

## UNITED STATES PATENT OFFICE

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## DEEP-HARDENING BORON STEELS

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This invention relates to steels, and more specifically to steels the hardness of which may be increased by rapid cooling from temperatures within or above the critical range. For the sake of simplicity of presentation, the application of the invention will be described herein principally as it may be applied to carbon steels containing 0.1% to 1% carbon, up to about 2% manganese, and up to about 1% silicon; but as the description proceeds it will be evident that the invention may be applied to a wide variety of hardenable steels.

When hardening steels by rapid cooling from high temperatures, it is often desired to produce a deep or thick zone of hardened material rather than a thin or shallow hardened case. The depth to which a piece of steel will harden, at a given rate of heat extraction, is different in different steels. The property of the steel which involves this relative susceptibility to mass effect in hardening seems to be inherent, and for convenience it will be termed herein "deep-hardenability."

An accepted, convenient measure of deep-hardenability is afforded by the "Jominy" test, described in detail in "A Hardenability Test for Carburizing Steel" by W. E. Jominy and A. L. Boegehold, Trans. Am. Soc. for Metals, vol. 26, p. 574 (1938). To summarize briefly, the test is made on a small bar of steel of standardized shape and dimensions, and comprises heating the entire bar to the desired hardening temperature, quickly extracting heat through one end face of the bar, grinding off superficial scale and decarburized skin and producing a flat surface suitable for making a hardness test, and measuring the Rockwell "C" hardness along the length of the bar. As a means for readily expressing the relation between the hardness and distance from the hardened end, the distance from the hardened end at which the hardness becomes less than Rockwell "C" 50 is used and is referred to herein as the "Jominy depth." If the same hardening temperature and cooling conditions be used for a series of steels, the relative depths of the hardened zones indicate the relative deep-hardenability of the steels of that series, each to the others.

An object of this invention is to improve the deep-hardenability of hardenable steels generally, and of plain carbon and low alloy (less than 5% in the aggregate of elements other than iron and carbon) steels especially.

The deep-hardenability of steel may be enhanced in some degree by adding in suitable percentages any one of the elements which can be

taken into solid solution in steel at high temperatures, for instance boron, silicon, molybdenum, tungsten, chromium, or nickel. These hardening elements differ widely in the minimum percentage required to impart a useful degree of deep-hardenability, and in the maximum degree of deep-hardenability obtainable while maintaining other necessary properties of the steel.

I have observed that some combinations of the above-listed elements may be used to impart an even further enhanced deep-hardenability without substantial sacrifice of other desirable properties of the steel. I have further observed that combinations of certain of these elements with suitable percentages of one or more of the alkali metals, alkaline earth metals, beryllium, aluminum, titanium, zirconium, uranium, cerium, thorium, vanadium, columbium, and tantalum, considerably enhance the effect of the combination on deep-hardenability.

In the course of my research on this subject I have discovered that a few of these combinations of elements are particularly effective in imparting deep-hardenability, and the present invention is based on this discovery.

A particularly effective combination is boron and silicon, preferably with one or more of the further elements aluminum, beryllium, magnesium, calcium, barium, strontium, the alkali metals, titanium, zirconium, cerium, hafnium, thorium, vanadium, columbium, tantalum, uranium, in a suitable proportion greater than that required for grain refinement.

In accordance with the present invention, boron may be present in a percentage between 0.0005% and 0.05%, but should ordinarily be between about 0.001% and 0.015%. The silicon content may suitably be between 0.1% and 1% or 2%, and will usually be between 0.15% and 0.35%. The minimum total proportion of said further element or elements to be added is any proportion greater than that required for grain refinement, and preferably up to several times that required for grain refinement. The percentage required for grain refinement will depend on the kind of steel, the steel-making conditions, and the kind and number of deoxidizing and grain-refining elements used, and may be determined empirically by the methods now in common use by metallurgists and steelmakers. In most instances the total percentage of such further elements to be added will be between 0.03% and 0.5% or 1%, and a preferred range is between 0.05% and 0.3%.

For each element and each combination of elements there appears to be an optimum percentage which imparts a maximum depth of hardenability and a frequent result of an increase in percentage beyond the optimum is a decrease of deep-hardenability below that imparted by the optimum. For reasons of economy, or to obtain a steel having a certain desired combination of physical properties, it will often be desired to add either less or more of the elements than will impart a maximum depth of hardening. Hence, the invention is not limited to the use of the optimum percentages.

The relatively great efficacy of combinations of boron and silicon may be appreciated from an inspection of the figures, derived from test data, in Table A which indicate the relative Jominy hardenability depths, in hundredths of an inch, of steels containing about 0.45% carbon, 1.5% manganese, the indicated added percentage of 20 other elements, and the remainder iron.

Table A

| Percent Si | Percent B | Percent Al | Percent Zr | Percent V | Hardenability depth |
|------------|-----------|------------|------------|-----------|---------------------|
| None       | None      | 0.035      | 0.035      | 0.035     | 21                  |
| 0.25       | None      | 0.035      | 0.035      | 0.035     | 22                  |
| None       | 0.01      | 0.035      | 0.035      | 0.035     | 27                  |
| 0.25       | 0.01      | 0.035      | 0.035      | 0.035     | 31                  |

Each of the steels in Table A contains a total proportion of the elements aluminum, zirconium, and vanadium slightly above that required for grain refinement. It will be observed that neither 0.25% silicon nor 0.01% boron alone has any substantial effect on the deep-hardenability of the fine-grained steel; but that the addition of both silicon and boron increases the deep-hardenability to a remarkable extent.

The respective and relative effects of additions of the single elements aluminum, zirconium, vanadium, and titanium on the deep-hardenability of steels containing about 1.6% Mn, 0.25% Si, 0.45% to 0.55% carbon, and 0.01% added boron, are indicated by the figures in Table B, derived from test data. The carbon contents of the steels used in such tests ranged from 0.42% to 0.53%, and the Jominy hardness depth, given in hundredths of an inch is the measured depth to Rockwell "C" 50, corrected by the factor ( $\pm 0.01\% \text{ C} = \pm 0.012 \text{ inch}$ ) to indicate the depth for a corresponding 0.45% carbon steel.

Table B

| Percentage added → |                                   |       |      |      |      |
|--------------------|-----------------------------------|-------|------|------|------|
|                    | 0.00                              | 0.025 | 0.05 | 0.10 | 0.15 |
| Element added..... | Jominy hardness depth (corrected) |       |      |      |      |
| Aluminum.....      | 37                                | 38    | 60   | **   | 85   |
| Titanium.....      | 37                                | 59    | **   | 64   | 65   |
| Zirconium.....     | 37                                | 48    | **   | 35   | 68   |
| Vanadium.....      | 37                                | 83    | 93   | **   | 46   |

\*\*Not determined.

Table C is similar to Table B, except that it indicates the relative effect of the addition of various combinations of two elements of the group aluminum, calcium, zirconium, vanadium, and titanium.

Table C

| Percentage of elements added |            |           |            |            | Jominy hardness depth (corrected) |
|------------------------------|------------|-----------|------------|------------|-----------------------------------|
| Percent Al                   | Percent Zr | Percent V | Percent Ti | Percent Ca |                                   |
| 0.035                        | 0.035      | (*)       | (*)        | (*)        | 61                                |
| 0.07                         | 0.07       | (*)       | (*)        | (*)        | 65                                |
| 0.035                        | (*)        | 0.035     | (*)        | (*)        | 79                                |
| 0.07                         | (*)        | 0.07      | (*)        | (*)        | 110                               |
| 0.035                        | (*)        | (*)       | 0.035      | (*)        | 55                                |
| 0.07                         | (*)        | (*)       | 0.07       | (*)        | 56                                |
| 0.035                        | (*)        | (*)       | (*)        | 0.035      | 63                                |
| 0.07                         | (*)        | (*)       | (*)        | 0.07       | 79                                |
| (*)                          | 0.035      | 0.035     | (*)        | (*)        | 94                                |
| (*)                          | 0.07       | 0.07      | (*)        | (*)        | 101                               |
| (*)                          | 0.035      | (*)       | 0.035      | (*)        | 54                                |
| (*)                          | 0.07       | (*)       | 0.07       | (*)        | 57                                |
| (*)                          | (*)        | 0.035     | (*)        | 0.07       | 73                                |
| (*)                          | (*)        | 0.07      | 0.035      | (*)        | 85                                |
| (*)                          | (*)        | 0.07      | 0.07       | (*)        | 70                                |
| (*)                          | (*)        | (*)       | 0.035      | 0.07       | 73                                |
| (*)                          | (*)        | (*)       | 0.07       | 0.035      | 61                                |
| (*)                          | (*)        | (*)       | 0.07       | 0.07       | 52                                |

\*None.

Table D is similar to Tables B and C, except that the relative effects of various combinations of three, four, and five elements of the group aluminum, calcium, zirconium, vanadium, and titanium are indicated.

Table D

| Percentage of elements added |            |           |            |            |               | Jominy hardness depth (corrected) |
|------------------------------|------------|-----------|------------|------------|---------------|-----------------------------------|
| Percent Al                   | Percent Zr | Percent V | Percent Ti | Percent Ca | Percent other |                                   |
| 0.025                        | 0.025      | 0.025     | (*)        | (*)        | (*)           | 93                                |
| 0.025                        | 0.025      | (*)       | 0.025      | (*)        | (*)           | 79                                |
| 0.035                        | 0.035      | (*)       | (*)        | 0.035      | (*)           | 74                                |
| 0.025                        | (*)        | 0.025     | 0.025      | (*)        | (*)           | 74                                |
| (*)                          | 0.035      | 0.035     | 0.035      | (*)        | (*)           | 76                                |
| (*)                          | 0.025      | 0.025     | (*)        | 0.025      | (*)           | 95                                |
| (*)                          | 0.025      | (*)       | 0.025      | 0.025      | (*)           | 57                                |
| (*)                          | (*)        | 0.035     | 0.035      | 0.035      | (*)           | 79                                |
| 0.035                        | 0.035      | 0.035     | 0.035      | (*)        | (*)           | 90                                |
| 0.035                        | 0.035      | 0.035     | (*)        | 0.035      | (*)           | 101                               |
| 0.035                        | 0.035      | (*)       | 0.035      | 0.035      | (*)           | 67                                |
| 0.025                        | (*)        | 0.025     | 0.025      | 0.025      | (*)           | 66                                |
| (*)                          | 0.035      | 0.035     | 0.035      | 0.035      | (*)           | 92                                |
| 0.035                        | 0.035      | 0.035     | 0.035      | 0.035      | (*)           | 93                                |
| 0.035                        | 0.035      | (*)       | (*)        | 0.035      | 0.025 Na      | 83                                |
| 0.035                        | 0.035      | (*)       | (*)        | 0.035      | 0.05 Sr       | 84                                |
| 0.035                        | 0.035      | (*)       | (*)        | 0.035      | 0.025 U       | 91                                |
| 0.035                        | 0.035      | (*)       | (*)        | 0.035      | 0.10 Ba       | 81                                |
| 0.035                        | 0.035      | (*)       | (*)        | 0.035      | 0.025 Th      | 90                                |
| 0.035                        | 0.035      | (*)       | (*)        | 0.035      | 0.01 Cb       | 79                                |

\*None.

The fact that considerable deep-hardenability is imparted by any of a large number of combinations of elements is an important one, because the latitude in choice of elements affords an opportunity to control the cleanness, grain size, tensile strength, and toughness of the steel through selection of appropriate combinations. In general, the deep-hardening steel of best quality for most purposes will be obtained by the addition of more than two of the "further elements" described above, within the range of percentages suggested herein. This generalization holds true not only for the steels of the S. A. E. 1345 type (medium manganese oil hardening) chosen for purposes of exemplification in Tables B, C, and D, but for low-alloy steels of all types, including those containing one or more of the elements chromium, tungsten, molybdenum, nickel, phosphorus, sulfur, etc. However, it is not to be understood that all properties necessarily improve in a consistent procession as the number and percentage of added elements increases. It must be borne in mind that the relative effectiveness of different elements is not the

same, and also that certain combinations of elements are better in some respects than other combinations comprising the same number of elements.

The high quality attainable in steels according to this invention is indicated in Tables E and F by test data of the physical properties of several representative steels after forging, quenching from 850° C., and drawing at 400° C. for one hour. In Table E, the indicated percentages of carbon and manganese are by analysis, the percentage of silicon in all steels is 0.25%, nominal, and the percentages of the remaining elements are the percentages added to the steel just before casting. In Table F, the yield point (Y. P.) and tensile strength (T. S.) of the steels of Table E are given in thousands of pounds per square inch; % El. designates percentage elongation in a two inch initial gage length, and per cent R. A. designates percentage reduction in area, upon fracture of the 0.505 inch diameter standard (A. S. T. M.) tensile test specimens. Under "Izod" are given the Izod impact test results, in foot-pounds, using a standard specimen one-centimeter square with standard V notch one mm. deep. The Jominy Hardness Depth is that actually measured, in hundredths of an inch, to Rockwell "C" 50.

Table E

| Steel No. | Composition of steels<br>(rest substantially iron and 0.25% Si) |                    |                   |                    |                    |                   |                    |                    |
|-----------|-----------------------------------------------------------------|--------------------|-------------------|--------------------|--------------------|-------------------|--------------------|--------------------|
|           | Per-<br>cent<br>C                                               | Per-<br>cent<br>Mn | Per-<br>cent<br>B | Per-<br>cent<br>Al | Per-<br>cent<br>Ca | Per-<br>cent<br>V | Per-<br>cent<br>Zr | Per-<br>cent<br>Ti |
| 1.....    | 0.51                                                            | 1.6                | (*)               | 0.06               | (*)                | (*)               | (*)                | (*)                |
| 2.....    | 0.51                                                            | 1.7                | 0.01              | 0.01               | (*)                | (*)               | (*)                | (*)                |
| 3.....    | 0.50                                                            | 1.7                | 0.01              | 0.15               | (*)                | (*)               | (*)                | (*)                |
| 4.....    | 0.50                                                            | 1.6                | 0.01              | 0.07               | (*)                | (*)               | (*)                | (*)                |
| 5.....    | 0.51                                                            | 1.6                | 0.01              | 0.07               | (*)                | 0.07              | (*)                | (*)                |
| 6.....    | 0.49                                                            | 1.7                | 0.01              | 0.07               | (*)                | (*)               | 0.07               | (*)                |
| 7.....    | 0.49                                                            | 1.6                | 0.01              | 0.07               | 0.07               | (*)               | (*)                | 0.07               |
| 8.....    | 0.46                                                            | 1.6                | 0.01              | (*)                | (*)                | 0.07              | (*)                | (*)                |
| 9.....    | 0.50                                                            | 1.6                | 0.01              | (*)                | (*)                | 0.07              | 0.07               | (*)                |
| 10.....   | 0.49                                                            | 1.7                | 0.01              | 0.025              | (*)                | 0.035             | (*)                | 0.035              |
| 11.....   | 0.49                                                            | 1.7                | 0.01              | (*)                | (*)                | 0.025             | 0.025              | (*)                |
| 12.....   | 0.49                                                            | 1.7                | 0.01              | (*)                | (*)                | 0.035             | 0.035              | 0.035              |
| 13.....   | 0.51                                                            | 1.6                | 0.01              | 0.035              | (*)                | 0.035             | 0.035              | 0.035              |
| 14.....   | 0.50                                                            | 1.7                | 0.01              | 0.035              | 0.035              | 0.035             | 0.035              | (*)                |
| 15.....   | 0.48                                                            | .74                | (*)               | 0.025              | 0.025              | 0.025             | 0.025              | (*)                |
| 16.....   | 0.50                                                            | .75                | 0.01              | 0.035              | (*)                | 0.035             | 0.035              | (*)                |
|           |                                                                 |                    |                   |                    |                    |                   |                    | 1.0                |
|           |                                                                 |                    |                   |                    |                    |                   |                    | 1.0                |

\*=None.

Table F

| Steel No. | Properties of steels of Table E |       |                |                  |      |                 |
|-----------|---------------------------------|-------|----------------|------------------|------|-----------------|
|           | Y. P.                           | T. S. | Percent<br>El. | Percent<br>R. A. | Izod | Jominy<br>depth |
| 1.....    | 112.0                           | 139.5 | 17.5           | 47.2             | 27.5 | 26              |
| 2.....    | 174.0                           | 202.0 | 6.0            | 18.8             | 16.7 | 44              |
| 3.....    | 178.5                           | 201.5 | 9.0            | 32.5             | 8.3  | 91              |
| 4.....    | 182.0                           | 205.5 | 10.5           | 37.6             | 8.5  | 116             |
| 5.....    | 180.0                           | 261.5 | 11.0           | 35.7             | 7.7  | 72              |
| 6.....    | 182.0                           | 196.5 | 11.0           | 40.4             | 8.5  | 61              |
| 7.....    | 169.0                           | 191.0 | 11.0           | 39.8             | 12.0 | 84              |
| 8.....    | 181.0                           | 202.0 | 11.0           | 41.0             | 9.5  | 105             |
| 9.....    | 182.0                           | 202.0 | 11.0           | 41.6             | 9.0  | 91              |
| 10.....   | 187.5                           | 214.0 | 9.5            | 37.9             | 7.0  | 98              |
| 11.....   | 203.0                           | 229.5 | 10.0           | 39.1             | 8.0  | 81              |
| 12.....   | 200.0                           | 229.5 | 7.5            | 32.8             | 7.5  | 95              |
| 13.....   | 192.0                           | 217.0 | 10.0           | 36.6             | 7.8  | 103             |
| 14.....   | 200.0                           | 224.0 | 9.5            | 37.0             | 7.0  | 83              |
| 15.....   | 206.0                           | 229.0 | 10.5           | 40.4             | 7.5  | 54              |
| 16.....   | 212.0                           | 242.0 | 9.0            | 35.0             | 7.3  | 103             |

In all of the Jominy hardness tests used as the bases of figures used in the tables herein, the same hardening temperature and cooling conditions were used.

As described in applications filed jointly by Walter Crafts and James H. Critchett, Serial 75

Numbers 201,931 (Patent 2,221,781) and 201,932 (Patent No. 2,221,782), both filed April 14, 1938; and Serial Numbers 243,324 (Patent No. 2,221,783) and 243,325 (Patent No. 2,269,407), both filed December 1, 1938; and Serial Number 296,914 (Patent 2,221,784), filed September 28, 1939, of which applications this is in part a continuation, clean, fine-grained irons and steels of improved properties may be produced by adding to the molten iron or steel up to 5% of a complex deoxidizing agent containing iron, 25% to 85% silicon, and either: (A) at least two elements selected from the groups (1) beryllium, magnesium, calcium, barium, strontium, boron, aluminum; (2) titanium, zirconium, cerium, hafnium, thorium; (3) vanadium, columbium, tantalum, elements from at least two groups being present each in an amount preferably at least 3%; or (B) at least 3% of each of at least two elements selected from the group titanium, zirconium, cerium, hafnium, and thorium. In general, it is preferred that the sum of the elements other than iron and silicon be between 10% and 20%, and not exceed at the most 25% plus an additional percentage which equals 5% multiplied by the number of elements in excess of two. For grain refinement, it is not ordinarily necessary to add more of the complex deoxidizing agent than enough to increase the silicon content of the steel by 0.25%. Thus, the maximum percentage that is really necessary for these purposes will not ordinarily exceed 1% of the iron or steel.

The complex deoxidizing agents described in the said prior applications are admirably suited for use in accordance with the present invention, provided they are used in a proportion greater than that required for grain refinement.

Such hardening agents as for instance boron may be introduced into the steel with the deoxidizing and grain refining agent, for instance as an ingredient of one of the above-described complex deoxidizing agents, or it may be separately introduced into the molten steel either before, during, or after the addition of the deoxidizing and grain refining agent. Boron, for example, may be added to molten steel as borax, calcium borate, boron carbide or ferro-boron, i. e. in almost any convenient form.

The advantages of the invention may be expounded in any of several ways. For instance, the cheaper steels among those described above may be used instead of more expensive, more highly alloyed steels heretofore used to obtain the desired strength. Or, present high strength steels may be even further strengthened by applying the principles of the invention, either by deeper hardening to a lower average hardness or by deeper hardening to the same or even higher hardness. Among the various steels described, there is a wide range of choice in respect to such factors as cost, grain size control, ductility, strength, toughness, and types of inclusions. Thus, the invention is capable of a wide field of application, which will be apparent to metallurgists and steelmakers. Therefore, although numerous specific examples have been given herein to illustrate the principles of the invention, it will be understood that such examples are merely illustrative and do not restrict the invention beyond the requirements of the claims and the state of the art.

I claim:

1. Method of imparting increased deep-hardenable to a hardenable steel which comprises adding to such steel while it is molten between

0.1% and 2% of silicon, at least 0.001% but materially less than 0.05% boron, and at least one grain refining element in a total percentage greater than that required for grain refinement and between 0.03% and 1%.

2. In the method defined in claim 1, the improvement which comprises maintaining the boron content of the steel between 0.001% and 0.015%, the silicon content between 0.15% and 1%, and the amount of grain-refining element added is between 0.03% and 1%.

3. Method of imparting improved deep-hard-  
enability to a hardenable steel which comprises adding boron and silicon thereto and adjusting the proportions of such elements in said steel to at least 0.0005% but materially less than 0.05% boron and between about 0.50% and 2% silicon.

4. Method as defined in claim 3, wherein the proportion of boron is between 0.001% and 0.015% and the proportion of silicon is between about 0.50% and 1.00%.

5. In a hardenable steel, at least 0.0005% but materially less than 0.05% boron and about 0.50% to 2% silicon which boron and silicon impart improved deep-hard-  
enability to said steel, remainder iron and incidental impurities.

6. In a hardenable steel, 0.0005% to 0.015% boron; 0.1% to 1% silicon; and at least one further element chosen from each of the groups consisting of (1) aluminum, magnesium, calcium, barium, strontium, the alkali metals, and (2) titanium, zirconium, cerium, hafnium, thorium, vanadium, columbium, tantalum, and uranium, in a total percentage greater than that required for grain refinement and between 0.03% and 1%, which boron, silicon, and further elements impart improved deep-hard-  
enability to said steel; 0.01% to 1% carbon; manganese in a substantial proportion not over 2%; remainder iron.

7. Method of imparting improved deep-hard-  
enability to a hardenable steel which comprises adding thereto between 0.0005% and 0.015%

boron; between 0.1% and 2% silicon; and at least one further element of the group consisting of aluminum, magnesium, calcium, barium, strontium, and the alkali metals, in a total percentage greater than that required for grain refinement and between about 0.03% and 1%.

8. Method of imparting improved deep-hard-  
enability to a hardenable steel which comprises adding thereto between 0.0005% and 0.05% boron; between 0.1% and 2% silicon; and at least one further element of the group consisting of titanium, cerium, hafnium, thorium, vanadium, columbium, tantalum, and uranium, in a total percentage greater than that required for grain refinement and between about 0.03% and 1%.

9. Method of imparting improved deep-hard-  
enability to a hardenable steel which comprises adding thereto between 0.0005% and 0.05% boron; between 0.1% and 2% silicon; and at least one further element from each of the groups consisting respectively of (1) aluminum, magnesium, calcium, barium, strontium, and the alkali metals, and (2) titanium, cerium, hafnium, thorium, vanadium, columbium, tantalum, and uranium; the total percentage of such further elements being greater than that required for grain refinement and being between about 0.03% and 1%.

10. Method of treating molten steel of a hardenable type to improve its deep-hard-  
enability when solidified, which comprises adding thereto 0.0005% to 0.05% boron and an amount, greater than that required for grain refinement but less than 5%, of a composition of matter containing iron, 25% to 85% silicon, and at least two further elements selected from the group titanium, zirconium, cerium, hafnium, thorium, vanadium, columbium, tantalum, and uranium, the total amount of said further elements being between about 3% and about 20%.

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