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HIGH STRENGTH, NOTCH DUCTILE STAINLESS STEEL PRODUCTS

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No Drawing. Filed July 27, 1964, Ser. No. 385,459

7 Claims. (Cl. 148—12)

The present invention is a continuation-in-part of our copending patent application Serial No. 244,861, filed December 17, 1962.

The present invention relates to the production of stainless steel products, and more particularly, to the production of stainless steel products characterized by high strength and improved toughness qualities.

Heretofore, the art has endeavored to produce special corrosion-resistant metal products, e.g., corrosion-resistant metal sheet, for use in structures which must sustain high stresses while the structures are in contact with corrosive materials or are in the presence of corrosive environments. Pressure vessels for holding corrosive fluids under high pressures are examples of such structures. Although the prior metallurgical art has achieved considerable success in producing corrosion-resistant metals, the corrosion-resistant metals produced by prior art methods still have serious shortcomings as engineering materials for use where high stresses must be sustained. In order for a metal to be entirely satisfactory for use in highly stressed structures, it is not only necessary that the metal be characterized by sufficiently high yield strength or ultimate tensile strength such as are determined by conventional tension tests of smooth (unnotched) specimens of the metal, but it is also necessary that the metal be characterized by adequate resistance to brittle failure. Past experience has proven that brittle failure can occur in a highly stressed structure made of a ductile metal even though the average stresses in the metal of the structure do not exceed the yield strength of the metal. Brittle failures of metal structures, particularly steel structures, have occurred since steel was first used as a structural material and have included failures in pressure vessels, gas transmission pipe lines, storage tanks, ships, bridges and power shovel booms. However, it was not until the Second World War that brittle fractures became recognized as a serious problem meriting systematic study. With respect to this problem, stress analysis has established that stresses in a structure can concentrate at the roots of notches in the structure to develop localized stress concentrations that are many times greater than the average stresses in the structure. Stress concentrations can develop at intentionally formed notches such as threads and sharp fillets. Metallic discontinuities such as internal flaws and surface scratches also often act as notches and give rise to stress concentrations. Metallurgical investigations of the effects of stress-concentrating notches on the behavior of metals have found that these effects cause some metals to behave in a brittle manner, whereas other metals behave in a ductile manner when such notches are present. These latter metals are referred to as being "notch ductile" or "insensitive to notch effects" or as "characterized by adequate notch toughness." Notch toughness is the capability or capacity of a metal to yield plastically under high localized stress such as might occur at the root of a notch. By so yielding, a metal characterized by adequate notch toughness or notch ductility can relieve itself of localized stress concentrations. Thus, brittle failure due to stress concentration at notches is avoided if a metal is characterized by notch ductility. Special tests have been developed for the purpose of evaluating notch toughness since it has been found

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that data obtained by conventional testing of smooth specimens, e.g., data such as yield strength, ultimate tensile strength, elongation and reduction of area, do not accurately portray the notch toughness characteristics of metals. While early investigations employed Charpy or Izod impact tests of notched specimens to evaluate notch toughness, more recent investigations have indicated that these impact tests are not sufficiently severe evaluations for many present day purposes; also, these impact tests are not well suited for evaluation of sheet metal products because of the shape of the specimen required for these tests. Particular importance is attached to the problem of evaluating notch toughness of sheet metal products, especially sheet metal products of high strength steel, i.e., steel characterized by a yield strength approaching or exceeding 230,000 p.s.i., because there exist pressing needs for such materials for the manufacture of lightweight, thin-walled pressure vessels. The notch tension test, wherein a notched specimen is fractured in tension, has become widely accepted by metallurgists as a means of accurately evaluating notch toughness of metals in sheet form and also in other forms. For evaluating notch toughness of high strength steel, special sharp-notch tensile test specimens having critically dimensioned sharp notches must be employed since it has been shown that the minimum critical size of a flaw that can induce brittle failure in steel decreases with an increase in the strength level of the steel. Such a sharp-notch tensile test specimen that is specially adapted for accurate evaluation of notch toughness of high strength steel is described in the paper of G. B. Espey, M. H. Jones and W. F. Brown, Jr., "The Sharp Edge Notch Tensile Strength of Several High-Strength Steel Sheet Alloys," published in American Society for Testing Materials Proceedings, vol. 59, 1959, and is illustrated in FIGURE 1 of that paper. Although some of the dimensions of a sharp-notch tensile specimen are not critical, it is most important for the purpose of accurately evaluating notch toughness of high strength steel that the notch root radius of a sharp-notch tensile specimen be not greater than 0.001 inch and that the notch configuration and dimensions be such as to result in a stress concentration factor K_t of at least 18 in the undeformed specimen.

In evaluating notch toughness, the notch-tensile test is used to determine notch strength and, in conjunction with the conventional tensile test, is also used to determine the notch/tensile strength ratio. This strength ratio is the criterion for determining whether a metal is notch brittle or notch ductile. Notch strength (notch tensile strength) is the ratio of the maximum load sustained in a tensile test of a notched specimen to the original minimum cross-sectional area of the specimen. The notch/tensile strength ratio is the ratio of notch strength to ultimate tensile strength. For purposes of describing the invention metals characterized by notch/tensile strength ratios of at least about 1, i.e., 0.95 or greater, are deemed notch ductile, whereas metals characterized by lower notch-tensile strength ratios are deemed notch brittle or notch sensitive. Correspondingly, where sharp-notch tensile specimens are used in making similar determinations, the notch toughness characteristics that thereby are determined are referred to as sharp-notch strength, sharp-notch/tensile strength ratio, sharp-notch ductility, etc. For high strength steels, the sharp-notch tension test provides, in conjunction with the conventional tension test, a direct indication of the ability of a metal to eliminate high stress concentrations by plastic flow.

Austenitic nickel-chromium stainless steels have been found useful and satisfactory for a wide variety of structures wherein corrosion resistance and relatively low, or moderate, levels of strength are required. The term austenitic is used to designate a class of steels on the

basis of the behavior of the steels. Austenitic steel is defined in the ASM Metals Handbook, 8th edition, page 3, as "an alloy steel whose structure is normally austenitic at room temperature." Austenitic nickel-chromium stainless steels ordinarily contain about 16% to about 26% chromium, about 6% to about 22% nickel, about 0.5% to about 2% manganese, about 0.5% to about 1% silicon and small amounts of carbon, e.g., 0.1% carbon. Other elements can also be present in these steels either as impurities or as alloying elements added to develop certain desirable characteristics. The chemical composition of austenitic stainless steel is so proportioned that the steel is austenitically structured, i.e., at least a major proportion of the steel in austenite, when the steel is at room temperature and in the annealed condition. Some compositions of austenite are described as "metastable" to denote the fact that such austenite is not a phase in a physico-chemical sense because it does not maintain its identity and characteristics under all conditions of heat or mechanical treatment but instead can become transformed into martensitic ferrite (martensite). The metastability of austenite is relative in the sense that the chemical composition of austenite effects its transformability by thermal and/or mechanical methods. Stainless steels containing metastable austenite of such a chemical composition that this austenite is stable at room temperature and can be transformed by some practical method, such as cold working at a temperature not lower than the boiling point of liquid hydrogen, are described as transformable austenite stainless steels. The elements which have the most important effect upon transformability of stainless steel are nickel, chromium, manganese, silicon, carbon and nitrogen. These alloying elements do not have the same relative effect on the transformability of austenite. From experimental data it has been determined that the net effect of these alloying elements upon transformability of austenitic nickel-chromium stainless steel can be approximated by means of the equivalent nickel index (ENI). This number is computed by the formula

$$\text{ENI} = \text{Percent Ni} + 0.68 (\text{percent Cr}) + 0.55 (\text{percent Mn}) + 0.45 (\text{percent Si}) + 27 (\text{percent C} + \text{percent N})$$

wherein the numerical factors are the empirical values of nickel equivalents determined by G. H. Eichelman and F. C. Hull and reported in Transactions of American Society for Metals, vol. 45, page 95, and wherein percent Ni, percent Cr, percent Mn, percent Si, percent C and percent N are the weight percentages of these elements in the steel. In general, transformable austenitic stainless steels have an equivalent nickel index of at least about 17 and not greater than about 30. Transformable austenitic stainless steels are well known in the metallurgical art and this art includes a number of teachings whereby one skilled in the art can readily determine whether a stainless steel is transformable.

Although the strength of annealed austenitic nickel-chromium stainless steels is normally low, prior art methods are available for producing stainless steel products whereby the strength of these steels is increased to moderate levels and even high levels. These processes include work hardening, transformation hardening and precipitation hardening, this last-named process being accomplished by both alloying and heat treating. The prior art of steel processing also includes processes wherein the strengths of some austenitic nickel-chromium stainless steels are greatly increased by subzero working, i.e., by deforming the steels while the steels are at temperatures below zero degrees Fahrenheit. However, increasing difficulty in obtaining adequate notch toughness, especially sharp-notch ductility, has been encountered as the strength of austenitic nickel-chromium stainless steel is progressively increased from a relatively low level to a moderate level and up to a high level by processes of the prior art, and these processes still have serious shortcomings as processes for producing stainless steel product characterized

by both high strength and sharp-notch ductility. One of the difficulties is that a disadvantageously high degree of anisotropy is developed in stainless steel products when the steel is cold rolled by large amounts, i.e., amounts of cold rolling resulting in 50% or more reduction in cross-sectional area. Another difficulty is that high strength stainless steel products produced by subzero and room temperature working processes of the prior art are sharp-notch brittle. Further, the corrosion resistance and/or notch toughness of high strength stainless steel products produced by precipitation hardening processes is not satisfactory for some purposes. These difficulties are even greater in the case of the need for corrosion resistant, high strength metal products for use in structures which are used at low temperatures, e.g., pressure vessels for containing liquid oxygen, since it is well established that the notch toughness of stainless steel generally decreases as the temperature of the steel decreases. Thus, there is need for an improved process whereby austenitic nickel-chromium stainless steel products characterized by an improved combination of high strength and sharp-notch ductility may be successfully produced. Although many attempts were made to overcome the foregoing difficulties and disadvantages, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that austenitic nickel-chromium stainless steel products characterized by an improved combination of high strength and sharp-notch ductility can be produced by a new and improved process, whereby a special austenitic nickel-chromium stainless steel workpiece is deformed by cold working at or below room temperature including temperatures below zero degrees Fahrenheit.

It is an object of this invention to provide a new and improved process for producing improved austenitic nickel-chromium stainless steel products.

The invention also contemplates providing a new and improved austenitic nickel-chromium stainless steel product characterized by an improved combination of high strength and sharp-notch ductility.

It is another object of the invention to provide a new sharp-notch ductile stainless steel which provides a yield strength of the order of 230,000 p.s.i. after having been cold worked at about room temperature and heat treated and to also provide a new stainless steel product having a yield strength of the order of 250,000 p.s.i.

Broadly stated, the present invention contemplates the production of a sharp-notch ductile, nickel-chromium stainless steel product by a new process comprising the steps of providing a workpiece of a special transformable austenitic, low-silicon, nickel chromium stainless steel, the structure of said workpiece comprising a major proportion of austenite, cold working the workpiece at or below room temperature such as by subzero working the workpiece to thereby produce a martensitic structure therein and thereafter heat treating the cold worked workpiece for about 1 hour to about 48 hours at about 700° F. to about 850° F. The special low-silicon stainless steel of the workpiece contains, in weight percent, not more than about 0.15% silicon, about 4% to about 12% nickel and about 15% to about 22% chromium and is a transformable austenitic steel that is normally austenitically structured when at room temperature or when at subzero working temperatures for short periods of time, e.g., up to about 1 hour, and can be transformed to be martensitically structured by cold working at room or subzero temperatures. Metalworking operations which can be performed to cold work (plastically deform) the special workpiece to produce new and improved stainless steel products in accordance with the invention include rolling, forging, stretching, drawing, spinning, bending, swaging, hydroforming, explosive forming and roll forming. Stainless steel products produced in accordance with the invention have improved strength and hardness and improved

notch toughness characteristics, including sharp-notch ductility and notch impact strength and are also characterized by the corrosion resistance of austenitic stainless steel in normal conditions. The present invention incorporates the discovery made by us that in processes of subzero working or cold working at about room temperature and subsequently heat treating transformable austenitic nickel-chromium stainless steel workpieces to produce stainless steel products of improved strength and hardness, it is advantageous for the purpose of obtaining sharp-notch ductility, especially in high strength stainless steel products, that the stainless steel workpieces be characterized by containing not more than 0.15% silicon, i.e., that the workpieces be of low-silicon stainless steel.

In order to produce high strength stainless steel products having a yield strength of at least about 230,000 p.s.i. together with sharp-notch ductility by subzero working in accordance with the invention, a transformable austenitic stainless steel workpiece is provided which contains at least about 90% austenite, which has an equivalent nickel index of not less than about 19 and not more than about 25 and which contains not more than about 0.15% silicon, about 6% to about 10% nickel, about 16% to about 21% chromium, about 0.01% to about 1% manganese, about 0.01% to about 0.1% carbon, about 0.005% to about 0.1% nitrogen, with the balance essentially iron.

The new low-silicon stainless steel cold worked at room temperature, e.g., 40° F. to 100° F., and/or slightly below room temperature, i.e., temperatures as low as zero degrees Fahrenheit (0° F.), possesses good sharp-notch ductility and high yield strengths on the order of 230,000 p.s.i., e.g., 220,000 p.s.i. to about 240,000 p.s.i., and is characterized by an equivalent nickel index from 20.5 to 23. These steels contain not more than 0.15% silicon, about 4% to about 10% nickel, e.g., 5% to 10% nickel, and about 15% to about 19% chromium with the total percentage of nickel plus chromium being not greater than 25.2% and advantageously being within the range of from 22% to 25%, about 0.01% to about 1% manganese, 0.01% to about 0.1% carbon, about 0.005% to about 0.1% nitrogen with the balance iron. For obtaining a particularly good combination of yield strength and sharp-notch ductility, the stainless steels rolled at room temperature contain 5% to 7% or 8% nickel, about 16% to 19% chromium and have an equivalent nickel index of 21.1 to about 22, more advantageously 21.1 to 21.6, and the nickel plus chromium content is about 23 to 25. For obtaining good yield strength it is advantageous that the carbon content be 0.04% to 0.10% and it is essential that the steel contain at least 0.01% carbon.

Although the balance of the stainless steel compositions that are satisfactory for the workpiece of the invention are characterized herein as being essentially iron, it is to be understood that the term "balance essentially iron" does not exclude small amounts of other elements which can serve some useful purpose ancillary to the objects of the invention, e.g., up to about 1% columbium, up to about 0.5% titanium, up to about 0.2% aluminum, up to about 0.1% each of calcium, magnesium and/or zirconium, and up to about 0.01% boron. Columbium or titanium can serve the purpose of carbide stabilization and, for this purpose, columbium should be present in amounts equal to about ten times the carbon content or titanium should be present in amounts equal to about five times the carbon content of the steel. Titanium, aluminum, calcium, magnesium, zirconium and boron can serve purposes of deoxidation, malleabilization and/or purification. The balance of the stainless steels used in practicing the invention may also contain very small amounts of impurities such as sulfur, phosphorus, bismuth, antimony, tin, lead, arsenic, etc. However, the total amount of these impurities must be less than 0.03% of the steel, e.g., about 0.02% or less.

In practicing the invention by subzero working to produce a high strength stainless steel product character-

ized by sharp-notch ductility and a yield strength of at least 230,000 p.s.i., e.g., 250,000 p.s.i. and above, the aforescribed workpiece in advantageously subzero worked at a deformation temperature, i.e., the temperature of the workpiece at the time when deformation is commenced, not higher than about minus 40° F. and is thereafter heat treated as described hereinbefore. When deformation is accomplished in a series of steps, the steel is cooled sufficiently between each step to achieve the deformation temperature for the following step. Sufficient deformation is accomplished to transform austenite of the workpiece to martensite and to provide that the product comprise at least about 60% but not more than about 99% martensite, advantageously 85% to about 99% martensite. Amounts of deformation that are equivalent to reductions in thickness of about 20% to about 50% of the original thickness are sufficient for producing high strength products. The optimum amount of deformation required for developing high yield strength is a function of the nature of the deforming operation, the temperature of the metal at the start of deformation and the equivalent nickel index of the composition of the workpiece. In processes of the invention wherein deformation temperatures are in the range of about minus 40° F. to about minus 320° F. and deformation is accomplished by rolling a workpiece of the aforescribed composition characterized by an equivalent nickel index in the range of about 20 to about 25, sufficient amounts of rolling are those which reduce the thickness by at least about 20%. For example, where the deformation temperature is about minus 106° F., a satisfactory amount of deformation for producing high strength stainless steel products of the invention is accomplished by rolling to reduce the thickness of the workpiece by about 40%.

When cold working is performed at near room temperature or a little lower, the workpiece, which is in an austenitic condition, is deformed an amount equivalent to a reduction in thickness of about 20% to about 50% and the deformation temperature is controlled, if necessary, by cooling the sheets between passes to obtain a deformation temperature in the range from 0° F. to about 100° F. After cold working is completed, the product comprises at least about 60% but not more than about 99% martensite. However, it is to be pointed out that in performing the plastic deformation at room temperature, the summation of the nickel plus chromium contents, as indicated above herein, advantageously does not exceed a level of 25%.

In carrying the invention into practice, the ingredients for the stainless steel are melted in an induction furnace or any of the other furnaces employed for production of similar alloys. Vacuum melting or inert atmosphere melting can be employed if desired but such practices are not necessary for attaining the objects of the invention. When the stainless steel products of the invention are produced commercially, the workpieces will usually be hot worked and sometimes cold worked before being worked at subzero temperatures. Advantageously, workpieces which have been hot and/or cold worked are annealed before being cold worked at room temperature or subzero worked. A satisfactory annealing treatment is accomplished by heating the workpiece for about 1 hour to about 24 hours at a temperature of about 1800° F. to about 2050° F. and thereafter air cooling to room temperature. Annealing serves the purpose of austenitizing and softening the workpiece. For subzero working the workpieces are cooled prior to subzero working by any method that lowers the temperature of the workpieces to the deformation temperature of the process without transforming more than a small amount of austenite. For example, workpieces that are not more than 1 inch thick can be satisfactorily cooled to about minus 106° F. by immersion in a bath of Dry Ice and isopentane for about one-half hour, or such workpieces can be satisfactorily cooled to about minus 320° F. by immersion in

liquid nitrogen for about one-half hour. For best results, the workpieces should consist entirely of austenite at the beginning of subzero deformation, although the presence of small amounts, e.g., about 5%, of delta ferrite in the workpieces at this stage of the process are not highly detrimental to the characteristics of the finished product and satisfactory results can be produced even with workpieces comprising as little as 75% austenite. Maximum strength and hardness in the subzero rolled and heat treated product of the invention is achieved by producing a product comprising a very high proportion of martensite, e.g., 75% or 95% martensite.

Especially in regard to subzero rolling, particularly advantageous results including production of nickel-chromium stainless steel products characterized by yield strengths of at least 250,000 p.s.i. and sharp-notch tensile strength ratios of at least 0.95 are achieved in accordance with the invention by employing workpieces of chemical compositions characterized by an equivalent nickel index of about 21 to about 23 and containing about 0.01% to about 0.15% silicon, about 7% to about 8.5% nickel, about 18% to about 19% chromium, about 0.1% to about 1% manganese, about 0.04% to about 0.08% carbon, about 0.01% to about 0.04% nitrogen with the balance essentially iron. A satisfactory subzero working operation for producing such a product is to roll the workpiece at a deformation temperature in the range of about minus 100° F. to about minus 150° F., e.g., about minus 106° F., to reduce the thickness thereof by about 30% to about 50%, e.g., about 40%.

After room temperature or subzero working is complete, the product is heat treated for about 4 hours to about 48 hours, e.g., 24 hours, at a temperature in the range of about 750° F. to about 850° F., e.g., 800° F.

For the purpose of giving those skilled in the art a better understanding of the invention, the production of stainless steel products by subzero working processes in accordance with the invention and by other processes is illustrated by the following examples. Twelve heats of stainless steel alloys were melted in induction furnaces and cast into ingots. Six of these heats (Alloys 1 through 5, and A) were melted in vacuum and the other six (Alloys 6, 7, 8, B, C and D) were melted in an air atmosphere. Compositions of these alloys are set forth in Table I.

Table I

Alloy No.	Composition in Weight Percent							ENI ¹
	Ni	Cr	Mn	C	N	Si	Fe	
1.....	7.6	18.0	0.95	0.05	0.01	0.09	Bal.....	21.9
2.....	10.1	19.8	0.45	0.04	0.01	0.10	Bal.....	25.4
3.....	7.7	18.9	0.78	0.05	0.02	0.11	Bal.....	22.9
4.....	8.6	18.8	0.75	0.06	0.01	0.10	Bal.....	23.7
5.....	8.2	18.4	0.01	0.05	0.01	0.10	Bal.....	22.4
6.....	7.4	18.7	0.05	0.07	0.02	0.13	Bal.....	22.6
7.....	9.0	18.4	1.01	0.05	0.02	0.01	Bal.....	23.7
8.....	8.0	18.7	0.06	0.06	0.05	0.02	Bal.....	23.4
A.....	8.8	18.6	0.49	0.05	0.01	0.57	Bal.....	23.6
B.....	9.0	18.4	0.92	0.05	0.03	0.50	Bal.....	24.1
C.....	7.6	18.5	0.44	0.04	0.05	0.44	Bal.....	23.3
D.....	8.1	18.5	0.46	0.05	0.03	0.46	Bal.....	23.5

¹ ENI = Equivalent nickel index.

Alloys 1 through 8 are stainless steels of the special compositions contemplated by the invention. The compositions of Alloys A through D are not in accordance with the invention; instead, these compositions have silicon contents which are representative of the typical silicon contents of stainless steels usually sold in commerce. The description of the compositions, processing and results of testing of Alloys A through D are included herein to illustrate the inferior sharp-notch toughness qualities of stainless steel products produced by using stainless steel workpieces that are outside the invention.

Ingots of the aforementioned Alloys 1 through 8 and A through D were hot forged and hot rolled to one-quarter inch thick plates and then cold rolled to sheets about

0.110 inch thick. These sheets were annealed by heat treating for one hour at 1950° F. and air cooling to room temperature in order to insure that the sheets consisted predominantly of austenite and to eliminate hardening resulting from prior cold work. The annealed sheets were finish machined to 0.100 inch thickness. This machining operation was simply for the purpose of providing that all of the sheets be equal in thickness at the start of the subzero working operation and did not affect the metallurgical characteristics of the finished products.

The machined sheets were subzero worked by rolling the sheets at a deformation temperature of about minus 106° F. The temperature of the rolls was about room temperature (65° F. to 75° F.). Before being subzero rolled, the sheets were cooled to a temperature of about minus 106° F. in a bath of Dry Ice and isopentane. Each sheet was removed from the bath, immediately thereafter passed once through a pair of rolls, and then returned to the bath and cooled again to minus 106° F. The sheets were rolled a sufficient number of passes to reduce the thickness of the sheets to 0.060 inch (40% reduction in thickness). The reduction in thickness per pass was generally 0.005 to 0.008 inch except for that of the final pass, which was usually a lesser reduction in order to produce the desired final thickness of 0.060 inch.

After rolling was completed, the sheets were heat treated for 24 hours at 800° F. for the purpose of increasing the yield strength thereof. Although the reason for this increase is uncertain, an explanation is that the increase in strength is due to relief from residual stresses. Metallurgical examination of specimens of the finished products of these examples established that these products comprised at least 75% martensite. Products produced from Alloys 1, 3 and 6 comprised at least about 85% but not more than about 95% martensite.

To test the results of the foregoing exemplary processes, both smooth (unnotched) and sharp-notched sheet tensile specimens were machined from the sheets. Longitudinal axes of the specimens were in alignment with the direction in which the sheets were subzero rolled. The dimensions of these sheet tensile specimens were the dimensions shown in FIGURE 1 of the aforeidentified paper of G. B. Espey, M. H. Jones and W. F. Brown. Thus, the sharp-notched specimens used to test the stainless steels of the foregoing examples had stress-concentration factors K_t of at least 18 and sharp notches with root radii not greater than 0.001 inch. These tensile specimens, both the smooth specimens and the sharp-notched specimens, were tested at room temperature at a strain rate of 0.005 inch per inch per minute until the yield strength was reached and thereafter at an increased strain rate of 0.05 inch per inch per minute until the specimens fractured. Yield strength, as employed herein, is yield strength at 0.2% offset. The results of these tests are set forth in Table II.

Table II

Alloy No.	0.2% Yield Strength, p.s.i.	Ultimate Tensile Strength, p.s.i.	Sharp-Notch Strength, p.s.i.	Ratio, SNTS/TS ¹
1.....	263,000	264,000	252,000	0.96
2.....	222,000	232,000	240,000	1.03
3.....	262,000	263,000	255,000	0.97
4.....	249,000	250,000	262,000	1.04
5.....	257,000	259,000	271,000	1.04
6.....	274,000	274,000	277,000	1.01
7.....	236,000	239,000	238,000	1.00
8.....	236,000	239,000	249,000	1.04
A.....	254,000	264,000	246,000	0.93
B.....	246,000	254,000	222,000	0.88
C.....	261,000	261,000	236,000	0.90
D.....	254,000	255,000	238,000	0.93

¹ Ratio, SNTS/TS = Ratio of sharp-notch tensile strength to ultimate tensile strength.

As a further demonstration of the superior characteristics of stainless steel products produced in accordance with the present invention, other specimens of sheet produced by the foregoing exemplary processes were tested

at minus 320° F. using the aforesaid strain rates. The results of these tests are set forth in Table III.

Table III

Alloy No.	0.2% Yield Strength, p.s.i.	Ultimate Tensile Strength, p.s.i.	Sharp-Notch Strength, p.s.i.	Ratio, SNTS/TS ¹
8-----	296,000	297,000	300,000	1.01
A-----	312,000	313,000	223,000	0.71

¹ Ratio, SNTS/TS=Ratio of sharp-notch tensile strength to ultimate tensile strength.

The results set forth in Tables II and III show that low-silicon stainless steel products produced in accordance with the invention are characterized by sharp-notch ductility whereas the products having silicon contents typical of commercial stainless steels are sharp-notch brittle. Furthermore, the results of Table III demonstrate that the special products produced in accordance with the invention display particularly improved sharp-notch ductility and strength at very low temperatures such as minus 320° F.

Chemical compositions of low-silicon stainless steel products produced by cold working at room temperature and heat treating in accordance with the invention are set forth in Table IV, wherein the compositions of Alloys Nos. 9 through 13 are in accordance with the invention. Also, for purposes of further illustrating advantageous and novel features of the invention, Table IV shows chemical compositions of two alloys, Alloys E and F, which are unsatisfactory for cold working at room temperatures. Thus, Alloy E has a nickel plus chromium content of about 26.1, which is too high, and Alloy F has an equivalent nickel index of only 19.4, which is too low.

Table IV

Alloy No.	Composition in Weight Percent								Ni+Cr ¹
	Ni	Cr	Mn	C	N	Si	Fe	ENI	
9-----	7.2	16.3	0.25	0.06	0.04	0.03	Bal-----	21.1	23.5
10-----	5.4	17.8	0.31	0.08	0.04	0.08	Bal-----	21.1	23.2
11-----	5.6	17.8	0.18	0.10	0.03	0.07	Bal-----	21.3	23.4
12-----	6.1	18.8	0.21	0.07	0.03	0.02	Bal-----	21.4	24.9
13-----	6.0	17.7	0.25	0.08	0.04	0.05	Bal-----	21.4	23.7
E-----	7.4	18.7	0.05	0.07	0.02	0.13	Bal-----	22.6	26.1
F-----	7.2	14.4	0.50	0.06	0.02	0.03	Bal-----	19.4	21.6

¹ Ni+Cr=Total percentage of nickel plus chromium.

Stainless steel workpieces of Alloys Nos. 9 through 13 and Alloys E and F which had been annealed and thus were in an austenitic condition, were cold rolled, at deformation temperatures of about 70° F. to 85° F., to about 40% reduction in thickness. The preparation of the workpieces before cold rolling at room temperature was substantially the same, with the exception of subzero cooling, as the preparation for the subzero working of Alloys Nos. 1 through 8. After cold rolling, the workpieces were heat treated for 24 hours at 800° F.

Smooth and sharp-notched tensile specimens as described in conjunction with the tensile testing of Alloys Nos. 1 through 8 were made from room-temperature cold-worked sheet of Alloys Nos. 9 through 13 and Alloys E and F. Test results set forth in Table V illustrate the advantageous sharp-notch ductility and yield strength properties characteristic of these steels. Yield strengths of the order of 230,000 p.s.i. are readily obtainable in accordance with the invention. In this connection, it will be noted that the yield strengths of both Alloys E and F were markedly inferior to those afforded by steels within the invention.

Table V

Alloy No.	0.2% Yield Strength, p.s.i.	Ultimate Tensile Strength, p.s.i.	Sharp-Notch Strength, p.s.i.	Ratio, SNTS/TS ¹
9-----	239,000	239,000	228,000	0.96
10-----	238,000	240,000	227,000	0.95
11-----	221,000	223,000	228,000	1.02
12-----	252,000	253,000	250,000	0.99
13-----	222,000	223,000	230,000	1.03
E-----	198,000	209,000	216,000	1.03
F-----	197,000	197,000	217,000	1.10

¹ Ratio, SNTS/TS=Ratio of sharp-notch tensile strength to ultimate tensile strength.

The process of the invention provides sharp-notch ductile stainless steel products characterized by the corrosion resistance of austenitic nickel-chromium stainless steel. Further, such products of the invention can be produced as products characterized by high yield strengths of at least about 230,000 p.s.i. and even as high as at least about 250,000 p.s.i. Stainless steel products that can be produced in accordance with the invention include sheets, plates, strips, rods, bars, tubing, forgings, wire, extrusions, stampings and pressings. Products of the invention are useful for making highly stressed structures and articles for use in corrosive environments. Such structures and articles include pipes, couplings, pressure vessels, beer barrels, wheel spokes, hydrofoils, bolts, rivets and screws. Processes and products of the invention are also useful for making hard, corrosion resisting articles including knives, surgical instruments, dental tools, saws and chisels. Since the stainless steel products of the invention are sharp-notch ductile at subzero temperatures as low as minus 320° F. or lower, the process of the invention is particularly applicable to the production

of stainless steel products for use in cryogenic environments, including environments wherein the temperature is at or below the boiling point of liquid oxygen (minus 297° F.), or at other subzero temperatures. Thus, the products of the invention are particularly useful for making rocket motor cases that are to be subjected to subzero temperatures and are also useful for making articles, structures and apparatus for producing, handling, storing and transporting liquefied gases, e.g., liquid propane, liquid oxygen or liquid nitrogen, including metal flanks, storage tanks, tanks for ships, railroad cars, trucks, airplanes, rockets and spacecraft, pumps, condensers, piping and tubing. The process of the invention is applicable in the production of stainless steel articles by room temperature working down through subzero working operations including rolling, forging, drawing, extruding, spinning, stretching, hydroforming, roll forming, upsetting, swaging, peening and explosive loading. The invention is also applicable to the production of welded structures and articles whereby a welded stainless steel workpiece including weld metal of the special low-silicon transformable austenitic nickel-chromium stainless steel

of the invention is deformed at or below room temperature including subzero temperatures. For instance, an article such as a tank or barrel can be produced by expanding a welded workpiece of low-silicon stainless steel in accordance with the invention in a closed die while the workpiece is at a subzero temperature by internal hydraulic pressure using a very cold liquid such as liquid nitrogen.

It is to be observed that the present invention provides a new process for making stainless steel products characterized by sharp-notch ductility and high strength.

Furthermore, the invention provides a new stainless steel product characterized by sharp-notch ductility and high strength at room temperature and at subzero temperatures. The product of the invention is also characterized by a very high ratio of strength to density (the Shapiro index).

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. 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 producing a stainless steel product characterized by improved notch toughness characteristics including sharp-notch ductility comprising the steps of providing a low-silicon transformable austenitic nickel-chromium stainless steel workpiece consisting essentially of not more than about 0.15% silicon, about 4% to about 12% nickel, about 15% to about 22% chromium, about 0.1% to about 1% manganese, about 0.01% to about 0.1% carbon, about 0.005% to about 0.1% nitrogen, up to about 0.2% aluminum, up to about 0.1% each of calcium, magnesium and zirconium, up to about 0.5% titanium, up to about 1% columbium, up to about 0.01% boron, with the balance essentially iron and also characterized by an equivalent nickel index (ENI) of at least about 17 but not greater than about 30 as computed by the formula

$$\text{ENI} = \text{percent Ni} + 0.68(\text{percent Cr}) + 0.55(\text{percent Mn}) + 0.45(\text{percent Si}) + 27(\text{percent C} + \text{percent N})$$

the structure of said workpiece comprising at least 75% austenite, plastically deforming said workpiece at a temperature below zero degrees Fahrenheit to transform austenite of the workpiece to martensite and thereafter heat treating the workpiece in the range of about 700° F. to about 850° F. for about one hour to about 48 hours.

2. A process for producing a stainless steel product characterized by sharp-notch ductility and a yield strength of at least about 230,000 p.s.i. comprising the steps of providing a workpiece of low-silicon transformable austenitic nickel-chromium stainless steel characterized by a chemical composition consisting essentially of not more than about 0.15% silicon, about 6% to about 10% nickel, about 16% to about 21% chromium, about 0.01% to about 1% manganese, about 0.01% to about 0.1% carbon, about 0.005% to about 0.1% nitrogen, with the balance essentially iron and also characterized by an equivalent nickel index (ENI) of at least about 20 but not greater than about 25 as computed by the formula

$$\text{ENI} = \text{percent Ni} + 0.68(\text{percent Cr}) + 0.55(\text{percent Mn}) + 0.45(\text{percent Si}) + 27(\text{percent C} + \text{percent N})$$

the structure of said workpiece comprising at least about 90% austenite, plastically deforming said workpiece by a metalworking operation at a deformation temperature in the range of about minus 40° F. to about minus 320° F. to reduce the thickness of said workpiece at least about 20% and to transform austenite of the workpiece to martensite and thereafter heat treating said workpiece

within the range of 700° F. to about 850° F. for about one hour to about 48 hours.

3. A process as set forth in claim 2 wherein the metalworking operation is performed by rolling.

4. A wrought, sharp-notch ductile stainless steel product having a microstructure consisting essentially of martensite and austenite with about 60% to about 99% of the structure being martensite, made of an alloy consisting of not more than about 0.15% silicon, about 6% to about 10% nickel, about 16% to about 21% chromium, about 0.01% to about 1% manganese, about 0.01% to about 0.1% carbon, about 0.005% to about 0.1% nitrogen with the balance essentially iron, characterized by an equivalent nickel index (ENI) of at least about 20 but not greater than about 25 as computed by the formula

$$\text{ENI} = \text{percent Ni} + 0.68(\text{percent Cr}) + 0.55(\text{percent Mn}) + 0.45(\text{percent Si}) + 27(\text{percent C} + \text{percent N})$$

and also characterized by a sharp-notch/tensile strength ratio of at least 0.95 and a yield strength of at least about 230,000 pounds per square inch.

5. A process for producing a stainless steel product characterized by a sharp-notch/tensile strength ratio of at least 0.95 and a yield strength of at least about 250,000 p.s.i. comprising the steps of providing a workpiece of low-silicon transformable austenitic nickel-chromium stainless steel characterized by a chemical composition consisting essentially of about 0.01% to about 0.15% silicon, about 7% to about 8.5% nickel, about 18% to about 19% chromium, about 0.1% to about 1% manganese, about 0.04% to about 0.08% carbon, about 0.01% to about 0.04% nitrogen, with the balance essentially iron and also characterized by an equivalent nickel index (ENI) of at least about 21 but not greater than about 23 as computed by the formula

$$\text{ENI} = \text{percent Ni} + 0.68(\text{percent Cr}) + 0.55(\text{percent Mn}) + 0.45(\text{percent Si}) + 27(\text{percent C} + \text{percent N})$$

the structure of said workpiece comprising at least about 90% austenite, plastically deforming said workpiece by a metalworking operation at a deformation temperature in the range of about minus 100° F. to about minus 150° F. to reduce the thickness of said workpiece by at least about 30% and not more than about 50% and to transform austenite in the workpiece to martensite and thereafter heat treating said workpiece at a temperature in the range of about 750° F. to about 850° F. for about four hours to about 48 hours.

6. A process as set forth in claim 5 wherein the metalworking operation is performed by rolling.

7. A wrought, sharp-notch ductile stainless steel product having a microstructure consisting essentially of martensite and austenite with about 85% to about 99% of the structure being martensite, made of an alloy consisting of about 0.01% to about 0.15% silicon, about 7% to about 8.5% nickel, about 18% to about 19% chromium, about 0.01% to about 1% manganese, about 0.04% to about 0.08% carbon, about 0.01% to about 0.04% nitrogen with the balance essentially iron, characterized by an equivalent nickel index (ENI) of at least about 21 but not greater than about 23 as computed by the formula

$$\text{ENI} = \text{percent Ni} + 0.68(\text{percent Cr}) + 0.55(\text{percent Mn}) + 0.45(\text{percent Si}) + 27(\text{percent C} + \text{percent N})$$

and also characterized by a sharp-notch/tensile strength ratio of at least 0.95 and a yield strength of at least about 250,000 pounds per square inch.

No references cited.

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