% NaF or 5-10% \( K_4[\text{Fe(CN)}_6] \) the depth of the boride case increases 30 and 20% respectively. The saturation rate is somewhat lower than in the bath consisting of 30% \( \text{B}_4\text{C} \) +70% \( \text{Na}_2\text{B}_4\text{O}_7 \), but the new baths are considerably cheaper. The addition of the new deoxidizers in place of \( \text{B}_4\text{C} \) makes it possible to reduce the cost of the process to one-third to one-half.

The formation rate of the boride layer is also substantially affected by the chemical composition of the steel [2]. The boride case depth is reduced most by elements that narrow the \( \gamma \)-region: chromium, titanium, molybdenum, tungsten, and carbon.

The boride case consists of two zones differing sharply in structure: a boride zone in which the boron occurs in chemical compounds, a "transition" zone in which the boron is in solid solution. The structure and reasons for the formation of the transition zone can be found in [6].

The boride case formed in electrolytic boriding has a characteristic "acicular" structure and consists of \( \text{FeB} \) and \( \text{Fe}_2\text{B} \). The \( \text{FeB} \) phase is distributed in the surface of the boride case, followed by the \( \text{Fe}_2\text{B} \) phase, and then the transition zone. The concentration of high-boron phase in the boride case on Armco iron...
Fig. 1. Effect of boriding conditions on the brittleness (grade) of the case. 1) Liquid boriding in 35% \( \text{B}_4\text{C} + \text{borax} \) at 1000°C for 8 h; 2) electrolytic boriding in \( \text{borax} \) at 1000°C for 4 h (current density 0.3 A/cm²).

Fig. 2. Wear resistance of steel 45 in relation to boriding method and case depth. 1) Not borided (quenched + tempered at low temperature); 2) liquid boriding in \( \text{borax} \) with silicon carbide (1000°C, 4 h); 3) liquid boriding in \( \text{borax} \) with boron carbide (1000°C, 4 h).

Fig. 3. Heat resistance of steel 20. 1) Not borided; 2) borided in 35% \( \text{SiC} + 65\% \text{ Na}_2\text{B}_4\text{O}_7 \) at 1000°C for 6 h.

Under optimal saturation conditions (950°C, 3 h, current density 0.25 A/cm²) reaches 64-66%; in steel 45 it reaches 56-59%; in steel U8 it reaches 54-55%. Nickel, manganese, chromium, tungsten, and molybdenum (in the order of increasing effect) slightly increase the relative concentration of high-boron phase in the diffusion layer, while aluminum, carbon, and particularly copper decrease it.

In liquid boriding in a bath of \( \text{borax} \) with boron carbide (30-40%) or calcium – silicon (10-15%) a two-phase boride case (FeB + Fe₂B) is also formed, but the concentration of high-boron phase is considerably lower than in electrolytic boriding. Under optimal saturation conditions (1000°C, 5 h) the relative concentration of high-boron phase in the case on Armco iron does not exceed 30-35%, or 22-24% on steel 45. An increase of the temperature to 1000-1050°C and an increase of the saturation time are accompanied by some increase in the concentration of FeB in the diffusion layer. In other respects the diffusion layers obtained in liquid boriding are almost indistinguishable from those obtained in electrolytic boriding.

The effects of alloying elements on the phase composition of the diffusion layer obtained in \( \text{borax} \) with boron carbide and calcium – silicon match those given above.

Saturation of low- and medium-carbon steels in baths of \( \text{borax} \) with ferrosilicon silicon, ferromanganese, and silicon carbide under ordinary conditions (950-1000°C, 3-5 h) results in a single-phase case consisting of Fe₂B. The second phase occurs in medium-carbon steels only after processing 8 h at 1000°C. The alloying elements chromium, nickel, and tungsten favor the occurrence of a second phase in the case. However, in notable quantities (under optimal saturation conditions) the second phase occurs only in high-alloy steels R18, Kh12, and 3Kh2V8. After saturation in these baths the most widely used alloyed structural and tool steels (40Kh, 40KhN, 5KhNM, 5KhVG, ShKh15, KhG, KhVG) form a "single-phase" boride case (x-ray diffraction analysis reveals the presence of FeB in the case, but its concentration is so small that it cannot be observed in metallographic analysis). It should be noted that in boriding highly alloyed steels containing strong carbide-forming elements (chromium, molybdenum, tungsten) the boride case retains inclusions of nonetching carbides \( \text{Cr}_2\text{C}_6 \) and \( \text{Fe}_3\text{W}_2\text{C} \).

Below the boride case on high-carbon steels one observes lamellar precipitates of boron cementite \( \text{Fe}_3(\text{C, B}) \) of variable composition. The boron concentration of the boron cementite depends on the composition of the steel and the boriding method. The texture of the boron cementite is similar to that of the boride phase, although its orientation depends not on the diffusion front but the orientation of the matrix – austenite.

The boride phases have a high microhardness. The results of microhardness measurements of single-phase and double-phase boride layers are given in Table 2. The carbon content of the steel has a strong effect on the hardness of the borides. Apparently this is due not to the composition of the borides but to the...