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COLD-WORKED STAINLESS STEEL

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

Heretofore, the art has endeavored to produce stainless steel products, for instance, stainless steel sheet and strip, having to a high degree special characteristics which are required of metal products for use in highly stressed corrosion resistant structures. It is well known that some austenitic stainless steels are improved in strength by cold working and stainless steels of well known compositions have been produced for many years as cold rolled products. Although cold-worked stainless steels have been highly satisfactory for many uses, there are needs in industry and commerce for stainless steels having improved characteristics. A particular problem in the improvement of stainless steels involves providing stainless steel products which are characterized not only by improved high strength such as yield strength but in addition by adequate sharp-notch toughness. Sharp-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 sharp notch and steels having adequate sharp-notch toughness are referred to as being sharp-notch ductile. The sharp-notch (tensile strength)/tensile strength ratio is used as a criterion of toughness and, as referred to herein for sheet specimens, metals characterized by sharp-notch/tensile strength ratios of at least about 1, i.e., 0.95 or greater, are deemed sharp-notch ductile, whereas metals characterized by lower sharp-notch/tensile strength ratios are deemed notch brittle or notch sensitive.

In providing stainless steel products for commercial use in highly stressed structures, it is not only important to produce steels of improved strength and toughness qualities but, in addition, it is also important that such improved products can be produced by commercially practical production methods that do not involve unusually high cost. For instance, it is commercially advantageous that improved metal products can be produced by unidirectionally rolling, or other simple working techniques, the metal at temperatures which are typically employed for cold working commercial stainless steels, without necessity for resorting to cross-rolling or to unusually high or low working temperatures. Most conveniently and economically, working is accomplished at room temperature.

A further aspect of the problem of producing high strength stainless steel products is that although it is possible to greatly strengthen some known stainless steels by cold rolling the steels to very high reductions in cross-sectional area, it has been found that stainless steels which are in the condition obtained by cold rolling to cross-sectional reductions of 50% or greater are often adversely characterized by poor characteristics in the direction transverse to the rolling direction. Accordingly, there are needs for special stainless steel alloys and production processes therefor which enable production of high strength, sharp-notch ductile stainless steel products without necessity of cold working the steel to amounts of deformation equivalent to cross-sectional reductions in area of 50% or greater. Although many attempts were made to overcome the foregoing difficulties and other disadvantages, none, as far as I am aware, was entirely successful when carried into practice commercially on an industrial scale.

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It has now been discovered that stainless steel produtcs characterized by an improved combination of high strength and toughness can be produced by a new commercially practical process involving working and heat treating a workpiece of a new stainless steel alloy.

It is an object of the present invention to provide a new process for making high strength, sharp-notch ductile stainless steel products.

Another object of the invention is to provide improved stainless steel products, including stainless steel sheet, strip, bar, rod, wire, tubing and the like, produced by a special process.

The invention also contemplates providing a new stainless steel alloy having a controlled chemical composition that is of sufficient scope to enable commercial production of stainless steel products which are consistently characterized by a combination of high yield strength and sharp-notch ductility.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates production of a high strength, sharp-notch ductile stainless steel product in accordance with a new strengthening process comprising the steps of providing an austenitically structured workpiece of a special nickel-chromium-cobalt stainless steel alloy which is initially of a structure including at least about 90% austenite, plastically deforming the initially austenitically structured workpiece at a temperature within the range of about 5° F. to about 100° F. by an amount at least equivalent to about 20% reduction in cross-sectional area to thereby transform the austenitically structured workpiece to a martensitically structured workpiece having at least about 60% to about 99% martensite and with the remainder of the structure substantially all austenite and thereafter heat treating the martensitically structured workpiece for about 1 hour to about 48 hours at about 750° F. to about 850° F.

The invention also provides a special nickel-chromium-cobalt stainless steel alloy, which is the special alloy of the workpiece required in the process of the invention, containing about 3% to about 8% nickel, about 12% to about 17% chromium, about 7% to about 13% cobalt, about 0.01% to about 1% manganese, about 0.01% to about 0.15% carbon, about 0.005% to about 0.1% nitrogen, up to about 5% molybdenum, not more than about 0.15% silicon, with the balance essentially iron and characterized by an equivalent nickel index (ENI) of at least about 19.5 but not greater than about 22 as computed by the formula

$$\text{ENI}=\text{percent Ni}+0.68\ (\text{percent Cr})+0.55\ (\text{percent Mn})+0.45\ (\text{percent Si})+27\ (\text{percent C}+\text{percent N})+0.2\ (\text{percent Co})+\text{percent Mo}$$

All alloy percentages set forth herein are by weight and in the foregoing formula, which is the equivalent nickel index formula, the expressions percent Ni, percent Cr, percent Mn, percent Si, percent C, percent N, percent Co and percent Mo are the weight percentages of nickel, chromium, manganese, silicon, carbon, nitrogen, cobalt and molybdenum, respectively, in the alloy of the invention. Although the balance of the nickel-chromium-cobalt stainless steel alloy composition of the invention is 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 0.2% aluminum, up to about 0.1% each of calcium, magnesium and/or zirconium, and up to about 0.01% boron. Aluminum, calcium, magnesium, zirconium, and/or boron can serve purposes of deoxidation, malleabilization and/or purification. Although small amounts of silicon, e.g., 0.05% silicon, can be present, the maximum silicon content of the alloy of the invention is restricted to about 0.15% in order that the alloy be characterized by sharp-notch ductility. The balance of the alloy of the invention may contain small amounts of relatively harmless impurities such as up to 2% copper and may also contain very small amounts of other more detrimental impurities such as sulfur, phosphorus, bismuth, antimony, tin, lead, arsenic, beryllium, etc. However, the total amount of these impurities must be less than 0.03% of the steel, e.g., about 0.02% or less.

The alloy of the invention is characterized by an improved combination of high strength, hardness and toughness, including a yield strength which is consistently at least 240,000 pounds per square inch (p.s.i.) together with sharp-notch ductility, i.e., a sharp-notch/tensile strength ratio of at least about 1 or greater, when in a martensitic condition obtained by plastically deforming and heat treating the alloy in accordance with the process of the invention. Thus, the present invention provides a new alloy characterized by ranges of chemical composition and equivalent nickel index which are specially controlled to provide for consistently obtaining a high yield strength of at least 240,000 p.s.i in combination with sharp-notch ductility and which are also of sufficient scope to permit consistent commercial production of specific embodiments of this new high strength alloy on a practical basis and with the normal tolerances for variation in composition (within the ranges set forth herein) demanded for successful commercial practice.

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 necessarily required for successfully practicing 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 processed in accordance with the process of the invention. Advantageously, workpieces which have been hot worked and especially workpieces which have been cold worked are annealed prior to being subjected to a deformation step of the process of the invention. 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 2100° F., e.g., about 1950° F., and thereafter air cooling to room temperature. Variations in annealing temperatures within the range 1800° F. to 2100° F. have little effect but annealing below 1800° F. is to be avoided because of possible embrittlement by carbides or sigma phase.

The plastic deformation of the workpiece which is accomplished in the process of the invention can be performed by rolling the workpiece at near room temperature and deformation temperatures in the range 5° F. to 100° F. are satisfactory for obtaining good results. Rolling is normally accomplished by multiple passes and it is to be recognized that it may be necessary to allow the workpiece to cool between passes in order that the workpiece temperature be within the range of 5° F. to 100° F. at the start of each pass. The amount of reduction in cross-sectional area is advantageously at least 20% and less than 50%, e.g., 45%. Reductions of less than 20% do not provide for developing full strength in the products and larger reductions, e.g., 60%, can cause mechanical anisotropy and poor transverse toughness in the product. Deformation in accordance with the invention can be accomplished not only by rolling but also by drawing, forging, spinning, or other forming techniques. Of course, it is to be understood that the deformation step can comprise a number of substeps, such as multiple passes through a rolling mill or through a series of drawing dies. It is to be emphasized that the workpiece is initially, i.e., at the start of deformation, austenitic in structure and that the working thereof in accordance with the invention results in transformation of austenite to martensite. To develop the full strength of the alloy, plastic deformation in accordance with the process of the invention accomplishes in succession plastic deformation of austenite, transformation of austenite to martensite and plastic deformation of martensite.

The strengthening heat treatment which is accomplished in the process of the invention is performed by heating the workpiece, after deformation is complete, for a period of about 1 hour to about 48 hours at a temperature from about 750° F. to 850° F. Either lower or higher heat treating temperatures will not develop the full strength of the products. Also, the full strength of the new stainless steel product will not be achieved if a heat treatment of too short duration or a heat treatment of extremely long duration greater than 48 hours is performed instead of the strengthening heat treatment of the process of the invention.

It is advantageous in order to produce stainless steel products of especially high strength and hardness in combination with sharp-notch ductility that the alloy of the invention contain about 4.5% to about 5.5% nickel, about 14.5% to about 16% chromium, about 7.5% to about 10% cobalt, about 0.1% to about 0.5% manganese, about 0.04% to about 0.09% carbon, about 0.01% to about 0.05% nitrogen, not more than about 0.1% silicon, with the balance essentially iron and have an equivalent nickel index of about 20 to about 21. Stainless steel products of this advantageous composition, when in a martensitically strucured condition obtained by deforming a workpiece of this advantageous alloy by an amount equivalent to at least about 30% reduction in area and by heat treating at about 750° F. to about 850° F. for about 1 hour to about 48 hours, advantageously about 4 hours to about 48 hours, are characterized by especially high yield strengths of at least about 260,000 p.s.i. and a sharp-notch/tensile strength ratio of about 1 or greater. For instance, Alloys 2 and 3 referred to hereinafter are particularly advantageous alloys of the invention.

For the purpose of giving those skilled in the art a better understanding of the invention and a better appreciation of the advantages of the invention, the production of stainless steel products of alloys and by processes in accordance with the invention as compared to the production of other alloy products or by other processes is illustrated by the following examples. Nine heats of stainless steel alloys were melted in induction furnaces in air atmospheres and cast into ingot. Five of these heats (Alloys 1 through 5) are examples of alloys within the invention and the chemical compositions of these five alloys are set forth in Table I:

TABLE I

Alloy No.	Percent Ni	Percent Cr	Percent Co	Percent Mn	Percent Si	Percent C	Percent N	Percent Mo	Percent Fe	ENI
1	6.7	16.1	7.6	0.40	0.01	0.06	0.03	--------	Bal	21.8
2	5.1	15.7	8.4	0.14	0.02	0.06	0.03	--------	Bal	20.1
3	5.1	14.6	7.7	0.24	0.05	0.05	0.03	2.05	Bal	20.6
4	5.2	12.7	7.8	0.07	0.05	0.07	0.03	3.90	Bal	22.0
5	6.1	14.3	11.1	0.23	0.05	0.04	0.03	--------	Bal	20.0

Bal.=Balance including small amounts of impurities, residual deoxidizers, etc.
ENI=Equivalent Nickel Index.

The other four of these heats (Alloys W, X, Y and Z) are of compositions outside the scope of the invention. The compositions of these four Alloys W, X, Y and Z are set forth in Table II:

TABLE II

Alloy No.	Percent Ni	Percent Cr	Percent Co	Percent Mn	Percent Si	Percent C	Percent N	Percent Mo	Percent Fe	ENI
W	6.0	18.7	3.48	0.21	0.01	0.06	0.03		Bal	22.0
X	6.5	16.8	3.10	0.45	0.01	0.06	0.03		Bal	21.2
Y	5.2	13.7	7.82	0.19	0.05	0.06	0.03		Bal	18.7
Z	4.2	13.6	10.7	0.20	0.05	0.05	0.02		Bal	18.5

Bal.=Balance including small amounts of impurities, residual deoxidizers, etc.
ENI=Equivalent Nickel Index.

From Table II it is apparent that Alloys W and X contain only about 3.5% and about 3.1% cobalt, respectively, which amounts are less than the amount of cobalt required in the alloys of the invention. These low cobalt contents of about 3.1% and about 3.5% are insufficient to provide for obtaining the high yield strength of at least about 240,000 p.s.i. which is a characteristic of the alloy of the invention. In order to provide for consistently obtaining high strength and hardness, the alloy of the invention contains at least about 7% cobalt. Alloys Y and Z are characterized by equivalent nickel indexes of only about 18.7 and 18.5, respectively, whereas for the purpose of obtaining high strength and hardness, the alloy of the invention is characterized by an equivalent nickel index of about 19.5 to about 22.

Ingots of Alloys 1 through 5 and W through Z were hot forged and hot rolled to about one-quarter inch thick plates and then cold rolled to about 0.1 inch thick sheet. These sheets were annealed by heat treating for one hour at 1950° F. and air colling to room temperature to insure that the sheets consisted predominantly of austenite and to eliminate hardening effects resulting from the prior hot and cold working steps. Thus, sheets of Alloys 1 through 5, which were characterized by a structure comprising at least about 90% austenite, up to about 10% martensite and possibly also delta ferrite in small amounts not greater than about 1%, were provided as workpieces for carrying out the process of the invention.

The annealed sheets of Alloys 1 through 5 and Alloys W through Z were cold rolled at room temperature (about 70° F.) to a reduction of about 40% in thickness, which reduction is approximately equal to a cross-sectional reduction in area of about 40%. Rolling was accomplished in several passes and the sheets were cooled to room temperature between passes. As a result of rolling, austenite in the sheets was transformed to martensite. After rolling was completed, the sheets, which were then about 0.06 inch thick, were heat treated for 24 hours at 800° F. for the purpose of increasing the yield strength and insuring the toughness thereof. Thus, finished stainless steel products of Alloys 1 through 5 were produced in accordance with the invention along with finished products of Alloys W through Z which were made by the same rolling and heat treating steps which were performed on Alloys 1 through 5.

To test characteristics and results of the foregoing alloys and 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 rolled. The dimensions of these sheet tensile specimens of one inch width were in accordance with dimensions for specimens shown in FIGURE 1 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, volume 59, 1959. 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. The term "yield strength," as employed herein, is the yield strength of 0.2% offset. The results of these tests are set forth in Tables III and IV wherein the results in Table III show characteristics of examples in accordance with the invention and the results in Table IV show characteristics of stainless steel products of alloys which are not in accordance with the invention:

TABLE III

Alloy No.	0.2% Yield Strength, p.s.i.	Ultimate Tensile Strength, p.s.i.	Sharp-Notch Tensile Strength, p.s.i.	Ratio SNTS/TS
1	243,000	244,000	244,000	1.00
2	268,000	269,000	270,000	1.00
3	270,000	270,000	267,000	0.99
4	251,000	251,000	277,000	1.10
5	255,000	255,000	250,000	0.98

SNTS/TS=Ratio of Sharp-Notch Tensile Strength to Ultimate Tensile Strength.

TABLE IV

Alloy No.	0.2% Yield Strength, p.s.i.	Ultimate Tensile Strength, p.s.i.	Sharp-Notch Tensile Strength, p.s.i.	Ratio SNTS/TS
W	231,000	236,000	241,000	1.02
X	224,000	225,000	239,000	1.06
Y	219,000	219,000	239,000	1.09
Z	223,000	223,000	221,000	0.99

In addition, smooth sheet tensile specimens from sheets of Alloy 5 were tested in conditions resulting from cold rolling the sheets to reductions of about 40% as referred to hereinbefore and thereafter either not heat treating the rolled sheet or heat treating the rolled sheet for 24 hours at one of the temperatures 800° F., 900° F. or 1000° F. Characteristics of these specimens of stainless steel sheet made from Alloy 5 are set forth in conjunction with heat treatment conditions thereof in Table V:

TABLE V

Heat Treating Temperature, ° F.	0.2% Yield Strength (p.s.i.)	Ultimate Tensile Strength (p.s.i.)
N.H.T.	204,000	209,000
800	255,000	255,000
900	216,000	221,000
1000	166,000	176,000

N.H.T.=Not Heat Treated.

The results set forth in Tables III and IV, when taken in conjunction with the compositions set forth in Tables I and II, demonstrate that Alloys 1 through 5 of the invention are all characterized by high yield strengths which are consistently greater than about 240,000 p.s.i. and by sharp-notch ductility whereas Alloys W, X, Y and Z which are not alloys in accordance with the invention do not possess the high yield strengths which characterize products made of alloys of the invention. In addition, results set forth in Table V illustrate the achievement of superior strength that is obtained by heat treating in accordance with the invention.

The present invention is particularly applicable to the production of sharp-notch ductile stainless steel products characterized by high corrosion resistance, hardness, yield strength and tensile strength. 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. The alloy and process of the invention are useful for making highly stressed structures and articles for use in corrosive environments and also in cryogenic temperature environments. Such structures and articles include pipes, couplings, pressure vessels, barrels, wheel spokes, bolts, rivets and screws. Furthermore, the alloy and process of the invention are also useful for making hard, corrosion resisting articles including knives, surgical instruments, dental tools, saws and chisels.

In addition, it is to be observed that the alloy of the invention is a transformable stainless steel that is particularly adapted for cold working at near room temperature in the austenitic condition to transform austenite of the alloy into martensite and increase the strength of the alloy and thereby produce a martensitically structured alloy which can be heat treated to still further increase the strength thereof. Accordingly, it is to be understood that the alloy of the invention is especially useful where it is desired to make stainless steel products and articles characterized by high strength in combination with sharp-notch ductility by methods involving plastically deforming a stainless steel alloy at or near room temperature.

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.

I claim:

1. A wrought and heat treated martensitic-structured nickel-chromium-cobalt stainless steel consisting essentially of 3% to about 8% nickel, about 12% to about 17% chromium, about 7% to about 13% cobalt, about 0.01% to about 1% manganese, about 0.01% to about 0.15% carbon, about 0.005% to about 0.1% nitrogen, up to 5% molybdenum, not more than about 0.15% silicon, with the percentages of the aforesaid elements proportioned to characterize the composition with an equivalent nickel index (ENI) of at least 19.5 but not greater than 22 as computed by the formula

$$\text{ENI}=\text{percent Ni}+0.68\ (\text{percent Cr}) +0.55\ (\text{percent Mn})+0.45\ (\text{percent Si})+27\ (\text{percent C} +\text{percent N})+0.2\ (\text{percent Co})+\text{percent Mo}$$

and with the balance essentially iron, cold worked to at least about 20% and less than 50% reduction in cross sectional area and thereafter heat treated for about 1 hour to about 48 hours at 750° F. to 850° F., having a microstructure of at least about 60% to about 99% martensite and the remainder essentially austenite and possessing a yield strength of at least 240,000 pounds per square inch and a sharp-notch/tensile strength ratio of at least about 1.

2. A stainless steel as set forth in claim **1** consisting essentially of about 4.5% to about 5.5% nickel, about 14.5% to about 16% chromium, about 7.5% to about 10% cobalt, about 0.1% to about 0.5% manganese, 0.04% to 0.09% carbon, 0.01% to 0.05% nitrogen, not more than 0.1% silicon, not more than 3.7% molybdenum, with the percentages of the aforesaid elements proportioned to characterize the composition with an equivalent nickel index (ENI) of at least 20 but not greater than 21 as computed by the formula

$$\text{ENI}=\text{percent Ni}+0.68\ (\text{percent Cr}) +0.55\ (\text{percent Mn})+0.45\ (\text{percent Si})+27\ (\text{percent C} +\text{percent N})+0.2\ (\text{percent Co})+\text{percent Mo}$$

and with the balance essentially iron, cold worked to at least about 30% and less than 50% reduction in cross sectional area and thereafter heat treated for about 4 hours to about 48 hours at 750° F. to 850° F., having a microstructure of about 60% to 99% martensite and the remainder essentially austenite and possessing a yield strength of at least 260,000 pounds per square inch and a sharp-notch/tensile strength ratio of at least about 1.

3. An alloy consisting essentially of 3% to about 8% nickel, about 12% to about 17% chromium, about 7% to about 13% cobalt, about 0.01% to about 1% manganese, about 0.01% to about 0.15% carbon, about 0.005% to about 0.1% nitrogen, not more than about 0.15% silicon with the balance essentially iron and characterized by an equivalent nickel index (ENI) of at least about 19.5 but not greater than about 22 as computed by the formula

$$\text{ENI}=\text{percent Ni}+0.68\ (\text{percent Cr}) +0.55\ (\text{percent Mn})+0.45\ (\text{percent Si})+27\ (\text{percent C} +\text{percent N})+0.2\ (\text{percent Co})$$

4. An alloy consisting essentially of about 4.5% to about 5.5% nickel, about 14.5% to about 16% chromium, about 7.5% to about 10% cobalt, about 0.1% to about 0.5% manganese, about 0.04% to about 0.09% carbon, about 0.01% to about 0.05% nitrogen, not more than about 0.1% silicon, not more than 3.7% molybdenum with the balance essentially iron and characterized by an equivalent nickel index (ENI) of at least about 20 but not greater than about 21 as computed by the formula

$$\text{ENI}=\text{percent Ni}+0.68\ (\text{percent Cr}) +0.55\ (\text{percent Mn})+0.45\ (\text{percent Si})+27\ (\text{percent C} +\text{percent N})+0.2\ (\text{percent Co})+\text{percent Mo}$$

5. An alloy as set forth in claim **4** wherein the alloy consists essentially of nickel, chromium, cobalt, manganese, carbon, nitrogen and silicon in amounts in accordance with claim **4** and a balance that is iron.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,340,048 September 5, 1967

Stephen Floreen

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

Column 4, line 42, for "strucured" read -- structured --; column 7, line 48, before "5%" insert -- about --.

Signed and sealed this 26th day of November 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents