

[54] METHOD OF STRENGTHENING LOW CARBON STEEL AND PRODUCT THEREOF

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[58] Field of Search..... 148/12.1, 16, 16.6

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[57] ABSTRACT

Deep drawing steel is strengthened by alloy-nitrogen precipitation strengthening to a minimum average yield strength of 50 ksi. A deoxidized, low carbon steel sheet stock or article formed therefrom, containing from about 0.02 percent to 0.2 percent titanium in solution, from about 0.025 percent to 0.3 percent columbium in solution, from about 0.025 percent to about 0.3 percent zirconium in solution, alone or in admixture, is heat treated at 1,100° – 1,350°F in an atmosphere containing ammonia in an amount insufficient, at the temperature and time involved, to permit formation of iron nitride.

21 Claims, No Drawings

METHOD OF STRENGTHENING LOW CARBON STEEL AND PRODUCT THEREOF

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of strengthening stamped or deep drawn articles after forming. Currently available high strength sheet stock cannot be extensively formed directly by stamping or deep drawing because of its limited ductility and drawability. The method of this invention involves the novel concept of producing stamped or deep drawn parts from a low strength, deep drawing quality steel, and subsequently strengthening the parts by alloy-nitrogen precipitation strengthening. Cold rolled and annealed sheet stock can also be strengthened in the same manner before forming to attain higher yield strength than has hitherto been possible.

2. Description of the Prior Art

The hardening of steel surfaces by heat treating in an ammonia-containing atmosphere to form an iron-nitrogen austenitic structure which is transformed by quenching to a martensitic structure having high surface hardness, has been practiced for many years. Prior art nitriding practices are described in *ASM Metals Handbook*, 1948 edition, pages 697 - 702, and the references cited therein. Under present practice, nitriding is performed on particular types of steels (such as Nitralloy type, austenitic stainless steels, SAE and similar steels) in the machined and heat treated condition to provide great wear resistance, retention of surface hardness at elevated temperature and resistance to certain types of corrosion. Reference may also be made to U.S. Pat. No. 3,399,085 issued Aug. 27, 1968, to H. E. Knechtel and H. H. Podgurski, relating to nitriding of a "Nitralloy" type steel.

The nitriding of steels containing nitride-forming alloying elements is discussed in *Transactions AIME*, volume 150 (1942), pages 157 - 171, by L. S. Darken. The nitriding of iron-aluminum alloys in an ammonia-hydrogen atmosphere is described in *Transactions Met. Soc. AIME*, volume 245 (1969), pages 1,595 - 1,602 and in *Transactions Met. Soc. AIME*, volume 245 (1969), pages 1,603 - 1,608, by H. H. Podgurski et al.

A comparison of nitrided iron-aluminum alloys and iron-titanium alloys is given in *Transactions Met. Soc. AIME*, volume 242 (1968), pages 2,415 - 2,422, by V. A. Phillips and A. V. Seybolt. It was concluded in this article that an alloy containing 1 percent titanium developed substantially higher surface hardening than a 1 percent aluminum alloy due to the very small particle size of the titanium nitride which was formed, less than about 15 Angstroms. It was suggested that the nitride particles must be within a range of about 10 to 40 Angstroms or smaller in diameter, in order to produce maximum hardening. The particle size of aluminum nitrides in the aluminum-bearing alloy was substantially coarser.

Boron, Calcium, Columbium and Zirconium in Iron and Steel, by R. A. Grange et al., John Wiley and Sons, Inc., publishers, pages 173 - 179, discusses columbium as an alloying element in nitriding steels. It was concluded therein that columbium readily combines with nitrogen at temperatures above 750°F if present in excess of the amount required to combine with all the carbon to increase the surface hardness of the steel.

U.S. Pat. No. 3,671,334, issued June 20, 1972 to J. H. Bucher et al, discloses a medium-carbon columbium-modified renitrogenized steel containing less than about 0.02 percent total of aluminum, zirconium, vanadium and titanium. Sufficient free nitrogen is added to the molten steel before teeming to impart strain aging properties thereto. In the hot rolled or cold rolled condition the steels have a yield strength of 50 to 70 ksi, which is increased to a range of 70 to 90 ksi after straining and aging.

U.S. Pat. No. 3,673,008, issued June 27, 1972, to M. E. Wood, discloses carbonitriding of a columbium-containing steel by heating an article formed from the cold worked steel to a temperature above the strain recrystallization temperature but below the A₃ critical temperature of the steel in a carbonitriding atmosphere containing hydrocarbons and ammonia.

The purpose of the Wood patent is to prevent strain induced grain coarsening by addition of from 0.006 percent to 0.018 percent columbium to a carbon steel containing from 0.05 percent to 0.15 percent carbon. The carbonitriding is stated to produce a hard, wear-resistant case on the formed article. A person skilled in the art would conclude that the undesirable ferritic grain coarsening is inhibited by columbium-carbide precipitates. Such carbide precipitates must exist in a fine dispersion in order to provide resistance to grain coarsening. A fine dispersion is obtained in steels of the type disclosed in Wood because of the high carbon content which significantly lowers the A₁ critical temperature (to about 1,333°F). The behavior of low carbon steels to which the present invention relates would be considered non-analogous to that of medium or high carbon steels since low carbon steels have a substantially higher A₁ critical temperature, and columbium-carbide particles formed by following the process of the Wood patent would be expected by a person skilled in the art to be too coarse to inhibit ferritic grain growth.

The case hardening of relatively massive parts by nitriding, as practiced conventionally, is distinguishable from the concept of strengthening hot rolled or cold rolled low carbon sheet stock. The prior art suggestions of addition of alloying elements such as columbium for the purpose of case hardening or prevention of grain coarsening, would not provide a person skilled in the art with a teaching which would lead to the solution of the problem of increasing the strength of stamped or deep drawn parts formed from deep drawing quality steel sheet stock.

Despite the above background, no successful approach has as yet been made to the problem of increasing the strength of deep drawn parts or stampings formed from sheet stock without loss of the necessary ductility and drawability of the steel required to make the part. Present practice is still governed by the fundamental precept that enhancement of strength is accomplished only by a sacrifice in ductility, drawability, and/or stretchability. To the best of applicant's knowledge the prior art has never previously suggested the application of alloy-nitrogen precipitation strengthening to a deep drawing quality, low carbon steel. As is well known, when such steel in sheet form is subjected to drawing or stamping, the finished article will have areas of low yield strength where the part has not been work hardened by straining or deformation, and will have other areas of high yield strength hardened by straining

or deformation in forming the article. Typically the yield strength of unstrained areas is the same as or slightly higher than the yield strength of the steel sheet from which the part was formed, i.e., about 20 - 30 ksi. The areas which have been work hardened may have yield strengths ranging upwardly from about 30 ksi to about 80 or 100 ksi, depending upon the severity of straining or deformation. When such article is subjected to heat treatment, the strained areas exhibit recrystallization and excessive grain growth, with consequent undesirable softening.

The prior art approach, illustrated by the above-mentioned Bucher patent, which utilizes strain-aging by carbon or nitrogen to strengthen a formed article, cannot be applied where deep drawing properties are required. Steels which can be strengthened more than a negligible amount by strain-age hardening inherently possess relatively high strength and low ductility in the hot rolled or cold rolled condition and hence cannot be subjected to deep drawing. Moreover, the gain in strength resulting from strain-age hardening is relatively small, on the order of about 10 ksi, and virtually no strengthening in unstrained areas of parts formed from such steels can be achieved.

SUMMARY

It is a principal object of the present invention to provide a process for producing articles by drawing or stamping from a deep drawing quality steel of a specific composition and subsequently to treat the articles after forming by a nitriding treatment which enhances the strength thereof.

It is a further object of the invention to provide a cold rolled sheet stock, and a method for production thereof, in the thickness range of 0.02 to 0.09 inch having a yield strength of at least about 70 ksi.

The present invention provides a method of increasing the yield strength of a low carbon steel sheet stock of deep drawing quality, and articles formed therefrom, by adding to a killed, drawing quality steel a nitride-forming alloying element chosen from the group consisting of titanium, columbium, zirconium, and mixtures thereof, in amounts such that titanium in solution at room temperature is from about 0.02 percent to 0.2 percent, columbium in solution is from about 0.025 percent to 0.3 percent, and zirconium in solution is from about 0.025 percent to 0.3 percent by weight, reducing the steel to final thickness, annealing if an article is to be formed therefrom, and heating the steel, or articles formed therefrom, in an atmosphere comprising ammonia and hydrogen at a temperature between 1,100° and 1,350°F for a period of time sufficient to cause reaction of the nitride-forming element with the nitrogen of the ammonia to form small, uniformly dispersed nitrides. The concentration of ammonia in the annealing atmosphere ranges between about 2 percent and 10 percent by volume and must be insufficient, at the temperature and time involved, to permit formation of iron nitride or an iron nitrogen austenite.

Unlike prior art nitriding practice, the alloy-nitrogen precipitation strengthening process of the present invention avoids the formation of an iron-nitrogen austenitic structure by heating at a higher temperature, for a shorter time, and with a lower ammonia concentration in the atmosphere than a typical nitriding operation.

Moreover, no quench is applied after the heat treatment, contrary to conventional practice in nitriding. The present invention does not obtain or seek the properties desired in nitriding other types of steels, viz. high surface hardness at elevated temperature, great wear resistance, increased endurance limit, and resistance to certain types of corrosion.

The process of the present invention involves relatively low and hence inexpensive alloying additions to low carbon steel, and relatively low heat treatment temperature for a relatively short period of time, thereby providing a commercially economical process which does not require specialized facilities or equipment.

A composition suitable for the practice of the invention comprises, in broad ranges:

Carbon	About 0.002 to 0.015%
Nitrogen	Up to about 0.012
Aluminum	Up to about 0.08
Manganese	About 0.05 to 0.6
Sulfur	Up to about 0.035
Oxygen	Up to about 0.01
Phosphorus	Up to about 0.01
Silicon	Up to about 0.015
Titanium	About 0.02 to 0.2 in solution
Columbium	About 0.025 to 0.3 in solution
Zirconium	About 0.025 to 0.3 in solution
Iron	Remainder, except for incidental impurities

In the above composition all percentages are by weight, and the titanium, columbium and zirconium may be present singly or in admixture, the sum total not exceeding about 0.3 percent.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A preferred composition is as follows:

Carbon	Less than about 0.010%
Nitrogen	About 0.004
Aluminum	About 0.02 to 0.04 (total)
Manganese	About 0.05 to 0.6
Sulfur	Up to about 0.035
Oxygen	Up to about 0.01
Phosphorus	Residual
Silicon	Residual
Titanium and either Columbium or Zirconium	About 0.08 to 0.10 (total)
Iron	About 0.03 to 0.06 (total)
	Remainder, except for incidental impurities

As indicated previously, the ammonia concentration in the annealing atmosphere is maintained at a concentration sufficiently low, at the temperature and time involved, to avoid the formation of iron nitride or an austenitic structure, thereby avoiding high surface hardness, low toughness and embrittlement. Preferably, the atmosphere in which the heat treatment is conducted contains from 3 percent to 6 percent ammonia by volume, with the balance hydrogen. An inert gas, such as nitrogen or argon may be substituted for part of the hydrogen, provided proper adjustments are made in the ratio of ammonia to hydrogen contents so that the formation of iron nitride or an iron-nitrogen austenite does not occur.

It has been found that a heat treatment conducted in this atmosphere within the temperature range of 1,100° to 1,350°F, preferably 1,100° to 1,300°F, results in relatively rapid diffusion of nitrogen into the steel and reac-

tion of the nitrogen with the nitride-forming alloying element to form small, uniformly dispersed nitride particles, probably ranging in size between about 20 and about 30 Angstroms. A time of 1 to 3 hours at temperature is ordinarily sufficient.

When heat treating a drawn or stamped article having strained and work hardened areas, it is preferred to provide both titanium and columbium, or both titanium and zirconium, as the nitride-forming elements. The presence of at least about 0.025 percent columbium or zirconium (as determined by analysis at room temperature) prevents the recrystallization and consequent softening of the strained areas of the formed article when subjected to heat. Thus, in the preferred practice of the invention as applied to deep drawn or stamped articles, the yield strength in the unstrained areas is increased to a minimum of 50 ksi and the yield strength of the strained areas is maintained or even increased.

Where the method of the invention is applied to the strengthening of a cold rolled sheet stock in the unformed condition having a thickness ranging between about 0.02 inch and about 0.09 inch, preferably 0.02 to 0.06 inch, the yield strength will be increased to at least about 70 ksi, a value never previously attainable in a low carbon steel. Such a product has sufficient formability to permit fabrication into articles of various types (other than deep drawn) wherein bends are mainly involved.

According to studies reported by L. S. Darken and R. W. Gurry in Physical Chemistry of Metals, McGraw-Hill Book Company, Inc. (1953), pages 372 - 395, the maximum ammonia concentrations which can be used within the temperature ranges of 1,100° to 1,350°F and still avoid the formation of iron nitride, are as follows:

1100°F	about 10% ammonia
1200°F	about 6% ammonia
1300°F	about 3% ammonia
1350°F	about 2% ammonia

1,100°F the rate of diffusion is so slow that the time required at temperature is commercially uneconomical. Above 1,350°F, the ammonia concentration must be kept so low that the driving force for diffusion becomes insufficient. In addition, the nitrides formed at 1,350°F and above are coarser in size and hence contribute less strengthening effect. Finally, when heat treating deep drawn or stamped articles having cold worked areas, a temperature above 1,350°F should be avoided because of excessive grain growth and consequent softening.

Within a preferred temperature range of 1,100° to 1,300°F and a preferred ammonia concentration of 3 percent to 6 percent by volume, the heat treatment time can range between about 1 hour and about 2 hours. Under such conditions nitrogen diffuses to a depth sufficient to increase the average yield strength of material having an as-received yield strength of 30 ksi to a minimum of 50 ksi.

The thickness of steel sheet treated in accordance with the process of the invention does not constitute a limitation, although its greatest utility resides in the treatment of hot rolled thin bar ranging in thickness from about 0.06 inch to 0.25 inch and cold rolled strip material ranging in thickness from about 0.02 to about 0.09 inch. Thin cold rolled material (i.e., up to about 0.06 inch) heat treated at about 1,300°F for 1 to 2 hours will be strengthened by alloy-nitrogen precipitation in finely dispersed form substantially all the way through the thickness and will achieve a yield strength of about 70 ksi. Thicker hot rolled material can be heat treated at somewhat lower temperatures, in which case it will be nitrided only part way through, but to a depth sufficient to obtain an average yield strength in excess of 50 ksi and up to about 85 ksi.

Experimental data are presented in the tables below for a series of heats of steels containing titanium, columbium, zirconium or mixtures thereof. For purposes of comparison a typical drawing quality aluminum-killed steel sheet containing no nitride-forming alloy other than aluminum has been included.

TABLE I

Composition - Percent by Weight										
Example	Heat	C	N	O	S	Mn	Al	Ti	Cb	Zr
1	B1090073	.040	.015	.0029	—	.30	.068(totl) .035(in sol)	—	—	—
2	V845-2	.0042	.0036	.0041	.019	.31	.004	.109	—	—
3	V845-3	.0043	.0045	.0022	.019	.31	.031	.110	—	—
4	800162-V	.0044	.0057	.0012	.011	.4	.030	—	.12	—
5	2250350-V	.002	.0036	—	.019	.32	.047	.095	.066	—
6	2260778-V	.0042	.0031	—	.011	.33	.029	.049	.039	—
7	V796-3	.0055	.0050	.0018	.017	.30	.12	—	—	.19
8	2260566-V	.004	.0030	—	.015	.33	.040	.084	.063	—
9	2260914-V	.003	.0045	—	.014	.32	.044	.078	.058	—

The above values represent equilibrium between ammonia-hydrogen mixtures and solid phases of the iron nitride system at one atmosphere pressure.

It will be apparent from the above information that the temperature and ammonia concentration are interdependent and should be varied inversely with respect to one another in the practice of the present process. Similarly, time is a further interdependent variable also inversely proportional to the temperature and ammonia concentration. It has been found that the rate of diffusion of the nitrogen into the steel is the controlling factor since the reaction rate of nitrogen with the alloying elements is relatively rapid. Below a temperature of

Example 1 was a mill-produced, aluminum-killed drawing-quality heat which was not subjected to vacuum degassing, but was mill hot-rolled and laboratory cold-rolled. Examples 2, 3 and 7 were laboratory-produced vacuum melted heats, subjected to laboratory hot-rolling and cold rolling. Examples 4, 5, 6, 8 and 9 were mill-produced, vacuum degassed heats, aluminum-killed, mill hot-rolled and laboratory cold-rolled.

In Table II below, properties and nitrogen contents at various stages of processing are reported for representative heats. In the "As-Received" condition all samples were cold-rolled to 0.040 inch thickness and fully

annealed. Samples were also subjected to 20 percent cold reduction to 0.032 inch thickness after annealing

in order to simulate strained and/or deformed areas of drawn articles.

TABLE II

Heat Treated in 3% NH - 97% H By Volume					
Example 1					
Condition	Y.S. ksi	T.S. ksi	% Elong.	Y.P.E.	%N
As-Received	26.6	43.9	46.0	0.0	.015
1100°F-1 hr.	35.9	50.5	37.0	3.7	.015
-2 hrs.	38.8	53.5	30.5	3.3	—
1200°F-1 hr.	47.9	62.4	26.5	3.0	.056
-2 hrs.	52.0	64.9	23.0	3.0	.078
1300°F-1 hr.	51.4	70.5	24.5	2.2	.13
-2 hrs.	51.4	71.2	21.5	1.6	—
Cold Rolled 20%	59.6	59.6	10.5	0.0	—
1100°F-1 hr.	51.7	63.0	19.0	2.6	—
-2 hrs.	49.9	62.0	25.5	2.5	—
1200°F-1 hr.	56.1	69.0	19.0	2.6	—
-2 hrs.	57.1	69.9	19.0	2.6	—
1300°F-1 hr.	48.9	70.9	20.0	0.0	—
-2 hrs.	48.9	73.7	17.0	0.0	—
Example 4					
Condition	Y.S. ksi	T.S. ksi	% Elong.	% Y.P.E.	%N
As-Received	23.8	48.6	37.0	0.0	.0057
1100°F-1 hr.	39.8	50.8	35.5	5.0	.012
-2 hrs.	55.9	65.1	15.0*	4.3	—
1200°F-1 hr.	51.2	59.3	18.0	2.7	.029
-2 hrs.	71.2	79.9	12.0	3.3	.069
1300°F-1 hr.	56.6	70.9	20.0	3.2	.074
-2 hrs.	62.5	77.1	22.0	2.9	—
Cold-Rolled 20%	67.9	73.2	4.0	0.0	.0057
1100°F-1 hr.	60.8	66.8	14.0	1.8	—
-2 hrs.	74.6	78.1	9.0	0.8	—
1200°F-1 hr.	66.7	71.0	13.0	4.3	—
-2 hrs.	82.3	86.9	11.0	3.9	—
1300°F-1 hr.	80.8	87.3	13.0	3.5	—
-2 hrs.	78.9	85.6	5.0*	1.8	—
Example 5					
Condition	Y.S. ksi	T.S. ksi	% Elong.	% Y.P.E.	%N
As-Received	22.1	45.5	40.0	0.0	.0036
1100°F-1 hr.	37.4	55.6	28.0	0.3	.010
-2 hrs.	66.3	76.7	19.0	1.1	—
1200°F-1 hr.	70.0	81.1	17.0	0.9	.029
-2 hrs.	103.6	111.6	11.0	2.0	.079
1300°F-1 hr.	87.0	95.5	15.5	1.9	.098
-2 hrs.	89.4	100.4	13.0	1.5	—
Cold-Rolled 20%	69.0	73.4	3.5	0.0	.0036
1100°F-1 hr.	65.6	70.3	11.0	0.0	—
-2 hrs.	90.5	92.9	9.0	0.0	—
1200°F-1 hr.	90.5	94.5	11.5	1.7	—
-2 hrs.	114.3	118.4	10.0	2.6	—
1300°F-1 hr.	94.8	100.1	12.5	3.5	—
-2 hrs.	97.2	103.5	12.0	2.5	—
Example 6					
Condition	Y.S. ksi	T.S. ksi	% Elong.	% Y.P.E.	%N
As-Received	20.7	44.8	40.5	0	.0031
1100°F-1 hr.	43.8	55.7	29.5	2.5	.0093
-2 hrs.	68.0	74.1	19.0	3.6	—
1200°F-1 hr.	74.8	82.1	15.0	2.7	.032
-2 hrs.	89.6	98.7	13.0	2.0	.067
1300°F-1 hr.	73.8	81.9	17.0	2.5	.080
-2 hrs.	76.5	86.8	16.0	2.1	—
Cold-Rolled 20%	63.4	68.2	5.0	0.0	.0031
1100°F-1 hr.	64.2	69.3	14.0	3.7	—
-2 hrs.	84.0	88.3	11.0	3.7	—
1200°F-1 hr.	82.8	86.6	11.0	3.0	—
-2 hrs.	94.3	98.7	14.0	2.8	—
1300°F-1 hr.	82.4	88.6	16.0	2.8	—
-2 hrs.	81.4	88.6	16.0	2.8	—

TABLE II—Continued

Heat Treated in 3% NH ₃ - 97% H ₂ By Volume				
Example 7				
Condition	Y.S. ksi	T.S. ksi	% Elong	% Y.P.E.
As-Received	23.1	48.5	37.5	0.0
1100°F-1 hr.	32.7	49.8	37.5	1.5
-2 hrs.	41.5	54.2	32.0	4.1
1200°F-1 hr.	54.1	62.7	24.0	5.1
-2 hrs.	66.6	71.5	19.0	3.8
1300°F-1 hr.	62.9	73.6	17.5	3.3
-2 hrs.	68.3	79.8	18.0	3.7
Cold-Rolled 20%	68.7	73.2	3.5	0.0
1100°F-1 hr.	57.7	63.3	13.0	0.0
-2 hrs.	65.2	69.8	14.5	2.2
1200°F-1 hr.	64.6	70.5	12.0	2.0
-2 hrs.	86.1	90.2	9.5	2.5
1300°F-1 hr.	80.5	87.0	12.0	3.9
-2 hrs.	83.9	92.8	13.0	2.8

*Broke near or outside gage mark.

Table II indicates that the aluminum-killed drawing quality steel of sample 1 showed very little strengthening when nitrided under the same conditions as the remaining steels of examples 2 - 7. The moderate increase in yield strength is due primarily to the return of the yield point elongation. In addition, some strengthening occurs as a result of nitrogen in solid solution in the steel.

A more direct comparison of the strengthening effect of titanium to that of aluminum is obtained from examples 2 and 3, example 2 containing only titanium as a nitride former, with example 3 containing the same amount of titanium plus 0.031 percent aluminum. It is apparent that no beneficial effect with respect to strengthening is obtained by addition of aluminum. The only difference is that the steel of example 2 containing only titanium developed yield point elongation while that of example 3 did not do so at the same total nitrogen concentrations. This is of course due to the fact that aluminum was available to scavenge nitrogen, thus resulting in less nitrogen in solid solution.

It is further apparent that the increase in yield strength produced in the columbium-bearing and zirconium-bearing steels of examples 4 and 7, respectively, is not as great as that for the titanium-bearing steels. However, yield strengths in excess of 50 ksi were obtained in both cases by heat treatment at 1,200° - 1,300°F for 1 hour.

Example 5 was an embodiment of a relatively highly alloyed titanium and columbium-bearing steel which exhibited an increase in yield strength substantially the same as that of examples 2 and 3.

Example 6, illustrative of lower alloying additions of titanium and columbium than example 5, exhibited significant increase in yield strength, although not as high as that of the more highly alloyed example 5.

The yield strengths reported for samples subjected to 20% cold reduction (simulating the strain or deformation resulting from deep drawing) show that the strengthening which accompanies the precipitation of

alloy nitrides is additive to the cold work strengthening so that a net gain in strength is obtained even though there is a small loss in strength due to partial recovery. The strength advantage in nitrided cold worked material over nitrided as-annealed material is attributable to alloy nitride nucleation and precipitation on dislocations and to enhanced solubility of nitrogen in a strained lattice.

The elongation values after nitriding are relatively high in view of the yield strength levels attained. These elongation values indicate that some limited forming could be performed after nitriding strip material such as bending or a restrike operation. The samples subjected to 20 percent cold reduction increased in elongation values along with an increase in yield strength, because of recovery.

As indicated previously the heat treatment step of the present process results in an increase in nitrogen in solid solution in the steel as well as nitrogen combined as nitrides with titanium, columbium, and/or zirconium. It has been found that the total amount of nitrogen taken up by the steel can exceed that required to satisfy normal equilibrium solution requirements plus that needed to convert the alloys to nitrides. This excess nitrogen can be attributed to nitrogen trapped on dislocations, adsorbed at the nitride-ferrite interface, and as enhanced lattice solubility in strained ferrite.

Of further significance in Table II are the values reported for nitriding at 1,300°F in 3 percent ammonia for 2 hours. In most instances a decrease in yield strength from the maximum values obtained at 1,200°F for two hours occurred, due to the formation of coarser alloy nitride particles. A thin austenite rim formed on the surfaces of samples nitrided at 1,300°F; therefore, to avoid the formation of an iron nitrogen austenite rim, the ammonia concentration should be slightly less than 3 percent at 1,300°F for a 2 hour heat treatment.

A comparison of the strengthening achieved by heat treating in a 3 percent ammonia - 97 percent hydrogen mixture with that achieved in a 6 percent ammonia - 94 percent hydrogen mixture is given in Table III below.

TABLE III

Effect of Ammonia Concentration
Cold-Rolled and Annealed 0.40" Sheets

Example & Condition	3%NH ₃ - 97%H ₂					6%NH ₃ - 94%H ₂				
	Y.S. ksi	T.S. ksi	%Elong.	%Y.P.E.	%N	Y.S. ksi	T.S. ksi	%Elong.	%Y.P.E.	Aust. Rim
Steel 2										
1100°F-1 hr.	37.6	54.2	23.5	0.7	.012	57.3	71.4	18.0	0.8	No
1200°F-1 hr.	76.4	92.6	14.0	1.4	.047	109.7	122.3	12.5	0.5	No
1300°F-1 hr.	88.3	98.3	14.0	1.5	.094	93.0	104.4	3.0	0.7	Yes
Steel 3										
1100°F-1 hr.	33.5	51.2	30.0	0.7	.011	52.8	67.5	20.0	0.5	No
1200°F-1 hr.	79.9	89.5	11.0	0.0	.047	121.3	128.6	8.0	0.0	No
1300°F-1 hr.	88.1	98.6	12.5	0.0	.11	98.3	104.7	1.5	0.0	Yes
Steel 4										
1100°F-1 hr.	39.8	50.8	35.5	5.0	.012	44.8	55.7	28.0	5.0	No
1200°F-1 hr.	51.2	59.3	18.0	2.7	.029	73.6	83.4	9.5	2.5	No
1300°F-1 hr.	56.6	70.9	20.0	3.2	.074	64.9	79.7	15.0	2.9	Yes
Steel 5										
1100°F-1 hr.	37.4	55.6	28.0	0.3	.010	54.8	68.8	18.0	0.7	No
1200°F-1 hr.	70.0	81.1	17.0	0.9	.029	107.0	114.5	5.5	0.0	No
1300°F-1 hr.	87.0	95.5	15.5	1.9	.098	97.9	110.0	4.0	1.2	Yes
Steel 6										
1100°F-1 hr.	43.8	55.7	29.5	2.5	.0093	56.4	66.1	18.5	3.8	No
1200°F-1 hr.	74.8	82.1	15.0	2.7	.032	98.2	106.7	12.0	3.5	No
1300°F-1 hr.	73.6	81.9	17.0	2.5	.080	82.6	96.7	11.0	1.7	Yes
Steel 7										
1100°F-1 hr.	32.7	49.8	37.5	1.5		40.6	54.7	30.0	3.9	No
1200°F-1 hr.	54.1	62.7	24.0	5.1		66.7	76.1	19.0	4.0	No
1300°F-1 hr.	62.9	73.6	17.5	3.3		72.9	84.4	14.0	2.5	Yes

It is apparent from Table III that any given steel achieves a higher yield strength when nitrided in 6 percent ammonia under the same time and temperature conditions than is attained by nitriding in 3 percent ammonia. Higher strength is obtained by nitriding at 1,200°F for 1 hour in 6 percent ammonia than by nitriding at 1,200°F for 2 hours in 3 percent ammonia. However, due to diffusion phenomena, the surface to mid-thickness strength gradient would be greater in a 6 percent ammonia atmosphere than in a 3 percent ammonia atmosphere. For some applications it may be desirable to obtain a lower average strength with a lesser gradient to mid-thickness. The present invention makes it possible to select readily temperature, time and ammonia concentrations which will result in a wide range of average yield strengths and surface to mid-thickness strength gradients.

Table III again indicates that nitriding in 6 percent ammonia at 1,300°F results in formation of an iron-nitrogen austenite rim which will transform either to martensite or an eutectoid structure, depending upon the cooling rate. In example 5, an austenite rim about 1 mil thick resulted from annealing in 6 percent ammonia at 1,300°F for 1 hour.

As the thickness of the steel stock subjected to the heat treatment of the present invention increases, the

time required to reach saturation at the equilibrium nitrogen content in solution (for a given temperature and ammonia concentration in the atmosphere) increases as the square of the thickness. For example, for nitrogen diffusion in pure iron at 1,200°F, to reach an average fractional saturation (i.e., N Avg/N Equil.) of 0.7 it has been found that 1 hour is required for sheet stock of 0.040 inch thickness while 5.6 hours is required for sheet stock of 0.090 inch thickness. However, an important feature of the present invention is the discovery that marked increases in average yield strength can be realized within relatively short times, (i.e., not more than 2 hours), by partial alloy-nitrogen precipitation strengthening. Table IV below indicates the substantial increase in yield strength achieved by nitriding the titanium-columbium bearing steel of example 8 in a 3 percent ammonia - 97 percent hydrogen atmosphere within the temperature range of 1,100° - 1,300°F for 1 - 2 hours. It will be noted that nitriding at 1,200°F for only one hour resulted in an average yield strength of 66.5 ksi. Even greater strengthening could be attained by heat treating for longer periods of time or by increasing the ammonia concentration to 6 percent. In Table IV 1,300°F again proved to be an unacceptable temperature when using a 3 percent ammonia atmosphere because of formation of an austenite rim.

TABLE IV

Properties of 0.090 Inch Hot Rolled Steel of Example 8 Heat Treated in 3% NH ₃ - 97% H ₂					
Condition	Y.S. ksi	T.S. ksi	%Elong.	%Y.P.E.	%N
As Hot Rolled	27.3	49.1	40.5	0.0	.0027
1100°F-1 hr.	46.8	63.3	30.0	0.0	.010
-2 hrs.	56.8	70.3	22.0	0.0	.013
1200°F-1 hr.	66.5	81.1	21.0	0.0	.027
-2 hrs.	83.9	94.9	16.0	1.0	.043
1300°F-1 hr.	77.7	91.1	20.0	1.3	.066
-2 hrs.	83.9	94.2	13.0	1.8	.080

The criticality of providing at least about 0.02 percent titanium in solution is illustrated in Table V below.

TABLE V

	Effect of Amount of Available Nitride-Forming Element		
	0.0044%C	0.010%C	C Saturated (0.024%C)
Available titanium in Solution	0.047%	0.025%	0%
Y.S.-ksi(nitrided in 6% NH ₃ , 1200°F-2 hrs.)	102.5	85.3	64.0
Y.S.-ksi(nitrided and then denitrided)	65.9	44.7	
Δ Y.S.-ksi(Y.S.nitrided-Y.S.denitrided)	20.7	19.4	19.3

In Table V a steel of the invention containing 0.077 percent total titanium, 0.037 percent total columbium, 0.31 percent aluminum, 0.0035 percent nitrogen, and remainder substantially iron, was carburized from an original carbon level of 0.0044 percent to a carbon level of 0.010 percent and to saturation with carbon in order to vary the amount of titanium in solution available to react with ammonia in the nitriding operation. It is apparent from Table V that a substantial decrease in yield strength occurs progressively with decrease of available titanium in solution from 0.047 percent to 0.025 percent and to 0 percent successively.

In order to ascertain the degree of strengthening contributed by nitrogen taken into solid solution in the steel, the samples of Table V were denitrided by heating in a hydrogen atmosphere at about 1,200°F for 2 hours. Table V reports the yield strength in the denitrided condition and further sets forth the differential at each of the different carbon contents, from which it is apparent that nitrogen taken into solid solution contributes about 20 ksi to the yield strength. It is further apparent that denitrided material at the 0.010 percent carbon level (resulting in 0.025 percent available titanium in solution) retains a substantially increased yield strength of 65.9 ksi in the denitrided condition.

concentrations, just less than that which results in the formation of iron nitrides or an iron-nitrogen austenite,

is desirable from the standpoint of producing maximum strengthening in the shortest possible time. However, it has been discovered that if nitriding conducted for the purpose of strengthening (and which results in an undesirably high excess nitrogen content in solid solution) is followed by a denitriding step, such as annealing in hydrogen gas, the excess nitrogen is removed with only a 10 to 20 percent reduction in yield strength. Removal of the excess nitrogen eliminates welding porosity and significantly reduces the ductile to brittle transition temperature while improving the impact energy values. The present invention thus provides low carbon, high strength steel stock suitable for welding applications.

Table VI demonstrates the above observations regarding the effect of denitriding. A steel of the invention initially containing 0.006 percent carbon, 0.077 percent titanium, 0.037 percent columbium, 0.031 percent aluminum, 0.0035 percent nitrogen, and balance substantially iron, cold rolled to 0.058 inch thickness and annealed, was nitrided as indicated in Table VI. Sample A was not denitrided, Sample B was partially denitrided, and Sample C was still further denitrided. Both the yield strength and the ductile to brittle transition temperature decreased gradually with the decrease in nitrogen in solution.

TABLE VI

Sample	Treatment	Effect of Denitriding					
		Y.S. ksi	T.S. ksi	%Elong.	Measured %Ntotal	Calc. %N(soln.)	Ductile to Brittle Transition Temp.°F
A	Nitrided in 6%NH ₃ -94%H ₂ 1200°F - 3 hrs.	88.3	100.7	18	0.10	0.067	0
B	Nitrided as in A, then denitrided in H ₂ 1200°F - 2 hrs.	80.8	92.0	17	0.053	0.020	-60
C	Nitrided as in A, then denitrided 1200°F - 4 hrs.	77.1	87.1	16	0.043	0.010	<-60

It has been discovered that the excess nitrogen content of the steels following alloy-nitrogen precipitation strengthening at higher allowable ammonia contents can present weldability problems and result in high ductile to brittle notched sheet Charpy impact transition temperature. The welding problems involve porosity resulting from the liberation of this excess nitrogen as nitrogen gas. These problems can be overcome by special welding techniques. The use of high ammonia

Steel having the composition specified herein can be melted by any conventional operation such as open hearth, basic oxygen furnace or electric furnace. The molten steel is then vacuum degassed in order to achieve the desired carbon and nitrogen levels, killed preferably with Al, and the nitride-forming alloying element or elements are added to the ladle after degassing with suitable mixing. The melt is then teemed into ingots, or cast into slabs. The solidified ingots or slabs are

then subjected to conventional hot rolling and to conventional subsequent processing steps to obtain sheet stock of the desired final thickness. The steel is then subjected to the process of the present invention either in the form of sheet or strip, or after forming into articles by drawing or stamping.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of increasing the yield strength of a low carbon steel sheet stock, which comprises:

providing a deep drawing quality steel containing from about 0.002 percent to about 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, and a nitride-forming element chosen from the group consisting of titanium, columbium, zirconium, and mixtures thereof, in amounts such that titanium in solution is from about 0.02 to about 0.2 percent, columbium in solution is from about 0.025 percent to about 0.3 percent, and zirconium in solution is from about 0.025 percent to about 0.3 percent, all percentages being by weight;

reducing said steel to final thickness; and heating the resulting sheet stock in an atmosphere comprising ammonia and hydrogen at a temperature between 1,100° and 1,350°F for a period of time sufficient to cause reaction of said nitride-forming element with the nitrogen of said ammonia to form small, uniformly dispersed nitrides, whereby to increase the average yield strength of said sheet stock to a minimum of 60 ksi, the concentration of ammonia in said atmosphere ranging between about 2 percent and 10 percent by volume and being insufficient, at the temperature and time involved, to permit formation of iron nitride.

2. The method of claim 1, wherein said steel initially consists essentially of from about 0.002 percent to about 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, from about 0.05 percent to about 0.6 percent manganese, from about 0.02 percent to about 0.2 percent titanium in solution, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, and remainder iron except for incidental impurities, all percentages being by weight.

3. The method of claim 1, wherein said steel initially consists essentially of from 0.002 percent to about 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, from about 0.05 percent to about 0.6 percent manganese, from about 0.025 percent to about 0.3 percent columbium, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, and remainder iron except for incidental impurities, all percentages being by weight.

4. The method of claim 1, wherein said steel initially consists essentially of from about 0.002 percent to about 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, from about 0.05 percent to about 0.6 percent manganese, from about 0.025 percent to about 0.3 percent zirconium, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, and remainder iron except for incidental impurities, all percentages being by weight.

5. The method of claim 1, wherein said steel initially

consists essentially of less than about 0.010 percent carbon, from about 0.05 percent to about 0.6 percent manganese, from about 0.02 percent to about 0.04 percent total aluminum, up to about 0.004 percent nitrogen, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, from about 0.08 percent to about 0.10 percent total titanium, from about 0.03 percent to about 0.06 percent total columbium, and remainder iron except for incidental impurities, all percentages being by weight.

6. The method of claim 1, wherein said steel initially consists essentially of less than about 0.010 percent carbon, from about 0.05 percent to about 0.6 percent manganese, from about 0.02 percent to about 0.04 percent total aluminum, up to about 0.004 percent nitrogen, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, from about 0.08 percent to about 0.10 percent total titanium, from about 0.03 percent to about 0.06 percent total zirconium, and remainder iron except for incidental impurities, all percentages being by weight.

7. The method of claim 1, wherein said sheet stock is cold rolled to a thickness of from about 0.02 inch to 0.09 inch, and wherein said heating step increases the yield strength of said sheet stock to at least about 70 ksi.

8. The method of claim 1, wherein said atmosphere contains from 3 percent to 6 percent ammonia by volume, and remainder hydrogen.

9. The method of claim 1, wherein said atmosphere contains ammonia and hydrogen, and the balance an inert gas, with the ammonia to hydrogen ratio adjusted in such manner that the formation of iron nitride or iron-nitrogen austenite is avoided.

10. The method of claim 7, wherein said heating is conducted at 1,100° to 1,300°F for a period of time inversely proportional to the temperature and directly proportional to the square of the thickness.

11. A method of increasing the yield strength of an article formed from a low carbon steel sheet stock of deep drawing quality, which comprises:

providing a steel containing from about 0.002 percent to 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, and a nitride-forming element chosen from the group consisting of titanium, columbium, zirconium, and mixtures thereof, in amounts such that titanium in solution is from about 0.02 percent to 0.2 percent, columbium in solution is from about 0.025 percent to 0.3 percent, and zirconium in solution is from about 0.025 percent to 0.3 percent, all percentages being by weight;

reducing said steel to final thickness;

annealing to soften and impart excellent drawing quality properties;

forming said article from said reduced and annealed steel; and

strengthening said article in an atmosphere comprising ammonia and hydrogen at a temperature between 1,100° and 1,350°F for a period of time sufficient to cause reaction of said nitride-forming element with the nitrogen of said ammonia, whereby to increase the average yield strength of said article to a minimum of 50 ksi, the concentration of ammonia in said atmosphere being between about 2 percent and about 10 percent by volume and being insufficient, at the temperature and time involved,

to permit formation of iron nitride or iron-nitrogen austenite.

12. The method of claim 11, wherein said steel initially consists essentially of from about 0.002 percent to about 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, from about 0.05 percent to about 0.6 percent manganese, from about 0.02 percent to about 0.2 percent titanium in solution, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, and remainder iron except for incidental impurities, and percentages being by weight.

13. The method of claim 11, wherein said steel initially consists essentially of from about 0.002 percent to about 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, from about 0.05 percent to about 0.6 percent manganese, from about 0.025 percent to about 0.3 percent columbium in solution, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, and remainder iron except for incidental impurities, and percentages being by weight.

14. The method of claim 11, wherein said steel initially consists essentially of from about 0.002 percent to about 0.015 percent carbon, up to about 0.012 percent nitrogen, up to about 0.08 percent aluminum, from about 0.05 percent to about 0.6 percent manganese, from about 0.025 percent to about 0.3 percent zirconium in solution, up to about 0.035 percent sulfur, up to about 0.01 percent oxygen, residual silicon and phosphorus, and remainder iron except for incidental impurities, and percentages being by weight.

15. The method of claim 11, wherein said steel initially consists essentially of less than about 0.010 percent carbon, from about 0.05 percent to about 0.6 percent manganese, from about 0.02 percent to about 0.04 percent total aluminum, up to about 0.004 percent nitrogen, up to about 0.035 percent sulfur, up to about

0.01 percent oxygen, residual silicon and phosphorus, from about 0.08 percent to about 0.10 percent total titanium, from about 0.03 percent to about 0.06 percent total columbium, and remainder iron except for incidental impurities, all percentages being by weight.

16. The method of claim 11, wherein said steel initially consists essentially of less than about 0.010 percent carbon, from about 0.05 percent to about 0.6 percent manganese, from about 0.02 percent to about 0.04 percent total aluminum, up to about 0.004 percent nitrogen, up to about 0.035 percent sulfur, up to 0.01 percent oxygen, residual silicon and phosphorus, from about 0.08 percent to about 0.10 percent total titanium, from about 0.03 percent to about 0.06 percent total zirconium, and remainder iron except for incidental impurities, all percentages being by weight.

17. The method of claim 11, wherein said atmosphere contains from 3 percent to 6 percent ammonia by volume, and remainder hydrogen.

18. The method of claim 11, wherein said atmosphere contains ammonia and hydrogen, and the balance an inert gas, with the ammonia to hydrogen ratio adjusted in such manner that the formation of iron nitride or iron-nitrogen austenite is avoided.

19. The method of claim 11, wherein said heating is conducted at 1,100° to 1,300°F for a period of time inversely proportional to the temperature, and directly proportional to the square of the thickness.

20. The method of claim 11, wherein said article is deep drawn.

21. The method of claim 1, including as a final step denitriding said sheet stock in a hydrogen atmosphere at a temperature between about 1,100° and 1,350°F for a period of time sufficient to decrease the ductile to brittle transition temperature to at least about -60°F.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,847,682Dated November 12, 1974Inventor(s) Rollin E. Hook

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8 (Table II), between Example 1 and Example 4 there should be inserted the following:

<u>Condition</u>	<u>Example 2</u>				
	<u>Y.S.</u> <u>ksi</u>	<u>T.S.</u> <u>ksi</u>	<u>%Elong.</u>	<u>%Y.P.E.</u>	<u>%N</u>
As-Received	18.3	42.1	42.0	0.0	.0036
1100°F-1 hr.	37.6	54.2	23.5	0.7	.012
-2 hr.	71.0	81.5	17.0	1.4	----
1200°F-1 hr.	76.4	92.6	14.0	1.4	.047
-2 hrs.	102.6	114.5	12.5	1.5	.079
1300°F-1 hr.	88.3	98.3	14.0	1.5	.094
-2 hrs.	85.2	97.6	13.0	0.0	----
Cold-Rolled 20%	60.0	63.1	7.0	0.0	.0036
1100°F-1 hr.	57.9	64.3	16.0	0.0	----
-2 hrs.	85.0	91.2	12.0	0.8	----
1200°F-1 hr.	96.3	102.5	10.0	1.1	----
-2 hrs.	107.0	113.5	12.0	1.8	----
1300°F-1 hr.	90.6	98.3	11.0	1.8	----
-2 hrs.	85.8	100.2	7.0*	0.0	----

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,847,682Dated November 12, 1974Inventor(s) Rollin E. Hook

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Example 3

<u>Condition</u>	<u>Y.S.</u> <u>ksi</u>	<u>T.S.</u> <u>ksi</u>	<u>%Elong.</u>	<u>%Y.P.E.</u>	<u>%N</u>
As-Received	17.8	42.3	42.0	0.0	.0045
1100°F-1 hr.	33.5	51.2	30.0	0.7	.011
-2 hrs.	68.4	79.6	18.0	1.4	----
1200°F-1 hr.	79.9	89.5	11.0	0.0	.047
-2 hrs.	104.5	116.7	9.0	0.0	.092
1300°F-1 hr.	88.1	98.6	12.5	0.0	.11
-2 hrs.	90.7	102.7	12.0	0.0	----
Cold-Rolled 20%	58.3	65.6	4.5	0.0	.0045
1100°F-1 hr.	58.9	64.8	15.0	0.0	----
-2 hrs.	85.7	92.1	10.5	0.0	----
1200°F-1 hr.	89.9	96.4	10.5	0.0	----
-2 hrs.	112.9	119.4	10.0	0.0	----
1300°F-1 hr.	95.2	104.4	10.5	0.0	----
-2 hrs.	93.9	105.4	11.0	0.0	----

Column 13, line 14, "65.9" should read --81.8--; "44.7" should read --65.9--; in the blank space (under the heading "C Saturated ...") there should be inserted --44.7--.

Signed and Sealed this

Seventh **Day** of September 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks