An Investigation on Boron-Treated Steels. I : On the Hardenability of Boron-Treated Medium-Carbon Steels, especially the Effect of Nitrogen-Content in Steels

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An Investigation on Boron-Treated Steels. I
On the Hardenability of Boron-Treated Medium-Carbon Steels, especially the Effect of Nitrogen-Content in Steels*

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Synopsis

As fundamental studies on boron-treated steels, the hardenability and the effect of nitrogen in it were studied with medium carbon steel.

The maximum hardenability is obtained with the addition of boron by the order of 0.003%, being decreased sharply with further increase of boron. When the nitrogen content is less than about 0.008%, the effect on the improving action of boron on the hardenability is almost nil, but with increasing of its amount over 0.008% the effect of boron decreases markedly, until the nitrogen content increases up to about 0.02% in which the effect of boron almost diminishes. When steel is strongly deoxidized and denitrogenized by adding aluminium or titanium, prior to boron addition, the effect of boron appears markedly. These results may be attributed to fact that boron accerelates to crystallize out a nitrogen compound during quenching or tempering of steels.

I. Introduction

Recently, it is noticed that the hardenability of steels is increased with addition of a small amount of boron, 0.002~0.003%, and in U. S. A., additional agents such as Silvaz No. 3, Silcaz No. 3, etc., produced in many companies, are used commercially.

The binary equilibrium diagram of "Fe-B" was proposed by Hannsen(1), Tschishewsky & Herdt(2), Tammann & Vogel(3), and Wever & Müller(4), and the ternary system of "Fe-B-C" by Tammann & Vogel(5); among them, however, Wever & Müller's result only is qualitatively accepted.

According to their results, the maximum solubility of boron in γ_{Fe} is about 0.15% and about 0.1% in α_{Fe}, therefore the behavior of the improving effect of boron, as mentioned above, can not be explained by the difference of solubility in γ_{Fe} and α_{Fe}. Moreover, when a small amount of an order of about 0.003% boron is added, precipitation of Fe_2B or double compound of boron, insoluble in γ_{Fe} at the ordinary hardening temperatures, is detected clearly; therefore the effective amount of boron, dissolved in γ_{Fe}, will be less than 0.003%.

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* The 566th report of the Research Institute for Iron, Steel and Other Metals.

(1) G. Hannsen: Z. anorg. Chem., 89 (1914), 257/78.

(2) N. Tschishewsky & A. Herdt: Iron Age, 98 (1916), 396.

(3) R. Vogel & G. Tammann: Z. anorg. Chem., 123 (1932), 225/75.

(4) F Wever & A. Müller: Mitt. K.-W.-Inst. Eisenforschg., 11 (1929), 193/218.
Z. anorg. Chem., 192 (1930), 317.
Stahl u. Eisen, 49 1929), 1528/30.

(5) R. Vogel & G. Tammann: Z. anorg. Chem., 123 (1932), 225/75.

From these facts, it is considered by many investigators that nitrogen dissolved in steels has a very close connection with boron, and the nitride-precipitation during cooling is very finely dispersed by the boron additions.

The present investigation was undertaken to study on the interaction between boron and nitrogen dissolved in steel, and also on the hardenability of boron-treated medium-carbon steel, especially on the effect of nitrogen-content in steel.

II. Preparation of specimens

As boron has a slightly more strong affinity with oxygen than with silicon, the degree of deoxidation prior to boron-addition is a very important factor.

In the present experiments, the deoxidation of steels was carried out with sufficient amount of metallic silicon (0.1～0.2%), prior to boron-addition, and the required amount of boron was easily added. The chemical compositions of ferro-boron used, were:

Name	C%	Si%	Al%	B%
Ferro-boron No. 1	0.31	2.26	11.87	11.09
Ferro-boron No. 2	0.30	2.31	10.71	9.38

Although aluminium contents in these alloys are comparatively high, the amount of aluminium induced in steel from these alloys is negligibly small to affect the mechanical properties of these steels, since the amount of Boron to be added is about 0.003%.

III. Results of experiments

(1) Effect of a small amount of boron-addition on nitride-precipitation.

It is a known fact that on tempering of hardened steels, the nitride precipitates prior to the carbide; that is, by Heidenreich(6), Fe_3N-precipitation was recognized with electron microscope when the hardened steels were tempered at about 200°C.

In the present work, an effect of a small amount of added boron on the nitride-precipitation was studied.

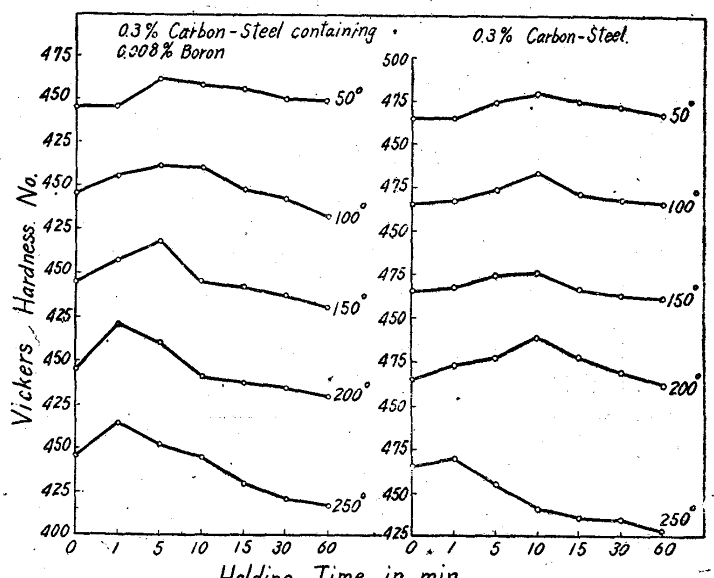

Fig. 1. 950°C(30min)→quenched in water and tempered for various length of time at 50°, 100°, 150°, 200° and 250°C.

(6) R. D. Heidenreich, L. Surkey and H. L. Woods: Jr.App. Phy., 12 (1946), 127.

For these purpose, specimens which contain 0·3% carbon with and without 0.008% boron were used. These specimens were heated at 950°C for 30 min, quenched in water, and tempered at temperature ranges from 50°C to 250°C for various length of time, then measured with Vickers hardness tester.

The results are shown in Fig. 1. From the figures, it is recognized that the maximum points of tempered hardness in steels, added boron, appear in shorter length of time on tempering than in those without boron, that is to say, nitride-precipitation is promoted with boron. In order to know in detail these effects of boron-addition, and also to study the relation of nitride and carbide precipitations, the change of magnetic coercive-force on tempering was meausred with specimens containing 0.2% carbon, 1.8% manganese, with and without 0.008% boron.

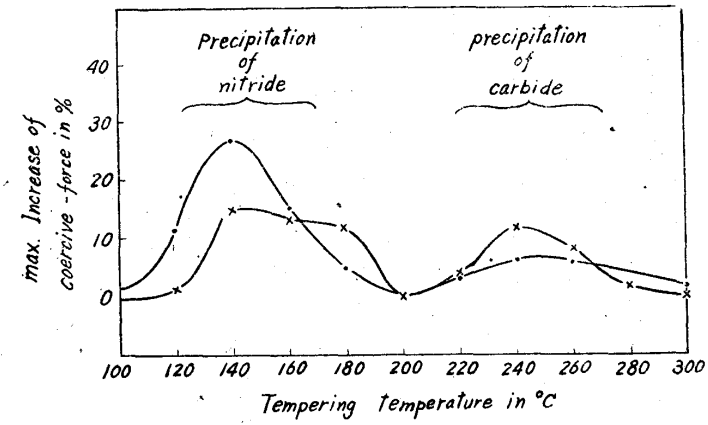

Fig. 2, Change of magnetic coercive-force on tempering.
•——• : 0.2% C, 1.8% Mn, 0.008% B.
×——× : 0.2% C, 1.8% Mn.

The results are shown in Fig. 2. From the figure, it is clearly recognized that the nitride-precipitation takes place at lower tempering temperatures in boron-treated steels than in no boron steels, and the carbide-precipitation is to some extent suppressed in these steels with boron.

These relations, are also recognized when the specimens were isothermally transformed at temperatures below 400°C, as shown in Fig. 3; the microscopic examinations show the nitride-precipitation, using a modified Fry's reagent for etching, as described below:

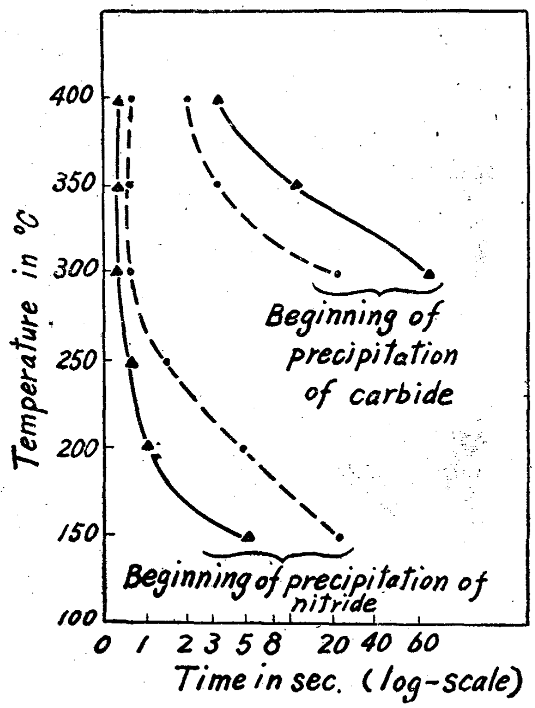

Fig. 3. Beginning curves of the carbide- and nitride-precipitations below 400°C.
▲——▲ 0.3% C, 0.05% B.
•— — • 0.3% C.

$$5\,g\text{-}(CH_3COO)_2Pb + 5\,g\text{-}CuCl_2 + 100\,cc\text{-Water} \rightarrow (CH_3COO)_2Cu + PbCl_2 \ (ppt.)$$

which was filtered and then a little amount of $FeCl_3$ was added.

After all these results, it can be considered that the nitride-precipitation is much promoted by adding 0.003% boron near the Ar'' temperature when the steels were quenched, and these precipitants promote the formation of martensite which act as a transformation nucleus, and, at the same time, these promoted nitride-precipitation increases the stability of super-saturated carbon, and then the hardenability are improved.

(2) Boron content to be obtained the maximum hardenability.

To determine the suitable amount of boron to be added, in order to obtain the maximum hardenability, specimens shown in Table 1 were used.

Table 1

Specimens	Chemical analysis					Length of hardened part in mm (50% M.+50% T.)
	C %	Si %	Al %	B %	N_2 %	
C.	0.31	0.13	0.027	0.0027		4.60
D.	0.29	0.12	0.069	0.005		4.15
E.	0.30	0.15	0.13	0.016		3.65
F.	0.21	0.13	<0.01	0.008	0.004~0.006	3.90
G.	0 26	0,13	<0.01	0.028		3.70
H.	0.29	0.13	0.01	0.041		3.60
I.	0.30	0.15	—	—		2.70

Hardenability was measured by "gradient quench" using ϕ 5mm × 100mm bars; specimens were heated at 900°C, for 10 min, one end quenched in water of about 12 mm depth, and measured a length of hardened part, that is, a length from quenched end to a point consisting of 50% martensite and 50% troostite in a longitudinal section.

The results are shown in Fig. 4, in which we can see a fact that the maximum hardenability is obtained with addition of about 0.0027 % boron, and somewhat decrease with increasing boron content up to 0.005%, and on further increase up to 0.041%, the hardenability decreases slightly. This is explained as mentioned below. The precipitation of Fe_2B or a double compound of boron at grain boundaries takes place by a small amount of addition of 0.0027% boron, the amount being markedly increased with increasing boron-content.

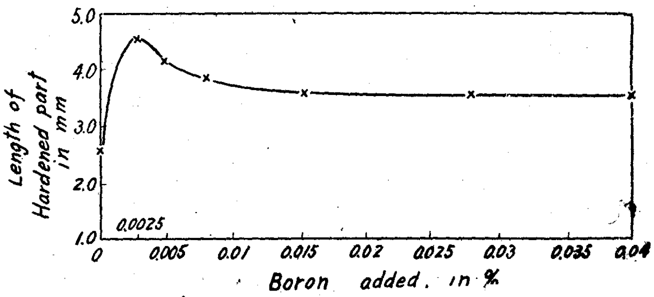

Fig. 4. Effect of boron content on length of hardened part in 0.3% C steels.

The amount of boride or double compound do not show any change when the steel was quenched from the ordinary hardening temperatures. Hence, on cooling from the hardening temperature, it may be considered that these precipitations act as nucleus for the formation of pearlite and promote the reaction, the maximum hardenability being obtained by the order of about 0.0027% boron-addition.

The suitable amount of boron coincides with many experimental results obtained by investigators in America.

The precipitations of Fe_2B or double compound are detected even by addition of 0.0027% boron at grain boundaries, as mentioned above, being not dissolved in austenite in ordinary hardening temperatures. Hence, the critical amount of boron, to give the maximum hardenability, which dissolves in austenite at hardening temperatures and acts effectively, should be lower in amount than 0.0027%.

On the other hand, the nitrogen-content in steels have a marked effect on the improving action of boron, that is, some quantity of added-boron is fixed as nitride which does not dissolved in austenite in ordinary hardening temperatures; and some quantity of boron added are lost as oxide which has no effect on the hardenability of steel, as reported by Mr. Udy(7).

From these facts, it is very difficult to determine the critical amount of boron to obtain the maximum hardenability, though the maximum hardenability can be obtained with an order of about 0.003% boron in steels containing 0.004~0.006% of nitrogen as shown in Table 1, provided the steels were well deoxidized prior to the addition of boron.

(3) Effect of nitrogen-content in steels on the improving action of boron.

According to many studies in America, the improving action of boron added appears markedly in steels made by basic open-hearth, but in those of electric arc-furnace or high frequency induction furnace, the effect is not so pronounced: the most serious difference is due to the nitrogen content, that is, in the former, the content is in the order of 0.001~0.008% while in the latter two, it is much higher, such as of 0.006~0.040%.

It is considered that such difference in nitrogen-content exerts a marked influence upon the improving action of added boron. Digges & Reinhalt(8) report that the high content of nitrogen in steels gives a harmful effect for the improving action of boron and the effect almost diminishes when the nitrogen-content is highly increased.

The writers made a study on the effect of the nitrogen-content in steels to the improving action of boron employing specimens shown in Table 2.

Table 2

Specimens	Chemical analysis					Length of hardened part in mm (50%M.+50%T.)	Remarks
	C %	Si %	Mn %	B %	N_2 %		
No. 1	0.34	0.12	0.28	0.004	0.004	4.60	ordinary melting.
No. 2	0.34	0.06	0.30	0.004	0.008	4.45	Added nitrogen with Mn-nitride
No. 3	0.33	0.06	0.29	0.004	0.011	3.31	
No. 4	0.31	0.08	0.29	0.003	0.019	2.88	
No. 5	0.31	0.07	0.30	0.004	0.022	2.70	
No. 6	0.33	0.07	0.31	0.002	0.028	2.75	
No. 27	0.34	0.12	0.28	—	0.005	2.65	no boron.

The nitrogen content of specimens Nos. 2~6 was controlled by quantity of manganese-nitride containing 7.4% nitrogen added prior to boron-addition, while in specimen No. 1 the manganese-nitride was not added.

The hardenability of these specimens was determined by the gradient-quench,

(7) M. C. Udy: Metal Progress, 52 (1947), 257.

(8) T. G. Digges & F. M. Reinhart: T. A. S. M., 40 (1948), 1124

as already mentioned (chapter 2). The results of experiments are shown in Figs. 5 and 6. From the figures, it is clearly recognized that the hardenability decreases as the nitrogen-content increases; the amount of decrease is slight when the nitrogen content increases from 0.004% to 0.008%, but when the nitrogen-content exceeds 0.008%, the decrease is remarkable and when the nitrogen-content increases up to 0.02%, the effect of boron almost diminishes, provided the boron-content is about 0.004%.

These changes may be explained as follows: the crystal grain size is refined with high content of nitrogen, and hence the hardenability decreases.

In the present experiments, actually, the crystal grain size was refined to some extent, but such a large decrease of hardenability, as shown in the figures, can not be attributable to these refinement.

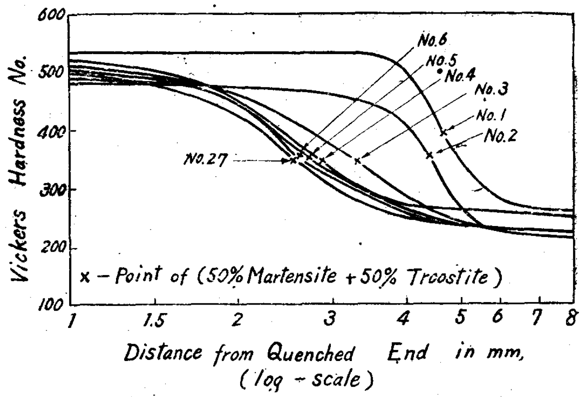

Fig. 5. "Hardness" curves of high nitrogen-boron steels.
900°C. (10 min) → Quenched

It can be considered, from the affinity of boron with nitrogen being rather strong, that is, some quantity of added boron is fixed as nitrides, dissolved in austenite in very small quantities even at high temperatures. And the quantity of effective boron, dissolved in austenite, decreases markedly with increasing nitrogen. Recently, Speight[(9)] reported that boron in steels is contained in "acid-soluble" and "insoluble" forms, and that the nitride of boron is "acid insoluble".

Hence, from the results shown in Figs. 5 and 6, it may be concluded that the fixed nitrides increase with the increase of nitrogen-content in steels, and when the content exceeds 0.02%, almost all amount of boron added are fixed as nitrides, and hence the amounts of effective boron are minimized almost to zero.

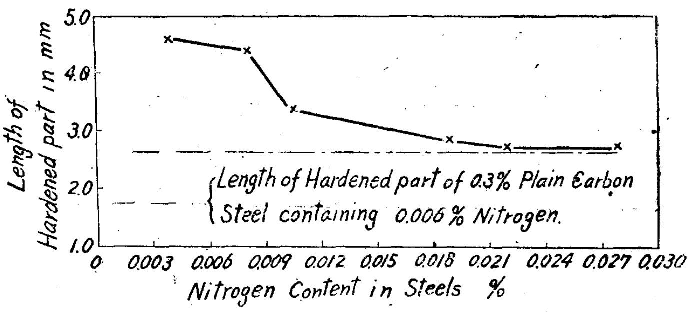

Fig. 6. Effect of nitrogen content on the hardenability of 0.3% C, 0.003% B steels.

In order to ascertain of these facts, the change of hardness on tempering of these specimens was measured; that is, these specimens were heated at 900°C, quenched in water and then tempered at 150° and 200°C with various length of time.

The results are shown in Fig. 7, from which it can be recognized that the effect of boron on the tempered hardness is as mentioned in chapter (1) up to 0.011%

(9) G. Speight: Jr Iron & Steel Inst. 22 (1949), 601

nitrogen, but as the nitrogen-content increases over 0.019%, the effects of boron almost diminish and are similar to the specimen No. 27, containing no boron.

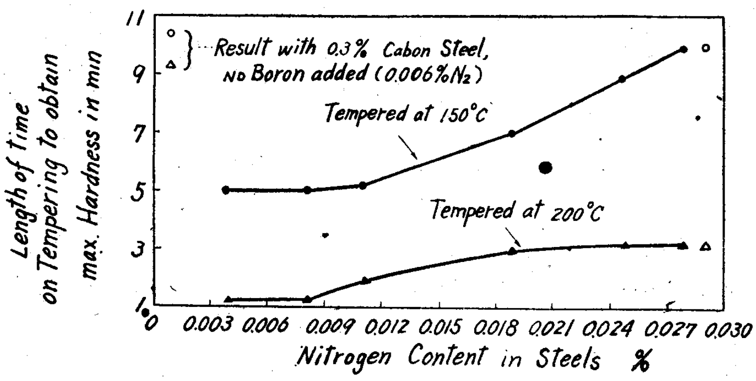

Fig. 7. Effect of nitrogen content in steels on holding time for tempering to obtain the max. precipitation -hardness with 0.3% C, 0.003% B steels.
900°C (30min) → W. Q. and tempered at 150°&200°C.

From these results, it is very desirable to lower the nitrogen-content in steels prior to boron-addition, and if the nitrogen-content is raised up to 0.02%, almost all the boron added is fixed or lost as nitride, and the effect of boron to increase the hardenability almost diminishes.

(4) Effect of aluminium to the improving action of boron.

As before mentioned, the nitrogen-content in steels gives a marked influence on the effect of boron. From the foregoing results, much more excellent effects of boron would be undoubtedly expected when the nitrogen-content in steels was lowered by the addition of aluminium or titanium, which has very strong affinity for nitrogen, prior to boron-addition.

At first, the effect of aluminium was studied with specimens containing 0.03, 0.1 and 0.2% aluminium.

The chemical compositions of the specimens made for this purpose are shown in Table 3.

Table 3

Specimens	Chemical analysis						Length of hardened part in mm (50%M.+50%T.)	Remarks.
	C %	Si %	Mn %	B %	Al %	N_2 %		
No. 7	0.26	0.08	0.24	0.002	0.03	0.004~0.006	4.50	Al & B added.
No. 8	0.32	0.09	0.26	0.003	0.11		5.00	
No. 9	0 29	0.17	0.28	0.004	0.26		5.20	
No. 13	0.35	0.08	0.28	—	0.009	0.007	2.70	ouly Al added
No. 15	0.34	0.08	0.26	—	0.04	0.008	2.75	
No. 16	0.29	0.10	0.24	—	0.13	0.006	3.42	
No. 17	0.35	0.12	0.28	—	0.25	0.005	3.80	
No. 1	0.34	0.12	0.28	0.004	—	0.004	4.60	only B added
No. 27	0.34	0.12	0.28	—	—	0.005	2.65	no B, no Al.

Specimens Nos. 7 to 9 were made by adding aluminium (0.03, 0.1 and 0.2%) prior to boron-treating, using a steel containing carbon 0.3%, manganese 0.3% and boron 0.003%, while for specimens Nos. 13 to 17 aluminium was added to a steel not treated with boron.

When these specimens were melted, first deoxidation was carried out with metallic silicon, and the loss of aluminium as oxides was minimized. Using these specimens, the hardenability was compared.

The results are shown in Figs. 8 and 9. From the figures, it will be recognized that the addition of 0.03% aluminium decreases the hardenability in a few degrees, compared with the boron-treated steel No. 1 without aluminium.

When the added amount of aluminium is increased up to 0.1 ~0.2%, however, the hardenability increases, as expected.

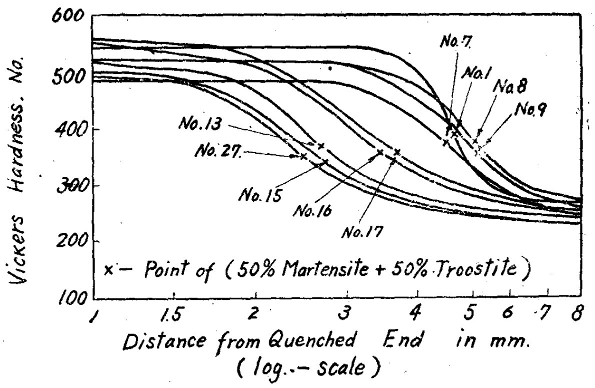

Fig. 8. "Hardness" curves of boron steels, in which various amount of Al added.

For the reasons of these results, it can be considered that the grain size of steels is refined markedly, when the added amount of aluminium was in the order of 0.03%, and the decrease of hardenability due to such a refined size of crystal grains masked the desirable denitrogenizing action of aluminium. From the results, it will be recognized that when aluminium was added prior to boron-addition, the nitrogen-content to fix the boron as nitride was minimized, and the improving effect of boron was enlarged.

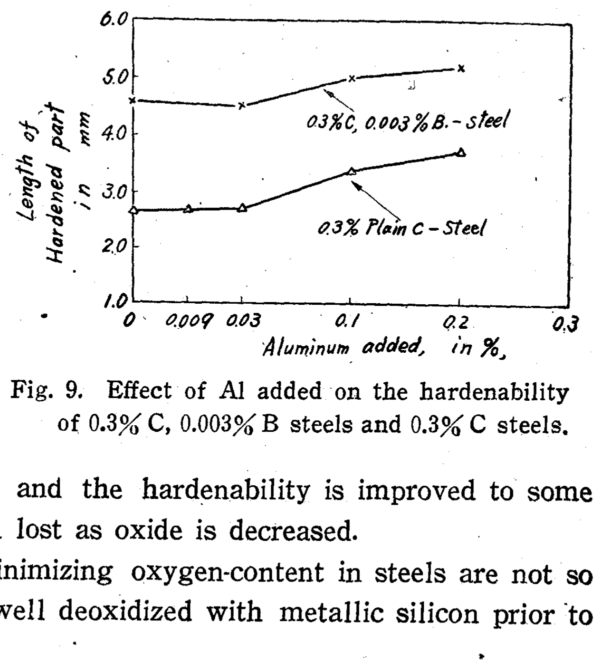

Fig. 9. Effect of Al added on the hardenability of 0.3% C, 0.003% B steels and 0.3% C steels.

Moreover, the following two facts seem worthy of consideration: (1) when aluminium is added in steels, deoxidation is more powerful than by metallic silicon alone, and the hardenability is improved to some extent, and (2) the amount of boron lost as oxide is decreased.

But these two effects, due to minimizing oxygen-content in steels are not so essential because the steels were well deoxidized with metallic silicon prior to aluminium-addition.

Therefore, above all, the principal factor for the improving effect of boron should be attributed to the denitrogenization by aluminium. In Figs. 8 and 9, the change of hardenability of steels, added aluminium alone without boron, are also shown; that is, aluminium alone was added by an order of 0.009~0.03%, but the improving effect to hardenability is almost negligible, while the amount of aluminium is increased up to 0.1~0.2%, the hardenability increases markedly.

(5) Effect of titanium on the improving action of boron.

The effect of titanium was studied using steels which were denitrogenized with titanium prior to boron-addition, as in the case of aluminium, as before mentioned.

The results of analysis of specimens made for the purpose, are shown in Table 4.

Table 4

Specimens	Chemical analysis						Length of hardened part in mm (50%M.+50%T.)	Remarks.
	C %	Si %	Mn %	B %	Ti %	N_2 %		
No. 10	0.33	0.12	0.25	0.005	0.04	0.004~0.006	4.95	Ti & B added.
No. 11	0.34	0.17	0.26	0 003	0.15		5.20	
No. 12	0.29	0.17	0.24	0.002	0.27		5.50	
No. 18	0.35	0.10	0.26	—	0.03	0.006	2.88	only Ti added.
No. 19	0.33	0.12	0.27	—	0,13	0.004	3.50	
No. 20	0.32	0.11	0.25	—	0.24	0.007	3.84	
No. 1	0.34	0.12	0.28	0.004	—	0.004	4.60	only B added.
No. 27	0.34	0.12	0.28	—	—	0.005	2.65	no B, no Ti.

Specimens Nos. 10~12 were made by adding 0.03, 0.1 and 0.2% of titanium to a steel containing carbon 0.3%, manganese 0.3% and boron 0.003% prior to boron-addition.

The hardenability of these specimens was measured by the "gradient-quench" method, and the results are shown in Figs. 10 and 11. From the figures, we can recognized clearly that titanium-addition is more effective for hardenability of the boron-treated steel, than aluminium-addition.

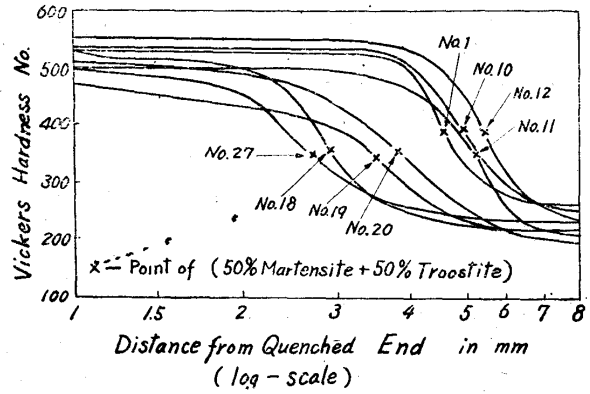

Fig. 10. "Hardness" curves of boron steels, in which various amount of Ti added.

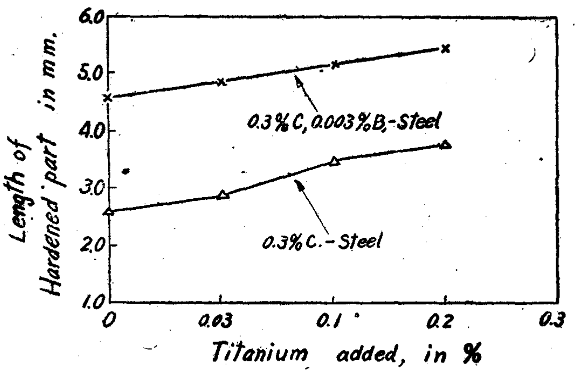

Fig. 11. Effect of Ti added, to the hardenability of 0.3% C, 0.003% B steels and 0.3% plain carbon steels.

It is also recognized that considerable improving effect is obtained when only 0.03% titanium was added, and the improving effect increases linearly with further increase of titanium up to 0.1 and 0.2%.

From the results with microscopic examinations of these steels, the crystal grain size were found to be refined, but not so much markedly as in the cases of aluminium-additions.

The superiority of titanium to aluminium for improving action of boron is attributed to the stronger affinity of the former with nitrogen.

In Figs. 10 and 11, the change of hardenability of steels to which only titanium was added is also shown.

In this case, the hardenability of boron-treated steel markedly increases by the strong deoxidation with titanium or aluminium.

Conclusion

(1) The precipitation of nitride, prior to that of carbide takes place on tempering

of hardened steels in a comparatively low temperature range from 150° to 200°C, being markedly promoted by the addition of a small amount of boron.

(2) The maximum hardenability of boron-treated medium-carbon steels is obtained with the addition of boron by the order of 0.003%. But it decreases sharply with increasing amount of boron, and when the amount exceeds about 0.015%, it is nearly constant.

(3) The nitrogen content less than about 0.008%, does not much affect the improving action of boron, but with increasing its amount beyond 0.008%, the effect of boron decreases markedly, until the nitrogen content increases up to 0.02%, in which the effect of boron almost diminishes owing to the fact that the more the nitrogen the more boron is fixed as nitride, and the amount of soluble active boron decreases markedly.

(4) When steels are strongly deoxidized and denitrogenized by adding alumiuium or titanium, prior to boron-addition, the improving effect of boron appears more sharply.

For these purposes, the required amount of aluminium is 0.1% at least. The addition of titanium is more effective than the aluminium-addition for the improving effect of added-boron; that is, by addition of a small amount of titanium, such as 0.03%, it's effect is recognized clearly.

In conclusion, the authors wish to express their sincere thanks to Emeritus Prof. T. Murakami for his kind advices during the course of this work.