BORON STEELS

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Abstract

A small amount of boron (0·0005 per cent minimum) is successfully used in the United States as a replacement of appreciable quantities of nickel, chromium and molybdenum in structural low-alloy steels. The standard AISI grades are designed to replace conventional alloy steels of equivalent hardenability. The boron steels are normally manufactured by the basic open-hearth process, although the basic electric furnace process is also used. Special equipment is not required in their manufacture and fabrication, but certain precautions are essential in making the boron addition and finishing the heats. The production of boron steels attained a maximum of about 0·7 million tons in 1952 and thereafter decreased to about 0·5 and 0·25 million tons in 1953 and 1954 respectively.

Examples are given to show the general influence of boron on hardenability and mechanical properties of selected steels. A review is made of the literature on the mechanism of boron in increasing hardenability and a summary is presented of known facts on the behaviour of boron in iron and steel.

Introduction

AT the beginning of World War II, it was recognized that the hardenability of certain structural steels was materially enhanced by the addition of minute amounts of boron. As one of the main roles of alloying elements in a structural steel is to increase its hardenability, this significant effect of boron suggested the possibility that it might be substituted for a part or all of the strategic elements commonly used as alloying agents in these steels. Because of the accelerated use of steel in the war effort, the availability of boron, and the scarcity of alloying elements, especially nickel and chromium, considerable attention was directed during this period of emergency to the development of boron-treated steels. A continuation of the study and development of boron-treated steels after the close of the war was dictated by a continuing scarcity of alloying elements and the economy of the nation in its ever-expanding use of steels. As a result of the extensive investigations that have been conducted, a voluminous literature exists today concerning the properties of these steels.

Chemical Composition, Manufacture, Production and Uses of Boron Steels

The chemical compositions of boron steels now recognized as standards, tentative standards and alternates by the American Iron and Steel Institute[1] are given in Table 1. They consist of both carburizing and hardenable steels; the latter are designed to have hardenability equivalent to certain non-boron steels of the same carbon but higher alloy content. For example, 81B45 is designed to have the same hardenability as 4145. (0·20-0·40 Ni, 0·35-0·55 Cr, 0·08-0·15 Mo, plus boron, is about equivalent in hardenability to 0·80-1·10 Cr, 0·15-0·25 Mo).

The procedures used in the manufacture and fabrication of boron steels are not markedly different from those used for low-alloy grades. Special equipment is not required, but some additional precautions are essential in the final processing of the heats and in making the boron additions. The boron steels are manufactured principally by the basic open-hearth process, although the basic-electric process is also used to some extent, especially for steels of aircraft quality. In each process, the boron additions are made to thoroughly deoxidized steel preferably as it is tapped into the ladle. Two types of agents, simple and complex, are available

TABLE 1 — AMERICAN IRON AND STEEL INSTITUTE STANDARD, TENTATIVE STANDARD AND ALTERNATE BORON STEELS (BARS, BILLETS, BLOOMS AND SLABS)

These steels can be expected to have 0·0005 per cent minimum boron content

CHEMICAL COMPOSITION RANGES AND LIMITS PER CENT

AISI Number	C	Mn	P max.	S max.	Si	Ni	Cr	Mo	V
TS 14B35	0·33-0·38	0·75-1·00	—	—	0·20-0·35	—	—	—	—
TS 14B50	0·48-0·53	0·75-1·00	—	—	0·20-0·35	—	—	—	—
TS 43BV12	0·08-0·13	0·75-1·00	—	—	0·20-0·40	1·65-2·00	0·40-0·60	0·20-0·30	0·03 min.
TS 43BV14	0·10-0·15	0·45-0·65	—	—	0·20-0·35	1·65-2·00	0·40-0·60	0·08-0·15	0·03 min.
46B12	0·10-0·15	0·45-0·65	0·040	0·040	0·20-0·35	1·65-2·00	—	0·20-0·30	—
50B30(a)	0·27-0·34	0·70-1·00	—	—	0·20-0·35	—	0·35-0·60	—	—
50B35(a)	0·32-0·39	0·70-1·00	—	—	0·20-0·35	—	0·35-0·60	—	—
50B40(a)	0·37-0·45	0·70-1·00	—	—	0·20-0·35	—	0·35-0·60	—	—
50B44(a)	0·42-0·50	0·70-1·00	—	—	0·20-0·35	—	0·35-0·60	—	—
50B46	0·43-0·50	0·75-1·00	0·040	0·040	0·20-0·35	—	0·20-0·35	—	—
50B50	0·48-0·53	0·75-1·00	0·040	0·040	0·20-0·35	—	0·40-0·60	—	—
50B60	0·55-0·65	0·75-1·00	0·040	0·040	0·20-0·35	—	0·40-0·60	—	—
51B60	0·55-0·65	0·75-1·00	0·040	0·040	0·20-0·35	—	0·70-0·90	—	—
81B45	0·43-0·48	0·75-1·00	0·040	0·040	0·20-0·35	0·20-0·40	0·35-0·55	0·08-0·15	—
86B45	0·43-0·48	0·75-1·00	0·040	0·040	0·20-0·35	0·40-0·70	0·40-0·60	0·15-0·25	—
94B15	0·13-0·18	0·75-1·00	0·040	0·040	0·20-0·35	0·30-0·60	0·30-0·50	0·08-0·15	—
94B17	0·15-0·20	0·75-1·00	0·040	0·040	0·20-0·35	0·30-0·60	0·30-0·50	0·08-0·15	—
TS 94B30	0·28-0·33	0·75-1·00	—	—	0·20-0·35	0·30-0·60	0·30-0·50	0·08-0·15	—
TS 94B40	0·38-0·43	0·75-1·00	—	—	0·20-0·35	0·30-0·60	0·30-0·50	0·08-0·15	—

These grades are normally manufactured by the basic open-hearth process, but may be manufactured by the basic electric process with adjustments in phosphorus and sulphur. The phosphorus and sulphur limitations for each process are: Basic electric furnace — 0·025 maximum per cent.; Basic open-hearth — 0·040 maximum per cent.

Maximum allowable amounts of unspecified and incidental elements are: copper 0·35 per cent; nickel 0·25 per cent; chromium 0·20 per cent; molybdenum 0·06 per cent.

NOTES — TS denotes tentative standard steels; (a) denotes alternate steels.

commercially for making the additions. Typical analyses of some of these agents are given in Table 2. These ferro-alloys differ principally in that the simple types (A and B, Table 2) have a higher concentration of boron than the complex types (C and D) and the latter types also contain appreciable amounts of one or more of the elements titanium, zirconium and vanadium. Thus, the complex agents carry their own nitride-formers for the protection of the boron. The amount of the agent added is sufficient to retain about 0·0005-0·005 per cent of boron in the steel. The preferable ranges are approximately 0·002-0·0025 per cent boron with the simple agents and 0·001-0·0015 per cent boron with the complex agents.

TABLE 2 — BORON ADDITION AGENTS (FERRO-ALLOYS)

DESIG-NATION	CHEMICAL COMPOSITION, PER CENT						
	B	Al	Mn	Si	Ti	V	Zr
A	11·6	—	—	2·6	—	—	—
B	3·7	—	—	45·0	—	—	—
C	0·6	13·0	8·0	3·0	19·0	—	5·5
D	0·5	6·7	—	38·0	9·0	9·5	9·0

The production of boron steels in the United States[2] during the period of 1951 through 1954 is given in Table 3. The sharp increase in the production of the boron steels in 1952 can be attributed to the scarcity of alloying elements, the restriction of their use in structural steels due to the Korean conflict and the co-operative efforts of the American Iron and Steel Institute and Society of Automotive Engineers to develop low-alloy steels containing boron. Nearly one-half of the production of boron steel in 1952 was of the triple alloy (nickel-chromium-molybdenum) grades (316, 502). The removal in 1953 of certain restrictions on the use of alloying elements was a factor contributing to the decrease in the production of boron steels. Apparently, some of the former successful users of the conventional alloy steels returned to using these grades when they became available. In 1954, the production of the formerly popular nickel-chromium-molybdenum grades (57,018 tons) was surpassed by the chromium grades (64,168 tons) and nearly equalled by the molybdenum grades (53,782 tons).

During World War II, the use of boron steel was confined principally to ordnance items. After the war, their use expanded to include parts for automobiles, tractors, locomotives, tools, etc.

Properties of Boron Steels

Tensile, Hardness and Impact Properties at Room Temperature — The beneficial effects of alloying elements on the mechanical properties of structural steels are fully obtained only when they are in the heat-treated conditions, that is, when fully hardened and tempered. The strength properties of structural carbon and conventional alloy steels are closely related to their hardness and are surprisingly similar for a selected hardness

TABLE 3 — PRODUCTION OF ALLOY STEEL INGOTS (OTHER THAN STAINLESS)

YEAR	NET TONS			PER CENT WITH BORON	CONSUMPTION OF BORON, lb.
	Without boron	With boron	Total		
1951	8689324	372131	9061455	4·1	29594
1952	7383806	702875	8086681	8·7	48973
1953	8711022	497215	9208237	5·4	35015
1954	6050663	244928	6295591	3·9	27266

Data from *Statistical Reports of the American Iron & Steel Institute*[2].

provided that the steels are originally hardened throughout their cross-sections. However, the tempering temperatures necessary to secure certain levels of hardness in these steels are affected by alloying elements and two steels may have to be tempered at different temperatures to secure the same hardness. If this is done, especially if the hardness is within the range of about 200-400 Brinell, the strength and ductility of the two steels will be remarkably similar. A steel that is incompletely hardened (that is, quenched at too slow a rate to prevent the formation of some fine pearlite) may have, after tempering, a hardness and tensile strength equal to that of a completely hardened and tempered steel, but its yield strength and ductility will be inferior.

The addition of boron to a steel causes no increase in resistance to softening by tempering. Therefore, to secure a certain hardness, the tempering temperature of a completely hardened boron steel is often lower than that of an equivalent alloy steel without boron, particularly if the latter contains appreciable amounts of molybdenum. The results of some recent work on boron-treated steels[3] indicated that the element boron has no effect on temper-brittleness. However, the evidence showed that the susceptibility to temper-embrittlement was increased by other elements introduced into the steel with the boron when certain complex agents were used.

The influence of boron on the tensile and Charpy impact properties and Rockwell hardness at room temperature of a 0·43 per cent C, 1·6 per cent Mn steel as completely hardened and tempered at temperatures ranging from 400° to 1200°F. is illustrated by the typical results summarized in Fig. 1. The two steels (15 and 10, Table 4) were processed from the same basic open-hearth heat, but they differed in that one contained no boron whereas sufficient boron was added in the mold with a complex agent (C, Table 2) to retain 0·0006 per cent B in the other steel. When these two steels were tempered alike, the values for yield strength, tensile strength and hardness were not materially affected by boron. Similarly, the ductility (elongation and reduction of area) was not appreciably improved by boron when the steels were tempered at 800°F. or higher. The spread in values obtained in each of these properties was no greater than the variations to be expected from heat to heat, duplicate specimens and testing procedure. However, when tempered at 400°-600°F. for relatively high hardness, the ductility of the boron steel was somewhat superior to that of the non-boron steel.

The trend for these particular steels was for the notch toughness (Charpy V-notch specimens fully hardened) to decrease with an increase in tempering temperature from 400° to 600°F. and thereafter to increase with

TABLE 4 — CHEMICAL COMPOSITION (PER CENT BY WEIGHT) OF SELECTED STEELS

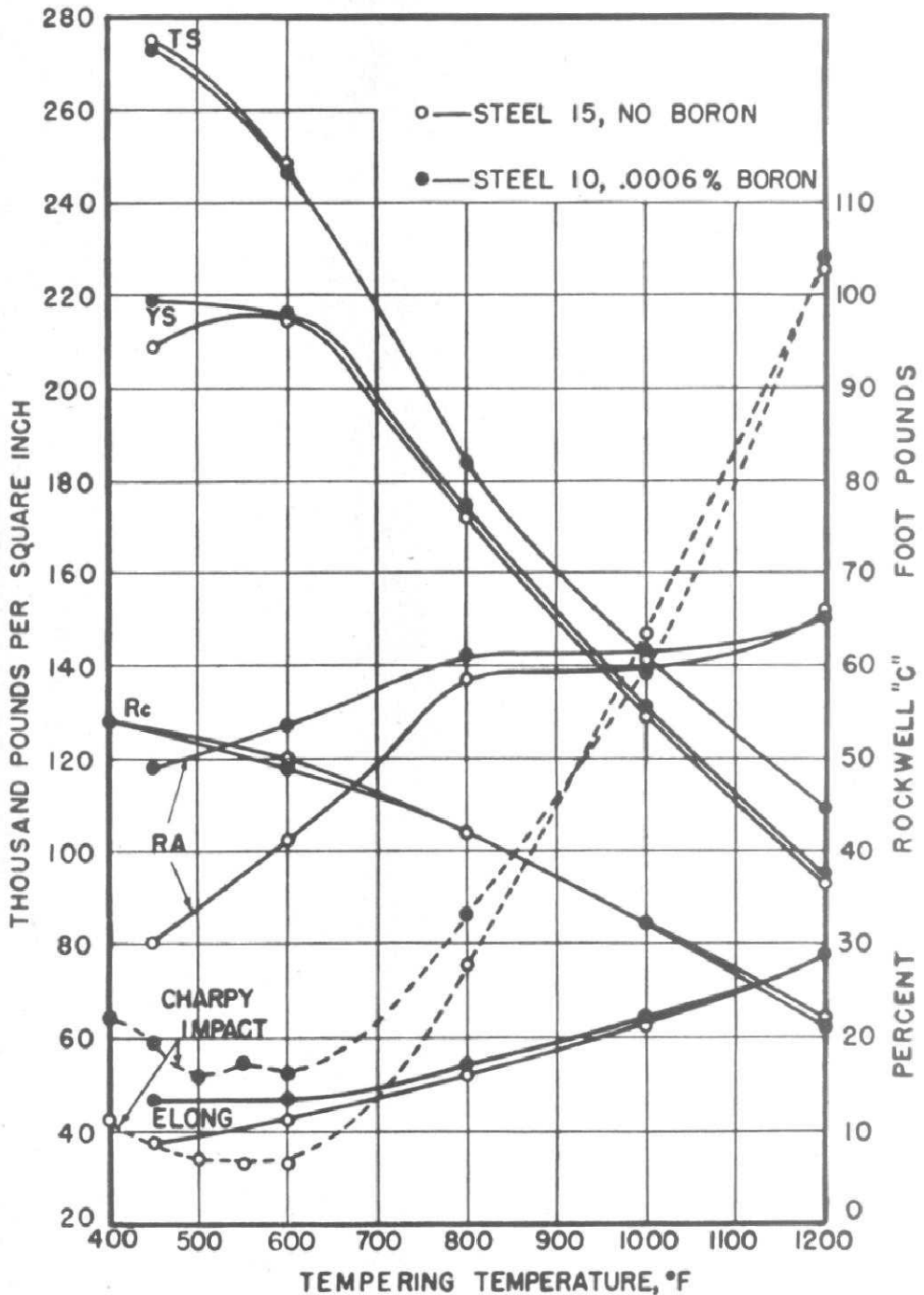| STEEL No.	C	Mn	P	S	Si	Ti	Zr	Al	N_2	B
Basic Open-hearth										
15	0·43	1·58	0·020	0·019	0·31	0·001	0·002	0·025	0·004	None
10	0·42	1·60	0·019	0·018	0·32	0·030	0·006	0·047	0·003	0·0006
Induction Furnace										
47	0·26	1·65	0·016	0·031	0·27	None	None	0·054	0·014	None
48	0·26	1·67	—	—	0·27	None	None	0·044	0·013	0·0053
49	0·26	1·65	—	—	0·31	0·17	None	0·053	0·015	0·0049

Fig. 1 — Effect of tempering temperature on the hardness, tensile properties, and notch toughness of 0·45 per cent carbon, 1·6 per cent manganese steel without and with boron

The chemical composition of the steels is given in Table 4.   Sections 0·53 in. in diameter for tensile and 0·43 in. sq. for impact (Charpy V-notch) tests were quenched from 1550°F. in oil and tempered at indicated temperatures for 1 hr. and then cooled in air.   A.S.T.M. grain number 8 at 1550°F.
The values plotted are the average for duplicate specimens tested at room temperature.

the temperature. The noticeable improvement in impact properties of the boron steel when heat-treated to high hardness has also been observed by other investigators. However, when low-alloy structural steels are fully hardened and tempered at high temperatures to relatively low hardness, the presence of boron, especially in relatively high amounts with complex agents, is usually without effect or is detrimental to notch toughness at room and subzero temperatures.

The tensile properties of normalized steels, obviously, will vary with the rate of cooling from the austenitizing temperature and with the presence or absence of elements, such as chromium, molybdenum and boron, that confer deep-hardening properties. When steels are normalized in relatively large sections, the presence of boron has no significant effect on the resulting tensile properties or hardness.

Hardenability — The principal use of boron in a steel is to increase its hardenability. Its effectiveness depends not only on the base composition, but also on the steel-making practice. Apparently, the effectiveness of boron in enhancing hardenability increases with the amounts (within limits) or manganese, chromium and molybdenum and decreases with increase in carbon content; its effectiveness is practically nil in steels of eutectoid carbon content. The hardenability of certain heats of boron steel has been found to be sensitive to prior thermal treatments.

The magnitude of the effect of boron on hardenability seems also to depend upon the form in which the boron exists in austenite and not critically upon the total amount present. The presence of either high-soluble nitrogen or oxygen is detrimental to the boron effect on hardenability. However, the detrimental effect of high nitrogen on hardenability in steels containing boron can be counteracted by the addition of small amounts of titanium or zirconium either as separate additions or by complex agents.

The role of titanium or zirconium in enhancing the hardenability of boron-treated steels containing high nitrogen is to act as a ' fixer ' for nitrogen by forming nitrides that are insoluble in austenite at hardening temperatures and thereby decrease the amount of soluble nitrogen available for reaction with the boron. Both titanium and zirconium appear to have a greater affinity than boron for nitrogen and the presence of sufficient amounts of either of these elements in high-nitrogen steels treated with boron has a desirable overall effect on hardenability similar to that of a boron addition to a low-nitrogen steel.

Boron lowers the grain-coarsening temperature of austenite. However, steels with relatively high additions of boron can be rendered fine-grained at heat-treating temperatures by the judicious use of grain-growth inhibitors, such as aluminium and titanium; the hardenability of a steel usually increases as the size of the grains increases at the austenitizing temperature.

The expected increase in hardenability by the addition of boron to 0·4 per cent C, 1·6 per cent Mn steel is illustrated by a comparison of the curves given in Fig. 2. The steels (Nos. 15 and 10, Table 4 and FIG. 1) were processed from a basic open-hearth heat of 32 ingots (each 22 × 25 in., 8600 lb.) in which the boron was added in the mold with one of seven different agents and the amount of boron retained ranged from 0·0001 to 0·0036 per cent. The curves for steel 10, which contains 0·0006 per cent boron added as a complex agent (C, Table 2), is typical for all the boron-treated steels of this heat. The hardenability of the steels comprising this heat was materially improved by the addition of boron, but the magnitude of the effect was independent of the amount of boron added or retained and the composition of the agents used. The nitrogen content of all of these steels ranged from 0·003 to 0·005 per cent. This is typical for good basic open-hearth practice.
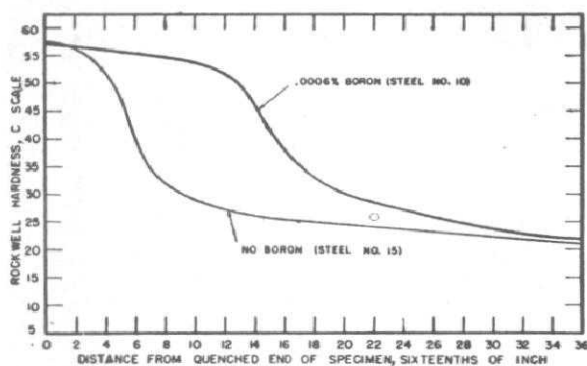
FIG. 2 — EFFECT OF BORON ON THE HARDENABILITY OF BASIC OPEN-HEARTH STEELS CONTAINING 0·45 PER CENT CARBON AND 1·6 PER CENT MANGANESE

The chemical composition of the steels is given in Table 4. Specimens were normalized at 1650°F. and end-quenched from 1550°F. A.S.T.M. grain number 8 at 1550°F. A.S.T.M. recommended procedures were followed in making the end-quench tests.

Relations have been established between the distances on the end-quench bar and equivalent hardnesses of rounds when quenched in either still oil or water. A hardness value of Rockwell C 50 (95 per cent martensite for 0·45 per cent carbon steel) will be produced at the centre of rounds of the above steels under conditions as follows:

Steel No.	Quenching medium	Diameter of bar, in.
15	Still oil	0·70
10	Still oil	2·30
15	Still water	1·25
10	Still water	3·00

Thus, treating the steel with boron resulted in tripling the diameter of the bar that can be hardened by a mild quench in oil.

The importance of maintaining the soluble nitrogen at a low value in boron-treated steels is emphasized by the results summarized in Fig. 3. The total nitrogen content of each of the three steels (47, 48 and 49, Table 4) comprising this experimental induction furnace heat was of the same order of magnitude (0·013-0·015 per cent N_2). The addition of about 0·005 per cent boron (steel 48) with a simple agent (A, Table 2) produced no significant increase in hardenability. However, considerable improvement in hardenability was obtained when a similar boron addition was made with the same agent in conjunction with 0·17 per cent titanium (steel 49).

Mechanism of Boron Effect on Hardenability

The action of boron in increasing the hardenability of steel is not definitely known, but tentative explanations have been reported in the literature. These theories may be conveniently classified on the basis that the improvement is due to: (1) a reaction of the boron with some other element to change the condition of the latter, and (2) boron in solid solution at the time of quenching.

Grossmann[4] suggested the possibility that boron was present as a carbide. Chandler and Bredig[5] and Carson[6] believed that boron acts as a fluxing agent. Dean and Silkes[7] were of the opinion that the boron effect was due to a dispersion and Boss[8] speculated that boron removed the last trace of oxygen.

Lippert[9] stated that boron, similar to any other alloying element, must be in solid solution to be effective in increasing hardenability. Grange and Garvey[10] assumed the presence of boron in steel in effective and ineffective forms. The effective form is capable of dissolving in austenite whereas the ineffective form does not enter into austenite solid solution. The boron atom is pictured as forming an interstitial solid solution with gamma iron. The boron atoms are preferentially located in the grain boundaries of the austenite just prior to its transformation, and their presence lowers the rate of grain boundary nucleation and thus increases hardenability. Only those boron atoms that remain in solid solution are effective in decreasing the rate of nucleation of ferrite and hence increasing the time required for austenite to transform. Heating steels at a high temperature for a long time may convert effective into ineffective boron. The latter may be some stable compound of boron that gradually forms at high temperature. Spretnak and Speiser[11] postulate that ferrite forms from austenite by a shear mechanism and boron increases hardenability by decreasing the rate of ferrite formation. It is possible
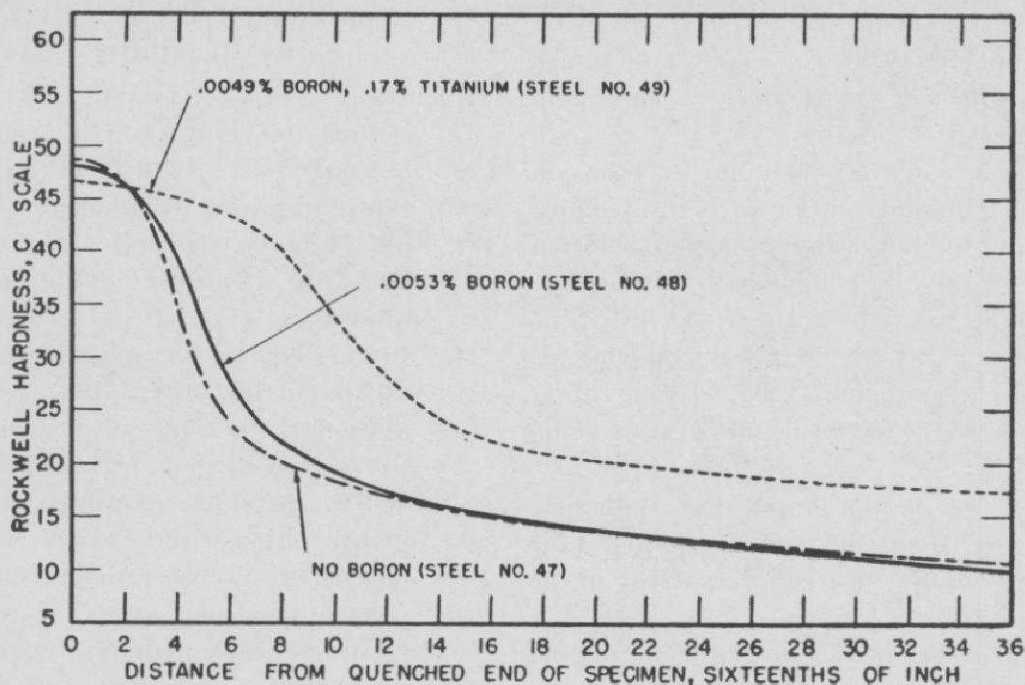
FIG. 3 — INFLUENCE OF NITROGEN, BORON AND TITANIUM ON THE HARDENABILITY OF 0·25 PER CENT
CARBON, 1·6 PER CENT MANGANESE STEELS

The chemical composition of the steels is given in Table 4. Specimens were normalized at 1650°F. and end-quenched from 1575°F. A.S.T.M. grain number 8 at 1575°F. A.S.T.M. recommended procedures were followed in making the end-quench tests.

that an effective concentration of boron occurs only in the vicinity of grain boundaries. Fisher[12] argues that since the primary influence of boron is to retard the nucleation of ferrite at grain boundaries, it is possible that this result comes about because of changes in the austenite grain-boundary free energy and the austenite/ferrite interfacial free energy due to the presence of boron. Adair, Spretnak and Speiser[13] state that it does not appear that boron sufficiently reduces the interfacial energy of austenite grain boundaries to explain the hardenability effect directly on this basis. They found indications of a consistent adsorption of boron to the austenite grain boundaries and more boron is forced to the grain boundaries as the austenitizing temperature is increased. Simcoe, Elsea and Manning[14] believe that boron increases the hardenability of hypoeutectoid steels by decreasing the rate of nucleation of ferrite and

bainite. They postulate that a concentration of lattice imperfections furnishes the necessary energy for nucleus formation. Boron concentrates at the imperfection where sites of suitable size are present and thereby decreases the energy and the number of sites favourable for nucleation to occur.

The facts that are fairly definitely known about the behaviour of boron in iron and steel can be summarized as follows:

(1) The solubility of boron in austenite is relatively low; the solubility is of the order of 0·001 per cent at heat-treating temperatures. The indications are that the solubility increases with temperature and is of the order of 0·003-0·004 per cent at 1800°F.

(2) The hardenability of a boron-treated steel does not depend critically upon the amount of boron present; 0·001 per cent or even 0·0001 per cent boron is often reported as effective as

0·002-0·006 per cent. Thus, one boron atom to 40,000 or more iron atoms is sufficient to produce a maximum effect.

(3) Boron can exist in different forms in steel, in solid solution or as compounds. Only the boron that is in solid solution is effective in enhancing hardenability. Boron can be converted from the effective (solid solution) to ineffective form (compounds) by heating to excessively high temperatures for long periods.

(4) The size of the boron atom is slightly larger than the carbon atom. Like carbon, it is located interstitially in the gamma iron lattice.

(5) The diffusion rate of boron in gamma iron is of the same order of magnitude as that of carbon.

(6) Boron, similar to carbon, is lost in the decarburized zone of boron-carbon steels.

(7) The effectiveness of boron in increasing hardenability decreases (within limits) as the carbon content of the steel is increased. Its effectiveness is practically nil in steels contaning 0·8 per cent or more carbon.   Boron does not improve the hardenability of steels having high-soluble nitrogen or oxygen. However, boron does improve the hardenability of high-nitrogen steels in which the nitrogen is in the form of titanium or zirconium nitrides.   It is also effective in thoroughly deoxidized steels low in soluble nitrogen.

(8) Boron has no significant effect in retarding the beginning of the transformation of austenite in steels isothermally transformed just below the Ae_1 temperature (about 1310°F.).   Boron in solid solution does have a marked effect in retarding the transformation rate of austenite to ferrite isothermally transformed at the nose of the S (TTT) curves (about 1100°-900°F.). This is a nucleation effect, not a decrease in the rate of growth.

(9) Boron has no material effect on the critical temperatures, A_3, A_1 and M_s, of steel.

(10) Boron increases the tendency of austenite grains to coarsen[15], but this can be offset by the use of grain-growth inhibitors.

(11) Boron appears to increase somewhat the impact (notched bar) toughness at room temperature of steels quenched to martensite and tempered (400°-500°F.) for high hardness. Boron is usually either without effect or is detrimental to notch toughness of completely hardened steels tempered at relatively high temperatures for low hardness[15].

A critical consideration of the above facts strongly supports the belief[16] that the effectiveness of boron in enhancing the hardenability of certain steels is due entirely to its action while in solid solution. The boron undissolved or in the form of compounds is either without effect or decreases hardenability by acting as nuclei for the transformation of austenite. When boron enhances the hardenability of a steel, it decreases the rate of nucleation of ferrite and not its rate of growth. The boron atom, located interstitially in the gamma iron lattice, is effective in either retarding the rate of formation of nuclei or the rate of their growth to the critical size necessary for transformation to begin, or both.

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