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A study on the electroboronizing of steel by superimposed cyclic current

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The effect of various activators such as Na_2CO_3, B_4C, NaCl and NaOH in molten borax on the electroboronizing process of low carbon steel at 800° C, and the mechanism of boron formation have been studied. The effect of superimposed a.c. on the penetration depth of boron was also investigated. Experiments show that Na_2CO_3 is the most effective activator, followed by B_4C, NaCl. The most economic composition of activators is identified as 10 wt % Na_2CO_3, 10 wt % B_4C, 20 wt % NaCl. Applying superimposed a.c. has a considerable advantage, because cathodic polarization, affected by frequency and amplitude, is decreased and effective current densities are increased. The boronized layer is more uniform and two times thicker than that formed with conventional electroboronizing methods.

1. Introduction

The impregnation of metal surface with chemical elements is one of the most effective methods of increasing the wear and corrosion resistance of machine components. A number of chemicothermal treatment processes, such as carburizing and nitriding, have already been investigated extensively and are widely used in production. In recent years, a great deal of attention has been focused on the development and industrial application of new chemicothermal treatment techniques. Among these, a considerable advantage is shown in the use of the process of surface impregnation with pure boron or boron accompanied by other elements, such as chromium, aluminium, and titanium.

Electroboronizing in molten electrolytes results in a deeper boride layer at a relatively low cost and provides an expedient convenience compared to gaseous [1–3], solid [4–6] or liquid [7–9] boronizing processes. Electroboronizing is usually carried out by dipping iron or steel into a molten bath containing borax, boric acid and Na_2O, ZrO_2, SiC or NaCl as an activator for a definite period of time [10].

For industrial application, the development of a low-cost activator, as well as an appropriate construction of the apparatus, is essential. Diffusion annealing and the influence of the chemical composition of the steel on the process is still to be investigated. The purpose of this study is to investigate the low-temperature and low current density electroboronizing process and to develop a low-cost method by identifying the most effective activator and treatment.

2. Experimental details

2.1. Specimen and reagent

The specimens were prepared from commercial grade low carbon steel (AISI 1015). The composition is shown in Table I. The tetragonal specimen (10 mm x 10 mm x 20 mm) was polished and degreased in a sodium hydroxide solution (20%) using a ultrasonic cleaner for 30 min.

Borax ($Na_2B_4O_7 \cdot 10H_2O$) was first dehydrated at 200° C for 30 min, then at 650° C in a muffle furnace for 3 h and then ground. Complete dehydration was detected by X-ray diffractometer method. First grade Na_2CO_3, NaCl and B_4C were also used.

TABLE I Chemical composition of low carbon steel specimen (wt %)

C	Si	Mn	P	S	Cu	Al	Sn
0.15	0.07	0.084	0.019	0.031	0.25	0.003	0.031

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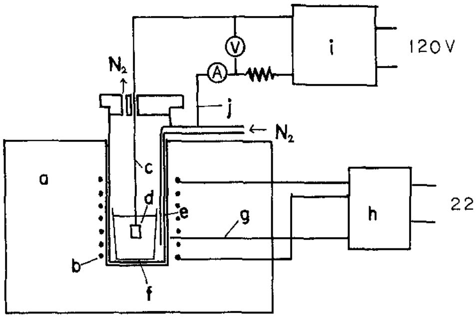


Figure 1 Apparatus for electroboronizing. (a) Cylinder furnace, (b) Fe–Cr wire, (c) Kanthal wire, (d) cathode (specimen), (e) stainless steel crucible, (f) graphite crucible, (g) thermocouple, (h) automatic temperature controller, (i) rectifier, (j) anode.

2.2.1. Apparatus

Fig. 1 shows the apparatus used in this experiment and the components are identified. Corrosion of the graphite crucible (a) and the kanthal wire heater is avoided by applying N_2 gas atmosphere. To maintain this neutral atmosphere in the furnace, the sensitive parts are enclosed in a stainless steel container (e). The specimen, acting as cathode, is connected to the negative output, and the graphite crucible, acting as anode, is connected to the positive output of the d.c. power supply.

2.2.2. Experimental procedure for conventional electroboronizing

To investigate the effect of different activators, the bath was kept at a constant temperature of 800° C, and a current density of 0.5 A cm^{-2} was used. Na_2CO_3, NaCl, or B_4C was added to the molten borax in predetermined quantities.

The effect of process time on the boronized depth using the most effective bath composition was tested after the specimen had been quenched in water.

2.2.3. Experimental procedure for superimposed cyclic current method

With a bath composition of 10 wt% Na_2CO_3 and 90 wt% borax at a temperature of 800° C, and a process time of 1 h, the frequency of the superimposed current was altered between 0 and 500 kHz. The frequency effect was determined by measuring the boride layer thickness.

In order to investigate the effect of the amplitude of the superimposed a.c., the voltage was changed between 2 and 8 V while bath temperature was fixed at 800° C, and the frequency of 5 kHz for a process time of 1 h. The process time was then altered from 1 h to 14 h at a fixed frequency of 5 kHz, a bath temperature of 800° C, and a current density of 1.2 ± 0.16 A cm^{-2}. The arrangement of the programmable d.c. power supply is given in Fig. 2.

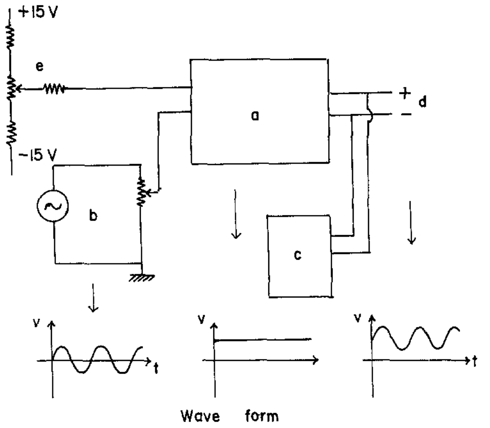


Figure 2 Block diagram of programmable d.c. power supply. (a) Direct coupled power amplifier, (b) oscillator, (c) oscilloscope, (d) output, (e) d.c. voltage adjust.

2.3. Measurement of boride layer

The thickness of the boride layer was measured from the surface to the deepest tip of the boride layer by using a metallographic microscope after cutting, polishing and etching the specimen in 3% nital solution for 5 sec. The FeB and Fe_2B layer is distinguished by colour difference after etching in picric acid natrium at 25° C for 1 min.

2.4. X-ray diffraction test

For all composition analyses, the X-ray diffraction method was used applying Diano (XRD-8000) at 35 kV and 10 mA through Cu$K\alpha$ target.

3. Results and discussion

3.1. Effect of current density

Fig. 3 shows the results of the conventional electroboronizing with the bath composition of 30 wt% NaCl, 10 wt% B_4C and 60 wt% borax at 800° C and with 1 h process time. The current density was varied from 0.03 to 1.47 A cm^{-2}. The results of this experiment are similar to those of Kunst and Schaaber [11]. The thickness of the boride layer decreased rapidly as the current density was set below 0.1 A cm^{-2}.

Fig. 5b indicates that the thickness of the boride layer increases as the Na_2CO_3 concentratios in fused borax increases. On the other

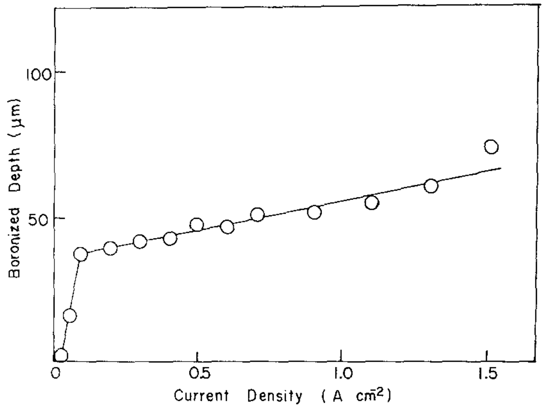


Figure 3 Relation between boronized depth and current density. (60 wt% borax + 30 wt% NaCl + 10 wt% B_4C, 800° C, 1 h.)

hand, the ion mobility of electrolytes decreases as the Na_2CO_3 concentration in molten borax increases. When Na_2CO_3 is added at 800° C, the thermal decomposition of Na_2CO_3 takes place according to the following reaction above 400° C [13–14]:

$$Na_2CO_3 \rightarrow Na_2O + CO_2 . \quad (1)$$

Pasechnik *et al.* [16] did not investigate the Na_2O decomposition, but Kawakami and Komuro [15] studied the decomposition of Na_2O. The decomposition of Na_2O takes place according to following reaction [11, 16]:

$$Na_2O \rightarrow 2Na + \tfrac{1}{2}O_2 . \quad (2)$$

Therefore, the reaction of electrolytes which are composed of fused borax and Na_2CO_3 at 800° C performs according to the following equations:

$$\begin{aligned} Na_2B_4O_7 &\rightleftarrows 2Na^+ + B_4O_7^{2-} \\ Na_2CO_3 &\rightarrow Na_2O + CO_2 \quad (3) \\ Na_2O &\rightarrow 2Na + \tfrac{1}{2}O_2 . \end{aligned}$$

As a result, only sodium ions are discharged at the cathode during electrolysis according to the following reaction:

$$Na^+ + e^- \rightarrow Na, \quad (4)$$

and at the anode

$$B_4O_7^{2-} \rightarrow 2B_2O_3 + \tfrac{1}{2}O_2 + 2e^- . \quad (5)$$

The thickness of the boride layer increases only slightly above 0.1 A cm^{-2}, because the formation of boron is restricted by the polarization effect on the cathode surface.

TABLE II X-ray diffraction data

2θ (°)	I/I_0	d	hk.l	$NaBO_2$ d	$NaBO_2$ I/I_0
22.6	28*	3.93			
29	100	3.07	10.2	3.07	90
32.7	79	2.74	20.2	2.73	70
34.4	99	2.61	31.1	2.62	100
36.2	19*	2.48			
40.7	80	2.22	32.1	2.23	70
42.3	23	2.13	31.2	2.14	30
44.7	44	2.03	40.2	2.02	40
45.8	54	1.98	33.0	1.99	80
47.4	14*	1.92			
49	30	1.86	42.1	1.87	40
51.4	20*	1.78			
59.4	18*	1.56			
60.2	15*	1.5			

*Unidentified peak.

3.2. Mechanism of the formation of boron and the effect of Na_2CO_3

Various mechanisms of boron formation have been reported. Therefore, the purpose of this study is to search for the most feasible explanation. At the interface between specimen and the fused electrolytes, solid products are created at 800° C, due to the electrochemical reaction at the current density of 0.5 A cm^{-2}, with a 3 h process time and a bath composition of 10 wt% Na_2CO_3 and 90 wt% borax.

The chemical composition and structure of this reaction product were analysed using an X-ray diffractometer. The results are shown in Fig. 4 and Table II. The reaction product is $NaBO_2$. The structure of $NaBO_2$ is hcp [12] and its melting point is 966° C [13].

This result indicates that $NaBO_2$ is created after the formation of boron due to the reaction between Na and B_2O_3 according to Pasechnik *et al.* [16]. Therefore, the thicker the solid $NaBO_2$ layer at the specimen surface is, the deeper is the boride layer of the treated specimen. The Na_2CO_3 concentration is varied from 10 to 50 wt% in fused borax at 800° C with a current density of 0.5 A cm^{-2} and a 3 h process time. Variation of the thickness of the boride layer is shown in Fig. 5b.

Fig. 6 shows the variation of thickness of the boride layer with process time and the Na_2CO_3 concentration in fused borax at 800° C with a current density of 0.5 A cm^{-2}. Na, which is formed according to Equations 2 and 4, and B_2O_3,

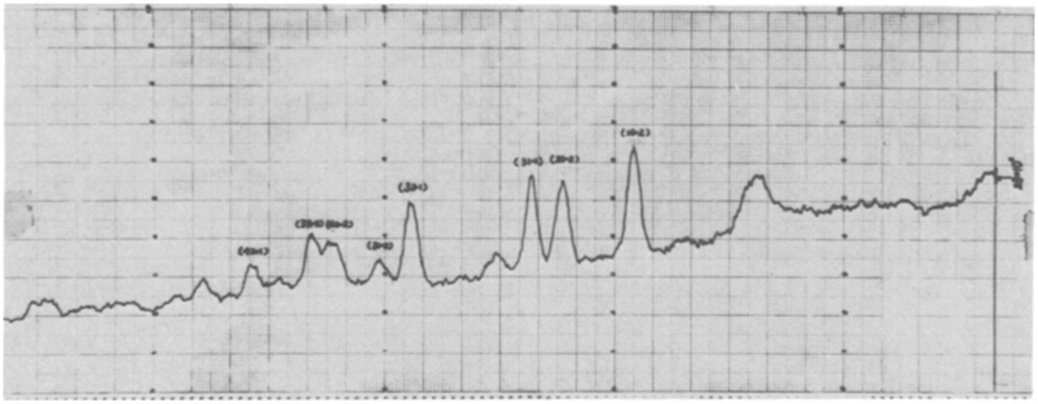


Figure 4 X-ray diffraction pattern of the solid product on the specimen surface after electroboronizing at 800° C. (Borax + 10 wt% Na_2CO_3, 3 h, 0.5 A cm^{-2}.)

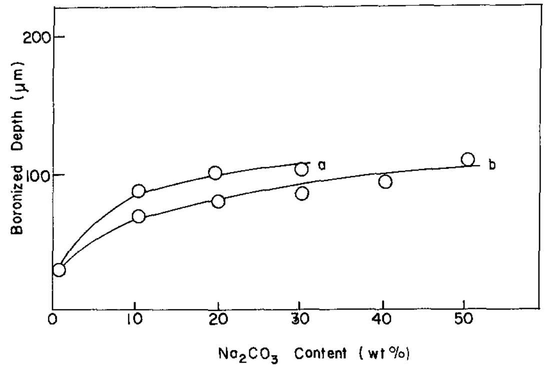


Figure 5 Relation between boronized depth and bath composition in molten borax. (800° C, 3 h, 0.5 A cm^{-2}.) (a) With 10 wt% B_4C, (b) without B_4C.

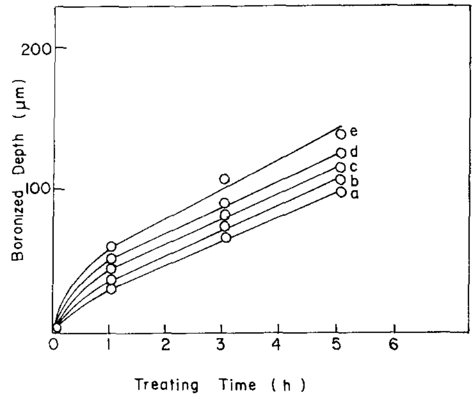


Figure 6 Relation between electrolytic boronizing time and boronized depth. (800° C, 0.5 A cm^{-2}.) (a) Borax–10 wt% Na_2CO_3, (b) borax–20 wt% Na_2CO_3, (c) borax–30 wt% Na_2CO_3, (d) borax–40 wt% Na_2CO_3, (e) borax–50 wt% Na_2CO_3.

which is formed according to Equation 5, react as follows:

$$3Na + 2B_2O_3 \rightarrow 3NaBO_2 + B. \qquad (6)$$

Na_2CO_3 in fused borax catalyses in favour of the formation of activated Na according to Equations 1 and 2, and so the activated boron concentration increases according to Equation 6. Therefore, higher Na concentration in borax increase the rate of chemicothermal treatment because the viscosity of the electrolytes is slightly increased, maintaining a higher Na^+ concentration on the cathode.

3.3. Effect of addition of NaCl

When the NaCl concentration is varied from 10 to 50 wt% in molten borax at 800° C, with a current density of 0.5 A cm^{-2} and a process time of 3 h, the thickness of boride layer slightly increases as shown in Fig. 7. The electrolyte, consisting of

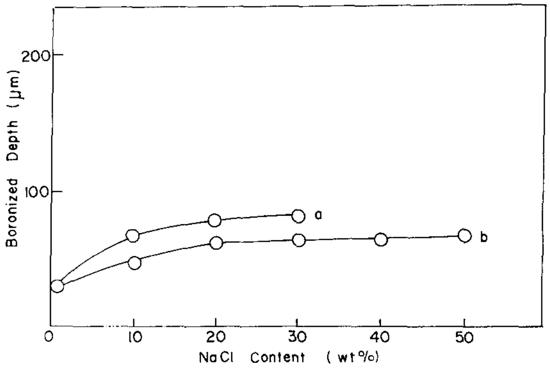


Figure 7 Relation between boronized depth and bath composition in molten borax. (a) With 10 wt% B_4C, (b) without B_4C. (800° C, 3 h, 0.5 A cm^{-2}.)

fused borax and NaCl, reacts according to the following equations [11]:

$$Na_2B_4O_7 \rightleftarrows 2Na^+ + B_4O_7^{2-}$$

$$NaCl \rightleftarrows Na^+ + Cl^-. \qquad (7)$$

Na and B_2O_3 react according to the following equation:

$$3Na + 2B_2O_3 \rightarrow 3NaBO_2 + B.$$

Higher NaCl concentrations in molten borax result in a higher viscosity of the mixed electrolyte at 800° C [13], because the melting point of NaCl is 801° C. Increased viscosity affects the formation reaction of boron because of the decreased mobility of the Na^+ ions. Therefore, the thickness of the boride layer does not increase substantially above 20 wt % NaCl.

3.4. Effect of B_4C addition in molten borax including Na_2CO_3 or NaCl

The NaCl or Na_2CO_3 concentration is varied from 10 to 30 wt% in molten borax including 10 wt% B_4C at 800° C, with a current density of 0.5 A cm^{-2} and a process time of 3 h.

Figs. 5a and 7a show the variation of thickness of the boride layer. The thickness of the boride layer increases by about 25 to 40% when 10 wt% B_4C is added to molten borax containing Na_2CO_3 or NaCl.

3.4.1. Effect of adding B_4C in molten borax containing Na_2CO_3

Hosokawa [18] has investigated the reaction mechanism of the mixed B_4C and metal carbonates by a powder method, and the following equations are suggested:

$$B_4C + Na_2CO_3 \rightarrow B_4C + Na_2O + CO_2$$

$$\rightarrow 4B + Na_2O + 2CO. \qquad (8)$$

B_4C melts at 2350° C [13] and does not ionize at 800° C. Borax reacts with adsorbed B_4C on the surface of the specimen according to the following equation:

$$6B_4C + Na_2B_4O_7 \rightarrow 28B + Na_2O + 6CO. \qquad (9)$$

The borax–Na_2CO_3–10 wt% B_4C system is more effective than the borax–Na_2CO_3 system, because B_4C catalyses to form activated boron according to Equations 8 and 9.

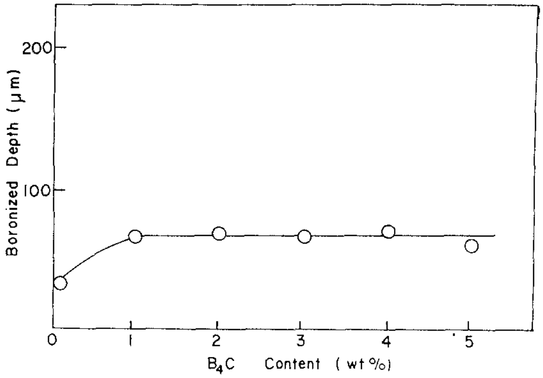


Figure 8 Relation between boronized depth and B_4C content in molten borax with 20 wt% NaCl (800° C, 3 h, 0.5 A cm^{-2}.)

3.4.2. Effect of adding B_4C to molten borax containing NaCl

Borax reacts with B_4C according to the following equation:

$$6B_4C + Na_2B_4O_7 \rightarrow 28B + Na_2O + 6CO. \qquad (9)$$

Na_2O has a low decomposition voltage; therefore, the reaction takes place as follows:

$$Na_2O \rightarrow 2Na + \tfrac{1}{2}O_2.$$

As a result the borax–NaCl–10 wt% B_4C system is more effective than the borax–NaCl system because B_4C catalyses to form activated boron according to Equation 9. Fig. 8 shows the relation between boronized depth and B_4C content in molten borax with 20 wt% NaCl (800° C, 3 h, 0.5 A cm^{-2}).

3.5. Effect of superimposing cyclic current on d.c.

Fig. 9 shows the influence of the frequency of the cyclic current on the boronized depth at 800° C,

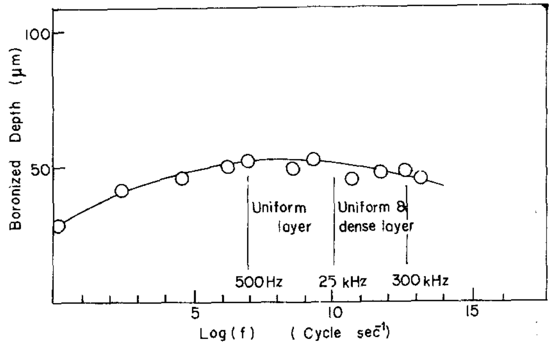


Figure 9 Variation of frequency of cyclic current with boronized depth at 10 wt% Na_2CO_3 in molten borax. (800° C, 0.1 ± 0.07 A cm^{-2}, 1 h.)

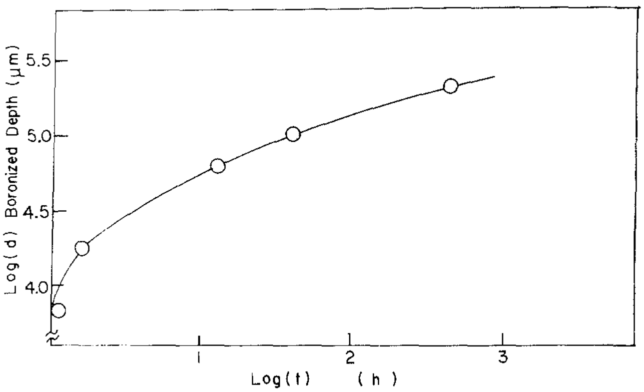


Figure 10 Variation of boronized depth with electrolysis time at 10 wt% Na_2CO_3 in molten borax (superimposed cyclic current; 0.2 ± 0.16 A cm^{-2}, 800° C, 5 kHz).

with a current density of 0.1 ± 0.07 A cm^{-2} and a process time of 1 h as 10 wt% Na_2CO_3 is added in fused borax.

When cyclic current is superimposed, a uniform boride layer is created above 500 Hz and a uniform and dense layer is created at frequencies between 50 and 300 kHz. The thickness of the boride layer also increases by 1.5 to 2 times above 100 Hz, compared to conventional electroboronizing.

Pasechnik *et al.* [16] have reported on the cathodic (concentration) polarization on the concentration of Na^+ ions at the interface between molten borax and the specimen. According to this report, this phenomenon interrupts electroboronizing, and cathodic polarization is decreased by the superimposing reversing square current. Another method of reducing cathodic polarization is the mechanical vibration technique [17]. It reduces the thickness of the diffusion layer and increases the limiting current density between the electrolyte and the surface of the specimen. In this work, superimposed cyclic current on d.c. above zero-potential is used to reduce cathodic polarization allowing no pole exchange.

The relation between the thickness and process time in a diffusion-controlled system is indicated as follows:

$$d = kt^n, \tag{10}$$

where d is thickness of the boride layer, k is a constant and t the processing time. Fig. 10 shows the variation of the thickness of the boride layer with processing time at 800° C, a frequency of 5 kHz and a current density of 0.2 ± 0.16 A cm^{-2} as 10 wt% Na_2CO_3 is added to molten borax. It can be seen that the boride thickness is not linearly related to the processing time.

Fig. 11 shows the variation of thickness of boride layer with processing time at 800° C and a current density of 0.5 A cm^{-2} as 20 wt% NaCl and 10 wt% B_4C are added to molten borax. For these conditions (Fig. 11), the thickness of boride layer is related linearly to the processing time and the slope n is about 0.56.

At constant temperature, the rate of diffusion is determined by the boundary conditions. The depth and degree of penetration increase with the increasing concentration of the diffusing element at the surface of the penetrated specimen. An increase of the layer thickness during electrolysis applying superimposed a.c., occurs on account of

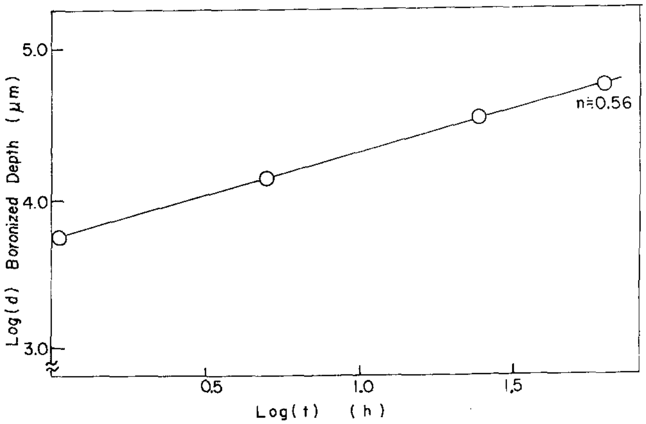


Figure 11 Variation of boronized depth with electrolysis time at 30 wt% NaCl + 10 wt% B_4C in molten borax. (800° C, 0.5 A cm^{-2}.)

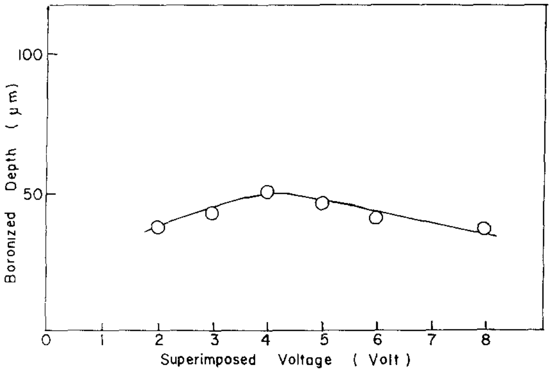


Figure 12 Variation of boronized depth with superimposed voltage. (800° C, 0.2 A cm^{-2}, 5 V, 1 h.)

the increased concentration of the penetrating element (boron) at the surface of cathode. The concentration of boron increases due to the decrease in cathodic polarization enabling current density to increase. Therefore, the thickness of the boride layer increases at a given current.

Referring to Fig. 10, the ion concentration at the cathode, resulting in a higher boronized depth, varies with increasing time because the kinetics between the cathode surface and the electrolyte are time-dependent in cases of superimposed a.c. on d.c. In other words, the boron concentration at the cathode varies with processing time at a constant temperature, constant bath composition, and constant current density. The boron concentration at the cathode surface is decreased as electrolytic time increased, because solid products, such as $NaBO_2$, grew at the cathode surface and slightly decelerated the rapid formation of active boron.

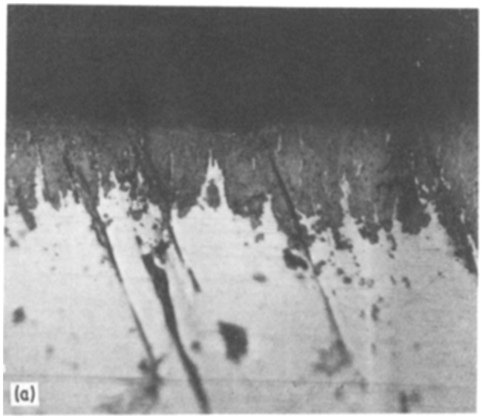
Fig. 12 shows the variation of thickness of the boride layer using superimposed cyclic voltage at amplitudes from 2 to 8 V. The maximum condition is that voltage amplitude is 4 V. The variation of superimposed voltage affected the boron concentration on the cathode surface. Summerizing the results, electroboronizing with superimposed cyclic current on d.c. increases the layer thickness by 1.5 to 2 times compared to conventional electroboronizing. Using superimposed cyclic current, it decreases cathodic polarization, and the effective current density for the formation of boron increases.

4. Conclusions

(1) The mechanism of boron formation in molten borax below 960° C takes place according to the following reaction:

$$3Na + 2B_2O_3 \rightarrow 3NaBO_2 + B,$$

and solid products of $NaBO_2$ at the surface prevent activated boron from diffusing into the specimen.



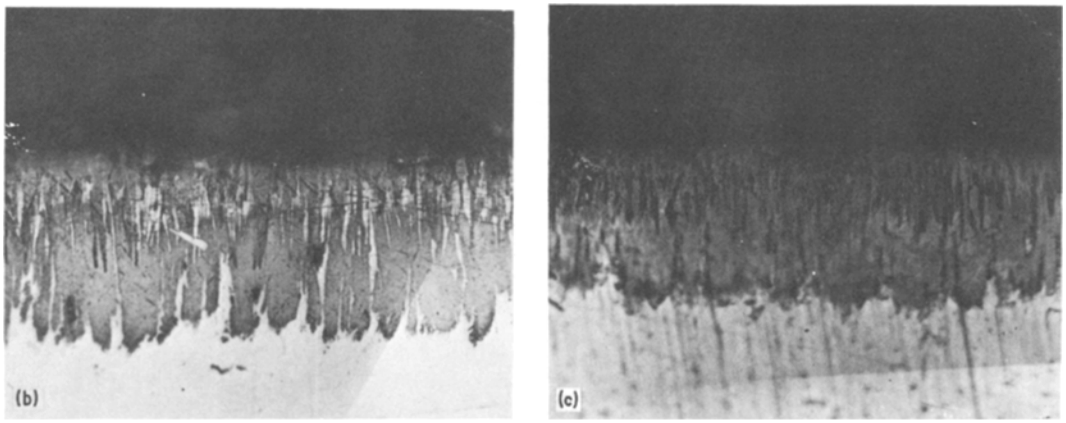


Figure 13 Microstructure of the boride layer formed by (a) the conventional method (borax + 10 wt% Na_2CO_3, 800° C, 1 h, 0.1 A cm^{-2}) × 360; (b) and (c) the superimposed cyclic current method (borax + 10 wt% Na_2CO_3, 800° C, 1 h, 0.1 ± 0.07 A cm^{-2}) × 360, frequency; (b) 5 kHz, (c) 300 kHz.

(2) The superimposed a.c. on d.c. decreases cathodic polarization depending on frequency and amplitude, and increases the effective current density for the formation of boron. At the cyclic current frequency between 500 Hz and 10 kHz and at a current density of 0.2 ± 0.16 A cm^{-2}, the boride layer was more uniform and 1.5 to 2 times thicker than that formed by conventional electroboronizing.

(3) The most effective activator is Na_2CO_3 followed by B_4C, NaCl, NaOH. The most economical composition of activators is identified as 10 wt% Na_2CO_3, 10 wt% B_4C, 20 wt% NaCl. In the case where only two kinds of activators are used, such as 10 wt% B_4C and Na_2CO_3 or 10 wt% B_4C and NaCl, the boronized layer is increased by 25 to 40%.

(4) Na_2O decomposes to O_2 and Na, which increases the amount of active boron.

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