

July 16, 1957

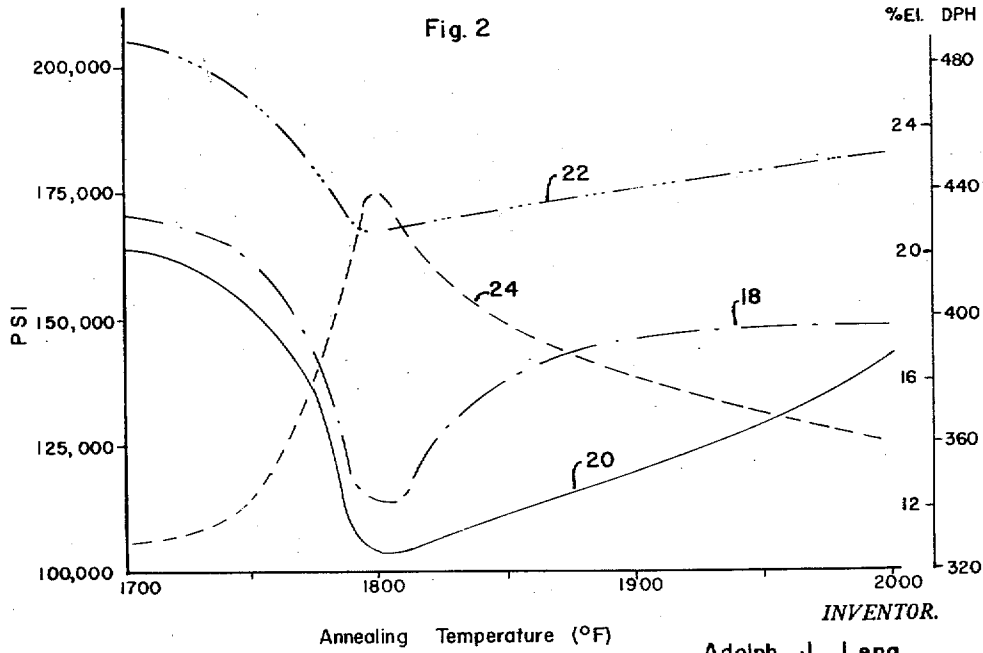
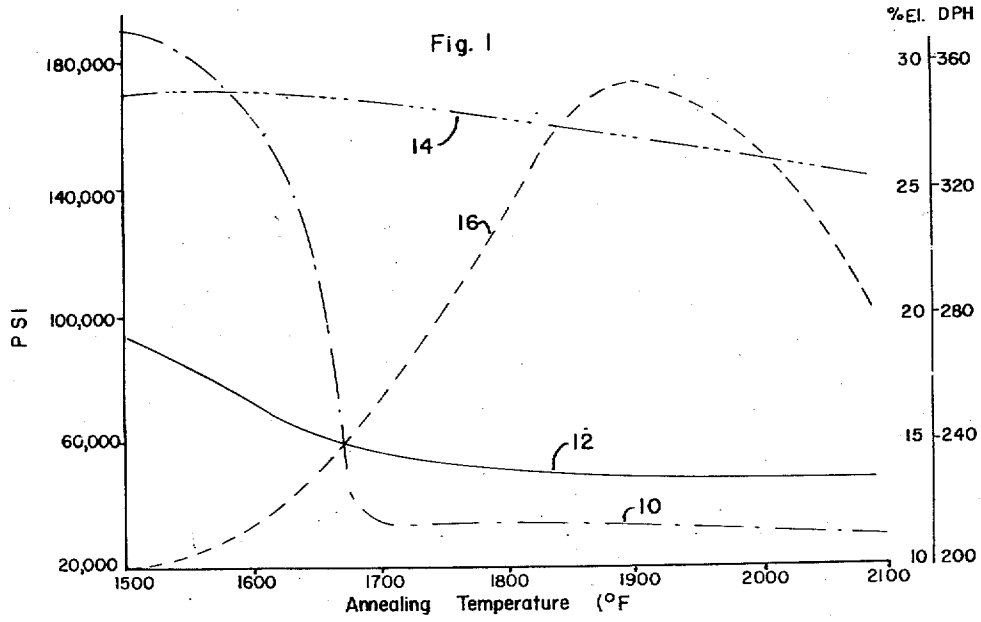
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2,799,602

PROCESS FOR PRODUCING STAINLESS STEEL

Filed Oct. 4, 1956

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

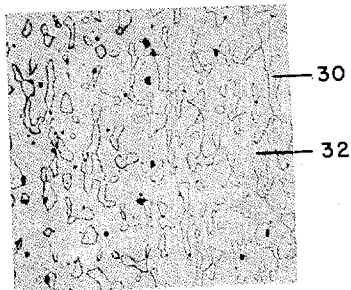


Fig. 3

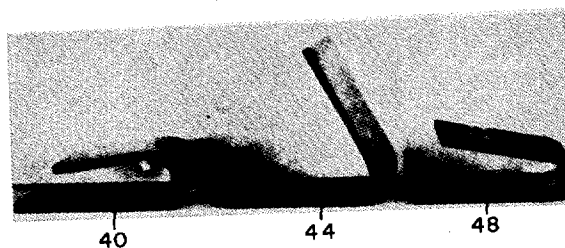


Fig. 6

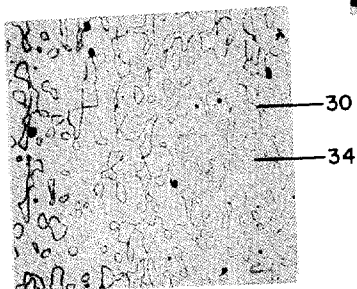


Fig. 4

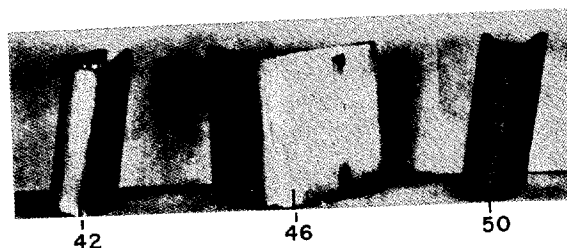


Fig. 7

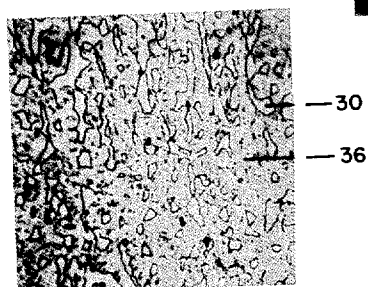


Fig. 5

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2,799,602

PROCESS FOR PRODUCING STAINLESS STEEL

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Application October 4, 1956, Serial No. 614,334

12 Claims. (Cl. 148—12)

This invention relates to the production of stainless steel containing as principal alloying elements chromium, nickel and molybdenum and having good hardness, strength, ductility and corrosion resistance.

It is well known that in stainless steels, the maximum ductility and the best fabrication properties are found in the austenitic type as characterized by the 300 series of stainless steels which are the standard chromium-nickel stainless steels of the 18-8 group, examples of which are types 301 and 302. These steels consist of a non-magnetic phase of steel called austenite when properly heat treated and cooled to room temperature. It is also known that adjustment of the physical and mechanical properties, such as hardness, strength and ductility, can only be achieved in these types of steels through what is known as the strain hardening method consisting of subjecting the steel to external cold deformation such as rolling or drawing. While the effect of the cold work is greater if it is performed at temperatures well below room temperature, for example, at subzero temperatures, subzero cooling alone without cold deformation does not produce the requisite properties of hardness, strength and ductility. The strain hardening method is obviously limited in application, for it cannot be employed in many cases such as, for example, in producing hardening in cast and fabricated articles. In addition, if steels of this type are strain hardened to produce the desired physical and mechanical properties and the steel is thereafter fabricated, for example, by welding, the welding operation in effect anneals the steel so that it no longer has the desirable strength or hardness in the vicinity of the weld which it possessed in the strain hardened condition.

On the other hand, it is well known that the physical and mechanical properties of certain other grades of stainless steel, namely the 400 series, examples of which are types 410 and 431, can be adjusted by heat treatment. This treatment usually requires heating to a high temperature such as 1800° F. and cooling at a sufficiently fast rate to permit the formation of martensite, an extremely hard phase of steel. Steels of this type in the annealed condition consist predominantly of ferrite, a magnetic phase of steel which possesses considerably less ductility than the austenitic grades of steel of the 300 series and hence, the steels of the 400 series are less amenable to fabrication.

From the foregoing it is apparent that it would be desirable to have a steel which possesses a combination of maximum ductility as exemplified by the austenitic steels for the best fabrication and still be amenable to heat treatment to develop the proper hardness and strength, as exemplified by the 400 series. Attempts have been made in the past to combine both the desirable properties of the 300 and 400 series stainless steels, but have met with little success. The ensuing heat treatments which were applied to such stainless steels have usually consisted of a double aging treatment which consisted of an intermediate aging treatment of from about one to two

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hours at a temperature within the range between about 1300° F. and 1400° F. followed by a final aging treatment consisting of about one to two hours at a temperature within the range from about 800° F. to 1000° F.

5 The double aging treatment, while sufficient or effective in increasing the hardness and strength, has an extremely deleterious effect on the corrosion resistance and impact strength of the steel to such a degree that they are no longer useful in applications to which the stainless steel

10 is applied.
An object of the invention is to provide for producing stainless steel having chromium, nickel and molybdenum as essential elements thereof in a predetermined balanced relation and having good hardness, strength, ductility and corrosion resistance.

15 A further object of this invention is to provide, in producing stainless steel, for selecting a balanced composition in which chromium, nickel and molybdenum are essential elements and for heat treating such balanced composition by annealing at a temperature between 1675° F. and 2000° F., cooling to room temperature, subzero cooling at a temperature between -80° F. and -110° F. and thereafter tempering at a temperature between 750° F. and 900° F. to impart to the stainless steel 20 an optimum balance in the hardness, strength, ductility and corrosion resistance characteristics of such steel.

These and other objects of this invention will become apparent when taken in conjunction with the following description and the accompanying drawings in which:

30 Figure 1 is a graph, the curves of which illustrate the effect of the annealing temperature on the tensile properties in the annealed condition;

Figure 2 is a graph, the curves of which illustrate the effect of the annealing temperature on the properties in the annealed subzero cooled, and tempered condition;

35 Fig. 3 is a photomicrograph taken at a magnification of 500 × showing the microstructure of a representative steel having a balanced composition selected in accordance with certain of the teachings of this invention after annealing;

40 Fig. 4 is a photomicrograph taken at a magnification of 500 × of the steel of Fig. 3 after subzero cooling;

Fig. 5 is a photomicrograph taken at a magnification of 500 × of the steel of Fig. 4 after tempering;

45 Fig. 6 is a photograph illustrating the bend angle ductility of the steel at various stages of heat treatment; and

Fig. 7 is a photograph taken from a different angle of the samples of Fig. 6 and illustrating the bend angle ductility of the steel samples of Fig. 6.

50 In general, the stainless steel produced in accordance with this invention comprises, up to about 0.15% carbon, from about 12.0% to about 18.0% chromium, from about 3.5% to about 7.0% nickel, from about 2.0% to 3.5% molybdenum, up to 0.5% maximum silicon, from about 0.25% to about 2.0% manganese, from about 0.05% to 0.15% nitrogen with the balance substantially all iron with incidental impurities, such as 0.04% maximum phosphorus, 0.04% maximum sulphur, and 0.25% maximum copper. Each element present in the steel has a 60 specific purpose. The carbon is necessary for proper hardening and strengthening, but it must be limited in amount to prevent the loss of corrosion resistance. The chromium is a necessary component of all stainless steels and is present in an amount to insure the proper corrosion resistance and to provide the proper "delta" factor, to be described more fully hereinafter. The nickel provides the ability to form austenite while the molybdenum provides added corrosion resistance and in this respect cannot be replaced by the other similar metals, for example, tungsten. For this reason, while steel having good corrosion resistance can be produced with a minimum of 2% molybdenum as given in the general range,

it is preferred to maintain the molybdenum content of the optimum ranges at a minimum of 2.25% to insure good corrosion resistance. Excellent results are obtained with a minimum of 2.45% molybdenum. Silicon and manganese are the steel making elements which are required for the proper purification and fabrication of the steel. The nitrogen contributes to the strengthening and hardening, to the formation of austenite, and also contributes to the proper "delta" factor.

Reference may be had to Table I for the chemical composition of the stainless steel which is amenable, when selected to have a balanced composition to be described hereinafter, to the heat treatment to be described. Table I sets forth the general range and two optimum ranges, it being understood that where the balance is given as iron, such balance includes incidental impurities usually present in stainless steel.

Table I

[Chemical composition—percent by wt.]

Element	General Range	Optimum Range 1	Optimum Range 2
C.....	0.03-0.15	0.06-0.15	.09-.15
Cr.....	12.0-18.0	16.0-17.5	14.5-16.0
Ni.....	3.5-7.0	4.0-4.5	4.0-4.5
Mo.....	2.0-3.5	2.25-3.50	2.25-3.50
Si.....	0.5 max.	0.20-0.40	0.20-0.40
Mn.....	0.25-2.0	0.40-0.80	0.40-0.80
N.....	0.05-0.15	0.05-0.10	0.07-0.13
Fe.....	Bal.	Bal.	Bal.

As illustrative of the steels made and produced in accordance with this invention, reference may be had to Table II giving chemical composition representative of steels produced within the general range given in Table I.

Table II

[Chemical composition—percent by wt.]

Element	DE 93	DK 43	74508	82661	92370	92608	92546	82401
C.....	0.073	.074	.077	.128	.14	.136	.133	.140
Cr.....	16.69	16.64	16.99	15.78	15.44	15.26	15.68	15.26
Ni.....	4.26	4.64	4.40	4.19	4.35	4.41	4.34	4.25
Mo.....	2.85	2.80	2.53	2.80	2.74	2.56	2.70	2.71
Si.....	0.34	0.24	0.25	.44	.37	.20	.28	.38
Mn.....	0.64	0.82	0.67	.96	.95	.89	1.02	1.03
N.....	0.69	.060	0.070	.13	.10	.12	.12	.11
Fe.....	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

In producing steel mill products, the stainless steel of this invention may be produced by any of the conventional steel mill practices, for example, melting in an electric arc furnace followed by casting of the steel into ingot form which when solidified may be thereafter hot rolled and/or cold rolled as desired. In practice, the steel is usually processed into the semi-finished mill product such as plate, bar, sheet and strip form before applying the heat treatment to be described hereinafter.

As was stated hereinbefore, a known manner of hardening austenitic type stainless steels is by the strain hardening method. With such steels there is no transformation of the austenite to martensite due to heat treatment alone. On the other hand, the known 400 series stainless steels have their hardness properties developed by heat treatment consisting of a high temperature anneal followed by a cooling at a rate sufficiently fast to transform the austenite which is formed at the high temperature annealing to martensite. Thus there are two distinctively different methods known for hardening the 300 and 400 series of stainless steels. The difference in the methods of hardening the respective steels is attributed to variations in chemical composition, to related microstructure associated with the chemical composition, and to the responsiveness or the ability of the microstructure to transform upon proper heat treatment. As is well known, the temperature at which the transformation from austenite to martensite takes place in such steel is well above room temperature for the 400 series stainless steels; whereas,

the temperature at which transformation starts in austenitic steels is considerably below room temperature and in some instances is below absolute zero. Because of the low transformation temperature of the commercial steels, they cannot be hardened to any appreciable extent by heat treatment regardless of the temperature to which they may be cooled. For instance, type 301 which has the highest transformation temperature of any of the commercial austenitic stainless steels (-78°F.) undergoes only a 15% transformation when cooled to -320°F. , an amount which is not sufficient to produce appreciable hardening. The temperature at which the martensite transformation begins is designated in the metallurgical trade as the "Ms" temperature.

I have found that by the proper selection of a combination of the elements, it is possible to obtain an Ms temperature which lies between a temperature that is slightly below room temperature and some conveniently fixed lower temperature so that when the steel is cooled to a temperature below such lower temperature, the retained austenite will readily transform to martensite. This transformation of austenite to martensite is a substantially instantaneous transformation. However, the amount of martensite to be formed is a function of temperature, for instance, a given steel containing substantially 100% austenite at room temperature may have an Ms temperature of 30°F. Therefore, cooling the steel at a temperature below 30°F. , for example, at 15°F. , will substantially instantaneously transform a certain proportion of the austenite to martensite. Holding for a longer period of time at that temperature will not result in any appreciable further transformation of the austenite of such steel to martensite. However, by decreasing the temperature, say to 0°F. , a certain greater proportion of the austenite will be transformed to martensite. Thus it follows that the amount of martensite which is formed upon cooling is a function of temperature for any given chemical composition of stainless steel.

While I have given a general range of composition in Table I, I have found that in order to produce stainless steel having sufficient ductility and hardness, the composition must be so selected that the steel will have at least 70% austenite in its microstructure in the annealed condition so that upon subsequent heat treatment, the steel will have the ability to transform to martensite, hereby effecting a hardening of the steel as will be referred to hereinafter. Under such condition it is found that the annealed steel can be drawn, rolled or deformed to a greater degree than that of the known hardenable stainless steels without the necessity of an intermediate anneal. If an excessive amount of cold work is applied to the steel having at least 70% austenite, the steel may be again annealed to relieve the stresses imparted thereto by such working without affecting the ability of the steel to be hardened as will be described hereinafter.

It has been found in producing the stainless steel having the balance of its physical properties as referred to hereinbefore that a definite relation must be maintained between the elements of the composition within the general range given in order for the steel to respond when treated, as will be described, to develop the hardness and strength thereof. Thus, in practicing this invention, the composition of the steel is selected within the general range given in Table I so that the resulting steel will have an Ms temperature in the range between 60°F. and -58°F. In order to satisfy such a requirement, it has been determined that the steel must have a balanced composition to provide a stability factor delta which is a measure of the austenite stability with respect to chemical composition of the steel in accordance with the formulae

$$\Delta = \% \text{Ni} - 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/12(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

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where $[\%Cr + 1.5(\%Mo)] < 20$; and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] > 20$,

of -3.82 to -4.65 when $\%C + \%N =$

.11 to .20 and $\%Cr = 16$ to 18 and

of -0.10 to -1.0 when $\%C + \%N =$

.20 to .28 and $\%Cr = 14.5$ to 16

Only those steels within the range given and having a delta factor in the ranges given depending upon the composition as determined by the equations given are satisfactory for the purpose of this invention, and even then such steel must have a microstructure such that at least 70% austenite is retained after the annealing treatment to be described hereinafter.

It is evident from the equations given hereinbefore that it is possible for a steel to have a delta factor within the range given by completely eliminating the nickel content and increasing the chromium content to excessive amounts. However, such a steel, while possessing the proper delta factor, will not harden because the microstructure of the steel will be ferritic and hence not susceptible to transformation upon cooling. In this respect the elements chromium, molybdenum and silicon which are normally referred to as ferritizing elements and which usually act oppositely to the austenitizing elements carbon, nitrogen, nickel and manganese, contribute to the stability of the austenite and thereby decrease the Ms temperature. At first glance this would seem to be in contradistinction to the recognized role of chromium, molybdenum and silicon which contribute to the formation of ferrite at elevated temperature. However, while this is true, when these elements are in solution in the austenite, they contribute to the stability of the austenite.

While steel selected within the general range in the manner specified hereinbefore will have a microstructure such that at least 70% austenite is retained after the annealing treatment to be described hereinafter, certain of the steels will have a preponderance of, that is, at least 90% austenite retained. For this reason two optimum ranges have been specified within the general range, the optimum range 1 compositions in which $\%C + \%N < .20$ and the $\%Cr = 16$ to 17.5, having from 70% to 85% austenite and from 30% to 15% delta ferrite present after the annealing treatment, whereas the steels of optimum range 2 in which the

$\%C + \%N > .20$ and the $\%Cr = 14.5$ to 16

will have from 90% to 100% austenite and from 10% to 0% delta ferrite present after the annealing treatment. All such steels selected as specified will respond to the heat treatment to be described having exceptionally good nondirectional strength characteristics.

That the steels when so selected will respond in the same manner when subjected to the heat treatment to be described will be understood when it is considered that it is only the austenite phase in the steel which transforms to develop the characteristics of the steel. The amount of austenite contained in the steel is, of course, dependent primarily upon the chemical composition of the steel. Thus a steel having a composition within the optimum range 1 when properly heat treated will contain between 70% and 85% austenite and from 30% to 15% delta ferrite. With these two phases present there is a partitioning of the alloying elements so that the austenite becomes richer in its concentration of the austenite forming elements nickel, carbon, nitrogen and manganese than the base analysis, whereas the delta ferrite becomes richer in the ferrite forming elements chromium, silicon and molybdenum. Where the two phases are present in the steel, as in the case of the steels in the optimum range 1, partitioning of the alloying elements occurs so that an austenite is produced containing, for example, about 15.5% chromium, 0.12% carbon and

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0.12% nitrogen. This may be explained on the basis that the austenite has a greater solubility for the austenite forming elements nickel, carbon, nitrogen and manganese, whereas the delta ferrite has a greater solubility for the chromium, silicon and molybdenum. Upon examination it is found that the steels of the optimum range 2, having little or no delta ferrite present, also have essentially the same approximate austenite composition as the austenite of the steel of the optimum range 1. Thus it is apparent that the steels of both optimum range 1 and optimum range 2 having an Ms temperature in the range given will respond to the same heat treatment. Also, it is for this reason that the delta factor equations are utilized in selecting the composition of the optimum ranges within the general range given for the delta factor equations utilized, depending upon the carbon, nitrogen and chromium contents of the steel, correlate the retained austenite with the Ms temperature to assure that a composition is obtained having an Ms temperature within the range of 60° F. to -58° F. and that the resulting composition will have at least 70% austenite which will transform to martensite upon proper heat treatment to develop the characteristics of the alloy.

In general, the process utilized in practicing this invention consists of first annealing the steel having chromium, nickel, and molybdenum as essential elements, and the composition within the range given in the balanced relationship as described hereinbefore, at a temperature within the range between 1675° F. and 2000° F. for from 10 minutes to 4 hours, depending upon the thickness. These limits on the annealing temperature have been established to insure that upon heating steel having the composition selected within the range given as stated hereinbefore, the microstructure of the steel is changed to at least 70% austenite. In some instances it may be desirable to anneal at a high enough temperature within the given range to dissolve all of the metal carbides within the austenite phase. As was stated hereinbefore, the Ms temperature is principally a function of the chemical composition; however, there are other significant considerations which have an effect upon the Ms temperature for any given chemical composition. In this respect, such variables as grain size and the relative amount of inclusions play a significant part in determining the relative stability of the austenite phase, and hence the Ms temperature. It is for this reason that a broad temperature range for initially annealing the steel must be maintained. For example, small heats of stainless steel having a chemical composition selected in accordance with the hereinbefore described manner and which, when melted without the benefit of a slag cover and only having a relatively small amount of hot deformation will necessarily possess a higher amount of inclusions as well as a relatively coarse equiaxed grain structure. These factors, together with the metal carbides which are usually precipitated at the grain boundaries, have a significant effect upon producing an unbalanced austenitic phase. The undissolved metal carbides and the inclusions act as nucleation points for further precipitation of metal carbides, thus seriously detracting from the balance and stability of the austenite phase. If sufficient metal carbides are precipitated, not only will the steel transform upon a subsequent cooling to room temperature, but the metal carbides may have an extremely deleterious effect upon the corrosion resistance and impact strength of the stainless steel. For this reason these steels, that is, heats made in an induction furnace without benefit of a protective slag covering and which usually have a high amount of inclusions and substantially small amounts of hot deformation which result in a relatively coarse equiaxed grain structure must be annealed at a temperature within the range between 1775° F. and 2000° F. in order to insure that substantially all of the metal carbides go into solution thereby stabilizing the austenite phase. On the other hand, large

heats of stainless steel, for example a 10-ton heat which is melted and produced in the conventional electric arc furnace using well known melting procedures which include the use of protective slag covering, the effect of which is usually to produce a cleaner steel than steels produced without the benefit of a slag covering and which will subsequently be subjected to large amounts of hot deformation, will necessarily have a more stable austenite phase. For this reason it is not necessary to anneal these steels at a temperature sufficient to dissolve all of the metal carbides within the austenite phase. In fact, I have found that it is sufficient if the annealing temperature is high enough to destroy any metal carbide envelope which may surround the grain boundaries. Annealing at higher temperatures which are sufficient to dissolve the metal carbides may stabilize the austenite phase to such a degree that it will not completely transform to martensite upon subsequent subzero cooling treatment, to be more fully described. I have found that by annealing these steels, that is, the steels produced in accordance with procedures well known to the art for producing commercial heats of steel, at a temperature within the range between 1675° F. and 1775° F., sufficient austenite is formed which, when transformed upon subsequent heat treatment, to be more fully described hereinafter, will produce the requisite properties needed within such steels. This will be more clearly demonstrated with respect to Figs. 1 and 2 to be described more fully hereinafter.

The temperature range as set forth must be limited to a maximum of 2000° F. because heating above such temperature, regardless of the grain size or the inclusions, will cause a large amount of delta ferrite to be formed, and this material will not transform upon subsequent cooling, regardless of the temperature to which the steel is cooled, and the steel therefore cannot be hardened.

After sufficient soaking at temperature between 1675° F. and 2000° F., preferably for a period of time of at least one half hour, the steel is cooled at a sufficiently fast rate in order to prevent any substantial precipitation of the metal carbides from the austenite phase. The cooling rate, of course, will depend upon section thicknesses; for example, sheet material of about 0.150 inch in thickness may be air cooled from 1800° F. to room temperature without the precipitation of any metal carbides or transformation of the austenite. It has been found, however, that larger sections may require a more severe quenching media, for example water, in order to prevent any metal carbide precipitation. After cooling to room temperature, the steel containing at least 70% austenite is in a soft ductile condition and may be fabricated to the shape and size of the article to be produced

therefrom in any well known manner. Where desired, the surface of such steel may be further treated in accordance with well known mill practice to produce a finish of predetermined character ranging from dull to bright thereon. However, if extreme cold deformation is to be applied to the steel, an intermediate annealing step may be necessary. This intermediate anneal must again be performed at a temperature within the range of 1675° F. to 2000° F. if the steel is to be subsequently hardened.

The steel having a delta factor in the ranges given and an Ms temperature between 60° F. and -58° F. is then subjected to a subzero cooling treatment at a temperature below -80° F. In practice it has been found that a temperature in the range between -80° F. and -110° F. is quite satisfactory. The subzero cooling treatment will substantially instantaneously transform the austenite which was retained at room temperature to martensite. With the compositions in the ranges given and having the delta factor in the ranges given, the lowest temperature at which the martensite transformation begins is -60° F. Thus it is evident that cooling the steel to a substantially lower temperature will transform a proportionate amount of retained austenite to martensite. It is only necessary to maintain the steel at the subzero temperature for a period of time sufficient to minimize any thermal gradients within the steel, and preferably for a time of up to three hours to insure transformation of the austenite to martensite.

Referring to Table III, there are listed the mechanical properties obtained on steels identified in Table II during the different steps of the process described hereinbefore. Also noted in Table III are the results obtained on two alloys identified as alloys A and B known to the prior art. Alloy A has a nominal composition of 0.10% carbon, 17% chromium, 7% nickel, 0.55% manganese, 0.4% aluminum, 0.7% titanium and balance iron, whereas alloy B has a nominal composition of 0.07% carbon, 17% chromium, 7% nickel and 1.1% aluminum. Alloy A is hardened by a simple aging treatment consisting of a solution heat treatment at a temperature in the range between 1850° F. and 1950° F. followed by an aging treatment of one half hour at a temperature of about 950° F. Alloy B is hardened by a double aging treatment consisting of annealing at 1900° F. for one half hour and air cooling, intermediately aging for one and one half hours at 1400° F., cooling to 60° F., and a final aging at 950° F. for one half hour. While neither alloy A nor alloy B is susceptible to the process disclosed herein, these alloys possess somewhat similar chemical compositions and clearly illustrate the superior results obtained in practicing this invention.

Table III

[Mechanical properties (room temperature).]

Heat No.	Condition	0.2% Offset Y. S. (p. s. i.)	T. S. (p. s. i.)	Percent Elong. in 2"	Hard- ness	Bend Angle, D=2t
DE-93	(1) Annealed 1,800° F., ½ hr., A. C.	44,900	163,000	19.5	R _b 93	180
	(2) Subzero cooled (1) for 1 hr. at -80° F.	118,000	200,000	10.0	R _c 42	120
	(3) Subzero cooled and tempered (2) for 2 hrs. at 750° F.	147,000	193,200	13.5	R _c 42	180
DK-43	(1) Annealed 1,900° F., ½ hr., A. C.	49,920	161,000	26.5	R _b 90	180
	(2) Subzero cooled (1) for 1 hr. at -80° F.	102,270	200,750	12	R _c 41	180
	(3) Subzero cooled and tempered (2) for 2 hrs. at 750° F.	133,555	181,900	19	R _c 41	180
74508	(1) Annealed 1,700° F., ½ hr., A. C.	48,800	164,000	18	R _b 95	180
	(2) Subzero cooled and tempered (1) for 2 hrs. at -100° F., 2 hrs. at 750° F.	166,850	205,000	11	R _c 44	180
82661	(1) Annealed 1,750° F., 1 hr., W. Q., 2 hrs. at -100° F., 2 hrs. at 850° F., A. C.	192,000	218,000	11.0	R _c 46.5	-----
92370	(1) Annealed 1,750° F., 1 hr., W. Q., 2 hrs. at -100° F., 2 hrs. at 850° F., A. C.	199,500	233,500	20	R _c 48	-----
92608	(1) Annealed 1,750° F., 1 hr., W. Q., 2 hrs. at -100° F., 2 hrs. at 850° F., A. C.	162,000	216,000	14	R _c 45.4	-----
92546	(1) Annealed 1,750° F., 1 hr., W. Q., 2 hrs. at -100° F., 2 hrs. at 850° F., A. C.	180,000	219,000	20	R _c 45.4	-----
82401	(1) Annealed 1,750° F., 1 hr., W. Q., 2 hrs. at -100° F., 2 hrs. at 850° F., A. C.	153,000	206,000	28	R _c 45.4	-----
Alloy A	(1) Annealed 1,900° F., 1 hr., cool to 60° F., 5 min.	75,000	120,000	3-10	R _c 22	-----
	(2) Annealed (1) and aged ½ hr. at 950° F.	180,000	195,000	3-10	R _c 39	-----
Alloy B	(1) Annealed 1,900° F., 1 hr., cool to 60° F., 5 min.	23,620	125,350	36	R _b 73	-----
	(2) Double aged	142,540	177,050	13	R _c 38	-----

By inspection of Table III it is evident that when the steel of heat No. DE-93, a 60-pound heat produced by induction melting without the benefit of a protective slag covering, is annealed at 1800° F., for one half hour, and thereafter air cooled to room temperature, the steel is in a soft and ductile condition as evidenced by the hardness and elongation data as tabulated. Upon subzero cooling for one hour at -80° F., there is a tremendous increase in the yield strength, tensile strength and hardness. As would be anticipated, however, the elongation is considerably reduced. However, the subzero cooling alone, while increasing the yield strength and hardness, does not impart all of the requisite properties needed in this steel. For that reason recourse is had to a tempering treatment which comprises heating the steel at a temperature in the range between 750° F. and 900° F. for a time period ranging between one and eight hours. The results of the tempering treatment illustrate the outstanding results achieved by the use of this process, namely, that the yield strength may be increased as much as 25% or greater without detracting from the hardness or tensile strength at the same time increasing the elongation over that which the steel possessed in the subzero cooled treatment. This is also illustrated by the results given for heat DK-43 in Table III. The effect of the annealing temperature may be readily seen by reference to the results given in Table IV which forms the basis of the curves of Figs. 1 and 2.

Table IV

[Effect of annealing temperature.]

Heat No.	Condition*	Annealing Temp., ° F.	Hardness, DPH	Yield Strength, p. s. i.	Tensile Strength, p. s. i.	El., per cent	Bend Angle, D=2.25t, degrees
74508	(1)	1,400	358	99,200	186,400	10	75
74508	(1)	1,500	373	44,000	170,400	10	180
74508	(1)	1,600	348	74,250	171,750	11	180
74508	(1)	1,700	210	48,800	164,000	18	180
74508	(1)	1,750	210	52,065	160,610	20	180
74508	(1)	1,800	216	53,700	157,500	25	180
74508	(1)	1,850	210	53,000	156,000	27	180
74508	(1)	1,900	216	51,200	153,300	29	180
74508	(1)	1,950	210	50,900	152,090	27	180
74508	(1)	2,000	210	53,750	150,500	27	180
74508	(1)	2,100	215	61,160	142,800	20	180
74508	(2)	1,700	435	166,850	205,000	11	180
74508	(2)	1,750	424	153,200	195,500	12	180
74508	(2)	1,800	343	104,500	168,500	22	180
74508	(2)	1,850	383	123,300	177,100	18	180
74508	(2)	1,900	393	115,640	171,450	17	180
74508	(2)	1,950	393	128,500	180,000	15	180
74508	(2)	2,000	393	136,300	181,200	14	180

* (1) As annealed. (2) Annealed at given temperature; 2 hrs. at -100° F.; 2 hrs. at 750° F.

These data are taken from tests performed on heat No. 74508 which is a commercial 10-ton heat of steel made and produced in accordance with the normal steel mill practice having the benefit of a protective slag covering. This heat was annealed at successively higher temperatures between 1500° F. and 2100° F., it being noted that the steel must be annealed at at least 1675° F. in order to possess at least 70% austenite as evidenced by the low tensile and yield strengths together with the low hardness of 95 Rb. Upon subzero cooling at a temperature of -100° F. for two hours, plus a tempering treatment at 750° F. for two hours, the yield strength in the tempered condition is greater than the tensile strength in the annealed condition as can be seen from Table III. A corresponding increase is also noted in the resulting hardness of this steel while at the same time a bend angle ductility of 180° is maintained. Subsequent tests upon this same heat of steel when initially annealed at 1800° F. and higher have resulted in a substantial decrease in the yield strength. A decrease is also noted in the hardness and tensile strengths, as is more clearly shown by the curves of Figs. 1 and 2. Thus it is evident that steels made with the benefit of a slag covering, as for example heat Nos. 74508, 82661, 92370, 92608, 92546 and 82401 identified in Table II and which inherently possess sub-

stantially smaller amounts of inclusions and do not have a substantially coarse equiaxed grain structure because of the substantially large amount of hot deformation in reducing the steel from its ingot form, must be heat treated within the annealing temperature range of 1675° F. and 1775° F. in order to develop their optimum properties. While all of the reasons for this are not known, it is believed that the primary factors which cause this effect are the inclusions and the amount of hot deformation which in turn is related to the grain size.

Referring now to the drawings, Fig. 1 illustrates the effect of the annealing temperature upon the properties of the tensile strength, yield strength, hardness and elongation of the steel in the annealed condition. Thus, as can be seen from the curves of Fig. 1, a temperature of about 1675° F. is needed in order to obtain low hardness, high elongation and low yield strength which are characteristic of this alloy when it contains at least 70% austenite. The effect of the temperature on the hardness, yield strength, tensile strength and elongation is illustrated by reference to curves 10, 12, 14 and 16, respectively, of Fig. 1.

It is significant to point out that where a double forming operation is required in producing the steel of this invention, it may be advantageous to conduct the first annealing treatment at about 1900° F., thereby obtaining the benefit of the high percentage of elongation as

shown by curve 16 with the substantially low hardness and yield strength as illustrated by curves 10 and 12, respectively. Upon subsequent annealing prior to the final forming operation, the steel may be heat treated at about 1700° F. and thereafter formed into its final shape and then subzero cooled at -100° F. and tempered at 750° F. to develop its optimum properties as shown by the curves 18, 20, 22 and 24 of Fig. 2 which illustrate the effect of the annealing temperature on the hardness, yield strength, tensile strength and elongation, respectively. Thus heat No. 74508, which is a 10-ton heat of steel made and produced with the benefit of a slag covering, will have its optimum properties developed when annealed at about 1700° F. followed by the subzero cooling and tempering treatment as described hereinbefore. In all cases where the steel is produced under a protective slag the steel should be subjected to a final anneal between 1675° F. and 1775° F., as a final anneal at 1800° F. gives poor results as illustrated by the curves of Fig. 2 when such annealed steel is subjected to the subsequent subzero cooling and tempering treatments described hereinbefore. In all cases, however, stainless steels which are selected in the manner set forth hereinbefore are amenable to the heat treatment described hereinabove, the only consideration being that the an-

nealing temperature required to develop the optimum properties when subsequently treated as described is influenced by the variables which affect the Ms temperature, namely the amount of metal carbides precipitated, the cleanliness of the steel, and the grain size, as influenced by the amount of hot deformation to which the alloys are subjected.

Referring to Figs. 3, 4 and 5 of the accompanying drawing, reference may be had to the microstructure of the steel DE-93 as produced during the different stages of heat treatment described hereinbefore. Each of the photomicrographs of Figs. 3, 4 and 5 is taken at a magnification of 500X.

Fig. 3 illustrates the microstructure of DE-93 as cooled from an annealing temperature of 1800° F., such steel consisting of a duplex structure of islands of ferrite 30 surrounded by a matrix of austenite 32. Since the austenite 32 is the continuous phase, the steel is in its ductile condition. Particular notice must be given to the fact that there is no evidence of undissolved or precipitated metal carbides at the grain boundaries between the austenite 32 and the ferrite 30 thus insuring a balanced and stable austenite 32 when the composition of the steel is selected in accordance with the hereinbefore mentioned equations and annealed and cooled to room temperature as previously described.

Referring now to Fig. 4, there is illustrated the microstructure of DE-93 steel of Fig. 3 as taken at a magnification of 500X after the subzero cooling treatment at a temperature in the range given for one half hour, it being noted that the basic duplex structure has not been changed. However, while the islands of ferrite 30 are still surrounded by a continuous matrix, the matrix has transformed to martensite 34. Since the martensite has been recently formed, it possesses little difference in etching characteristics than austenite 32 of Fig. 3; therefore the continuous phase of martensite 34 of Fig. 4 bears a close resemblance to the continuous phase of austenite 32 of Fig. 3. Again it is noteworthy to point out that in subzero cooled condition, there is no evidence of a metal grain boundary precipitate.

In Fig. 5, the microstructure of the steel DE-93 after tempering at 750° F. for two hours is illustrated. The basic duplex structure of islands of ferrite 30 surrounded by a matrix of tempered martensite 36 is maintained. There is no evidence of any metal carbide grain boundary precipitate thereby insuring a greater resistance to intergranular corrosion than similar steels hardened by a double aging treatment, for example, alloy B. The matrix of Fig. 5, while containing tempered martensite 36, does not show the characteristic acicular martensitic needle. This, however, is due solely to etching characteristics alone. While some change can be noted in the matrix of tempered martensite 36 as contrasted with the matrix of martensite 34 in Fig. 4, the change does not reveal the true character of the martensite.

The ductility of the steel of this invention is clearly illustrated by reference to Figs. 6 and 7 of the drawing, which figures comprise photographs of strips of the steel DE-93 as taken at two different angles at different stages of the treatment. Thus the strips 40 and 42 of Figs. 6 and 7, respectively, illustrate the bend angle ductility of 180° after cooling from the annealing temperature of 1800° F., 44 and 46 of Figs. 6 and 7, respectively, illustrate the loss of some of the bend angle ductility after the subzero treatment since such bend ductility is reduced to not more than 120°, and 48 and 50 of Figs. 6 and 7, respectively, illustrate the recovery of bend angle ductility after the steel is tempered for two hours at 750° F., the bend angle ductility for such tempered steel being again 180°.

One of the outstanding mechanical properties possessed by the steel selected and treated in accordance with this invention is the impact strength. Representative steels

of this invention possess an impact strength of about 50 ft.-lbs. at room temperature. When tested at -40° F., such steels have an impact strength of about 35 ft.-lbs. Comparing these results with those obtained upon testing alloy A in its heat treated condition which is found to have an impact strength of 10 ft.-lbs., it is seen that alloy A possesses but one-fifth of the impact strength of the steel produced in accordance with this invention. This is even more remarkably illustrated with alloy B which in its heat treated condition has an impact strength of but 5 ft.-lbs. at room temperature. In other words, the steel of this invention may have as much as ten times greater impact strength than prior art steels of similar composition. This holds true even when the impact strength is measured at -40° F. The difference in impact strengths between the steel produced in accordance with the teachings of this invention and alloys A and B, is primarily attributable to the selection of the composition and the method in which the hardening takes place. In the process employed in producing my steel, as was hereinbefore stated, one of the primary considerations is the prevention of the precipitation of a continuous envelope of metal carbides at the grain boundaries from the austenite phase. While alloy B is a stable austenitic alloy having an Ms temperature far below room temperature, the alloy is hardened by precipitating metal carbides which usually takes place at the grain boundaries thereby detracting from the balance and stability of the austenitic matrix. Upon the subsequent heat treatments, the steel transforms to increase the hardness and strength but with adverse effect upon the impact strength. The continuous envelope of carbide precipitation not only detrimentally affects the impact strength, but has an extremely detrimental effect upon the corrosion resistance. When alloys A and B were tested for two 48-hour periods in boiling 65% HNO₃, the tests had to be discontinued because of excessive losses at the rates of .0305 and .0847 inch penetration per month, respectively. On the other hand, the steel produced in accordance with this invention has a corrosion resistance in boiling HNO₃ of only about .005 inch penetration per month which is comparable to type 430, and a corrosion resistance in 20% salt spray at least as good as that obtained with type 316. The superior corrosion resistance may be attributable to the absence of precipitated metal carbides at the austenitic grain boundaries which, as is well known to the art, is the principal cause of intergranular corrosion.

The steel produced in accordance with this invention has excellent physical properties at elevated temperatures. As an example of the properties obtained at elevated test temperatures, reference may be had to the results recorded in Table V for tests on the steel of heat No. 92370 after the heat treatment specified in Table III.

Table V

Test Temp.	0.2% Offset Y. S. (p.s.i.)	T. S., p. s. i.	Percent El. in 2 Inch.
400° F.	137,640	193,400	15.5
600° F.	139,860	194,800	13.0
700° F.	129,880	196,800	10.5
800° F.	129,870	192,810	10.5
900° F.	111,930	178,550	15.0
1,000° F.	96,580	143,630	16.0

The steel which is selected in accordance with the teachings of this invention requires no special melting procedures or fabrication procedures foreign to any of the 300 series stainless steels. Further, the steel may be cast into the shape and size of articles of manufacture which do not require further fabrication and when subjected to the heat treatment described will respond thereto. The alloys of optimum range 2 are particularly adapted to the making of precision castings and the like, as well as wrought products such as sheet, strip and plate. The annealing equipment used in the processing of the steel

is the same as is used in general steel mill practices today. While refrigeration equipment may be desirable for the subzero treatment of this steel, a satisfactory temperature may be obtained by the use of a mixture of acetone and Dry Ice. The tempering treatment is accomplished in any standard equipment. Thus, the proper selection of steel followed by the treatment described results in a steel having an outstanding combination of physical properties in that it has good hardness, ductility, impact strength and corrosion resistance.

This is a continuation-in-part of my co-pending application Serial No. 477,216, filed December 23, 1954, and, now abandoned, which in turn is a continuation-in-part of my then pending application Serial No. 442,168, filed July 8, 1954, and which is now abandoned.

I claim:

1. In the process of producing stainless steel composed of from about 0.03% to 0.15% carbon, from about 12.0% to 18.0% chromium, from about 3.5% to about 7.0% nickel, from about 2.0% to about 3.5% molybdenum, up to about 0.5% maximum silicon, from about 0.25% to about 2.0% manganese, from about 0.05% to about 0.15% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a composition within the range given to provide a steel having a stability factor Δ in accordance with the formulae

$$\Delta = \% \text{Ni} + 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] < 20$, and

$$\Delta = \% \text{Ni} + 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] > 20$

of -3.82 to -4.65 when $\% \text{C} + \% \text{N} = < .20$ and $\% \text{Cr} = 16$ to 18 and

of -0.10 to -1.0 when $\% \text{C} + \% \text{N} = > .20$ and $\% \text{Cr} = 14.5$ to 16

annealing the steel at a temperature between 1675°F. and 2000°F. , cooling the steel to room temperature at a rate sufficient to retain at least 70% austenite, subzero cooling the steel at a temperature between -80°F. and -110°F. to transform the retained austenite to martensite to develop the hardness of the steel, and thereafter subjecting the steel to a tempering treatment at a temperature between 750°F. and 900°F. to develop the yield strength and ductility of the steel without adversely affecting the hardness and corrosion resistance.

2. In the process of producing stainless steel composed of from about 0.03% to 0.15% carbon, from about 12.0% to 18.0% chromium, from about 3.5% to about 7.0% nickel, from about 2.45% to about 3.5% maximum molybdenum, up to about 0.5% maximum silicon, from about 0.25% to about 2.0% manganese, from about 0.05% to about 0.10% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a composition within the range given to provide a steel having a stability factor Δ in the range between -3.82 and -4.65 when

$$\Delta = \% \text{Ni} - 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] < 20$, and

$$\Delta = \% \text{Ni} + 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] > 20$

annealing the steel at a temperature between 1675°F. and 2000°F. , cooling the steel to room temperature at a rate sufficient to retain at least 70% austenite, subzero cooling the steel at a temperature between -80°F. and -110°F. to transform the retained austenite to martensite to develop the hardness of the steel, and thereafter subjecting the steel to a tempering treatment at a

temperature between 750°F. and 900°F. to develop the yield strength and ductility of the steel without adversely affecting the hardness and corrosion resistance.

3. A corrosion resistant stainless steel composed of 0.03% to 0.15% carbon, 12% to 18% chromium, 3.5% to 7.0% nickel, from about 2.45% to about 3.5% maximum molybdenum, up to about 0.5% maximum silicon, 0.25% to 2% manganese, from about 0.05% to 0.10% nitrogen and the balance iron with incidental impurities, the steel having a balanced composition to provide a stability factor Δ between -3.82 and -4.65 when

$$\Delta = \% \text{Ni} - 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] < 20$, and

$$\Delta = \% \text{Ni} + 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] > 20$

the steel having a hardness in excess of 40 Rc together with good ductility and yield strength and produced by the heat treatment of claim 2 without impairment of the corrosion resistance thereof.

4. In the process of producing a ductile stainless steel having a hardness in excess of 40 Rc in the hardened condition and having as essential alloying elements 12% to 18% chromium, 3.5% to 7.0% nickel and from about 2.45% to 3.5% maximum molybdenum, together with not more than 0.15% carbon, not more than 0.5% silicon, 0.25% to 2% manganese, from about 0.05% to 0.10% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a balanced composition in the range given to provide a stability factor Δ which lies in the range between -3.82 and -4.65 when

$$\Delta = \% \text{Ni} - 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] < 20$, and

$$\Delta = \% \text{Ni} + 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] > 20$

annealing said steel at a temperature within the range between 1675°F. and 2000°F. , cooling said steel to room temperature at a rate sufficient to retain at least a 70% austenitic structure, subzero cooling the steel to a temperature between -80°F. and -110°F. , holding the steel at a subzero temperature for a period of time between about one half hour and two hours to develop the hardness thereof, and thereafter tempering said steel at a temperature in the range between 750°F. and 900°F. for a period of time ranging between one hour and eight hours to impart thereto the characteristics of good hardness, strength, ductility and corrosion resistance.

5. In the process of producing stainless steel composed of from 0.06% to 0.15% carbon, from about 14.5% to 18.0% chromium, from about 4.0% to about 4.5% nickel, from about 2.25% to about 3.5% molybdenum, up to about 0.5% maximum silicon, from about 0.25% to about 2.0% manganese, from about 0.05% to about 0.13% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a composition within the range given to provide a steel having a stability factor Δ in accordance with the formulae

$$\Delta = \% \text{Ni} - 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] < 20$, and

$$\Delta = \% \text{Ni} + 1/12[\% \text{Cr} + 1.5(\% \text{Mo}) - 20]^2 + 1/2(\% \text{Mn}) + 35(\% \text{C} + \% \text{N}) - 14$$

where $[\% \text{Cr} + 1.5(\% \text{Mo})] > 20$

of -3.82 to -4.65 when $\% \text{C} + \% \text{N} = < .20$ and $\% \text{Cr} = 16$ to 18 and

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of -0.10 to -1.0 when $\%C + \%N \geq .20$ and $\%Cr = 14.5$ to 16 ,

annealing the steel at a temperature between 1675° F. and 2000° F., cooling the steel to room temperature at a rate sufficient to retain at least 70% austenite, subzero cooling the steel at a temperature between -80° F. and -110° F. to transform the retained austenite to martensite to develop the hardness of the steel, and thereafter subjecting the steel to a tempering treatment at a temperature between 750° F. and 900° F. to develop the yield strength and ductility of the steel without adversely affecting the hardness and corrosion resistance.

6. A corrosion resistant stainless steel composed of 0.06% to 0.15% carbon, 14.5% to 18.0% chromium, 4.0% to 4.5% nickel, 2.25% to 3.5% molybdenum, up to about 0.5% maximum silicon, 0.25% to 2.0% manganese, from about 0.05% to about .13% nitrogen and the balance iron with incidental impurities, the steel having a balanced composition to provide a stability factor Δ in accordance with the formulae

$$\Delta = \%Ni - 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] < 20$, and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] > 20$

of -3.82 to -4.65 when $\%C + \%N < .20$ and $\%Cr = 16$ to 18 and

of -0.10 to -1.0 when $\%C + \%N \geq .20$ and $\%Cr = 14.5$ to 16

the steel having a hardness in excess of 40 R_c together with good ductility and yield strength and produced by the heat treatment of claim 5 without impairment of the corrosion resistance thereof.

7. In the process of producing stainless steel composed of from about 0.09% to 0.15% carbon, from about 14.5% to 16.0% chromium, from about 4.0% to about 4.5% nickel, from about 2.25% to about 3.5% molybdenum, up to about 0.5% maximum silicon, from about 0.25% to about 2.0% manganese, from about 0.07% to about 0.13% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a composition within the range given to provide a steel having a stability factor Δ in accordance with the formulae

$$\Delta = \%Ni - 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] < 20$, and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] > 20$

of -0.10 to -1.0 when $\%C + \%N \geq .20$ to .30 and $\%Cr = 14.5$ to 16

annealing the steel at a temperature between 1675° F. and 2000° F., cooling the steel to room temperature at a rate sufficient to retain at least 70% austenite, subzero cooling the steel at a temperature between -80° F. and -110° F. to transform the retained austenite to martensite to develop the hardness of the steel, and thereafter subjecting the steel to a tempering treatment at a temperature between 750° F. and 900° F. to develop the yield strength and ductility of the steel without adversely affecting the hardness and corrosion resistance.

8. In the process of producing stainless steel composed of from about 0.06% to 0.12% carbon, from about 16.0% to 17.5% chromium, from about 4.0% to about 4.5% nickel, from about 2.25% to about 3.5% molybdenum, up to about 0.5% maximum silicon, from about 0.25% to about 2.0% manganese, from about 0.05% to about 0.15% nitrogen and the balance iron with incidental im-

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purities, the steps comprising, selecting a composition within the range given to provide a steel having a stability factor Δ in accordance with the formulae

$$\Delta = \%Ni - 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] < 20$, and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] > 20$

of -3.82 to -4.65 when $\%C + \%N < .20$ and $\%Cr = 16$ to 17.5

annealing the steel at a temperature between 1675° F. and 2000° F., cooling the steel to room temperature at a rate sufficient to retain at least 70% austenite, subzero cooling the steel at a temperature between -80° F. and -110° F. to transform the retained austenite to martensite to develop the hardness of the steel, and thereafter subjecting the steel to a tempering treatment at a temperature between 750° F. and 900° F. to develop the yield strength and ductility of the steel without adversely affecting the hardness and corrosion resistance.

9. In the production of a stainless steel article composed of from about 0.03% to 0.15% carbon, from about 12.0% to 18.0% chromium, from about 3.5% to 7.0% nickel, from about 2.45% to 3.5% maximum molybdenum, up to about 0.5% maximum silicon, from about 0.25% to 2.0% manganese, from about 0.05% to 0.10% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a composition within the range given to provide a steel having a stability factor Δ in the range between -3.82 and -4.65 when

$$\Delta = \%Ni - 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] < 20$, and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] > 20$

fabricating the steel to a semi-finished mill product such as plate, bar, sheet and strip form, annealing the semi-finished mill product at a temperature in the range between 1675° F. and 2000° F. for a period of time sufficient to form at least 70% austenite, cooling the semi-finished mill product at a sufficiently fast rate to retain at least 70% austenite and without precipitating a continuous envelope of grain boundary metal carbides, forming said semi-finished mill product to the predetermined shape and size of the finished article, subzero cooling the article to transform the retained austenite to martensite, and tempering the article at a temperature in the range between 750° F. and 900° F. without precipitating any grain boundary metal carbides to develop the yield strength and ductility of the article without adversely affecting the hardness, corrosion resistance, finish and shape of the fabricated article.

10. In the process of producing stainless steel composed of from about 0.03% to 0.15% carbon, from about 14.5% to 18.0% chromium, from about 3.5% to about 7.0% nickel, from about 2.0% to about 3.5% molybdenum, up to about 0.50% maximum silicon, from about 0.25% to about 2.0% manganese, from about 0.05% to about 0.15% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a composition within the range given to provide a steel having a stability factor Δ in accordance with the formulae

$$\Delta = \%Ni - 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] < 20$, and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

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where $[\%Cr+1.5(\%Mo)] > 20$

of -3.82 to -4.65 when $\%C + \%N = < 0.20$ and $\%Cr = 16$ to 18 and
 of -0.10 to -1.0 when $\%C + \%N = > 0.20$ and $\%Cr = 14.5$ to 16

making the steel using a protective slag covering, annealing the steel at a temperature between 1675° F. and 1775° F., cooling the steel to room temperature at a rate sufficient to retain at least 70% austenite, subzero cooling the steel at a temperature between -80° F. and -110° F. to transform the retained austenite to martensite to develop the hardness of the steel, and thereafter subjecting the steel to a tempering treatment at a temperature between 750° F. and 900° F. to develop the yield strength and ductility of the steel without adversely affecting the hardness and corrosion resistance.

11. In the process of producing a ductile stainless steel having a hardness in excess of 40 Rc in the hardened condition and having as essential alloying elements 14.5% to 18% chromium, 4.0% to 4.5% nickel and from about 2.25% to 3.5% maximum molybdenum, together with from 0.06% to 0.15% carbon, not more than 0.5% silicon, 0.25% to 2% manganese, from about 0.05% to 0.13% nitrogen and the balance iron with incidental impurities, the steps comprising, selecting a balanced composition in the range given to provide a steel having a stability factor Δ in accordance with the formulae

$$\Delta = \%Ni - 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] < 20$, and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] > 20$

of -3.82 to -4.65 when $\%C + \%N = < 0.20$ and $\%Cr = 16$ to 18 and
 of -0.10 to -1.0 when $\%C + \%N = > 0.20$ and $\%Cr = 14.5$ to 16

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making the steel using a protective slag covering, annealing said steel at a temperature within the range between 1675° F. and 1775° F., cooling said steel to room temperature at a rate sufficient to retain at least a 70% austenitic structure, subzero cooling the steel to a temperature between -80° F. and -110° F., holding the steel at the subzero temperature for a period of time between about one half hour and two hours, and thereafter tempering said steel at a temperature in the range between 750° F. and 900° F. for a period of time ranging between one hour and eight hours to impart thereto the characteristics of good hardness, strength, ductility and corrosion resistance.

12. A corrosion resistant stainless steel composed of 0.03% to 0.15% carbon, 14.5% to 18% chromium, 3.5% to 7.0% nickel, from about 2.0% to about 3.5% molybdenum, up to about 0.5% maximum silicon, 0.25% to 2% manganese, from about 0.05% to 0.15% nitrogen and the balance iron with incidental impurities, the steel having a balanced composition to provide a stability factor Δ in accordance with the formulae

$$\Delta = \%Ni - 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] < 20$, and

$$\Delta = \%Ni + 1/12[\%Cr + 1.5(\%Mo) - 20]^2 + 1/2(\%Mn) + 35(\%C + \%N) - 14$$

where $[\%Cr + 1.5(\%Mo)] > 20$

of -3.82 to -4.65 when $\%C + \%N = < 0.20$ and $\%Cr = 16$ to 18 and
 of -0.10 to -1.0 when $\%C + \%N = > 0.20$ and $\%Cr = 14.5$ to 16

the steel having a hardness in excess of 40 Rc together with good ductility and yield strength and produced by the heat treatment of claim 10 without impairment of the corrosion resistance thereof.

References Cited in the file of this patent

Laurssen and Greene: Trans. A. S. S. T., vol. 19, pages 501-534, esp. pages 501-504; publ. 1932.