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AUSTENITIC STAINLESS STEEL AND METHOD

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ABSTRACT OF THE DISCLOSURE

A chromium-nickel-molybdenum austenitic stainless steel, primarily for superior corrosion resistance for special applications such as in the chemical and process industries, has been obtained by initial forging (rolling) of the same only between critical temperatures of 2050° to 2200° F., when said novel stainless steel has essentially the following composition on weight basis:

	Percent
Chromium	20.00 to 23.00
Nickel	23.00 to 26.00
Molybdenum	4.00 to 5.00
Silicon (maximum)	1.00
Manganese (maximum)	2.00
Columbium	0.20 to 0.40
Carbon (maximum)	0.04
Iron	Balance

An annealing step is not required to avoid intergranular corrosion in welding the novel alloy. The novel alloy can be employed in chemical apparatus used, for example in wet phosphoric acid processes.

This invention relates to a process for manufacturing an alloy, more particularly, this invention relates to a process for manufacturing high chromium-nickel-molybdenum-iron alloy having included therein certain additional components to give it unexpectedly high corrosion resistance; the novel alloy is also within the scope of the invention.

Austenitic stainless steels of various properties have been used with great success in corrosive environments. Nevertheless, it is recognized that many types of stainless steels are suitable only in certain corrosive environments and not in others. It is also well known that varying the ratio of the components or merely varying a component of an alloy, e.g., in a stainless steel, often causes far reaching changes in the observed corrosion properties. Moreover, omitting a component in one of the combinations of components in a stainless steel alloy may result in equally far reaching changes in respect to the corrosion properties of this alloy when the same is exposed to different corrosive environments.

Further, it is known to treat, by annealing, stainless steel alloys of certain compositions to obtain the dissolution of the various carbides which may form in the intergranular regions of the alloy, and to make the alloy more plastic at higher temperature.

Hot working of various stainless steels is effected by appropriate plastic deformation of the alloys at elevated temperatures. It is not possible to predict just what will result from variations in the forming of alloys, when a component is added, subtracted, or proportions of the components changed. Hence, the discovery of novel alloys and processes for producing the same are governed by empirical observations with predictability being almost nonexistent.

As it is well known, austenitic steels are subject to severe attack at the grain boundary, known as intergranular corrosion, under the corrosive attack of an aggressive medium when exposed to the same. It is thought that this

phenomenon is the result of chromium carbide precipitation and the concomitant depletion of chromium in the areas adjacent to the grain boundaries. With increase in carbon content, such intergranular corrosion problem is increased.

Further, it has been proposed to reduce the susceptibility to intergranular corrosion by certain annealing treatments, or by stabilizing the alloys as in the American Iron and Steel Institute's Type 321 or 347 stainless steels or by using alloys with extra low carbon content.

However, while these steps have moderated the corrosive attacks encountered in chemical process industries, still no satisfactory answer has been found for all of the many corrosion problems encountered under various circumstances. Consequently, for many applications, the only solution to the corrosion problems has been the use of steels which have less than desired properties. Thus, any stainless steel alloy which improves some of the corrosion properties beyond those previously obtainable with the available steels, is a desired addition to the selection of useful stainless steel alloys. Moreover, a stainless steel alloy which eliminates some of the components in a previously known alloy but still possesses its most desirable properties, is a worthwhile economic addition to the series of stainless steels for use in chemical process industries.

Chromium-nickel-molybdenum stainless steels which have been made and used heretofore have often been ruined by cracking during rolling. It was tried, at considerable expense to use temperatures up to 2300° F., but this did not prove successful. For example, an ingot made with the composition:

	Percent
Carbon	0.026
Manganese	1.62
Silicon	0.61
Nickel	25.00
Chromium	20.60
Molybdenum	4.63
Columbium	0.40
Balance	(1)

[1] Essentially iron including conventional impurities associated with iron and not intentionally added.

when tested, appeared to be wothless as working it at 2300° F. (the temperature which had been found best for closely related stainless steel formulae of chromium, nickel and iron both with and without molybdenum) showed that its plasticity was insufficient, the ingots cracked on rolling with only 10% reduction from original thickness. After many experiments, it was discovered that adequate workability and plasticity are obtained if the temperature is kept within the range of 2050° to 2200° F.—that is, these properties are improved by lowering the temperature whereas previous experience had shown that they were improved by raising the temperature and deteriorated by going to lower temperatures. It has now been found that if a specific high chromium-nickel-molybdenum-iron austenitic alloy is processed in a critical range of temperature conditions, the process unexpectedly results in the production of an alloy of especially advantageous properties as concerning intergranular corrosion resistance, corrosion resistance of weldments made from the alloy, corrosion resistance to corrosive slurries and corrosion resistance to corodents of various types, as well as having suprisingly good plastic properties for hot rolling, etc. The freedom from necessity for a weldment annealing step is especially welcome in chemical process industries where large process equipment often cannot be annealed.

In accordance with the invention, the novel chromium-nickel-molybdenum austenitic stainless steel has been

worked into desired products by initially forging (hot rolling) the same between the critical temperatures of 2050° to 2200° F., when said stainless steel has a composition essentially within the following range on weight basis:

	Percent
Chromium	20.00 to 23.00
Nickel	23.00 to 26.00
Molybdenum	4.00 to 5.00
Silicon (maximum)	1.00
Manganese (maximum)	2.00
Columbium	0.20 to 0.40
Carbon (maximum)	0.04
Iron	Base

The resulting stainless steel alloy is especially remarkable for its superior corrosion resistance for special applications such as in the chemical and process industries.

Any impurities in the iron should be taken into account, as is well understood in this art, when formulating the alloy; but smaller percentages of other impurities can be tolerated where their effects are known to be compatible with the desired result. For example, in the herein described alloy the balance is iron, and it contains phosphorus, sulfur, copper, cobalt, etc., components which are generally not defined. These minor components in iron are not added intentionally and, therefore, not mentioned. Thus, the present alloy may contain about 0.30% of copper as an unintended component of iron up to 0.50% maximum. Copper is sometimes added to improve acid resistance. However, copper materially affects the ease of workability of the alloy rendering such an alloy often prohibitively expensive to work or allowing only the productions of small plates or slabs. Obviously, achieving suitable corrosion properties in more economical manner, i.e., with less working while also producing large sheets, opens up new uses of an alloy from which an intentionally added, cost-increasing component such as copper is eliminated. Hence, the ready production of sheets in sizes commonly specified for conventional stainless steels is also a desideratum in the stainless steel art. In addition to the unintentional components which are present and do not materially interfere with the properties of the alloy, some of the components such as carbon are detrimental from corrosion standpoint. Hence, eliminating carbon in conventional manner is well known. Eliminating carbon beyond the minimum, acceptable limits as herein in combination with varying the other components, such as using larger proportions of molybdenum, give the unexpectedly desirable properties to the present alloy manifesting in improved corrosion resistance in combination with the properties attributable to the herein disclosed combination of alloy components. Thus, the columbium content should be at least 10 times the carbon content but less than 1.00%; and in this range it provides resistance to intergranular corrosion in the present alloy.

TABLE I

Typical results are listed below for a ferrous alloy with the following chemical composition of the alloying constituents:

Chemical composition (nominal percent)

C	.03
Mn	1.70
Si	.50
Cr	21.00
Ni	25.00
Mo	4.50
Cb	0.30
Balance	(1)

[1] Essentially iron.

Mechanical properties (representative)

Tensile strength, p.s.i.	85,000
Yield strength, p.s.i.	39,000
Elongation, percent	45
Reduction area, percent	50
Hardness, Brinnell	170

Physical properties

Microstructure—Austenitic

Ferromagnetism—Non-magnetic

Density

Lb. per cu. in.	0.29

Approximate thermal conductivity

B.t.u. per hr. per sq. ft. per ft. per degree F.	8.5
Mild steel=1.00	0.30

Approximate coefficient of thermal expansion

Per degree F., 32° to 212° F.	9.15×10^{-6}
Mild steel=1.00	1.37

Thermal treatment

Initial forging—2050/2200° F.

Solution annealing—cool rapidly from 1950/2000° F.

Hardening—hardenable by cold work

Sensitivity to intergranular corrosion after welding—none

BEND (cold)

180° around a pin equal to the thickness of material being bent.

TABLE II.—COROSION DATA FOR THE NOVEL ALLOYR

[48 hour laboratory tests—All concentrations are by weight percent]

Environment	Temperature ° F.	Corrosion rate inches per year, (IPY)
20% phosphoric acid	Boiling point	<0.002
54% phosphoric acid	250	0.0024
60% phosphoric acid	Boiling point	0.010
85% phosphoric acid	Boiling point	0.495
25% phosphoric acid–2% HF	167	0.008
60% acetic acid	Boiling point	<0.002
1:1 acetic acid/anhydride	do	0.001
5% nitric acid plus 3% HF	155	<0.002
25% nitric acid	Boiling point	<0.002
65% nitric acid, Huey test	do	<0.020
5% hydrochloric acid	do	0.304
10% hydrochloric acid	Room temperature.	0.018
Do	140	0.150
Do	Boiling point	2.93
10% HCl in EDA [1]	do	<0.001
Butyl acetate mixture [2]	do	0.022
Streicher test [3]	do	0.008

[1] 1 Volume concentrate HCl in 9 volumes ethylene diamine.
[2] 75% ester—11% butanol—10% acetic acid—4% water—0.3% H_2SO_4.
[3] 50% sulfuric acid plus 0.6% Fe+++ as ferric sulfate inhibitor.

In respect to the hot forging (rolling) of the corrosion resistant stainless steel, it is known that with higher and higher alloy content added to the composition of austenitic alloys containing chromium, nickel, molybdenum, and iron, the hot strength and resistance to deformation in hot working increases. Unless high alloy content steels are worked at high temperatures, these high alloy stainless steels are prone to cracking at temperatures at the lower end of the working ranges. For example, an austenitic class of alloys start from about 9% nickel and 18% chromium content with the balance essentially iron. At temperatures between 2000° F. to 2300° F., this alloy displays sufficient plasticity, the latter being more pronounced at the higher temperatures. As greater amounts of nickel and then molybdenum are added to the chromium-nickel-iron alloy composition, plasticity is reduced and tendency to crack is increased if the composition is worked at the lower temperature. Hence, the minimum working temperature must be increased with increased alloy content. For example, Type 310 stainless steel (25% chromium, 20% nickel, balance iron) is sufficiently plastic at hot working temperature of 2000° to 2300° F. It

is more plastic at or near 2300° F., and it is recognized that the higher the temperature within the above range, the more satisfactory is the workability.

The foregoing concerning Type 310 stainless steel holds true for Type 330 stainless steel (35% nickel, 15% chromium, balance essentially iron) as well as for Type 316 stainless steel (18% chromium, 13% nickel, 2½% molybdenum).

In sharp distinction in respect to the Type 310, 330, and 316, and like stainless steels, the novel alloy composition is satisfactorily hot workable throughout the range of 2050° to 2200° F. without deleterious cracking, which cracking is especially prevalent at the higher temperatures heretofore required for high alloy content stainless steels. This critical relationship of workability and obtaining highly corrosive resistant ferrous alloys was established by working ferrous base alloys with the following alloying compositions:

TABLE II

	C	Mn	Si	Ni	Cr	Mo	Cb
Heat No.:							
A	.038	1.62	.58	25.28	20.40	4.20	.39
B	.032	1.73	.50	24.78	20.30	4.22	.37
C	.029	1.68	.54	25.50	20.90	4.22	.40
D	.040	1.76	.53	25.13	20.45	4.22	.37
E	.039	1.64	.46	25.15	19.65	4.27	.35
F	.033	1.76	.66	25.10	20.25	4.00	.37
G	.029	1.78	.52	25.60	20.65	4.35	.39
H	.032	1.70	.56	24.60	20.70	4.25	.40
I	.040	1.75	.67	24.88	20.60	4.25	.37

In reference to the above list, working is carried out as described below. For example, reduction of ingot thickness per pass is approximately ½" and can vary between ¼" and 1" per pass. A standard ingot employed measures 26" wide x 8" thick x 48" long (2400#). Upon properly and uniformly heating the ingot in a furnace to the acceptable temperature of 2200° F., maximum, it is removed from the furnace and charged to the ingot-breakdown rolling mill. The rolling mill can be a two-high, non-reversing mill employing a pair of rolls 66" long x 31" diameter. The ingot enters the rolls in the "flat" position with the roll opening set at approximately 7½". The first pass and subsequent passes reduce the 8" thickness of the ingot in approximately ½" to ¾" increments to the intermediate thickness or finished plate thickness desired, for example, one inch. In the case of a 1" thick plate, the number of passes would be from 10 to 16. However, during the rolling, if the temperature of the ingot has decreased to 2050° F., the ingot must be re-heated in the furnace so that further reduction will be within the range of 2050° to 2200° F., to prevent cracking due to loss in plasticity.

In another example, if a ¼" thick plate is desired, rolling is carried out as above to an intermediate thickness of approximately ¾". Following cutting to appropriate width and length, cooling to room temperature, inspection, and surface grinding as necessary to remove scale, the ¾" thick intermediate plate is heated uniformly and properly to approximately 2200° F. maximum and rolled on a two-high, non-reversing plate mill to ¼" thickness while observing the requirement of 2050° to 2200° F. temperature range.

In testing for corrosion under field conditions at an average temperature of about 165° F. in a moderately to strongly agitated wet phosphoric acid slurry of 30% P_2O_5 and 2% to 3% H_2SO_4, the slurry consisting of phosphate rock and gypsum including usual impurities, e.g., fluorine, the corrosion rate of the novel alloy was found to be 1.35 mils/year. In respect to the corrosion caused by fluorine and other halogens in various chemical processes, the novel alloy shows good corrosion resistance.

Morevoer, because of the particular combination of the components in the herein disclosed proportions, the novel alloy exhibits a marked improvement against pitting corrosion as well as against overall corrosion compared with the standard stainless steels used for designing process equipment.

In testing the various properties of the alloy, ASTMS procedures are employed.

What is claimed is:

1. A chromium-nickel-molybdenum austenitic stainless steel of improved corrosion resistance obtained by initial forging of same between temperatures of 2050° to 2200° F., said stainless steel consisting essentially of the following composition on weight basis:

	Percent
Chromium	20.00 to 23.00
Nickel	23.00 to 26.00
Molybdenum	4.00 to 5.00
Silicon (maximum)	1.00
Manganese (maximum)	2.00
Columbium	0.20 to 0.40
Carbon (maximum)	0.04
Iron	Balance

2. An austenitic stainless steel of improved corrosion resistance, hot formed between 2050° to 2200° F., said stainless steel consisting essentially of iron alloyed with:

	Percent
Chromium	20.00 to 23.00
Nickel	23.00 to 26.00
Molybdenum	4.00 to 5.00
Silicon (maximum)	1.00
Manganese (maximum)	2.00
Columbium	0.20 to 0.40
Carbon (maximum)	0.04

3. An austenitic stainless steel of improved corrosion resistance, said stainless steel consisting essentially of iron alloyed with:

	Percent
Chromium	20.00 to 23.00
Nickel	23.00 to 26.00
Moybdenum	4.00 to 5.00
Silicon (maximum)	1.00
Manganese (maximum)	1.00
Columbium	0.20 to 0.40
Carbon (maximum)	0.04

4. A chromium-nickel-molybdenum austenitic stainless steel of improved corrosion resistance according to claim 2 and wherein iron is alloyed with:

	Percent
Chromium	21
Nickel	25
Molybdenum	4.5
Silicon	.5
Manganese	1.7
Columbium	0.3
Carbon	0.03

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