SURFACE IMPREGNATION AND TREATMENT

BOROZINING OF HIGH-ALLOY STEELS

Dr. tech. sc., Prof. Yu. M. Lakhtin and Eng. M.A. Pchelkina
Moscow Road Transportation Institute

This work reports on an investigation of gaseous impregnation with boron of high-alloy stainless and heat-resistant steels to incrase their hardness, resistance to wear erosion and scoring at high temperatures. We first studied the effect of chromium and nicket on the hardness, depth and phase composition of the boronized layer.

Impregnation with boron was conducted in diborane in a mixture with hydrogen (B_2H_6:H_2 = 1:25) at 950°C/6 hrs. [1]. After boronizing, the specimens were held at the impregnation temperature for 4 hrs. At this temperature, the high-chromium steels had a mixed structure consisting of λ and α -phases whle all the other steels were austenitic.

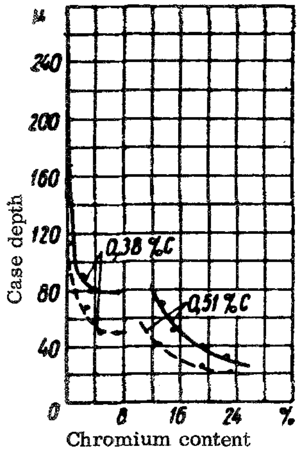

Fig. 1. Effect of Cr on depth of boronized layer: solid line - total layer depth; dashed line - depth of solid layer of borides.

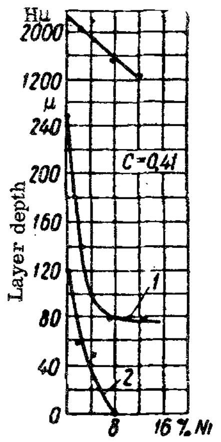

Fig. 2. Effect of nickel on depth and hardness of a boronized layer: 1 — total layer depth; 2 — depth of solid boride layer

Figures 1 and 2 contain data on the effect of Cr and Ni on the depth of the boronized layers. The distance between the surface of the specimens and the end of the layer containing boride phases (Figure 3) was considered the full layer depth. This included also the transition layer consisting of α -solid solution with borides.

It is seen in Figure 1 that small additions of Cr to medium carbon steels reduced considerably the depth of the diffusion layer. An increase of chromium to 3-8% did not affect the overall layer depth or the layer of massive borides. At 12-25% Cr in a 0.51% C steel, the depth of the boronized layer decreased, Figure 1.

The hardness of the boronized layer increased somewhat with chromium content. For instance, the hardness of a steel with 0.38% C and 1.06% Cr was 1290 $H\mu$. In steels with 0.51% C and 13-19.5% Cr, the hardness was 1850-2290 $H\mu$. Figure 3, c shows a typical microstructure of a boronized layer on a chromium steel. Addition of nickel up to 4-6% reduced the depth of the diffused layer. At still higher nickel contents the overall layer depth did not change but the continuous layer of borides became considerably thinner, Figure 2. In steels with 6-8% Ni, the all-boride layer was totally absent and only an austenitic zone with borides was observed at the impregnation temperature (Figures 2 and 3, a). However, boride "whiskers" (Figure 3, b) penetrating to a considerable depth formed in steels with 7-8% Ni. The hardness of the boronized case decreased with increasing nickel, Figure 2.

Addition of 6-7% Ni to a steel with 0.32% C and 15.52% Cr increased the overall depth of the boronized case as well as the depth of solid boride layer. At a still higher nickel content, the depth of the diffused layer either changed very little, if at all. Figure 4. The structures of the diffusion layer are shown in Figure 3, d. A solid layer of borides of sufficient thickness was observed in all cases. The presence of 2.2% W in a high-chromium steel reduced the boronized case thickness.

Addition to a chromium steel (0.32% C and 15% Cr) of up to 8% Mn had practically no effect on the depth and structure of the diffused layer. Figures 5 and 6 demonstrate that columbium and especially titanium reduce considerably the depth and hardness of the boronized case on 18-8 type steels.

The decrease of the depth of the diffusion layer owing to alloy elements is probably associated with an increased binding strength in the borides as was experimentally established during boronizing of alloyed ferrite [2].

We boronized several standard stainless and heat-resistant steels, with the results given in the Table on following page.

Figure 7 gives the distribution of hardness across the boronized case in steel "G". The hardness change pattern in other austenitic steels is the same as in this one.

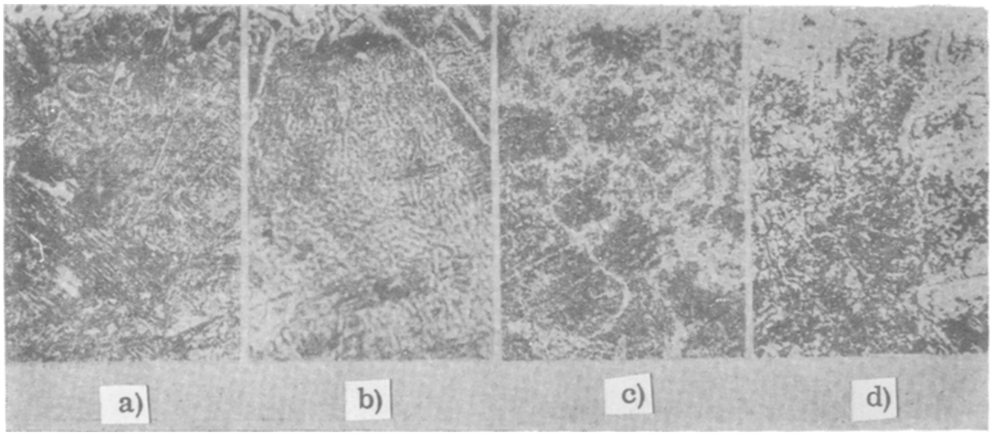

Fig. 3. Microstructure of boronized layer on various steels, 300 x: a — 0.41% C, 12.82_2 Ni; b — 0.41% C, 11% Ni; c — 0.38% C, 4.74 Ni; d — 0.32% C, 15.52% Cr, 6.6% Ni.

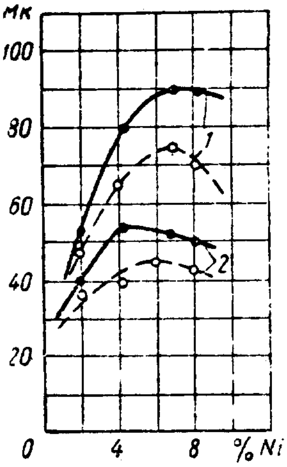

Fig. 4. Effect of nickel on the boronized case depth on a steel with 0.32% and 15.52% Cr: 1 — total layer depth; 2 — depth of continuous borides layer. (Dashed lines refer to a steel with 0.34% C, 15.45% Cr, 2.7% W).

The process of boronized layer formation in alloy steels differs from the mechanism taking place in iron or other pure metals [1]. During boronizing of iron (or other metal) mixtures of phases such as α-solid solution and borides cannot exist [1]. During the impregnation with boron of complex austenitic steels with high Ni, Cr and other elements, the formation of a diffusion layer apparently takes place as follows:

When the saturation limit for boron in the alloyed solid solution is reached, borides appear at the impregnated surface alongside the saturated α-solution. The formation of borides is accompanied by a depletion of the solid solution in boride-forming elements.

The borides are located within the solid solution in patches. With time, their formation takes place not only at the furface but within the layer at a certain depth as well. The higher the content of boride-forming elements (Ni, Cr and etc.), the more borides are formed during the treatment. As a result, a solid layer of borides appears on the surface and an austenite-boride zone follows underneath.

TABLE 1

Steel Grade	Boronizing schedule		Case depth, μ		Microhardness (superface)
	Tempera-ture, °C,	Time, hrs,	Borides	Total Depth	
1Kh18N9T (steel "A")	950 1100	6 2	25 20	100 120	2200 2200
Kh18N12M3T (steel "B")	900	4	20	100	2290
Kh18N25S2 (steel "C")	900 1100	4 2	25 70	115 150	2290 2200
Kh23N18 (steel "D")	950 1100	6 2	15 20	130 130	2190 2190
Kh25N20S2 (steel "E")	950	6	15	70	1890
Kh25N25T (steel "F")	950	6	12	130	2090
Kh15N37V3T (steel "G")	850 850 850 850 950 1050	2 4 6 10 2 2	15 25 30 45 30 50	60 75 125 160 80 120	2190 2190 2190 2190 2190 2190

Figure 8 shows microstructures of the boronized case of steels "D".

Short-time saturation with boron at high temperature

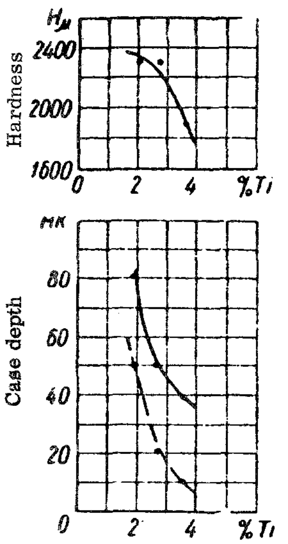

Fig. 5. Effect of titanium on depth and hardness of boronized case on steel with 0.15% C, 18.39% Cr, 8.4% Ni, 2.05% W: Solid lines - total layer depth, dashed lines - depth of solid borides layer.

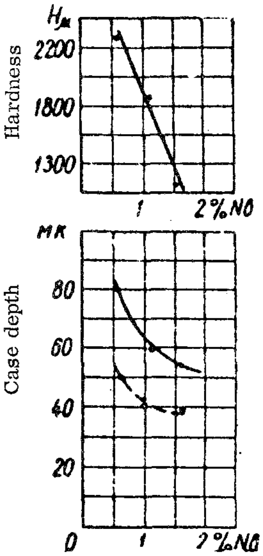

Fig. 6. Effect of columbium on case depth and hardness on steel with 0.27% C, 17.5% Cr, 8.1% Ni, 2.3% W.

results in the formation of an austenite-boride zone, Figure 2. In this case the solid boride layer does not form because of the vigorous escape of boron atoms from the surface into deeper strata. When the boronizing temperature is reduced and the holding time lengthened, a solid layer of boride forms on the surface and a mixed austenite-boride zone is found farther down, Figure 8, a.

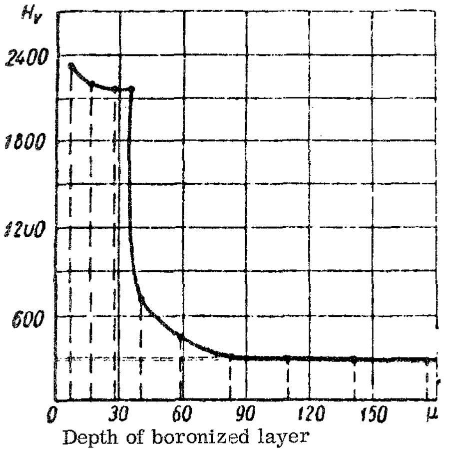

Fig. 7. Hardness distribution across thickness of boronized case on steel "G".

It is seen from Figure 8 that during formation of the mixed zone, the borides form at first at grain boundaries and grain junctions in the austenite and then within the grain body and the sub-boundaries between large mosaic blocks. Such a boride phase formation suggests that diffusion of boron occurs mainly along grain boundaries.

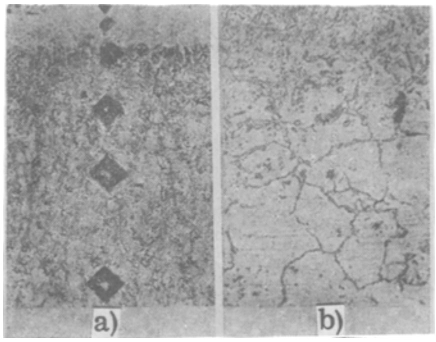

Fig. 8. Microstructure of boronized case, 500 x:
a — steel "D" boronized at 950°C/6 hrs.,
b — same steel boronized at 1100°C/2 hrs.

A saturation of steel with boron is accompanied by depletion in carbon of the austenite adjacent to the boride phases. The carbon diffuses into more remote volumes of the uastenite in the direction of the center. This is seen in Figure 9 showing the microstructure of a boronized case on a steel with 0.41% C and 12.82% Ni. Hence, the transitional austenitic-boridic zone contains, at the diffusion temperature, two α -solution with low and high carbon concentrations in addition to the boride phase.

X-ray studies of the phase composition of the boronized case on high-chromium (13% Cr), nickel (25% Ni) and 18-8 steels showed that it consists of iron borides in which a part of the iron atoms was replaced by alloy elements [3]. Boronizing of high-chromium steels is accompanied by formation of borides of the types (Fe, Cr)B, (Fe, Cr)$_2$B; in nickel steels, (Fe, Ni)B, (Fe, Ni)$_2$B; in Cr-Ni - - (Fe, Ni, Cr)B and (Fe, Ni, Cr)$_2$B. It is possible that part of the boron in the boride is substituted by carbon. Judging from an analogy with a carbide phase, we cannot exclude the possiblity of formation during boronizing of phases containing high amounts of boride-forming elements such as nickel, i.e., borides of the types of Ni$_3$B and Ni$_2$B.

Fig. 9. Microstructure of boronized case on a steel with 0.41% C, 12.82% Ni, 600 x.

CONCLUSIONS

1. The possibility of gas boronizing of high-alloy steels, including austenitic steels has been demonstrated.

2. It is shown that, during boronizing of high-alloy steels, a two-phase layer is produced in the early stages

at the treatment temperature: a saturated solid solution (borides) followed by formation of a solid boride layer.

3. The boronized case on high-alloy steels has a high hardness and wear resistance.

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EFFECT OF PRELIMINARY SURFACE TREATMENTS OF IRON AND STEEL ON THEIR INTERACTION WITH LIQUID ZINC

Cand. tech. sc. D.Ya. Gluskin

Leningrad Shipbuilding Institute

This work is concerned with the study of the possibilities of reducing the solubility of iron and steel in molten zinc. A successful solution of this problem is important for the manufacture of equipment with which hot dip galvanizing is effected. Iron and steel specimens were prepared by impregnation with chromium and silicon to explain the effect of these processes on the interaction of the base with molten zinc.

The study was conducted on technically pure iron (TPI), steels with 0.3, 0.5 and 1% C, and on technically pure zinc (99%) Specimens of iron and steel 7 mm dia. and 20 mm long were machined for the study.

Diffusion chromizing of the specimens was conducted in a mixture with 71% aluminum low-carbon ferrochromium (70% Cr), 25% aluminum oxide and 4% ammonium chloride.

Siliconizing was performed in a mixture of 71% ferrosilicon (90% Si), 25% aluminum oxide and 4% ammonium chloride. To study the effect of pure chromium on the interaction of a ferrous base with molten zinc, some specimens were electrolytically chromium plated.

Data on the specimens initially subjected to surface impregnation are listed in Table 1 and shown in Figure 1. Specimens not subjected to the above pretreatments were also tested in regard to their interaction with molten zinc.

A small amount (50 g) of zinc was melted in a porcelain crucible; specimens first wetted in zinc chloride were immersed into the bath. The interaction between the specimens of metal and the zinc was studied at 500°C since the maximum solubility of iron in liquid zinc is found at this temperature [1]. After holding for 2 to 10 hrs., the specimens were allowed cool in air.

Transverse specimen sections were etched with 4% alc. solution of HNO_3 and examined under the microscope. Table 2 and Figure 2 give information on the interaction of TPI and of steel (not subjected to any preliminary treatment) with liquid zinc at 500°C.

From the data in Table 2 it is seen that the thickness of the diffusion layer increased with longer reaction thimes and so did the amount of $FeZn_7$ crystals in the zinc; this was accompanied by a decreasing cross section of the specimens. Thus, the solubility of the metal in molten

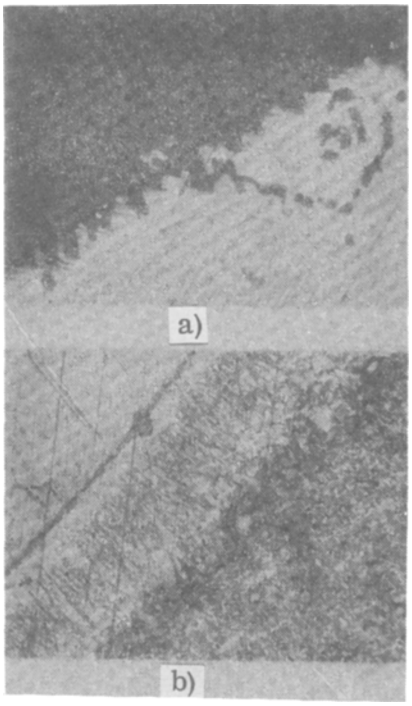

Fig. 1. Microstructure of specimens after impregnation with chromium, 200 x:
a — TPI; b — steel U10A (1% C).