On the Mechanism of Boron Hardenability

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Synopsis

The adsorptions of boron and other interstitial solute elements in the quenched state could be made well observable by etching the steel with NaOH–NaNO$_3$ aqueous solution. Boron atoms adsorbed upon a grain surface would fill up the lattice defects or diffusion holes, reducing the internal strains induced by these imperfections; in other words, these atoms would diminish the unstability of austenite grain boundaries and could suppress the transformation beginning at these places.

The decrease of boron hardenability with the increase of the austenitizing temperatures seemed to be caused by the re-dissolution of nitrogen in solid solution.

I. Introduction

As to the mechanism of boron hardenability, that is, the remarkable hardenability of steel due to the addition of a very small amount of boron, namely, 0.001 ~0.002 per cent, many works have been reported, but no satisfactory interpretation has yet been obtained. The reason for it will be that the behavior of boron in steels must be considered from the other point of view quite different from that in the case of Ni, Cr or Mn.

The following characteristic phenomena have been recognized in boron-treated steels.

(i) The characteristic precipitation of "boron-constituent"[1] observed only in boron-treated steels shows that boron atoms dissolve in austenite, most of them being localized about the parent austenite grain boundaries at the quenching temperature.

(ii) In the "martensite + troostite" regions in an end-quenched ordinary steel the grain boundary nodular troostites clearly delineate the parent austenite grains, while in a boron-treated steel the tendency of growth being decreased these troostites appear randomly as large "patches".

(iii) The boron hardenability reaches the maximum at the definite temperature of heat-treatment and then decreases gradually with the rise of the austenitizing temperature.

(iv) The boron hardenability is inversely proportional to the carbon content and essentially negligible in the eutectoid composition.

(v) Influences on the isothermal transformation are only to delay the beginning of transformation within the range from pearlite to upper bainite.

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(1) R. A. Grange and T. M. Garvey, Trans. Amer. Soc. Met., **37** (1946), 136.

(vi) The effect of boron does not appear when the rate of cooling is comparatively slow.

Among the above-mentioned experimental observations, (i) and (ii) seem to suggest directly the mechanism of boron hardenability. Grange and Garvey[1] stated that most atoms of boron added to a steel were concentrated in the vicinity of parent austenite grain boundaries at the quenching temperature and that in the subsequent cooling these locarizations of boron atoms might suppress the nucleation of the transformation beginning at grain boundaries. Assuming that a monatomic boron film would be formed around the austenite grain boundaries by surface adsorption, Spretnak and Speiser[2] calculated the extent of adsorption of boron atoms necessary to produce these continuous monatomic films, and found that the formation of such a film was quite unlikely.

Nevertheless, the adsorption of foreign atoms in a solid solution may generally be considered to be one of the most important causes for the hardenability, and so it must also be the case with boron. In the present work, the grain boundary adsorptions of boron and other interstitial solute elements were metallographically examined with a special etching reagent and the mechanism of the hardening was considered.

II. Metallographic test of boron adsorption

The mechanical properties of two kinds of steels used chiefly as the specimens are shown in Table 1. As shown in the table, the steel A clearly showed an excellent boron effect, that is, it has far better mechanical properties both in the

Table 1

Steel	Chemical analysis					Mechanical properties					
	C %	Mo %	Si %	Ti %	B %	Heat treatment	σ_B kg/mm²	σ_s kg/mm²	R.A.%	El. %	V.P.H.
A	0.08	0.5	0.2	0.15*	0.003*	950°(30min)→A.C.	61.0	48.7	70.5	31.0	142
						950°(30min)→W.Q. Tempered 550°	84.9	81.7	67.2	25.6	229
B	0.08	0.5	0.2	—	—	950°(30min)→A.C.	43.2	21.1	69.3	42.4	118
						950°(30min)→W.Q. Tempered 550°	54.6	41.6	56.8	23.4	178

* : amount of addition.

normalized state and the hardened and tempered state than the steel B not boron-treated. These two kinds of steels were heated at 950°C for 30 min and then quenched in water. The photomicrographs in quenched states, etched with 5 per cent picral as usual, are shown in Photos. 1 and 2; their structures are quite similar to each other, showing, on the whole, martensitic structures and neither pro-eutectoid nor eutectoid transformation product. When they are etched with NaOH-NaNO₃ solution* proposed by Beaujard[3] for revealing the segregations of

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(2)   J. W. Spretnak and R. Speiser, J. of Metals, 5 (1953), 445.

(3)   L. Beaujard, Rev. Mét., 49 (1952) 149.

  *   Boiling solution of 40 of NaOH, 15g of NaNO₃ and 60g of water.

solute elements, however, a difference was clearly recognized between them as shown in Photos. 3 and 4.

As shown in Photo. 3 in the boron-treated steel A dark brown colored narrow bands were clearly observable along the parent austenite grain boundaries, and sometimes also along some sub-grain boundaries of the parent austenite. On the other hand, in the case of the not boron-treated steel B, no colored band was observable as shown in Photo. 4. Recently, such a phenomenon as temper-enbrittlement appearing in several alloyed steels was regarded as being due to the heterogenuity in the vicinity of parent austenite grain boundaries, and such heterogenuities could clearly be revealed by etching the steel with picric acid solution containing a small amount of Zephiran chloride. Many workers[4,5,6,7] had explained the phenomenon to be that these heterogenuities were brought forth as the results of concentrating of carbon and some other solute atoms on the boundaries by the grain surface adsorption.

The dark brown colored narrow bands shown in Photo. 3 might be considered to be the same kind of heterogenuity as above-mentioned. In other words, they show the local concentration of several solute elements by the surface adsorption.
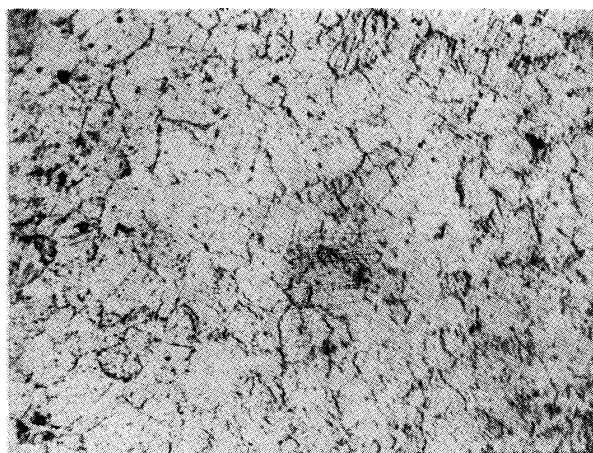

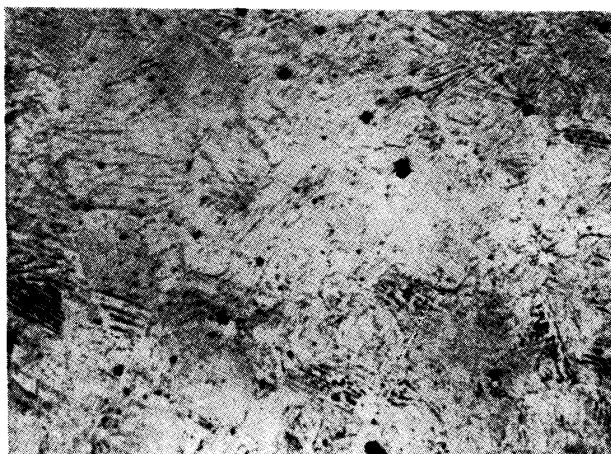Photo. 1.　Steel A, as-quenched from 950°C
picral etched.　　　　　　×350

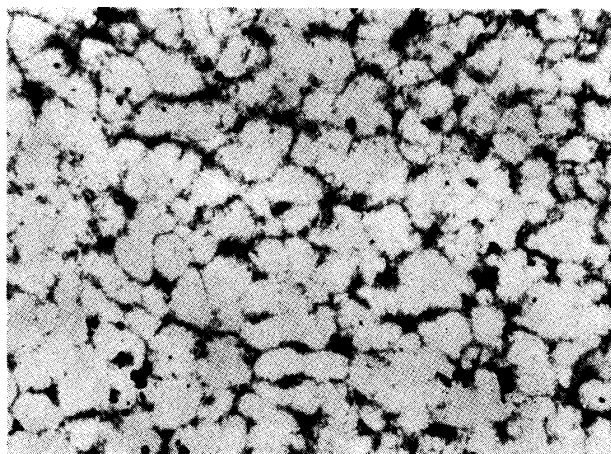Photo. 2.　Steel B, as-quenched from 950°C
picral etched.　　　　　　×350

Photo. 3.　The same specimen as shown in Phot. 1.
NaOH-NaNO₃ sol. etched.　　×350

(4)　J. W. Spretnak and R. Speicer, Trans. Amer. Soc. Met., **43** (1951), 734.
(5)　G. W. Austin A. R. Entwisle and G. C. Smith, J. Iron Steel Inst., **173** (1953), 376.
(6)　A. Preece and R.D. Cater, J. Iron Steel Inst., **173** (1953), 387.
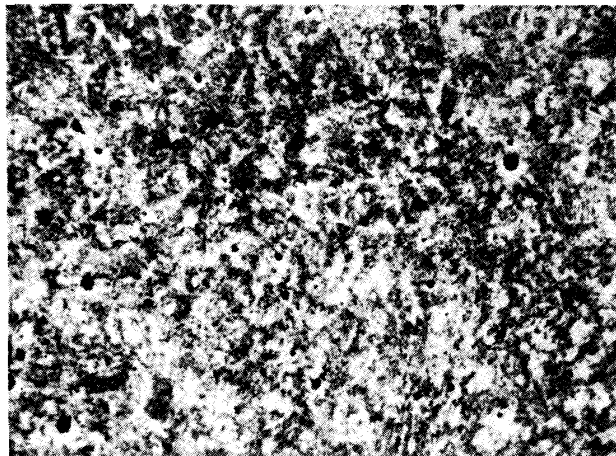(7)　B. C. Woodfine, J. Iron Steel Inst., **173** (1953), 340.

Photo. 4.   The same specimen as shown in Phot. 2.
            NaOH-NaNO$_3$ sol. etched.   ×350
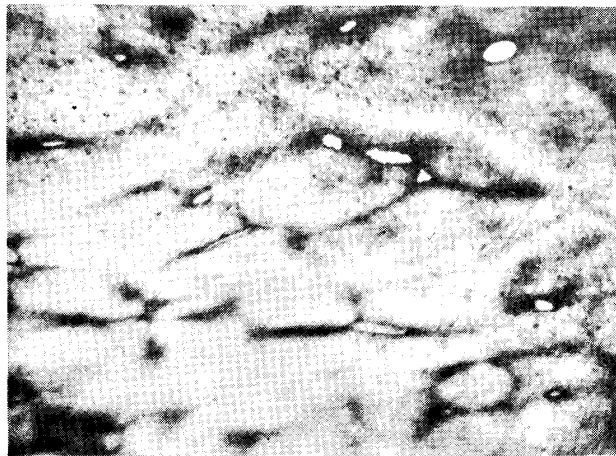

Photo. 5.   Steel C, as-quenched from 1000°C
            NaOH-NaNO$_3$ sol. etched.   ×350
(steel C : 0.01%C 0.0004%B, melten in vacua)
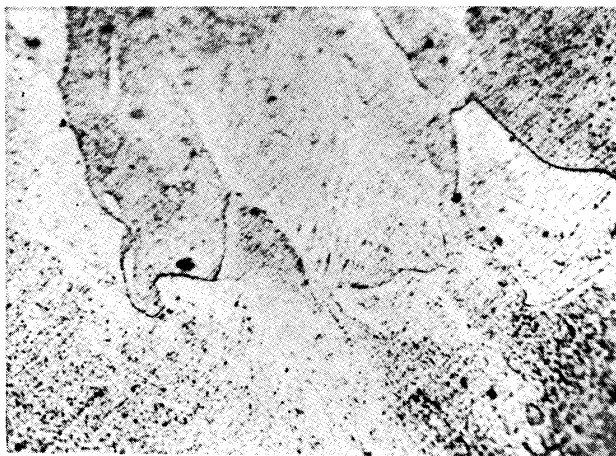

Photo. 6.   The same specimen as shown in Phot. 5.
            picral etched.   ×350

Considering the fact that the characteristic precipitation alike to "boron-constituent" is formed only in a boron-treated steel, it will be certain that the boron atoms are concentrated in the vicinity of parent austenite grain boundaries. To obtain the evidence of the adsorption of boron, a simple test was carried out with the steel C containing 0.01 per cent of carbon and 0.0004 per cent of boron and made from fairly high purity iron by melting in high vacuum. The steel was heated at 1000°C for 10 min and then quenched in ice water. The photomicrographs etched with NaOH-NaNO$_3$ solution and 5 per cent picral are respectively shown in Photos. 5 and 6, in which the small white products are considered to be ferrite transformed primarily during the quenching. The colored bands along the parent austenite grain boundaries similar to those shown in Photo. 3 are also seen in Photo. 5. In this case, however, the width is more or less increased and is broken along boundary, this breaking will be nothing but an indication of a comparatively low content of boron, 0.0004 per cent being perhaps the lowest limit for effective hardening.

Next, to examine what kinds of elements other than boron were also capable of being adsorbed, the micro-structures of four plain carbon steels shown in Table 2 were similarly examined. The steels D and E, deoxidized strongly by adding respectively 0.15 per cent

Table 2

Steel	Chemical analysis					Remarks
	C %	Si %	Mn %	Ti %	Al %	
D	0.13	0.2	0.2	0.15	—	
E	0.13	0.2	0.2	—	0.2	
F	0.15	—	—	—	—	Melted in vacuum (10^{-3}mmHg)
G	0.20	0.2	0.2	—	—	

of Ti and 0.2 per cent of Al, also showed the colored grain boundary bands as shown in Photo. 8. On the contrary, in case of the steel F (melted in vacuum), no colored grain boundary band appeared as shown in Photo. 10, and in the steel G deoxidized only by Si, also no boundary band was recognized. As mentioned above, it will be very interesting that no grain boundary band appears in the steels degassed almost perfectly by vacuum melting (steel F) or degassed insufficiently only by silicon (steel G), whereas it is easily formed in the steels deoxidized strongly by suitable amount cf Ti or Al (steel D and E). In the case of a plain carbon steel, it may be most reasonable to consider that the segregating element consists chiefly of carbon because of its high deffusion rate and of its high content compared with nitrogen, oxygen and others.

It may be considered that nitrogen in austenite has also a comparatively high mobility, being almost of the same order as that of carbon, and will perhaps be adsorbed alike to carbon. The principal element causing the grain boundary bands will be carbon, because its content is in these steels far higher than nitrogen content.

All boron-treated steels were always strongly deoxidized by Al, Ti, V, Ca and Zr etc. prior to the addition of boron. Therefore as mentioned above, it might be considered that the adsorption of solute element upon grain surface was in a very suitable condition. And the adsorbed boron atoms would be of service to produce the adsorption effects of carbon and
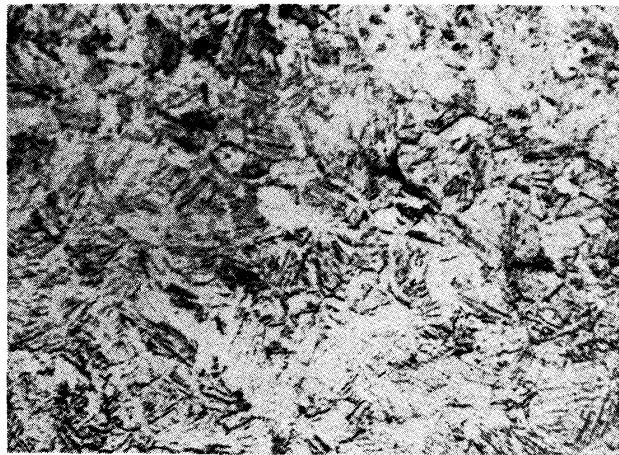

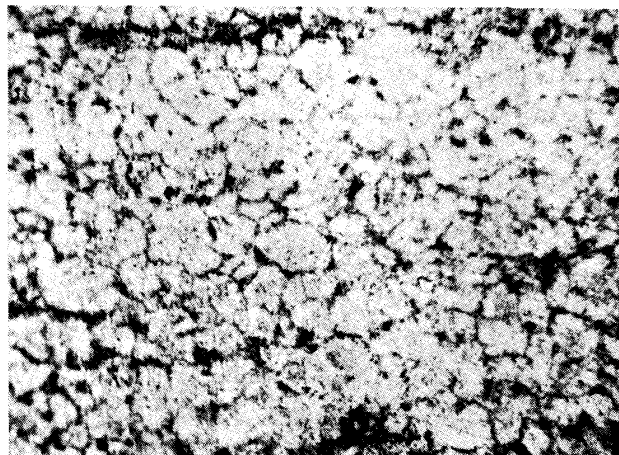Photo. 7. Steel D, as-quenched from 950°C
picral etched. ×350
(V.P.H. = 310)

Photo. 8. The same specimen as shown in Phot. 7.
NaOH-NaNO₃ sol. etched. ×350

other elements to the excellently high degree. For example, as shown in Fig. 1 (chemical compositions of materials are shown in Table 3), the normalized steel No. 2 deoxidized strongly by adding 0.15 per cent of Ti had a fairly high strength compared with the steel No. 1 deoxidized only with Si, that is, the former had a fairly good hardenability compared with the latter. In the case of boron-treated steel No. 3, however, the strength increased remarkably when normalized, that is, the steel No. 3 has an excellent hardenability compared with the steel No. 1 or No. 2.
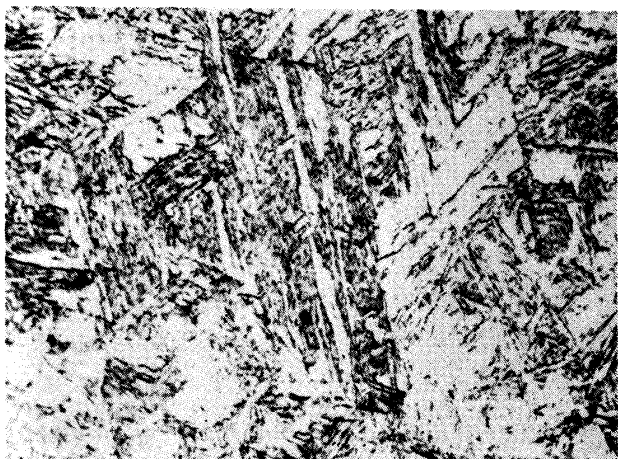
Photo. 9. Steel F, as-quenched from 950°C
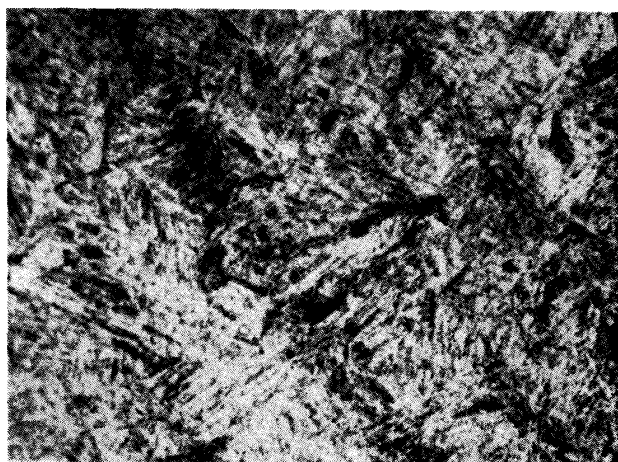   Picral etched.   ×350
               (V.P.H. = 280)

Photo. 10. The same specimen as shown in Phot. 9.
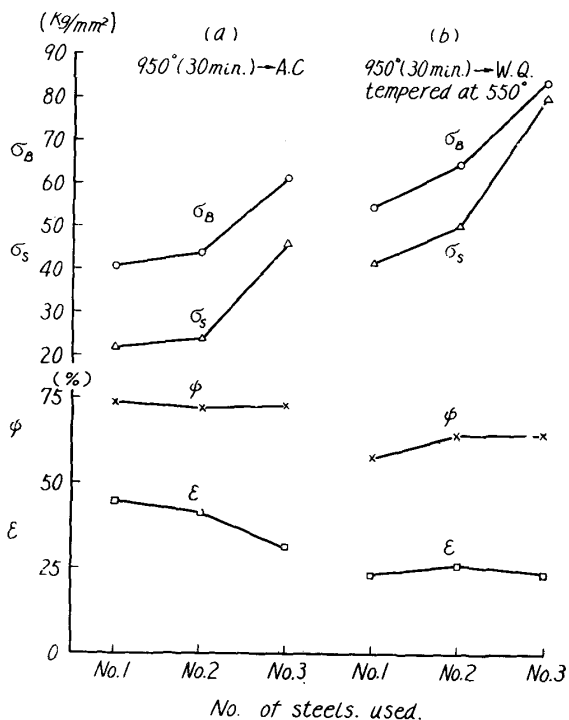   NaOH-NaNO₃ sol. etched.   ×350

Fig. 1. Mechanical properties of 0.5% Mo-, 0.5%Mo-0.15%Ti- and 0.5%Mo-0.15%Ti-0.003%B-steel.
   (a) as-normalized,
   (b) as-hardened and tempered.
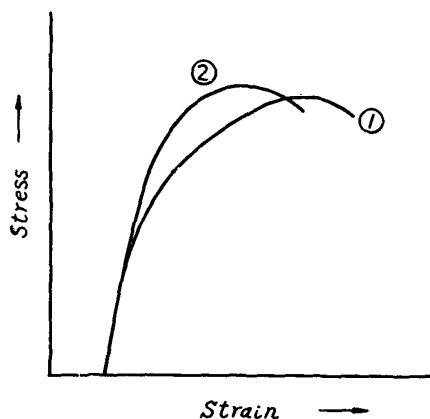
Fig. 2. Stress-strain diagrams for steel No.4.
   ① : as-normalized from 950°C.
        (material is as-forged)
   ② : as-normalized from 950°C.
        { material is after repeated heating between 950° and 650° in high vacuum. }

Table 3

Steel	Chemical analysis				
	C %	Mo %	Si %	* Ti %	* B %
No. 1	0.08	0.5	0.2	—	—
No. 2	0.08	0.5	0.2	0.15	—
No. 3	0.08	0.5	0.2	0.15	0.003

* : amount of added ferro-boron (10%B.)

Table 4

Steel	Chemical analysis			Mechanical properties				
	C %	Mo %	Si %	Heat treatment	σ_B kg/mm²	σ_s kg/mm²	R.A. %	El. %
No. 4	0.08	0.7	0.2	950°(30min)→A.C. (as-forged)	42.1	21.7	69.1	38.7
				950°(30min.)→A.C. (after replated heating 950~650°)	43.8	24.3	65.9	34.8

Moreover, to see the effect of gas content on the hardenability the steel No. 4 (chemical compositions are shown in Table 4) was annealed for a long time in high vacua (10^{-5} mmHg). Degasification was carried out by repeated heating and cooling within the temperature range from 950 to 650°C in the atmosphere below the pressure of 10^{-5} mmHg. From the results shown in Table 4 and Fig. 2 it will be seen that the mechanical strength or the hardenability increases with the degasification treatment when normalized and that the magnitude of increase is almost the same as in the steel No. 2 which was strongly deoxidized by adding 0.15 per cent of Ti. Therefore, the fairly good hardenability of the steel No. 2, compared with the steel No. 1, would be due to the effect of the gas content being controlled to obtain a suitable amount of carbon and other solute atoms for adsorption, but not due to the alloying effect of Ti.

III. The metallographic test for boron adsorption and the formation of "boron-constituent"

The characteristic precipitation of "boron-constituent" found first by Grange and Garvey[1] appears only in a boron-treated steel when it is rapidly cooled from an extremely high austenitizing temperature, say, about 1,100°C to the temperature below the eutectoid transformation point. The reason for it will be that the adsorptions of boron and other atoms will progress toward almost perfect state by heating the steel at the extremely high temperature.

Table 5

Steel	Chemical analysis				
	C %	Mo %	Si %	* Ti %	* B %
H	0.08	0.3	0.2	0.3	0.003

* : amount of added ferro-boron (10%B)

To see the effect of raising the austenitizing temperature on the adsorption, two specimens of the steel H (chemical compositions are shown in Table 5) were heated, one at 1,000°C for 30 min and the other at 1,100°C for 10 min, and then were quenched in water. The photomicrographs obtained by etching with NaOH-NaNO₃ solution are shown in Photos. 11 and 12 respectively. As shown in photomicrographs, the width of grain boundary bands became extremely narrow, especially in the case of the heating at 1,100°C, which might be said linear feature rather than band. Next, another specimen of the same steel H was heated at 1,100°C for
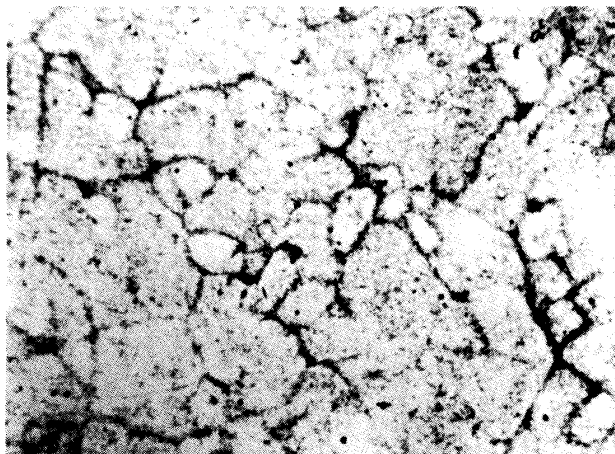
Photo. 11.   Steel H, as-quenched from 1000°C
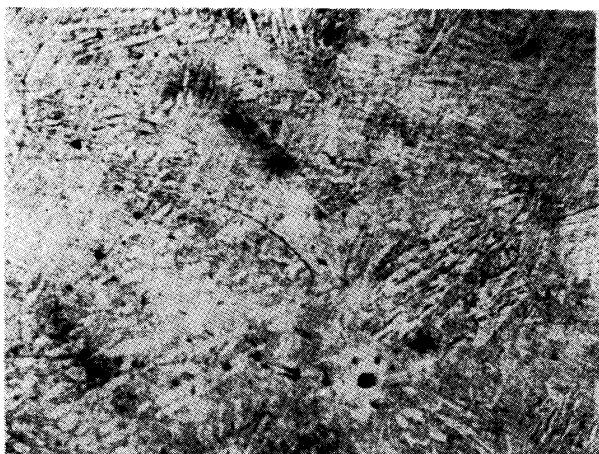   NaOH-NaNO₃ sol. etched.   ×350

Photo. 12.   Steel H, as-quenched from 1100°C
            NaOH-NaNO₃ sol. etched.   ×350
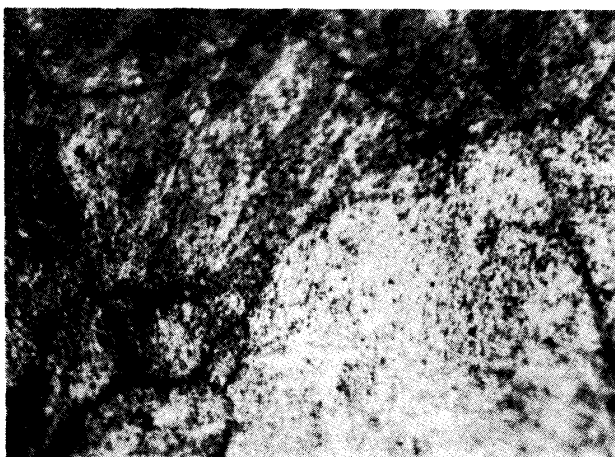

Photo. 13.   Specimen H,
    Heated at 1100°C for 10 min, cooled in the
    furnace to 1000°C, held for 30 min and then
    quenched in water.
    Ethed with NaOH-NaNO₃ solution.   ×350

10 min, cooled to the temperature of 1,000°C in the furnace, held for 30 min and then quenched in water. The photomicrograph in this case is shown in Photo. 13. The width of grain boundary bands became similar to the case of heating at 1,000°C for 30 min shown in Photo. 11.

From the changes of these features of grain boundary bands, it will be said that the adsorption of solute atoms upon grain surface is proceeded with the rise of the austenitizing temperature, resulting finally in revealing the "boron-constituent". In the case of such a high adsorption state, the rate of diffusion-back of the adsorbed atoms would relatively be slow during quenching, compared with the case of a low adsorption state which might be resulted from treating the steel at normal lower austenitizing temperatures. Further, the super-saturated state of adsorbed atoms in the vicinity of parent austenite grain boundaries will be brought up quickly and these atoms will be put forward to combine each other to form the compounds, prior to the diffusing back into grains.

Next, the question would arise what kinds of adsorbed atoms put forward to combine the precipitation of "boron-constituent", but its details were still unknown, and hence some further experiments were carried out.

IV. Influence of austenitizing temperature upon the harbenability of boron-treated steel

As to the influence of austenitizing temperature upon the hardenability of boron-treated steel, many experiments have been reported, but their results are not always in good agreement with one another. It is generally accepted, however, that the effect of boron on hardenability gradually decreases with the rise of the austenitizing temperature.

Table 6

Steel	Chemical analysis				
	C %	Si %	Mo %	Al %	* B %
No. 5	0.08	0.2	0.70	—	—
No. 6	0.09	0.2	0.73	0.11	0.003
No. 7	0.09	0.2	0.73	0.20	0.003
No. 8	0.09	0.2	0.73	0.33	0.003
No. 9	0.09	0.2	0.73	0.41	0.003

* : amount of added ferro-boron (10%B.)

To ascertain these circumstances, several low-carbon and low-alloy steels were prepared with the compositions shown in Table 6. Some of them were strongly deoxidized by various amounts of Al from 0.1 to 0.4 per cent and were added 0.003 per cent of boron, while others were not treated with boron and deoxidized only by Si. These specimens were austenitized at various temperatures from 950 to 1,100°C and then cooled in the air (normalizing).

As the indicator of the hardenability the hardness was measured, and the results are shown in Figs. 3 and 4.

With the rise of the austenitizing temperature, in the not boron-treated steel No. 5, the grains became coarse and homogeneous and the hardenability increased, while in the boron-treated steel No. 6, the hardenability gradually decreased and
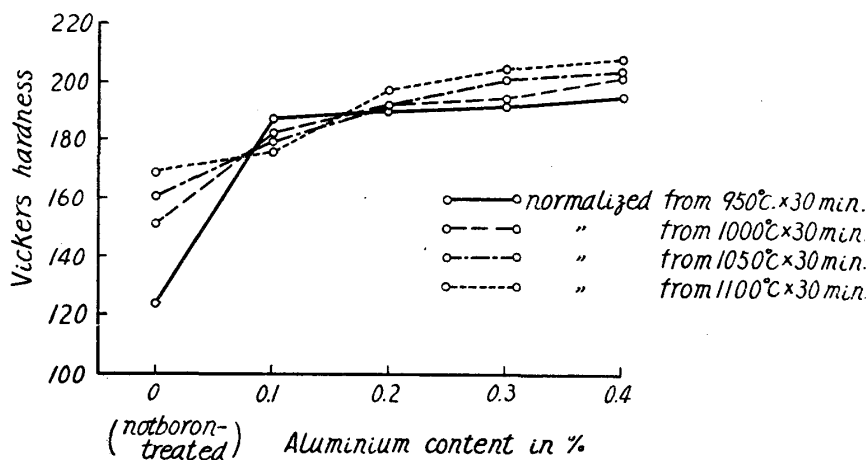

Fig. 3. Influence of austenitizing temperature upon the boron hardenability effect.
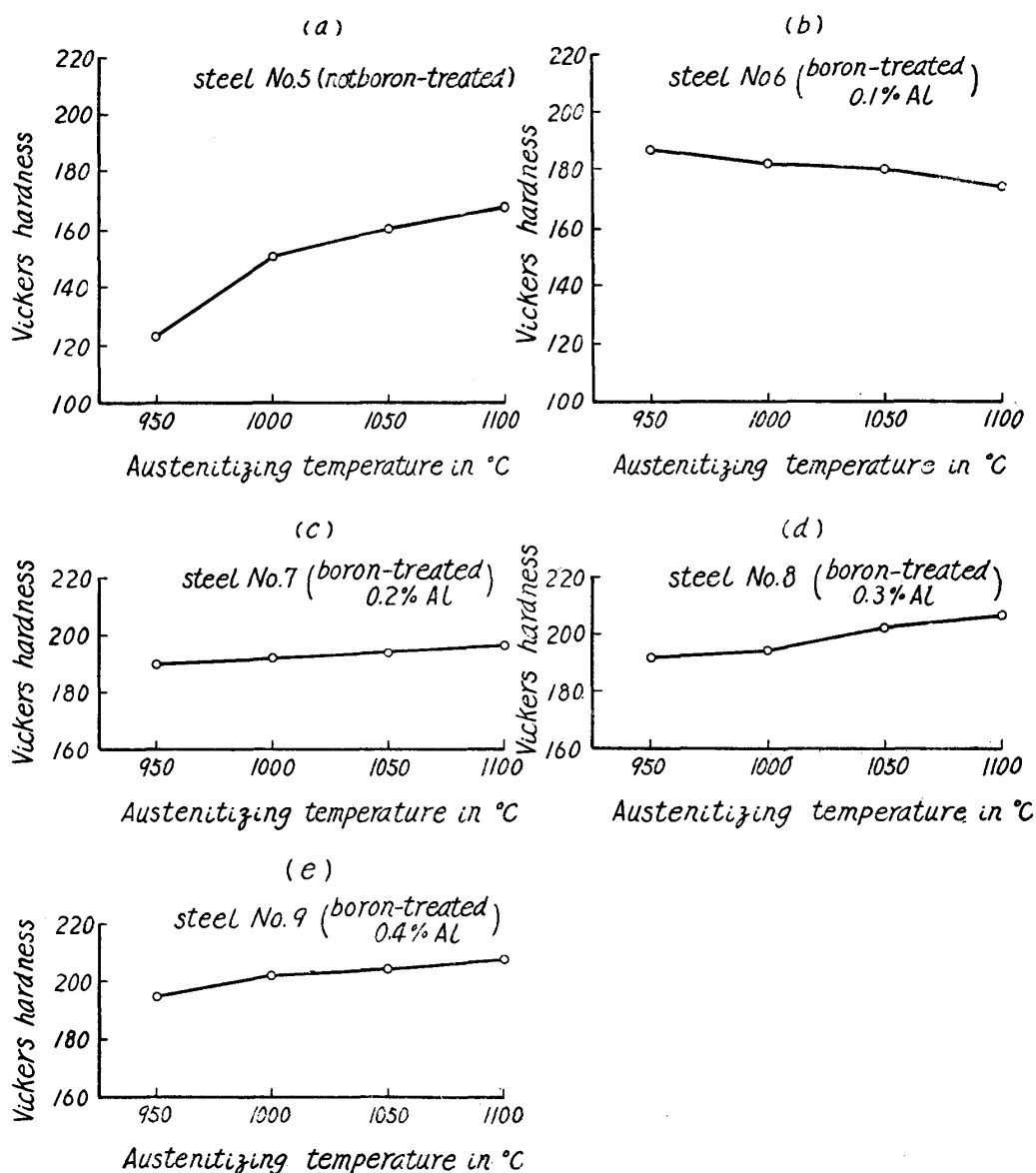The materials, used, were given in Table 6.

Fig. 4(a-e). Influence of austenitizing temperature upon the boron hardenability effect.

the effect almost disappeared when austenized at 1,100°C. In the cases of boron-treated steels No. 7, No. 8 and No. 9, all being strongly deoxidized by excessive addition of Al respectively of 0.2, 0.3 and 0.4 per cent, the effect of boron was fairly well recognized at the maximum austenitizing temperature (1,100°C).

From these observations, it might be said that the austenitizing temperature had no influence upon the boron hardenability when a steel was treated with an excessive amount of deoxidizing agent.

The reason for the disappearence of boron effect with the rise of austenitizing temperature under a relatively small amount of deoxidizing agent will be that the specimens are deoxidized and denitrogenized by the addition of Al, producing large amounts of Al-oxide and Al-nitride.

From the experiment of Born and Koch[8] it is well recognized that Al-nitride

(8) K. Born and W. Koch, Stahl u. Eisen, 72 (1952), 1268.

is easily re-dissolved in austenite above 1,000°C. Therefore, the nitrogen content in the steel will rapidly be increased when the austenitizing temperature is raised above about 1,000°C. Moreover, from the experiment by Digges and Reinhart[9] it is well recognized that the boron hardenability rapidly decreases with the increase of nitrogen content in the solid solution of steel.

When an excessive amount of Al was added to control the gas content, as in the steels No. 7, No. 8 and No. 9, the re-dissolving of nitrogen in austenite might be restricted by the excess of Al in the solid solution and, accordingly, the nitrogen content might be controlled within a relatively low value. On the contrary, in the steel No. 6, in which the amount of Al was relatively small, the nitrogen re-dissolution would easily take place. Therefore, its boron effect greatly decreased at extremely high austenitizing temperatures. When Ti was used instead of Al,

the decrease of boron hardenability with the rise of austenitizing temperature was not recognized even at the addition of 0.1 per cent of Ti, as shown in Fig. 5 (chemical compositions of steels used are shown in Table 7). From the experimental fact that Ti-nitride does not re-dissolve in the austenite at about 1,100°C, it may be concluded that the increase of nitrogen content in the solid so-

Fig. 5. Influence of austenitizing temperature upon the boron hardenability effect. The materials used were given in Table 7.

lution with the rise of the austenitizing temperature is not so conspicuous in the Ti-deoxidized steel as in the Al-deoxidized one. Consequently, in the Ti-deoxidized steel the boron hardenability can clearly appear at relatively high austenitizing temperatures.
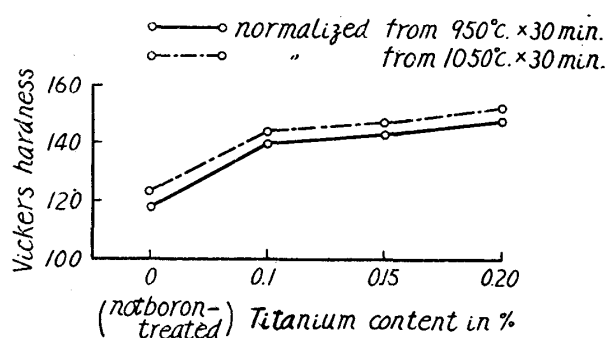
Table 7

Steel	Chemical analysis				
	C %	Si %	Mo %	Ti %	* B %
No. 10	0.08	0.2	0.5	—	—
No. 11	0.07	0.2	0.5	0.10	0.003
No. 12	0.08	0.2	0.5	0.15	0.003
No. 13	0.08	0.2	0.5	0.20	0.003

* : amount of added with ferro-boron (10% B)

V. Mechanism of boron hardenability

It has been reported[10][11] that boron has no important effect on the diffusivity of carbon in austenite. Further, from the various observations on boron-treated steels, it has been known that the mechanism of boron hardenability differs far

(9) T. G. Digges and F. M. Reinhart, Trans. Amer. Soc. Met., **40** (1948), 1124.

(10) J. W. Spretnak and R. Speicer, Trans. Amer. Soc. Met., Preprint No. 20 (1953).

(11) P. E. Busby, M. E. Warga and C. Wells, J. of Metals, **5** (1953), 1463.

from that of the usual alloying elements as Ni, Cr or Mn.

From the results mentioned in the foregoing sections, it becomes clear that the boron hardenability is due mainly to the grain surface adsorptions of boron and other atoms whose mobilities in austenite are comparatively high. The most characteristic aspect of boron hardenability may be said to be a remarkable suppression of the nucleation of transformation beginning at the austenite grain boundary. Owing to the large atomic size of boron as an interstitial solute element and to its high mobility[11] in austenite, boron atoms adsorbed on the grain surface will effectively fill up lattice imperfections there, and the internal strains due to these imperfections will be reduced. Thus, the nucleations beginning at grain boundaries will be suppressed until the steel is cooled to a sufficiently low temperature. The alternative interpretation will be as follows: boron atoms adsorbed on the grain surface may form "Cottrell atmosphere" during cooling, giving rise to the anchoring of dislocations in the vicinity of grain boundaries, because these dislocations play an important role in the formation of the nucleus of α-Fe by quenching.

Spretnak and Speiser[10] have proposed the following mechanism: the transformation of γ-iron into α will be carried out by the nucleation and shear mechanism instead of the usual nucleation and growth mechanism. The high strain energy in austenite lattice due to boron atoms will be effective to retard the shear transformation of γ-iron. Basing on the relations betweeen lattice parameters, concentrations and diameters of solute atoms, they calculated the ratios of hardenabilities due to carbon, nitrogen and boron with the result of 1:3:50. It will be more likely, however, that the weak points for shearing such as imperfections of lattice, dislocations or diffusion holes, will be remedied by boron atoms. As the boron atom, having high mobility in austenite, is of the largest size among the interstitial solute element, it would be most liable to fall into these holes, compared with carbon or nitrogen. Furthermore, carbon atoms are also well adsorbed on grain surface alike to boron atoms as shown in Photo. 8, especially in the steels in which the gas content was easily controlled.

It is well known that nitrogen content in a solid solution generally decreases with the increase of carbon content. Therefore, the increase of carbon content (within the ranges of eutectoid composition) will be useful to produce the good result for the adsorption of carbon atom, due directly to the increase of its concentration and indirectly to the decrease of gas content in the solid solution. In the same way as in the case of boron, the carbon hardenability will reach the degree equivalent to that gained with boron addition. Such a consideration will be most probable to explain the influence of carbon content upon the boron hardenability, that is, the boron effect is inversely proportional to the carbon content and essentially negligible at the eutectoid carbon content.

Summary

(1) Adsorption effect of boron on austenite grain surface was considered to

be the most important factor in the hardenability.

(2) The adsorptions of boron and other interstitial solute elements at the quenched condition were well revealed by etching the steel with NaOH-NaNO$_3$ solution. The dark brown colored narrow band developed usually around the parent austenite grains and sometimes around the subgrains. This colored band changed into a linear feature with the rise of the austenitizing temperature, which would be considered to be due to the high degree of adsorption.

(3) In the case of a plain carbon steel, the grain boundary bands were also seen when the steel was well deoxidized and denitrogenized by the addition of Al, Ti and so on. This would be due to the adsorption of carbon upon grain surface similar to the case of boron.

(4) The decrease of boron hardenability with the rise of austenitizing temperatures would be caused by the re-dissolution of nitrogen in the solid solution. At extremely high austenitizing temperatures, the concentrated nitrogen atoms resulted from the re-dissolution of nitrides would be adsorbed upon the grain surface in the same way as in the cases of boron and carbon. When the amount of nitrogen adsorbed upon the grain surface extremely increased, it would bring out the formation of compound with boron and made boron ineffective form.

(5) The adsorbed boron atoms well served for filling lattice imperfections or diffusion holes and perhaps for anchoring dislocations. Thus, the nucleation of transformation beginning at grain boundary was well suppressed.

(6) The adsorption of carbon atom upon grain surface was raised with the increase of the carbon content (within the eutectoid carbon content), and so the boron hardenability was inversely proportional to the carbon content and essentially negligible at the eutectoid carbon content.