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CORROSION RESISTANT METASTABLE AUSTENITIC STEEL

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mission

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9 Claims

ABSTRACT OF THE DISCLOSURE

A steel and a process for imparting to such steel a combination of high strength, high uniform elongation, high toughness and corrosion resistance. The process consists of subjecting single phase, austenitic steel which has an M_s below ambient temperature, a total carbon plus nitrogen content of from about 0.15% to about 0.5%, a chromium content of from about 11% to about 18%, and at least 0.5% of at least one alloying element selected from the group consisting of molybdenum, manganese, vanadium, niobium, tantalum and tungsten preferably molybdenum, to deformation at a temperature above about 400° F. but below the recrystallization temperature of the steel.

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of, or under, Contract No. W-7405-Eng-48 with the United States Atomic Energy Commission.

The invention relates to high strength, high elongation steel, and more particularly to a corrosion resistant high strength, high toughness, high uniform elongation steel, and to a process for making same.

High strength, high elongation steel and a process for making same is disclosed and claimed in U.S. Pat. No. 3,488,231, assigned to the same assignee. However, this prior steel is not corrosion resistant, thus limiting the applications for high strength, high elongation steels.

The composition of the present inventive corrosion resistance steel is generally similar to that of the steel disclosed in the above referenced patent, and is produced in a generally similar manner, but provides a substantial improvement over this prior high strength, high elongation steel.

SUMMARY OF THE INVENTION

The starting material of the inventive process, like that of the process of the above referenced patent, requires an M_s below ambient temperature, thus substantially differing from the commonly known steels. M_s is a standard metallurgical expression defined as the temperature at which the martensitic phase begins to form when the temperature is lowered. M_D is a metallurgical term defined as the temperature above which the martensitic phase cannot form during mechanical working of the metal. The M_s and M_D may readily be determined by tests familiar to those skilled in the art. An M_s of ambient temperature or below is extremely low compared to the M_s of commonly known heat treatable high strength steels.

It is also essential to the invention that the steel contains at least 0.5%, preferably about several percent of at least one alloying element selected from the group consisting of molybdenum, manganese, vanadium, niobium, tantalum, and tungsten, preferably molybdenum.

In addition, the inventive steel must contain chromium in the range from about 11% to about 18%, but preferably between about 11–13%.

The steel used in the starting material in the present process, as in the above referenced patented process, must have a total carbon plus nitrogen content of from about 0.15% to about 0.5%. Since the carbon content in conventional stainless steels is generally kept below 0.1%, the combined carbon and nitrogen content of the inventive steel is a sharp contrast to these commonly known stainless steels.

In the inventive process, if the combined carbon and nitrogen content of the steel is below about 0.2% the steel does not have high strength and high toughness, and when the combined carbon and nitrogen content of the steel is above about 0.5% the steel does not have good elongation.

Also, to be suitable for use as a starting material in the present invention, the steel, like in the patented process, must first be converted to a single phase, austenitic state, this being usually done by heating the steel above the critical temperature for austenite formation for a length of time sufficient so that the entire specimen has been heated throughout, as known in the art. In general, for the steels of the present invention, the temperature will be from about 1500° F. to about 2200° F.

The actual operation to produce the inventive corrosion resistant, high strength, high toughness, high uniform form elongation steel involves deforming a steel specimen having the above described composition within a particular temperature range with the lower limit being about 400° F. and the upper limit being the recrystallization temperature of the steel. Recrystallization temperature is a standard term customarily defined as that temperature above which a completely new set of strain-free grain are formed, and, as known in the art, may be determined by routine tests. The recrystallization temperatures of the steels of the inventive steels are generally in the range of about 1500° F. to about 1800° F., and thus the temperature range at which deformation occurs in the inventive steel is generally from about 400° F. to 1100° F., this being an unusual working range when compared with the temperature utilized for the commonly known high strength steels. However, some steels made in accordance with the invention may have a higher recrystallization temperature up to 2200° F. and a deformation temperature up to about 1800° F. The expression "deforming" is used in the description of the present invention to mean subjecting the specimen to a stress beyond its elastic limit and thereby causing a change in the shape of the entire specimen. Deformation may be carried out by any of the standard metal working techniques such as rolling, swaging, wire drawing, forging, shear forming, etc. Any application of mechanical force sufficient to cause a change in shape is effective provided the change in shape extends throughout the entire specimen. In general it is preferred that the amount of deformation be at least about 20% at temperatures in the middle of the operating range. At the lower end of the temperature range a greater amount of deformation may be required to induce the desired chemical and structural changes, while at the upper end of the temperature range a greater amount of deformation may be required because the higher temperatures may serve to modify the structure in an undesired way.

The benefits of the process are achieved once the steel of the proper composition has been deformed at the proper temperature. After deformation, the specimen may be treated in a variety of ways depending on the ultimate use. For example, the steel may be quenched rapidly to room temperature in an appropriate quenching medium, and, if desired, even subsequently cooled to a temperature below room temperature. Alternately, it may be quenched rapidly to the desired processing temperature.

While the high strength, high elongation steel of the above reference patent contained, for example, about 8% chromium, the present invention utilizes a chromium content of from about 11 to 18 percent, preferably about 11-13%, thereby providing good corrosion resistance, whereby not only does the present invention provide a steel simultaneously possessing high strength, high toughness and high elongation but provides the additional advantage of corrosion resistance, thereby substantially improving the steel of the above referenced patent.

As in the above mentioned patented steel process, the steel of the present invention provides increased elongation resulting directly from the control of the austenite to martensite transformation, while providing high strength and corrosion resistance.

Therefore, it is an object of the invention to provide a corrosion resistant metastable austenitic steel and process therefor.

A further object of the invention is to provide a high strength, high elongation, corrosion resistance steel.

Another object of the invention is to provide a high strength, high elongation steel having a total carbon plus nitrogen content of from 0.15% to about 0.5%, and a chromium content in the range from about 11% to about 18%.

Another object of the invention is to provide a process for producing a corrosion resistant steel possessing both high strength and high elongation, wherein the steel is composed of about 12 to 14% chromium, about 5 to 11% nickel, about 0.2 to 0.5% carbon, up to about 4% molybdenum, up to about 2% manganese, with minor amounts of silicon, phosphorus and sulfur, and the balance iron.

Other objections of the invention, not specifically set forth above will become readily apparent from the following description.

DESCRIPTION OF THE INVENTION

Recent developments have shown that high strength and ductility can be obtained by subjecting metastable austenitic steels to proper combinations of heat treatments and deformation processes (thermomechanical processing). When these materials are strained, they transform from face-centered cubic austenite to body-centered tetragonal martensite. If this transformation begins before necking (local plastic instability) occurs, a high rate of strain hardening results and the material can continue to deform plastically at high stress levels. Metastable austenitic alloys that exhibit this type of behavior have been called TRIP (Transformation Induced Plasticity) steels, such steels being disclosed and claimed in the above-identified patent.

In order for the material to undergo this austenite-to-martensite transformation, its chemical composition must be properly balanced. The M_S temperature must be below room temperature (or below the test temperature) and the M_D temperature must be above test temperature. The M_D temperature is always above the M_S temperature. The M_S and M_D temperatures are influenced both by chemical composition and thermo-mechanical processing. It was commonly held that after thermomechanical processing the M_S and M_D temperatures increase was due at least in part to some of the carbon being precipitated during processing to form finely dispersed carbides, this decreasing the stability of the surrounding austenite. Recently, however, the possibility of the M_S temperature being decreased, while simultaneously the M_D temperature is increased by thermomechanical processing, has been determined, as reported by the coinventor of this application, Dr. V. F. Zackay in a University of California report UCRL-18676 entitled Anticipated Developments in Physical Metallurgical Research, January 1969, see page 16.

It has been found that metastable austenitic steels (TRIP steel), as exemplified by the above-identified patent,

undergo an active to passive corrosion behavior similar to stainless steels. For example, corrosion tests on a typical TRIP steel, with a nominal composition, of 9% chromium (Cr), 8% nickel (Ni), 4% molybdenum (Mo), 2% manganese (Mn), 1% silicon (Si), and 0.25% carbon (C), Balance iron (Fe), have shown a corrosion rate 2 to 3 times greater than an 18% Cr- 8% Ni austenitic stainless steel in 10% sulfuric acid at room temperature.

The present invention provides a solution to this corrosion problem in the so-called TRIP steels, thereby providing a steel having both high strength and high elongation which is corrosion resistant as compared to the TRIP steels of the above-mentioned patent.

In accordance with the invention, it has been determined that good corrosion resistance in 10% sulfuric acid is obtained by increasing to chromium content to between 11% to 18%, with 11% to 13% being preferable. It has also been determined that molybdenum has a beneficial effort on the corrosion resistance of the TRIP steel alloy composition, whereas manganese above a certain amount is detrimental thereto.

The same elements that are present in common stainless steels, i.e., Cr, Ni, and Mo also influence the stability of the austenite-to-martensite transformation of the TRIP steels. When increasing the Cr content to obtain corrosion resistance in the TRIP steel, the amount of Ni, Mo, Mn and C must be adjusted to give the desired metastable austenitic structure after thermomechanical processing.

As pointed out above, it is essential that the steel contains at least 0.5%, preferably about several percent, of at least one alloying element selected from the group consisting of molybdenum, manganese, vanadium, niobium, tantalum, and tungsten, preferably molybdenum, in addition to the chromium content of preferably about 11-13%. The steel used as the starting material in the present process must have a total carbon plus nitrogen content of from about 0.15% to about 0.5%. To be suitable for use as a starting material in the operation of the present process, the steel must first be converted to a single phase, austenitic state. The usual way of doing this is by heating the steel above the critical temperature for austenite formation for a length of time sufficient so that the entire specimen has been heated throughout. Those skilled in the art are familiar with this operation and accordingly such need not be described in detail. In general, for the steels of the present invention, the temperature will be from about 1800° F. to about 2200° F.

The actual operation of the process involves deforming a steel specimen having the proper composition, for example constituting alloy F of Table I set forth below and composed of 12.3% chromium, 7.8% nickel, 3% molybdenum, 0.24% carbon, with not over 1% silicon, 0.045% phosphorus, 0.03% sulfur and with the balance iron. This deformation must take place within a particular temperature range. The lower limit of the temperature range is about 400° F. with the upper limit of the temperature range being the recrystallization temperature of the steel, generally, in this process, in the range of about 1500° F. to about 1800° F., thus the temperature at which deformation occurs is generally in the range of 400° F. to 1100° F. in practicing this invention.

Again, it is emphasized that expression deforming as used herein is intended to mean the subjecting of the specimen to a stress beyond its elastic limit and thereby causing a change in the shape of the entire specimen, and can be carried out by any of the standard metal working techniques such as rolling, swaging, wire drawing, forging shear forming etc., any application of mechanical force being sufficient provided it causes a change in shape which extends throughout the entire specimen. In general it is preferred that the amount of deformation be at least about 20% at temperatures in the middle of the operating range. At the lower end of the temperature range a greater amount of deformation may be required to induce the desired chemical and structural changes, while at

the upper end of the temperature range a greater amount of deformation may be required because the higher temperatures may serve to modify the structure in an undesired way.

The above exemplary steel composition, processed in accordance with the TRIP steel concept may be carried out as follows: Heat to 2080° F. and hold at this temperature for one hour; cool to 840° F. and deform 80% by rolling at this temperature; finally, water quench to room temperature. The above processing as shown for alloy F in Table II hereinafter results in the following properties: Yield strength: 187,000 p.s.i.; ultimate tensile strength: 231,000 p.s.i.; tensile strength to yield strength ratio: 1.24; percent elongation of 1 inch: 38; percent reduction in area: 38; R_e hardness: before: 45, after: 57; magnetic characteristics; before: non-magnetic, after: magnetic.

To illustrate the advantages of the present invention, a comparison of the mechanical properties as set forth in Table II between the above novel steel composition and those of the commercial type 316 stainless steel, the composition of which is set forth in Table I below, will show the corrosion resistant, high strength, high elongation steel of the present invention as having about 5.3 times greater yield strength and about 2.7 times greater tensile strength than the type 316 steel.

Fred J. Padilla, September 1970, published by Lawrence Radiation Laboratory, University of California, Berkeley, Calif. funded by United States Atomic Energy Contract No. W-7405-Eng-48.

In these tests the chromium content was held constant at selected percentages for each of the alloys A-I (see Table I) and the nickel, molybdenum, and manganese contents were systematically varied. In addition the two commercial stainless steels, commonly known as Type 304 and Type 316 were tested for comparison, these results being shown on Table II. These tables are as follows:

TABLE I.—CHEMICAL COMPOSITION OF ALLOYS
IN WEIGHT PERCENT

	Cr	Ni	Mo	Mn	C	Fe
Alloy:						
A.....	12.9	7.8	-----	-----	0.26	Bal.
B.....	13.0	10.5	-----	-----	0.26	Bal.
C.....	13.0	10.0	1.0	-----	0.26	Bal.
D.....	12.6	8.8	2.0	-----	0.25	Bal.
E.....	13.4	7.6	1.0	-----	0.236	Bal.
F.....	12.3	7.8	3.0	-----	0.24	Bal.
G.....	12.9	6.9	4.0	-----	0.25	Bal.
H.....	13.0	5.9	3.0	2.0	0.25	Bal.
I.....	12.8	5.8	3.0	4.0	0.185	Bal.
304.....	18.7	9.1	-----	1.8	0.08	Bal. ^a
316.....	18.0	13.5	3.0	1.0	0.04	Bal. ^a

^aThis alloy also contains a maximum of 1.00% silicon, 0.045% phosphorus and 0.030% sulfur.

TABLE II.—MECHANICAL PROPERTIES

Alloy	Yield strength K s.i.	Tensile strength K s.i.	T.S./Y.S.	Percent elong. 1 inch	Percent red. in area	R _e hardness		Magnetic characteristic ^b	
						Before test ^a	After test ^b	Before test	After test
A.....	164	253	1.54	28	32	48	55	Non-mag.	Mag.
B.....	187	187	1.0	8	51	41	41	Sl-mag.	Mag. ^c
C.....	194	194	1.0	11	51	42	42	Sl-mag.	Mag. ^c
D.....	200	209	1.05	46	44	45	55	Non-mag.	Mag.
E.....	190	264	1.39	27	35	48	56	Sl-mag.	Mag.
F.....	187	231	1.24	38	38	45	57	Non-mag.	Mag.
G.....	185	249	1.35	34	42	49	58	Non-mag.	Mag.
H.....	185	231	1.25	40	33	44	57	Non-mag.	Mag.
I.....	186	188	1.01	46	42	44	52	Sl-mag.	Mag.
304 ^d	35	85	2.42	55	65	80	-----	Non-mag.	-----
316 ^d	35	85	2.42	55	70	80	-----	Non-mag.	-----

^a Outside gage length of specimen.

^b Within gage length of specimen.

^c Magnetic around necked area only.

^d Values of mechanical properties taken from Metals Handbook, vol. 1, 8th edition, 1961.

^e 0.2% offset yield strength value.

^f 2 inch gage length.

The inventive steel composition may, for example, also be produced by the following treatment: heat to 2080° F. and hold for one hour at this temperature, water quench to room temperature, reheat to 840° F. and deform 80% by rolling at this temperature. Alternately, the specimen can be cooled from 2080° F. to 840° F. rather than to room temperature and reheated to 840° F.

The inventive steel of the above composition, for example, may also be processed by the following treatment: heat to 2080° F. and hold for one hour at this temperature, water quench to room temperature, heat to 840° F. and deform 80% by rolling at this temperature, cool to room temperature, strain 15% at room temperature, and finally, heat to 840° F. and hold at this temperature for thirty minutes.

To verify the inventive concept as well as to clearly illustrate that a steel may possess both high strength and high elongation and be corrosion resistant at least to certain corrosion type environments, extensive testing has been conducted to determine the effects produced by variations in the TRIP alloy composition. As a result of these tests the inventive concept has clearly been supported resulting in optimizing a steel with corrosion resistance and with the TRIP steel mechanical properties. Since the details of those tests do not constitute part of this invention, only a brief description thereof will be set forth. These tests were conducted under the supervision of the inventors of the present invention, and the procedures and results of these tests are fully described in Report UCRL-19065 entitled "Optimization of Corrosion Resistance in Metastable Austenitic Steel" authored by

In the tests the alloy processing was accomplished by producing heats of ingots by induction melting of high purity elements in a helium; forging the ingots at 1100° C. into flat bars; cross-rolling the flat bars at 1100° C. to a thickness of 0.4 inch; austenitizing the material at 1200° C. for 2½ hours in Sentry-Pac stainless steel bags to prevent decarburization; and quenching in an ice-brine solution. The thermomechanical treatment consisted of an 80% reduction in thickness by rolling at 450° C., the material being reheated to 450° C. after each pass of 10 to 15 mils until a thickness of 0.08 inch was reached, after which it was water quenched.

The mechanical testing was accomplished by machining tensile specimens from the 0.08 inch rolled materials, with 1 inch gage length specimens being used. The tensile tests were carried out at room temperature using a cross-head speed of 0.04 inch/min. Rockwell C hardness measurements were made on the tensile specimens before tensile testing outside of the gage length, and after the tensile test the hardness measurements were made within the gage length. Magnetic measurements were made along the gage length of each specimen before and after the tensile test by using a large hand magnet.

An electrochemical method of corrosion testing known as the potentiodynamic polarization technique was used in evaluating the corrosion resistance of the inventive alloy. The importance of this method is that it allows a series of alloys, exhibiting passivity, to be systematically tested for their corrosion properties in a relatively short time (3-4 hours). Briefly, a typical potentiodynamic anodic polarization curve was prepared, which is a plot

of the potential of the metal in an electrolyte (against a standard such as a calomel electrode) vs. the current density developed by the metal at this potential (with a suitable auxiliary electrode such as platinum), the curve being developed by slowly, but continuously varying, the potential. As known, the curve along the potential axis can be divided into three parts, i.e., (1) active, (2) passive, and (3) transpassive regions. From this curve it is possible to determine the following:

(1) The mixed or corrosive potential (E_{corr}): The potential of the metal in the environment without any current flowing, i.e., with no dissolution taking place.

(2) The primary passive potential (E_{pp}): Up to the primary passive potential, normal dissolution of the material takes place. As the potential is made more noble, up to the primary passive potential, dissolution of the material increases linearly, a behavior typical of all non-passivating materials. At the primary passive potential the material begins to exhibit a decrease in the dissolution rate (passivation), i.e., the current density decreases. This decrease is thought to be due to the formation of a protective film on the metal surface. The corrosion resistance of a material may be effectively increased by adding alloying elements which shift the primary passive potential in the active direction, since, for chemical passivation to take place, the environment (oxidizing agent) must have a higher (more noble) redox potential than the primary passivation potential of the metal. Hence, the lower (more active) the primary passivation potential of the metal, the greater its corrosion resistance, even in the presence of a weak oxidizing agent, i.e., one that has a low redox potential. In steels, the usual alloying additions of chromium, nickel, and molybdenum generally have only a minor effect on the primary passive potential. Hence, a more important parameter in improving corrosion resistance is the critical current density set forth herebelow.

(3) The critical anodic current density (I_{cr}): The maximum corrosion or dissolution rate for the metal in the environment, and indicates the current that must be achieved in order for the material to passivate. The lower the value of the critical current density, the lower the concentration of oxidizing agents necessary for achieving passivity. Hence, for increased corrosion resistance, alloying additions which lower the critical current density of a material are desirable. This lowering of I_{cr} is generally more effective in increasing passivating tendency than is the altering of the primary passivation potential. The reason for this is that in practical situations, the oxidizing environment (usually containing oxygen) has a redox potential higher than the primary passivation potential. Therefore, the main barrier to passivation becomes the ability of the environment, by its reduction on the metal, to produce a current density greater than the critical anodic current density.

(4) The passive potential region: Indicated by the vertical, low, constant-current-density part of a typical potentiodynamic curve. From a corrosion viewpoint the passive area should be as wide as possible. The material can remain passive under more varied conditions when the primary passive potential (E_{pp}), described above, and the transpassive potential (E_t) are farther apart.

(5) The passive current density (I_p): Given by the constant value of the current density in the passive range and indicates the passive corrosion rate. This represents the lowest amount of corrosion taking place. The current density can be related to the corrosion rate by Faraday's Law. Taking into account the percentage of each element in the alloy, an average value of 0.5 mil per year being equivalent to 1 $\mu\text{amp./cm.}^2$ is obtained. Since the rate of corrosion in the passive state is proportional to the passive current density, increased corrosion resistance can be obtained by lowering the passive current density. Also, the lower the value of I_p , the more stable the passive state becomes. The reason for this is that the lower

the passive current density becomes, the less current that must be supplied by the passivating (oxidizing) agent in order to re-establish a passive film that has been temporarily destroyed.

(6) The transpassive area: In the transpassive area the passive state is destroyed and the current density begins to increase again similar to that in the active region. In some steels a secondary passivity is frequently observed. From a practical standpoint, this secondary passivity is not important due to its small size and instability. Also steels cannot normally reach this high potential except when an external current is supplied. This secondary passivity has been ascribed to the adsorption of oxygen at the potential which is just before evolution of oxygen in gaseous form occurs.

It is thus seen that the above items 1-6 serve as a guide showing how an anodic polarization curve was used to systematically follow the effect of composition or other variables on the corrosion properties of the alloys tested. It should be noted also that cathodic reduction of the particular alloy has notable influence in the corrosion system, this being well known in the art.

Since the details of the experimental test technique do not constitute part of this invention, greater description thereof is deemed unnecessary.

In the tests conducted to verify the inventive corrosion resistant, high strength, high uniform elongation steel, the only variable in all of the alloys was the chemical composition. All other processing and testing factors were held constant, i.e., austenitizing temperature (2080° F.), deformation temperature (840° F.), amount of deformation (80%), and testing temperature (72° F.). The mechanical properties of the alloys indicate that the resulting structures ranged from metastable to completely stable austenite. A summary of these properties for alloys A-I is given in Table II, above, along with values from the literature for type 304 and type 316 stainless steel. Alloys A, E, F, G, and H were sufficiently metastable to undergo the TRIP steel phenomenon, and excellent strength-ductility values were obtained. The austenite in alloys D and I was metastable and underwent the austenite to martensite transformation, but at an insufficient rate to show appreciable strain-hardening (TS/YS ratios of 1.05 and 1.01, respectively).

Alloys A, D, F, G, and H were assumed to be completely austenitic before testing as indicated by their non-magnetic behavior. The remaining alloys were slightly magnetic before testing, indicating a small amount of martensite was present.

All of the alloys which underwent the austenite to martensite transformation exhibited a sharp yield point and Luder's strain. After the Luder's strain, the slope of the stress-strain curve (not shown) increased and a number of serrations appeared. These serrations have been attributed to the formation of martensite in local necked regions of the specimen. Due to the higher strain in these regions, martensite forms and strengthens this region against further necking, this being due to the TRIP phenomenon. Martensite is a more effective barrier to dislocation motion, hence deformation then proceeds in other areas of the specimen. These serrations may also be due to the Portevin-LeChatelier effect, but such effect probably plays only a minor role in these alloys due to the low diffusion rate of the solute elements at room temperature.

The difference between alloys A and B, see Table II, was that alloy B contained 2.7% more Ni, see Table I. Alloy B has a higher yield point, probably because of a combination of solution hardening and the fact that a small amount of martensite was initially present in alloy B. This martensite may have been produced either by the quenching after austenitizing or during deformation of the austenite at 450° C. Since the material behaved in a somewhat ductile manner, showing cup-cone fracture and 8% elongation, its non-TRIP behavior was prob-

ably due to the stability of the austenite against transformation by straining, and not to the initial martensite present. The influence of composition alone on the stability of the austenite in alloy B is indicated by its higher position in a Modified Schaeffler Diagram, not shown but widely utilized in the art.

Comparing alloys B, C, D, F, and G (see Tables I and II) it is seen that as Mo is added and Ni decreased,

corrosion potential (E_{corr}) of the alloys was indicated on the polarization curves, not shown. The passive potential region for all alloys tested ranged from approximately 0.1 v. to 0.95 v. The passive potential region was slightly larger for the alloys containing greater amounts of Mo.

The influence of nickel (Ni) on the inventive steel is seen by comparing alloys A and B in Table III below:

TABLE III.—SUMMARY OF ANODIC POLARIZATION RESULTS AND MECHANICAL PROPERTIES^a

Alloy	Weight percent					Fe	E_{pp}^b , V vs. S.C.E.	I_{cr}^c , $\mu\text{a}/\text{cm}^2$	I_p^d , $\mu\text{a}/\text{cm}^2$	Yield ^e strength, K s.i.	Tensile strength, K s.i.	Percent ^f elong. 1 in.
	Cr	Ni	Mo	Mn	C							
A.....	12.9	7.8	-----	-----	0.26	Bal.	-0.34	960	11	164	253	28
B.....	13.0	10.5	-----	-----	0.26	Bal.	-0.32	720	9.5	187	187	8
C.....	13.0	10.0	1.0	-----	0.26	Bal.	-0.31	98	11	194	194	11
D.....	12.6	8.8	2.0	-----	0.25	Bal.	-0.27	35	12	200	209	46
E.....	13.4	7.6	1.0	-----	0.236	Bal.	-0.32	76	13	190	264	27
F.....	12.3	7.8	3.0	-----	0.24	Bal.	-0.24	17	7	187	231	38
G.....	12.9	6.9	4.0	-----	0.25	Bal.	-0.25	12	9.5	185	249	34
H.....	13.0	5.9	3.0	2.0	0.25	Bal.	-0.28	30	8.5	185	231	40
I.....	12.8	5.8	3.0	4.0	0.185	Bal.	-0.38	38	9.5	186	188	46
304.....	18.7	9.1	-----	1.8	0.08	Bal. ^g	-0.22	84	4	35	85	55
316.....	18.0	13.5	3.0	1.0	0.04	Bal. ^g	-0.18	16	4	35	85	55

^a Mechanical properties for type 304 and type 316 taken from the Metals Handbook, 1961.

^b E_{pp} = Primary passive potential.

^c I_{cr} = Critical anodic current density.

^d I_p = Passive corrosion current density ($1 \mu\text{amp}/\text{cm}^2 \approx 0.5 \text{ mil per year}$).

^e 0.2% offset yield strength for type 304 and type 316 stainless steels.

^f 2 inch gage length for type 304 and type 316 stainless steels.

^g This alloy also contains a maximum of 1.00% silicon, 0.045% phosphorous and 0.030% sulfur.

a more unstable austenite is produced. This leads to excellent strength-ductility values as a result of the strengthening action of the austenite-to-martensite transformation. The increase in yield strength of alloys B, C, and D may be due to a combination of solution-hardening by the Mo, and hardening by precipitates of molybdenum carbides. At a Mo/Ni ratio of 3/8 (alloy F) the yield strength drops, and at a ratio of 4/7 (alloy G) the yield strength slightly decreases again. This indicates that the beneficial effects of solution and precipitation hardening may have been reached.

Comparing alloys F and H it is seen that Mn can be directly substituted for Ni. The two alloys have approximately the same mechanical properties.

While the tests did not establish a definite relationship between the position of the alloy in the Modified Schaeffler Diagram, its calculated M_s temperature, and its mechanical properties, it was observed that if the position of the alloy was too far above the austenite-martensite boundary the TRIP phenomenon did not occur. Also, while the Modified Schaeffler Diagram and the calculated M_s temperature serve as guides in selecting compositions that may undergo the transformation from austenite to martensite after yielding of the material takes place, these do not take into consideration the effect that the thermomechanical processing has on M_s and M_D , and hence on the resulting mechanical properties.

The effects of Ni, Mo, and Mn on the electrochemical parameters are summarized in Table III below. For comparison, the electrochemical values obtained for type 304 and type 316 stainless steel are also listed in Table III.

The electrochemical parameters listed in Table III are the primary passive potential (E_{pp}), the critical anodic current density (I_{cr}) and the passive corrosion current density (I_p). The effect of the alloying elements was most pronounced in the active region, where significant changes were observed in the critical current density (I_{cr}), and the corresponding potential (E_{pp}). Current density in the passive state (I_p) was approximately the same for all the materials tested and ranged from a minimum of $7 \mu\text{a}/\text{cm}^2$ (Alloy F) to a maximum of $13 \mu\text{a}/\text{cm}^2$ (Alloy E). On the other hand, the I_{cr} ranged from a low value of $12 \mu\text{a}/\text{cm}^2$ (Alloy G) to a high value of $960 \mu\text{a}/\text{cm}^2$ (Alloy A). The mixed or natural

As seen, the extra 2.7% Ni in alloy B decreased I_{cr} from $960 \mu\text{a}/\text{cm}^2$ to $720 \mu\text{a}/\text{cm}^2$ and I_p from $11 \mu\text{a}/\text{cm}^2$ to $9.5 \mu\text{a}/\text{cm}^2$. As expected E_{corr} and E_{pp} became slightly more positive. Regarding the column E_{pp} in Table III term (V vs. S.C.E.) defines the potential of volts vs. a saturated calomel electrode. As also seen, the effect of Ni on the mechanical properties of the alloys is significant as discussed above.

The influence of the Mo/Ni ratio can be seen by comparing alloys B, C, D, F, and G, the nominal ratios being 0/11, 1/10, 2/9, 3/8, and 4/7. The Mo content was increased by 1% steps as the Ni content was decreased by a similar amount. As can be seen from Table III, there is a tendency toward more positive primary passive potentials (E_{pp}) as the Mo is increased and Ni decreased. The outstanding effect that Mo has is in decreasing the critical anodic current density (I_{cr}). Comparing alloys B and C, it is seen that a very large decrease in I_{cr} is obtained by the simultaneous decrease of Ni by 1% and increase of Mo by 1%. I_{cr} is decreased by at least half of the previous value in going from a Mo/Ni ratio of 1/10 to 2/9 and from 2/9 to 3/8. When this ratio is changed from 3/8 to 4/7, I_{cr} only decreases by one-third, thus indicating the beginning of a leveling effect. The extent of the passive range also appears to have been maximized at a Mo/Ni ratio of 4/7. Molybdenum has been used to decrease the susceptibility of stainless steel to pitting by causing a more protective or more stable passive surface, and thus indicates from the test conducted that alloys F and G, which have the lowest I_{cr} may have a high resistance to pitting. The passive current density (I_p) of alloys C (1/10) and D (2/9) increased slightly over that of alloy B (0/11). Alloy F with a Mo/Ni ratio of 3/8 showed a decrease of I_p to a value of $7 \mu\text{a}/\text{cm}^2$. This was the lowest passive current density obtained for all the alloys tested. This corresponds to a corrosion rate of approximately 3.5 mils per year in the passive range. Examination of Table III shows that with an increase of the Mo/Ni ratio of 4/7 (alloy G), an increase in I_p to the value of alloy B (0/11) takes place, which appears to indicate that the beneficial effect of Mo/Ni is best at a ratio of 3/8 (alloy F).

The influence of Mo on alloys A-I with a fixed Ni content of 8% can be seen by comparing alloys A, E, and F

in Table III wherein the values of E_{pp} , I_{cr} , and I_p are given. As can be seen in Table III, a 1% addition of Mo resulted in a very large decrease in I_{cr} . The addition of Mo to 3% caused a further reduction of I_{cr} to a value of 17 $\mu\text{a./cm}^2$. The value of I_p actually increased slightly with the addition of 1% Mo, but decreased to the lowest value of all alloys tested when the Mo was increased to 3%. Thus, there is an increase in the stable passive potential range for alloy F over alloys A and E. Alloy F compares very favorably from a corrosion resistance standpoint with both types of stainless steels tested, as can be seen in Table III. The value of I_{cr} was much lower for alloy F than for type 304 stainless steel. This indicates that a much lower current (or lower concentration of oxidizing agent) is required in order to achieve passivity with alloy F or type 304 stainless steel. Once passivity is achieved, type 304 and type 316 stainless steels will corrode at a slightly lower rate than alloy F. The lower value of I_p for the stainless steels as compared to alloy F is due to their higher chromium content. All of the alloys tested, including type 304 and type 316 stainless steels indicate that their passive corrosion rate is well under 20 m.p.y., the maximum corrosion rate which would enable a material to be used in a process with only minor maintenance. Actual long term corrosion studies show that type 316 stainless steel corrodes at a rate less than 20 mils per year in an air-free, 10% sulfuric acid solution at room temperature. The test conducted indicate that alloy F, being very similar to the test results of type 316 stainless steel, may have similar corrosion resistance under the same environment, although verification has not yet been accomplished.

The influence of Mn on alloys A-I can be seen by comparing alloys H, I and F in Table III. Alloys H and I were identical in composition except for the Mn. The major effect of Mn was increasing the critical current density (I_{cr}), and hence decreasing the stability and ease of achieving passivity. Comparison of alloy H with alloy F, which has the same nickel equivalent, i.e., austenite forming elements (Ni, Mn, C) and the same mechanical properties, shows that I_{cr} is approximately double by the addition of 2% Mn. Addition of Mn up to 4% (alloy I) caused a further increase in I_{cr} , but due to the lower carbon content of this alloy, the increase is not very large. The passive current density (I_p) also increased slightly over those alloys without Mn. The potential range of the passive region was not greatly affected by the Mn additions.

Comparing alloy H (2% Mn) with type 304 stainless steel (Table III) shows that, even with the manganese addition, the critical current density (I_{cr}) of alloy H remains twice as low as for type 304 stainless steel.

As illustrated above, the effects of composition on the mechanical and corrosion properties of the inventive metastable austenitic steels have been determined, a summary of these properties being found in Table III. The base composition range for this series was 12.3%–13% Cr and 0.185%–0.26% C with the balance being iron, different amounts of Ni, Mo, and Mn being added to vary the composition.

In view of the foregoing, it has been shown that the present invention provides a metastable austenitic steel with greatly improved corrosion resistance but with similar mechanical properties of the previously known TRIP steels disclosed in the above referenced U.S. Pat. No. 3,488,231. The inventive concept has clearly been illustrated by tests which support the invention as producing a substantial step in the state of the art by providing a high strength, high elongation, corrosion resistant steel.

While particular compositions and operational sequences have been set forth to describe the inventive concept, modification and changes will become apparent to those skilled in the art, and it is intended to cover in the appended claims all such modifications and changes as come within the spirit and scope of the invention.

What we claim is:

1. In a process for producing a substantially austenitic steel having a combination of high strength, high uniform elongation, high toughness, and corrosion resistance by utilizing a strain-induced transformation which occurs in service, the steps of subjecting single phase, austenitic steel which has an M_s below ambient temperature, a total carbon plus nitrogen content of from about 0.15% to about 0.5%, a chromium content of from about 11% to about 18%, and which contains at least 0.5% of at least one alloying element selected from the group consisting of molybdenum, manganese, vanadium, niobium, tantalum, and tungsten, to deformation at a temperature above the M_D temperature, but below the recrystallization temperature of the steel, while maintaining same in substantially austenitic form, and cooling to ambient temperature while maintaining same in substantially austenitic form.

2. The process defined in claim 1, additionally, including the steps of forming the thus composed austenitic steel prior to the deformation thereof by heating the thus composed material thereof to a temperature above the critical austenite formation temperature thereof for a period of time sufficient to assure transformation of substantially all of the thus composed material to the austenitic phase, and bringing the temperature of the thus formed austenite steel to the temperature of deformation.

3. The process defined in claim 2, wherein the step of bringing the temperature of the thus formed austenitic steel to the temperature of deformation is accomplished by quenching the thus heated austenitic steel to room temperature and reheating the thus quenched austenitic steel to the deformation temperature.

4. The process defined in claim 2, wherein the step of bringing the temperature of thus formed austenitic steel to the temperature of deformation is accomplished by quenching the thus heated austenitic steel to the deformation temperature.

5. The process defined in claim 2, wherein the temperature above the critical austenite formation temperature is from about 1500° F. to about 2200° F., and wherein the temperature of deformation is from about 400° F. to about 1800° F.

6. The process defined in claim 2, wherein the step of forming the thus composed austenitic steel includes preparing the thus composed material to consist essentially of a composition of about 12.3% chromium, about 7.8% nickel, about 3% molybdenum, about 0.24% carbon-nitrogen, and the balance iron, and wherein the temperature above the critical austenite formation temperature is about 2080° F. with the time period being about one hour, wherein the temperature of deformation is about 840° F., and wherein the deformation of the austenitic steel is in the range of about 20% to about 80%.

7. The process defined in claim 1, additionally including the step of subjecting the thus formed substantially austenitic steel to strain thus inducing transformation of the substantially austenitic steel to martensitic steel, whereby the strength of the steel is increased.

8. The process defined in claim 1, wherein the single phase, austenitic steel has a carbon plus nitrogen content in the range of about 0.185% to about 0.26%, a chromium content in the range of about 12% to about 13.4%, a molybdenum content in the range of about 1% and about 4%, with the balance being essentially iron, and wherein the temperature above the critical austenite formation is about 2080° F. with the time period being about one hour, wherein the temperature of deformation is about 840° F., and wherein the deformation of the austenitic steel is in the range of about 20% to about 80%.

9. The process defined in claim 8, additionally including the steps of cooling the thus deformed austenitic steel to room temperature, straining the thus cooled steel about 15% at room temperature, and heating the thus straining steel to about 840° F. for a time period of about one-half hour.

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