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AUSTENITIC STAINLESS STEEL AND PROCESS THEREFOR

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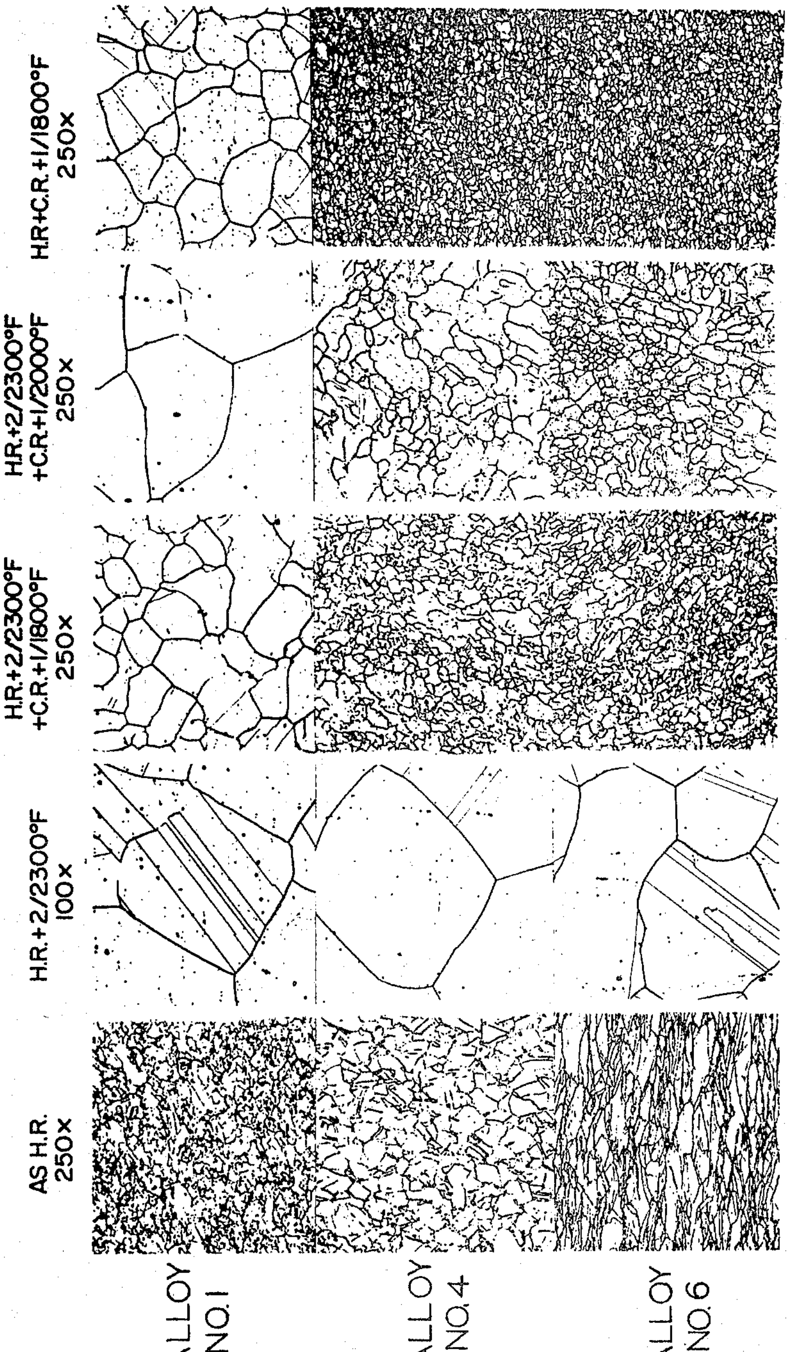

Fig.1. Fig.2. Fig.3. Fig.4 Fig.5.

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AUSTENITIC STAINLESS STEEL AND PROCESS THEREFOR

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The present invention relates to austenitic stainless steels and, more particularly, to austenitic stainless steels of special composition and of the AISI 300 series type which in the annealed condition are characterized by a combination of properties markedly superior to those characteristic of known austenitic stainless steels.

Of the three principal classes of stainless steels, to wit, the martensitic, ferritic and austenitic, the austenitic grades have by far found the greatest commercial use as is evident from the fact that present commercial production of the austenitic grades is more than double the combined production of the martensitic and ferritic grades. This is not, in retrospect, surprising in view of the combinations of properties characteristic of the austenitic stainless steels, including their high degree of resistance to corrosive environments, their excellent tensile strength levels at both normal and high temperatures, their established ability to be fabricated with relative ease on a commercial scale, etc. These factors, among others, have led to their wide acceptance and diversified utility and application.

In view of the fact that the austenitic stainless steels such as the 18–8 type (18% chromium, 8% nickel) containing up to 2% manganese and up to 1% silicon have been known for about a half-century, it is rather surprising to find that there is a dearth of literature with regard to the specific problem of improving their yield strength in the annealed condition while maintaining the high level of other properties, e.g., ductility, corrosion resistance, etc. This seems particularly significant when it is considered that a substantial percentage of 18–8 stainless is used in the annealed state. Actually, from the commercial viewpoint, the representative yield strength of such steels has remained virtually unchanged since their development. For example, in the authoritative treatise "Metals Handbook," the 1936 edition indicates at page 379 that the yield strength of the 18–8 type of stainless steel (18% chromium, 8% nickel) was about 35,000 pounds per square inch (p.s.i.) in the annealed condition and exhibited an elongation value of about 55% to 60% (2 inch gage length). The 1961 edition, page 414, reflects that a comparable 18–8 type, i.e., AISI 302 or 304, has approximately the same yield strength and ductility (elongation) levels in the annealed condition. This is not to say that very high yield strengths cannot be obtained with austenitic stainless. In the cold-worked condition, yield strengths above 200,000 p.s.i. have been obtained, but, as is well known, cold-worked austenitic stainless is rather the antithesis of austenitic stainless in the annealed condition.

The continuous rise in the production of 18–8 austenitic stainless and the rather concerted efforts to expand the applications and uses thereof, has stimulated the need for austenitic stainless steels capable of manifesting yield strengths in the annealed condition of a magnitude substantially superior to those exhibited by austenitic stainless steels presently available. For example, trailer tankers made of austenitic stainless have recently become more widely accepted. These tankers possess the virtues of disposing of, as a practical matter, the need for maintenance and economically provide for the transportation of a vast variety of otherwise corrosive media as a result of the resistance to corrosion afforded by austenitic stainless. However, it would be advantageous for such use to provide an austenitic stainless steel of higher yield strength in the annealed condition to thus afford greater resistance to external loads or stress. This aspect would also be economically attractive in enabling thinner sections of stainless steel to be used due to increased strength. The problem is intensified by the fact that other properties heretofore characteristic of such steels must not be detrimentally affected. That is to say, the ductility, toughness, corrosion resistance, etc., for which the austenitic stainless steels are so well known should not be sacrificed at the expense of improved yield strength. Thus, for example, rather close adherence to the heretofore prescribed compositional limits for austenitic stainless is necessary to preclude formation of secondary phases which would impair or adversely affect the mechanical and/or chemical properties of such steels.

It has now been discovered that austenitic stainless steels of the AISI 300 series type but containing special amounts of columbium in conjunction with correlated amounts of other essential constituents are capable of exhibiting yield strengths of 50,000 p.s.i. to 60,000 p.s.i. in the annealed condition provided the common process annealing treatment is eliminated. Such yield strength levels obtain without a concomitant deleterious impairment of other properties.

The incorporation of columbium in austenitic stainless steels as such is not new. It is believed that the use of columbium to overcome the problem concerning intergranular corrosion was first proposed about 1930 or shortly thereafter. Subsequent to the original development of the austenitic stainless steels, it was found that such steels were afflicted with intergranular corrosive attack. More specifically, it was found that slowly cooling such steels through the temperature range of about 750° F. or 800° F. to 1600° F. (now commonly referred to as "sensitizing") resulted in chromium carbide precipitation at the grain boundaries. This resulted in a depletion of effective chromium and thus created an enviroment conducive to corrosive attack. Among the many ways advanced to overcome this problem was the proposal, now well accepted, of stabilizing the austenitic stainless steels with various carbide stabilizers, one of which is columbium. Columbium, having a greater affinity for carbon than chromium, would combine with carbon to form columbium carbides which were practically insoluble in the austenite at the sensitizing temperature thereof. This preferential or selective columbium carbide formation prevented or greatly minimized the tendency for chromium carbides to form at the grain boundaries. A certain ratio of columbium to carbon had to be observed and the ratio that has been generally adopted is that the amount of columbium must be at least ten times the carbon content as is reflected by the standard columbium stabilized grade of stainless steel, i.e., AISI 347. The other carbide stabilizers act in a similar manner. Of course, as is well known, intergranular corrosion is also greatly minimized by maintaining the carbon level below 0.03%, thus rendering the use of columbium or other stabilizers unnecessary.

It is common commercial practice to subject austenitic stainless steels during processing to intermediate annealing treatments at temperatures of about 1900° F. to 2100° F. The final annealing treatment is also usually conducted over the range of 1900° F. to 2100° F. in commercial operation. In addition, the use of a process anneal is commonly employed between hot- and cold-working operations and is particularly utilized with regard to the production of austenitic stainless in the form of sheet. Among other principles of the invention, we have now found that by avoiding the process annealing step an optimal yield strength is attained apart from the economic benefits realized.

It is an object of the present invention to provide austenitic stainless steels of improved yield strength in the annealed condition without adversely affecting the other properties, including ductility, of such steels.

Another object of the invention is to provide a process for achieving a combined high level of yield strength and ductility in austenitic stainless steels in the annealed condition.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which:

FIGURES 1 to 5 are reproductions of photomicrographs showing the structure of various austenitic stainless steels after being subjected to different heat treatments.

In accordance with the invention an optimum combination of properties, including yield strengths of at least about 50,000 p.s.i. (0.2% offset) together with ductilities of at least 50% (using standard ASTM specimens) are obtained in the annealed condition with austenitic stainless steels having compositions (based on weight percentage) within the following most advantageous ranges: at least 0.05%, e.g., 0.06%, and up to about 0.08% carbon, about 17.5% to about 19.5% chromium, about 8% to about 12% nickel, about 0.18% to about 0.28% columbium, up to about 2% manganese, up to about 1% silicon, up to about 0.1% aluminum, up to 0.5% nitrogen and the balance essentially iron. The steels contemplated herein have a unique fine-grained structure, i.e., an ASTM grain size of 11 to 14 or finer, and are substantially free of coarse carbide precipitates. This characteristic of an extremely fine grain structure is discussed more fully hereinafter.

To obtain yield strength levels of 50,000 p.s.i. in the annealed condition it is most important that the aforediscussed process annealing treatment, i.e., the anneal between the hot working and cold working operations at temperatures above about 1900° F., be avoided as will be more fully illustrated herein. Further, the constituents of the alloy composition must be balanced and correlated such that at the working temperature employed in processing, i.e., 2300° F. down to above 1900° F., the presence of detrimental delta ferrite is avoided. If appreciable amounts of delta ferrite are present during the hot-working operation, delta ferrite will be retained in the final product and while it increases yield strength, it substantially adversely affects ductility and formability properties particularly when such properties are measured in the transverse direction. Most advantageously, the presence of delta ferrite should be avoided although up to 5% can be tolerated. Improved yield strength levels in the annealed condition can also be attained with austenitic stainless steels within the following compositional ranges and without detrimentally affecting other properties: carbon in an amount more than 0.03%, e.g., more than 0.04%, and up to 0.12%, at least 16% and up to 20% chromium, about 6% to about 12% nickel, 0.15% to not more than 0.5% columbium, up to 2% manganese, up to 2% silicon, up to 0.5% aluminum, up to 0.5% nitrogen and the balance essentially iron. Of course, the alloying constituents must be properly correlated to provide for an austenitic structure.

In carrying the invention into practice, it is preferred to soak the steel at a high temperature, such as 2250° F. to 2350° F., e.g., 2300° F., before hot rolling and to then apply and continue the hot-rolling treatment within the temperature range of 2300° F. down to above 1900° F. Temperatures as low as 1650° F. are commonly employed but it is most advantageous to hot work from a temperature of about 2300° F. down to 2000° F. After this treatment, the steel has a hardness as low as annealed material and is suitable for subsequent cold rolling. If the finishing temperature of the hot-working operation falls significantly below about 2000° F., e.g., below about 1950° F., a high temperature process annealing treatment may otherwise be required at, say, 2300° F. But since it is desirable to eliminate the process anneal, it is beneficial to maintain a minimum hot-working temperature of about 2000° F.

Subsequent to the hot-working treatment the steels are subjected to a cold reduction operation for control of gage and surface finish and to assure the occurrence of recrystallization during the final anneal treatment (the only annealing treatment required in accordance with the invention). The steel should be advantageously cold reduced at least 15% and up to about 70%. Cold reductions of less than about 15%, e.g., 5%, tend to cause excessive grain growth while reductions of over 70% result in a steel which is too hard to further work without difficulty on a commercial basis. Cold reductions of 40% to 60% are most advantageous with 50% being highly satisfactory. Where desired, intermediate annealing may be employed provided that the temperature range of 1900° F. to 2200° F. is avoided. If the cold-working operation or equivalent is omitted, it makes little difference at what temperature the final anneal is conducted since yield strengths of at least 50,000 p.s.i. will not be obtained.

In accordance with the invention, it has been found that the heat treatment employed (after cold working) to achieve the annealed condition is important. The most advantageous temperature range is 1750° F. to 1850° F. and the steel should be held within this range for about 3 hours to 0.4 hour, e.g., 1 hour at 1800° F. While the annealing temperature can be as high as 2000° F., the holding time should be not greater than 5 minutes and preferably not greater than 3 minutes, otherwise, adverse results can occur. This stems from the fact that in accordance with the invention it is considered that the unusually high yields strengths result, inter alia, partially from the very fine grain size, i.e., ASTM 11 to 14 or finer, and partially from dislocation tangles. High annealing temperatures, i.e., 2000° F., bring about a condition in which fine carbide particles go back into solution and this is accentuated with long holding times, e.g., one-half hour at 2000° F. Thus, there is a loss of fine particles which would otherwise retard grain boundary movement and this would be causative of grain growth. Also, the dislocation tangles tend to disappear or combine with each other such that there is an interference with the strengthening mechanism. On the other hand, the minimum annealing temperature must be above 1600° F., e.g., 1700° F. and above, to assure the occurrence of recrystallization. However, at the lower annealing temperature longer holding times would be required and this contributes to prolonged processing. At 1750° F. the steels should be annealed for about 3 hours. For optimum results the annealing treatment should be in accordance with the following formula:

$$45.3=(460+T)(\log t+20)\times 10^{-3}$$

where T is the temperature in degrees Fahrenheit and t represents time in hours. This formula is derived from the Larson-Miller parameter equation. Thus, at 1900° F. the holding time should be approximately 9 to 10 minutes. A temperature range of 1725° F. to 1950° F. is also satisfactory and the steels should be held at such temperatures for about 4 hours to 0.4 hour, the period of the shortest holding time being used at the highest temperature.

For the purpose of giving those skilled in the art a better understanding of the invention and/or a better appreciation of the advantages of the invention, the following illustrative examples are given:

A series of stainless steels (Alloys 1 to 11 and A to E) was prepared having the compositions given in Table I.

For purposes of comparison the compositions for AISI 304 and 347 as set forth at page 409 of the "Metals Handbook," 1961 edition, are also given in Table I.

TABLE I

Alloy No.	C, percent	Ni, percent	Cr, percent	Cb, percent	Si, percent	Mn, percent	Fe, percent
AISI304	0.08 max	8–12	18–20		1.00 max	2.00 max	Bal.[1]
AISI347	0.08 max	9–13	17–19	10 x C min[2]	1.00 max	2.00 max	Bal.
1	0.07	9.65	18.73	N.A.	0.39	1.20	Bal.
2	0.07	9.60	19.09	0.09	0.59	1.15	Bal.
3	0.08	9.60	18.86	0.16	0.57	1.28	Bal.
4	0.07	9.55	18.81	0.26	0.50	1.15	Bal.
5	0.07	9.60	19.01	0.28	0.48	1.15	Bal.
6	0.07	9.60	18.60	0.34	0.50	1.10	Bal.
7	0.07	9.60	18.94	0.46	0.45	1.20	Bal.
8	0.022	9.15	18.15	N.A.	0.39	0.92	Bal.
9	0.032	9.75	18.45	0.08	0.40	0.92	Bal.
10	0.026	9.75	18.60	0.17	0.45	0.93	Bal.
11	0.024	9.75	18.50	0.27	0.40	0.93	Bal.
A	0.06	10.65	18.08	N.A.	0.63	1.2	Bal.
B	0.07	9.85	18.14	0.1	0.57	1.1	Bal.
C	0.07	10.05	18.68	0.25	0.66	1.15	Bal.
D	0.07	9.8	17.56	0.51	0.67	1.13	Bal.
E	0.07	10.05	18.62	0.85	0.63	1.2	Bal.

[1] Bal.=Balance essentially iron.
[2] 10 x C min.=Columbium exceeds carbon by a minimum ratio of 10 to 1.
N.A.=None added.

The steels 1 through 11 and A through E were prepared in an air induction furnace, the ingredients being melted in magnesia crucibles. Silicon-manganese was used for deoxidation purposes with aluminum additions of less than about 0.1% being made. Final deoxidizing additions were made following slag removal and normal temperature adjustment. The steels were produced in ingot form and hot rolled at temperatures of 2000° F. or 2300° F. after a liberal soak. The hot-rolled product was in the form of ¾-inch round bars. Alloys Nos. 1 through 11 were subjected to a treatment which comprised cold reducing the bars about 45% and annealing for about 1 hour at 1800° F. followed by air cooling. No initial or process anneal was employed. Alloys A through E were treated in the same manner except a process anneal of 1 hour at 2000° F. was employed prior to cold working. It should be noted that Alloys Nos. 2 through 7 and B through E respond to the composition of AISI 304 except for the columbium content. It should also be noted that Alloys Nos. 8, 10 and 11 had carbon contents below 0.03% and, thus, are outside the scope of the present invention as are Alloys Nos. 1, 2 and 9 (columbium was not added to Alloy No. 1 and the amount present in Alloys Nos. 2 and 9 was below the minimum required in accordance with the invention). The yield strength (0.2% offset), ductility (elongation in percent using standard ASTM specimens) and percent reduction of area are given in Table II.

TABLE II

Alloy No.	Yield Strength (0.2% offset), p.s.i.	Elongation, Percent	Reduction of Area, Percent
AISI 304[1]	35,000	55	65
AISI 347[1]	35,000	50	65
1	39,300		76.1
2	44,500		75.7
3	52,300	55	74.8
4	55,300	55	75.2
5	53,000	52	
6	55,400	51	74.9
7	55,200	51	74.8
8	29,100	65.5	
9	34,100	65.0	
10	37,900	58.5	
11	41,400	54.5	
A	33,900	69.7	76.0
B	39,500	65.4	75.2
C	42,500	56.3	74.0
D	40,700	55.5	72.8
E	40,100	57.3	76.0

[1] Metals Handbook, 1961 ed., page 414.

Alloys Nos. 3 through 7 of Table II illustrate that yield strengths of well over 50,000 p.s.i., e.g., 55,000 p.s.i., together with high ductility (i.e., over 50% elongation and over 70% reduction in area) can be obtained in austenitic stainless steels in the annealed condition. Such strength levels represent an increase of about 50% or more as can be seen from a comparison of Alloys AISI 304 and 347 with Alloys Nos. 3 through 7. It will be further noted that Alloys A through E (which were given a process anneal) manifested significantly lower yield strengths than Alloys Nos. 3 through 7. Further, the steels containing less than 0.03% carbon (Alloys Nos. 8, 10 and 11) all manifested yield strengths much below 50,000 p.s.i. and such data illustrate that the steels should contain carbon contents in excess of 0.03%. In addition, Alloys Nos. 1 and A indicate that in the absence of columbium it is immaterial whether the steels are or are not given a process anneal treatment.

A striking feature is the effect of columbium in accordance with the invention as opposed to columbium-containing AISI 347 which has a representative yield strength of only 35,000 p.s.i. in the annealed condition. No special product ratio of columbium content times the carbon content is necessary. The data further reflects that for an optimum combination of properties, the columbium content should not exceed 0.3%.

Residual cold work was not responsible for or causative of the markedly enhanced yield strengths illustrated by the data in Table II. To demonstrate this, an austenitic stainless steel of the AISI 304 type but which contained 0.19% columbium (and also contained 0.08% carbon, 9.01% nickel, 18.27% chromium, 0.76% silicon and 1.08% manganese) was hot rolled to strip. The hot-rolled strip was fully recrystallized and had a Rockwell "B" hardness of 75 to 80. The hardness level did not fall further even after an annealing treatment of 1 hour at a temperature as high as 2100° F. Specimens of the steel were cold reduced 45% without an initial anneal and were annealed after cold reduction (the only anneal) at 1800° F. The 0.2% offset yield strength was 50,500 p.s.i. and the elongation was 55%. These results are in good agreement with Alloy No. 3 of Table II which contained 0.16% columbium.

While the theory which would perhaps explain the mechanism involved is not completely understood, it is deemed that columbium exerts a most unusual and pronounced influence in retarding grain growth when used in percentages in accordance with the invention, although solid solution hardening mechanisms might be involved This is considered quite opposite in conjunction with the elimination of the process annealing treatment This ostensible phenomenon is more effectively illustrated by reference to FIGURES 1 to 5 wherein there is shown the grain size of Alloys Nos. 1, 4 and 6, respectively, in various treated conditions. In FIG. 1 (250 magnification) there are illustrated photomicrograph reproductions of the three steels in hot hot-rolled condition (hot rolled at 2300° F.). FIG. 2 (100 magnification) depicts the grain size of each of the steels after a process anneal at 2300° F. for 2 hours following the hot-rolling operation. It will be noted that the process anneal completely eliminated all observable difference among the three steels. FIGURES 3 and 4 (both at 250 magnification) represent the microstructure obtained after a final anneal, i.e., the alloys were hot rolled, process annealed at 2300° F. for 2 hours, cold rolled (a reduction in area of about 45%) and given a final anneal at 1800° F. (FIG. 3) and 2000° F. (FIG. 4) for 1 hour. FIGURE 5 (250 magnification) depicts the extremely fine grain structure (finer than ASTM size 14) obtained for Alloys Nos. 4 and 6 (alloys within the invention) in the absence of the process annealing treatment. The steels (FIGURE 5) were hot rolled, cold rolled (45% reduction in area) and annealed at 1800° F. for 1 hour. Thus, austenitic stainless steels within the invention are uniquely characterized by a very fine grain structure, i.e., an ASTM grain size of 11 or finer, e.g., ASTM grain size 14 or finer, in the absence of a process anneal. This is thought surprising when considered in the light of the grain size heretofore given for the well established columbium-containing austenitic stainless AISI 347. For example, it has been reported that the AISI 347 austenitic steel of the following composition has a grain size of about 6 or 7.

AISI	C, percent	Ni, percent	Cr, percent	Cb, percent	Mn, percent
347	0.05	11.49	17.33	0.76	1.74

When hot rolled, pickled and then annealed at 1900° F., 2000° F. and 2100° F. this steel had a grain size of 8, 7 and 6, respectively. When hot rolled, annealed at 1900° F., 2000° F. and 2100° F., respectively, de-scaled, cold rolled 20% and final annealed at the same temperatures as the initial anneal, this steel had a grain size of 7, 7 and 6, respectively. This compares quite unfavorably with ASTM grain sizes of 11 to 14 achieved in accordance with the invention. It is considered that this conflicting behavior is somewhat attributable to the fact that columbium in amounts say above 0.5%, result in carbide agglomerates which paralyze the reactions taking place to the extent that grain growth is substantially uninhibited. We have found that high columbium contents should be avoided and are quite unnecessary. An alloy stainless steel containing 0.07% carbon, 10.05% nickel, 0.63% silicon, 1.2% manganese, 18.62% chromium and 0.85% columbium when hot rolled, cold reduced by 45% and annealed at 1800° F. for 1 hour had an ASTM grain size of about 8. Except for the columbium content, this steel would have been within the invention.

Whatever be the theoretical explanation, the austenitic stainless steels in accordance with the invention are characterized by extremely fine grain sizes, i.e., ASTM grain sizes of at least 11, e.g., 12 to 14. This fine grain size affords many other advantages, such as improved deep-drawing characteristics and machinability. It should be mentioned that grain size as referred to herein, was determined with the Standard ASTM Grain Size Chart at a magnification of 500×. This is higher than the 100× magnification normally used because of the extreme fineness of the grains of the steels within the invention. Correction for higher magnification was made by using the ASTM correction formula,

$$Q=6.64 \log \frac{M}{M_b}$$

where Q is the correction number to be added to the ASTM Grain Size Number observed at the higher magnification, M is the high magnification, i.e., 500×, and M_b equals 100×.

The austenitic stainless steels of the invention can, of course, be used in all applications for which such steels are presently used. However, by virtue of the increased yield strength coupled with good ductility, etc., characteristic of the steels, an expanded field of use is opened particularly where higher strength-to-weight ratios are necessary or advantageous, e.g., transportation tanks carrying various media, including corrosives.

As those skilled in the art will readily appreciate, "balance" or "balance essentially" as used herein in referring to the iron content of the steels does not exclude the presence of other elements commonly present as incidental elements, eg., deoxidizing and cleansing elements, and impurities ordinarily associated therewith in amounts which do not adversely affect the basic characteristics of the steels. For example, up to 3% molybdenum can be present in the steels. The term "austenitic" as used herein means that the structure of the alloys at room temperature is substantially or completely of an austenite matrix although up to not more than 10%, and most advantageously not more than 5%, of other phases, e.g., ferrite, can be present.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. For example, the present invention is applicable to the austenitic stainless steels of the AISI 201 and 202 types, i.e., the nickel content can be as low as 3% and the manganese content can be as high as 10%, the remainder of the composition being within the limits set forth before herein. Of course, the nickel and manganese contents in combination with the other elements would have to be correlated to insure an austenitic structure. In such instances the yield strength of the AISI 201 and 202 types is increased to above 70,000 p.s.i., e.g., 75,000 to 80,000 p.s.i. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for improving the yield strengths of and achieving finer grain sizes in austenitic stainless steels consisting of about 0.06% to about 0.08% carbon, about 8% to about 12% nickel, about 17.5% to about 19.5% chromium, about 0.18% to about 0.28% columbium, up to 1% silicon, up to 2% manganese, up to 0.1% aluminum, up to 0.3% nitrogen and the balance essentially iron which comprises hot working the steels within the temperature range of about 2300° F. to about 2000° F., cold working the steel without a prior process annealing treatment to obtain a reduction in area of 40% to 60% and thereafter recrystallizing the steel by subjecting it to an annealing treatment within the temperature range of about 1750° F. to about 1850° F. in accordance with the following formula:

$$45.3=(460+T)(\log t+20)\times 10^{-3}$$

wherein T represents temperature in degrees Fahrenheit and t is time in hours.

2. A process for improving the yield strengths of and achieving finer grain sizes in austenitic stainless steels consisting of carbon in an amount above 0.03% and up to about 0.12%, about 6% to about 12% nickel, about 16% to about 20% chromium, about 0.15% to less than about 0.3% columbium, up to 2% silicon, up to 2% maganese, up to 0.5% aluminum, up to 0.5% nitrogen and the balance essentially iron which comprises hot working the steels within the temperature range of about 2000° F. and up to 2300° F., cold working the steel without a prior process annealing treatment to obtain a reduction in area

of at least 15% and thereafter substantially recrystallizing the steel by subjecting it to an annealing treatment within the temperature range of about 1725° F. to 1950° F. for a period of about 4 hours to about 0.4 hour, the period of the shortest holding time being employed at the highest temperature.

3. The process as set forth in claim 2 wherein the carbon content is present in an amount of at least 0.04%.

4. The process as set forth in claim 2 wherein the carbon content is at least 0.05% and the columbium content is at least 0.18%.

5. A process for improving the yield strengths of and achieving finer grain sizes in austentic stainless steels consisting of about 0.05% to about 0.12% carbon, about 6% to about 12% nickel, about 16% to about 20% chromium, 0.15% to not more than 0.5% columbium, up to 2% silicon, up to 2% manganese, up to 0.5% aluminum, up to 0.5% nitrogen and the balance essentially iron which comprises hot working the steels within the temperature range of above 1900° F. and up to 2300° F., cold working the steel without a prior process annealing treatment to obtain a reduction in area of at least 15% and thereafter substantially recrystallizing the steel by subjecting it to an annealing treatment within the temperature range of above about 1700° F. and up to not more than about 2000° F.

6. An austenitic stainless steel in the annealed condition consisting of at least 0.05% and up to 0.12% carbon, about 3% to about 12% nickel, about 16% to about 20% chromium, about 0.16% to not more than 0.3% columbium, up to 1% silicon, up to 10% manganese, up to 0.1% aluminum, up to 0.3% nitrogen, up to 3% molybdenum and the balance essentially iron, said steel being characterized by a yield strength of at least 50,000 p.s.i., an elongation of at least 50% and a grain size of at least about ASTM No. 12 when hot worked at a temperature of about 2000° F. to about 2300° F. followed by cold working to obtain a reduction in area of at least 15% and then substantially recrystallized by subjecting it to an annealing treatment within the temperature range of over about 1700° F. to not more than 2000° F.

7. An austenitic stainless steel consisting essentially of carbon in an amount above 0.03% and up to 0.12%, about 3% to about 12% nickel, about 16% to about 20% chromium, about 0.15% to about 0.3% columbium, up to 2% silicon, up to 10% manganese, up to 0.5% aluminum, up to 0.5% nitrogen, up to 3% molybdenum, and the balance essentially iron, said steel having a yield strength of at least 50,000 p.s.i., an elongation of at least 50% and a grain size fineness of at least about ASTM No. 12.

8. The stainless steel as set forth in claim 7 and containing 0.04% to 0.12% carbon, 6% to 12% nickel, 16% to 20% chromium, 0.16% to 0.28% columbium, up to 2% silicon, up to 2% manganese, up to 0.1% aluminum, up to 0.3% nitrogen, and the balance essentially iron.

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Patent No. 3,284,250 November 8, 1966

Ralph B. G. Yeo et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 73, for "volved This is considered quite opposite" read -- volved. This is considered quite apposite --; line 74, after "treatment" insert a period; column 7, line 5, for "hot", first occurrence, read -- the --; line 49, for "amounts say" read -- amounts, say --; column 8, line 17, for "eg." read -- e.g. --; line 70, for "maganese" read -- manganese --.

Signed and sealed this 12th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents