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SEMI-AUSTENITIC Cr-Ni-Al-Cu STAINLESS STEEL

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ABSTRACT OF THE DISCLOSURE

A semi-austenitic chromium-nickel-aluminum stainless steel consisting essentially of, by weight percent, about 7.0–18.0% chromium, about 6.0–12.0% nickel, about .5–2.5% aluminum, manganese and silicon each not exceeding about 1.0%, carbon not exceeding about .042%, phosphorus not exceeding about .040%, sulfur not exceeding about .015%, nitrogen not exceeding about .05%, molybdenum up to about 8.0%, about 1.0–3.0% copper, about .0005–.003% boron, and the balance essentially iron. Said steel, in the precipitation hardenable conditions, is characterized by a U.T.S. of at least 230 ks.i. and improved toughness at room temperature as measured by a precracked sheet charpy with a value of 1000 in.-lbs./in.^{2}, provided that the carbon content plus 6X boron content does not exceed .045.

BACKGROUND OF THE INVENTION

This invention represents an improvement over the precipitation hardening stainless steel disclosed and claimed in U.S. Pat. 3,278,298, issued Oct. 11, 1966, to D Cameron Perry. The precipitation hardening stainless steels, particularly the semi-austenitic Cr-Ni-Al stainless steels to which the respective inventions relate, were developed and introduced in 1950. For instance, such steels are described in detail in U.S. Pat. Nos. 2,505,762, 2,505,763, 2,505,764, and 2,506,558, issued to G. N. Goller in May 1950.

The family of precipitation hardening stainless steels, which includes the Cr-Ni-Al steels of this invention, may be classified into three distinct groups, each characterized by a particular crystalline structure and a thermal treatment to achieve the superior properties. While each is generally known in the prior art, a brief description may help in the understanding of the present invention. One member of the family is the austenitic PH stainless steels which are characterized by an austenitic crystaline structure at all times throughout its processing and heat treatment. The hardening reactions are achieved by means of a single heat treatment. A second member is the martensite grades which are never austenitic at room temperature. In fact, the crystalline structure is always substantially martensitic. In the manner of the austenitic members, the thermal treatment involves a single step. The final member of the family is the semi-austenitic grades, the steels of the present invention. While greater detail will be given hereinafter, these steels may be solution treated to yield a stable austenitic structure. However, they can be heat treated to a martensitic structure by a suitable thermal treatment, then staged to high strength levels. In the practice known to the prior art, this treatment is termed a double heat treatment.

The semi-austenitic precipitation hardening stainless steels, precipitation hardening hereinafter referred to as PH, captured the imagination of designers looking for materials which possessed high strength at elevated temperatures, along with resistance to corrosive environments. Such steels combine the advantages of the well-known AISI 300 and 400 series stainless steels. However, the production of these PH stainless steels was not without the imposition of critical controls to develop the outstanding properties. Typically, the high strength in these

steels is achieved by a heat treatment which includes three essential steps.

(1) Austenite conditioning,
(2) Cooling below a critical temperature which may be subzero to effect transformation of austenite to martensite,
(3) Precipitation hardening.

The steels of this invention possess certain advantages over the standard stainless steels and others of the precipitation hardening varieties. For example, the steel may be shipped from the producing mill in very cold weather without the risk of premature hardening. After forming or fabrication the material may then be given the first of said three treatments.

Finally, the treatments may be continued to develop the desired high strength and toughness.

Generally speaking, such combination of properties are unique. Typically, toughness is sacrificed at the expense of strength. However, by the present invention, it was discovered that the proper combination and correlation of elements could produce a steel having a minimum U.T.S. of 230 k.s.i., and a pre-cracked sheet charpy with a value of 1000 in.-lbs./in.^{2} at room temperature.

SUMMARY OF THE INVENTION

Briefly in the practice of this invention, there is provided a semi-austenitic precipitation hardenable stainless steel having controlled additions of chemical elements in a ferrous base. Specifically, in the broadest and preferred range, said additions, by weight percent, are as follows:

Broad	Chemistry	Preferred
.042% max.	Carbon	.039% max.
1.00% max.	Manganese	.75% max.
.040% max.	Phosphorus	.020% max.
.015% max.	Sulfur	.010% max.
1.00% max.	Silicon	.75% max.
7.0–18.0%	Chromium	13.50–15.00%
6.0–12.0%	Nickel	7.25–8.75%
8.0% max.	Molybdenum	1.50–3.00%
.5–2.5%	Aluminum	1.00–1.75%
1.00–3.00%	Copper	1.50–2.50%
.05% max.	Nitrogen	.01% max.
.0005–.003%	Boron	.0005–.0015%
Balance	Iron	Balance

However, within these chemistry ranges, there is one particularly important control which must be exercised in attaining high strength and improved toughness in the doubly heat treated condition. Specifically, the carbon content plus six (6) times the boron content should not exceed about .045, preferably no greater than about .042.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

Turning now to the practice of this invention, there is provided a semi-austenitic chromium-nickel-aluminum-copper stainless steel. Said steel is a modification of the precipitation hardening stainless steel disclosed and claimed in U.S. Pat. No. 3,278,298, by D Cameron Perry. While all modifications, and the effects of same, will become apparent hereinafter, certain major ones are outlined below:

(1) Reduction of carbon
(2) Synergistic relationship of carbon and boron on toughness
(3) Addition of copper as supplemental precipitation hardening agent for improved strength

It should be clear from the preceding that the mechanical properties achieved hereby are due in large measure to the critical control of ingredients comprising the

chemistry of this steel. Considering now the said chemistry, in tabular form, by weight percent:

CHEMISTRY

	Percent
Carbon	.042
Manganese ---max--	1.0
Phosphorus ---max--	.040
Sulfur ---max--	.015
Silicon ---max--	1.0
Chromium	7.0–18.0
Nickel	6.0–12.0
Molybdenum ---max--	8.0
Aluminum	.5–2.5
Copper	1.0–3.0
Nitrogen ---max--	.05
Boron	.0005–.003
Iron	Balance

it will be noted that while some latitude is given to several of the elemental ranges, it is important that certain relationships be maintained. For example, to insure a U.T.S. in excess of 230 k.s.i., and a toughness at room temperature of 1000, as expressed in W/A (work/area, in.–lbs./in.^{2}), the carbon content plus six times the boron content should not exceed .042. Finally, it is preferred that the total aluminum and copper content, within the limits stated, should be at least 3.00% by weight. Supporting reasons for each said control will become more apparent by the description and examples to follow.

The significance of balancing the ingredients of this steel may be gained most by reviewing the heat treating cycle followed to achieve the desired properties herein.

Initially, the steel in the form of plate, sheet, strip, bars, rods, wire and the like, is given an annealing or solution-treatment at a temperature in the range of about 1800° F.–2000° F. Such a treatment may be affected either by the steel producer or the customer-fabricator. In any case, the material in this condition is ideally suited for fabrication, as the steel has a relative softness on the order of about R_B 80–90.

The annealing or solution-treatment apparently places the metal in an austenitic condition in which the aluminum and copper content of the steel are dissolved. Upon quenching the steel, the aluminum and copper constituents remain in solution. Thus, since the steel is essentially austenitic at this stage, it is relatively soft, ductile and readily formable to the shapes and sizes desirable.

As noted above, and to be discussed hereinafter, one of the significant steps of this total heat treating cycle is a refrigeration treatment which results in the transformation of the austenite to martensite. Accordingly, unless a proper balance is maintained in the steel of this invention, the shipment of the steel in the solution-treated condition might encounter cold weather, which could result in a partial transformation of the material or the steel might be so stable as to preclude good heat treatment response. Thus, chemistry balancing is critical within the ranges stated above. For example, the total alloy content, as well as the austenite-ferrite balance is critical. If the austenite balance (C, Ni, Mn, Cu, N) is too high at a given ferrite level (Cr, Si, Al, Mo), the steel is too stable to transform. At this same austenite level, however, a lower or higher ferrite level may result in a steel too unstable or too stable respectively. In addition, at a given ferrite level, a low or high austenite level will also result in a steel which is too unstable or too stable, respectively. Thus it can be seen that not only is the ferrite level and austenite level important, but their interrelationship and total alloy content, are important if this invention is to produce a steel which meets the stability requirements desired.

Following the fabrication of the steel, it is given an austenite-conditioning heat treatment at a temperature on the order of about 1300° F.–1750° F. for a period of time of at least one hour. Following said treatment, the steel is cooled or refrigerated at a sub-zero temperature of about −100° F. for about eight hours, to effect the transformation from austenite to martensite.

Final hardening of the steel is achieved by reheating the material at a temperature of about 700° F. to about 1200° F. and cooling to room temperature. Ordinarily, the preferred heating range is between about 900° F. to 1050° F. for about one hour. This treatment results in a material having a hardness on the order of R_C 40–53, a U.T.S. of at least 230 k.s.i., and a toughness of 1000 as measured in W/A [in.–lbs./in.^{2}].

Turning now more particularly to the several ingredients of the steel, it will be appreciated that while all of the additions are significant, certain ones are more critical. For example, the amounts of chromium, nickel, aluminum and copper employed in the steel of this invention and the correlation between same are particularly critical. For where lesser amounts of chromium are employed, the desired resistance to corrosion is not achieved. And where greater amounts are employed, the structural balance of the steel is upset, with a resultant loss in hardness in the precipitation-hardened condition. Thus, it is preferred that the chromium be present in an amount between about 10.0–15.0%, or more preferably at least 13.5–15.0%. Similarly, where either lesser amounts of nickel are used than the prescribed minimum a tendency towards instability results and the steel inclines to harden prematurely in cold weather. On the other hand, where greater amounts are used than the maximum of 12%, the structure of the steel is radically changed with a resulting loss of mechanical properties. Therefore, it is preferred that the nickel be present in an amount between about 7.0–10.0%, or more preferably in the range between about 7.25–8.75%.

While there may be some latitude with respect to the copper and aluminum content, it is believed that these ingredients which when found in the steel of this invention precipitate as an intermetallic compound, such as with nickel, to develop the higher final strengths obtained by the final agging treatment. Therefore, it is important to maintain the copper and aluminum within the prescribed limits so as not to disturb the structural balance and resulting undesired change in the overall mechanical properties. Preferably, it is desirable to include at least a total content of the two elements of at least 3.00%.

The inclusion of the interstitial elements, namely, carbon, sulfur, and nitrogen, are not without significance in the attainment of the properties of the steel of this invention. The carbon content, as noted above, must not exceed 0.042%, by weight, for the carbon-boron relationship will be exceeded and the toughness of the steel lowered. From the standpoint of mere toughness, the lower carbon contents are desirable, even though this may result in a lowering of the strength. Thus, while lower carbons are desirable, it is preferred that at least .02% be included. Another factor affecting the carbon content is the holding time required for the conditioning treatment. At carbon levels of about .02%, the conditioning treatment must be on the order of several hours. On the other hand, if the carbon is increased to even about .025%, the treatment time may be reduced to about one hour.

The sulfur content of this steel should not exceed about .015%, and preferably should not exceed .010%, for the reason that this ingredient appears as an interstitial in the crystal lattice of the metal. This may generate dislocations. Thus, by minimizing the sulfur content, hence, reducing the number of dislocations in the lattice structure, there results an increase in the toughness of the metal.

With respect to the nitrogen content, it is preferable to maintain same below about .05%, and more preferably below about .01%, so as not to impair the toughness and resistance to impact. Optimum toughness will be obtained with nitrogen below about .003%. It is believed that with larger amounts of nitrogen in the presence of the

aluminum of this steel, there is a tendency for the elements to form aluminum nitrides, which when dispersed throughout the steel may affect the properties thereof.

Boron is desirable in the steel of this invention as it helps to secure good hot-rolling and other hot-working properties. For this reason, at least .0005% is used. However, the boron content should not exceed about .003% because boron like the sulfur discussed above, is an interstitial in the crystal lattice structure, and this causes an attending loss in toughness. It was further discovered that when working with steels having a U.T.S. greater than about 230 k.s.i., the boron in the range described has six times the effect of carbon on the final toughness of the heat treated steel. Accordingly, to achieve both the high strength and good toughness it is important that the carbon content plus six times the boron content should not exceed .042. While this gives excellent toughness at room temperature, a lesser figure, namely, .039, is applied to the carbon-boron relationship for sub-zero temperatures. For example, in order to insure a toughness value of 500 at —70° F., as measured in W/A [in.-lbs./in.^{2}], the lower value of .039 should be used as the maximum.

Phosphorus normally is present in the steel of this invention in relatively small amounts. While the lowest values are most desirable, the phosphorus content should not exceed .040%. As to the manganese and silicon contents, optimum mechanical properties are achieved with maximum contents of .1%.

While the molybdenum content has been shown in this steel to be an optional element, it is preferred that the element be used to the extent of about 2%. Accordingly, the preferred figure for the molybdenum is a maximum of 6% with the most preferred range thereof being between about 1.50–3.00%.

Before putting these teachings together to illustrate some specific examples, it will be observed that throughout this discussion the toughness has been expressed in W/A values. This is a toughness test that was developed on sheet like materials for it was found that the Allison bend tests (also known as the instrumented band test) was incapable of separating very tough materials. The use of a pre-cracked sheet Charpy was found to be reliable, yet inexpensive, in measuring the toughness of the material. For more information on this means of evaluating toughness, reference may be made to the article by G. M. Orner and C. E. Hartbower, entitled "Sheet Fracture Toughness Evaluated by Charpy Impact and Slow Bend," Welding Research Supplement, September 1961, pages 405s–416s.

By way of specific illustration of the steels of this invention, attention is directed to Tables I and II which give the chemistry and mechanical properties of ten different samples which have been given the double heat treatment in the manner described previously. Samples 1–6 all have chemistry limits which fall within the broad ranges but fail to achieve both high strength and good toughness in the heat treated condition. One obvious failure of these steels is the fact that the carbon-boron relationship does not comply with the requirements established for this invention. In contrast to this, samples 7 through 10 comply with all of the requirements which have been established for the steels of this invention, and as a consequence achieve the mechanical property limits desired.

TABLE II. MECHANICAL PROPERTIES

Sample	Strength, k.s.i. .2% YS	Strength, k.s.i. UTS	W/A, in.-lbs./in.^{2} Room temp.	W/A, in.-lbs./in.^{2} —70° F.
1	207.6	235.0	865	161
2	213.6	237.4	806	168
3	219.8	239.5	520	128
4	197.3	219.0	1,961	1,529
5	175.5	194.6	1,191	968
6	212.8	228.1	1,281	897
7	221.8	239.8	1,714	1,384
8	214.3	241.3	1,439	1,324
9	214.1	239.3	1,735	1,500
10	229.8	255.4	1,235	744

The ten samples, identified as 1 to 10 above, were vacuum induction melted and cast as thirty pound 3"x 3" ingots. The resulting ingots were then heated to 2150° F. and hot rolled to 1" thickness. The hot rolled bars were then cut into 8–9" lengths, heated to 1950° F., further hot reduced to .100–110", annealed at 1825° F. and pickled, cold reduced to .050", annealed at 1825° F. and pickled, and finally sampled for testing.

The stability of all samples to cold treatment was determined by hardness tests before and after the following treatments:

(1) as annealed, the final process step,
(2) as annealed plus refrigeration at 0° F., for 16 hours (simulate conditions during transport of steel in cold weather from steel mill to customer-fabricator), and
(3) as annealed plus box anneal at 900° F. for 4 hours, plus refrigeration at 0° F. for 16 hours.

Response to the standard double heat treatment of 1700° F. for 1 hour, air cooled to room temperature, refrigeration at —100° F. and held for 8 hours, followed by heating to 950° F. for 1 hour and air cooling, indicated whether the samples were too stable to meet the minimum U.T.S. of 230 k.s.i.

All of the samples fall within one of four categories, namely: (a) suitable, (b) too stable for transformation, (c) too unstable and thereby resulting in premature transformation, (d) partial premature transformation but usable as a result of the intermediate box anneal at 900° F. With respect to this latter category, it was discovered that some samples would partially transform when tested under procedure (2) above. However, such samples could be salvaged by interposing the box anneal [procedure (3)] and preventing the premature transformation.

As a result of this testing and subsequent double treatment, it was determined that Samples 1, 2, 8 and 9 fell within category (a), Samples 4, 5 and 6 within category (b), Sample 3 within category (c), and Samples 7 and 10 within category (d). Thus, where seven of the samples satisfied the minimum strength requirements, only Samples 7–10 achieved both the strength and toughness limits established earlier.

While it should be apparent from the above that controls are critical to achieving the unique properties hereof, those skilled in the art may find areas wherein changes and modifications may be effected therein. Accordingly, no limitation is intended to be imposed herein except as set forth in the appended claims.

TABLE I.—CHEMISTRY

Sample	C	Cr	Ni	Mo	Al	Cu	N	B	C+6XB	Cu+Al
1	.044	14.39	8.37	2.24	1.32	1.14	.0015	.0034	.0644	2.46
2	.045	14.60	8.42	2.18	1.42	.57	.0015	.0024	.0694	1.99
3	.038	14.42	7.50	1.55	1.04	1.90	.0039	.0027	.0542	2.94
4	.040	14.30	8.31	2.30	.97	1.95	.0023	.001	.0460	2.92
5	.042	16.02	7.81	0.90	.94	1.96	.0040	.0029	.0594	2.90
6	.034	[1] 13.93	8.12	2.25	1.04	1.98	.0027	.0029	.0514	3.02
7	.033	14.44	7.94	2.28	1.20	1.95	.0018	.0017	.0432	3.15
8	.028	14.38	8.30	2.29	1.23	1.95	.0028	.0017	.0392	3.18
9	.024	14.60	8.16	2.31	1.30	2.05	.0018	.0017	.0342	3.35
10	.036	14.26	8.01	2.31	1.30	1.95	.0013	.0010	.042	3.25

[1] Sample 6 contained .27% V, where V=2Cr.

NOTE.—All samples contained Mn<.05, P<.005, S<.004, Si<.08.

I claim:

1. A semi-austenitic precipitation-hardenable stainless steel consisting essentially of, by weight percent, about 7.0–18.0% chromium, about 6.0–12.0% nickel, about .5–2.5% aluminum, a maximum of 1.0% manganese, a maximum of 1.0% silicon, a maximum of .042% carbon, a maximum of .040% phosphorus, a maximum of .015% sulfur, a maximum of .05% nitrogen, a maximum of 8.0% molybdenum, about 1.0–3.0% copper, about .0005–.0015% boron, with the balance essentially iron, the sum of the aluminum plus copper contents being at least 3.00%, and the carbon content plus six times the boron content not exceeding .045.

2. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 1, wherein the phosphorus, sulfur and nitrogen are limited to .02% maximum, .010% maximum, and .01% maximum, respectively.

3. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 2, wherein the carbon is present in an amount not exceeding .039%, and wherein the carbon content plus six times the boron content does not exceed .042.

4. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 3, wherein the chromium is present in an amount between 13.50–15.00%, and nickel is present in an amount between 7.25–8.75%.

5. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 4, wherein the aluminum is present in an amount between about 1.25–1.75%, and copper is present in an amount between 1.50–2.50%.

6. The semi-austentic precipitation-hardenable stainless steel claimed in claim 5, wherein the molybdenum is present in an amount between 1.50–3.00%.

7. A semi-austenitic precipitation-hardenable stainless steel consisting essentially of, by weight percent, about 10.0–15.0% chromium, about 7.0–10.0% nickel, about .75–2.0 aluminum, a maximum of .75% manganese, a maximum of .75% silicon, a maximum of .042% carbon, a maximum of .040% phosphorus, a maximum of .015% sulfur, a maximum of .05% nitrogen, a maximum of 6.0% molybdenum, about 1.0–3.0% copper, about .0005–.0015% boron, with the balance essentially iron, the sum of the aluminum plus copper contents being at least 3.00%, and the carbon content plus six times the boron content not exceeding .042.

8. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 7, wherein the phosphorus, sulfur and nitrogen are limited to .020% maximum, .010% maximum, and .010% maximum, respectively.

9. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 8, wherein the carbon is present in an amount not exceeding .039%.

10. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 9, wherein the chromium is present in an amount between 13.50–15.00%, and nickel is present in an amount between 7.25–8.75%.

11. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 10, wherein the aluminum is present in an amount between about 1.25–1.75%, and copper is present in an amount between 1.50–2.50%.

12. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 11, wherein the molybdenum is present in an amount between 1.50–3.00%.

13. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 13, wherein the manganese and silicon each do not exceed .10%.

14. The semi-austenitic precipitation-hardenable stainless steel claimed in claim 14, wherein the nitrogen does not exceed about .003%.

15. A semi-austenitic precipitation-hardenable stainless steel consisting essentially of, by weight percent, about 13.50–15.00% chromium, about 7.25–8.75% nickel, about 1.00–1.75% aluminum, a maximum of .75% manganese, a maximum of .75% silicon, a maximum of .039% carbon, a maximum of .020% phosphorus, a maximum of .010% sulfur, a maximum of .01% nitrogen, about 1.50–3.00% molybdenum, about 1.50–2.50% copper, about .0005–.0015% boron, and balance substantially iron with the sum of the aluminum plus copper contents being at least 3.00%, and the carbon content plus six times the boron content not exceeding about .039.

16. A precipitation-hardened stainless steel havng a hardness of about R_C 40–53, an ultimate tensile strength of at least about 230 k.s.i., and a pre-cracked sheet charpy toughness of at least 1000 W/A (in.–lb./in.^{2}) at room temperature, said steel consisting essentially of, by weight percent, about 10.0–15.0% chromium, about 7.0–10.0% nickel, about .75–2.0% aluminum, a maximum of .75% manganese, a maximum of .75% silicon, a maximum of .042% carbon, a maximum of .040% phosphorus, a maximum of .015% sulfur, a maximum of .05% nitrogen, a maximum of 6.0% molybdenum, about 1.0–3.0% copper, about .0005–.0015% boron, and the balance iron, with the sum of the aluminum plus copper contents being at least 3.00%, and the carbon content plus six times the boron content not exceeding .042.

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