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(71) Applicant(s)
ATI Properties LLC

(72) Inventor(s)
Berry, David C.;Bailey, Ronald E.

(74) Agent / Attorney
K&L Gates, Level 25 South Tower 525 Collins Street, Melbourne, VIC, 3000, AU

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(71) Applicant: ATI PROPERTIES, INC. [US/US]; 1600 N.E. Old Salem Road, Albany, OR 97321 (US).

(72) Inventors: BERRY, David, C.; 1232 Willowbrook Drive, Washington, PA 15301 (US). BAILEY, Ronald, E.; 313 Oak Forest Drive, Pittsburgh, PA 15216 (US).

(74) Agents: GROSSELIN, John, E., III et al.; ATI Properties, INC., 1000 Six PPG Place, Pittsburgh, PA 15222 (US).

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(54) **Title**: DUAL-PHASE STAINLESS STEEL

(57) **Abstract**: A dual-phase ferritic-martensitic stainless steel includes, by weight, about 11.5% to about 12% Cr, about 0.8% to about 1.5% Mn, about 0.75% to about 1.5% Ni, 0% to about 0.5% Si, 0% to about 0.2% Mo, 0% to about 0.0025% B, Fe, and impurities. In various embodiments, the steel has a Brinell hardness (HB) and Charpy V-notch impact energy at -40°C (CVN) such that CVN (ft-lb) + (0.4xHB) is about 160 or greater. Articles of manufacture including the stainless steels also are disclosed.

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TITLE

DUAL-PHASE STAINLESS STEEL

INVENTORS

David C. Berry

Ronald E. Bailey

BACKGROUND OF THE TECHNOLOGY

FIELD OF TECHNOLOGY

[0001] The present disclosure relates to a dual-phase stainless steel having a microstructure of ferrite and tempered martensite. In particular, the present disclosure relates to cost-effective stainless steels having improved hardness for abrasion-resistant and/or wear-resistant applications.

DESCRIPTION OF THE BACKGROUND OF THE TECHNOLOGY

[0002] Dual-phase stainless steels can exhibit a combination of desirable properties that make them useful for a wide variety of industrial applications, such as for oil sands extraction and in the sugar industry. These steels are generally characterized by a microstructure of tempered martensite dispersed in a ferrite matrix.

[0003] An example of a dual-phase stainless steel is ATI 412™ stainless steel (UNS 41003), which typically contains, by weight, 11.75% chromium (Cr), 0.90% manganese (Mn), 0.70% silicon (Si), 0.40% nickel (Ni), 0.030% sulfur (S), 0.020% carbon (C), 0% to 0.040% phosphorus (P), 0% to 0.030% nitrogen (N), and the balance iron (Fe) and other incidental impurities. ATI 412™ stainless steel typically has a Brinell hardness (HB) of about 177 when annealed at about 766°C, and a Brinell hardness of about 258 when annealed at about 843°C.

[0004] Another dual-phase stainless steel is Duracorr® steel, which contains, by weight, 11.0% to 12.5% Cr, 0.20% to 0.35% molybdenum (Mo), 0% to 1.50% Mn, 0% to

1.00% Ni, 0% to 0.70% Si, 0% to 0.040% P, 0% to 0.030% N, 0% to 0.025% C, 0% to 0.015% S, and the balance Fe. Notably, Duracorr® stainless steel contains Mo as an alloying element, *i.e.*, an intentional alloying addition, and not as an incidental impurity. Because of the rising costs of Mo, however, Duracorr® stainless steel may be too costly for certain applications. Although Duracorr® stainless steel typically has a hardness of about 223 HB, it can be processed to exhibit nominal hardness of 300 HB, which grade is commercially available as Duracorr® 300 stainless steel. Duracorr® and Duracorr® 300 stainless steels have largely the same composition, but the hardness of Duracorr® 300 stainless steel varies from 260 HB to 360 HB. The increased hardness of Duracorr® 300 stainless steel, however, is accompanied by a reduction in toughness. For example, the Charpy V-notch impact energy of Duracorr® 300 stainless steel at -40°C is only about 15 ft-lb on average.

[0005] In applications requiring a stainless steels having abrasion resistance and/or wear resistance, high hardness levels, for example, up to about 350 HB, may be desirable in combination with higher toughness than is available from Duracorr® 300 stainless steel. Moreover, an in-service work hardenability up to about 450–500 HB, for example, may be required in certain applications. Furthermore, it is desirable that any such alloys are cost-effective.

SUMMARY

[0006] According to one non-limiting aspect of the present disclosure, an embodiment of a high-hardness dual-phase ferritic-martensitic stainless steel is described. The stainless steel comprises, by weight, about 11.5% to about 12% Cr, about 0.8% to about 1.5% Mn, about 0.75% to about 1.5% Ni, 0% to about 0.5% Si, 0% to about 0.2% Mo, 0% to about 0.0025% B, Fe, and impurities. In certain non-limiting embodiments, the stainless steel according to the present disclosure exhibits Brinell hardness (HB) and Charpy V-notch impact energy at -40°C (CVN) such that CVN (ft-lb) + ($0.4 \times$ HB) is about 160 or greater.

[0007] According to another non-limiting aspect of the present disclosure, an embodiment of an article of manufacture including a high-hardness dual-phase ferritic-

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martensitic stainless steel is described. The stainless stell comprises, by weight, about 11.5% to about 12% Cr, about 0.8% to about 1.5% Mn, about 0.75% to about 1.5% Ni, 0% to about 0.5% Si, to about 0.2% Mo, 0% to about 0.0025% B, Fe, and impurities. According to certain non-limiting embodiments of the article, the stainless steel exhibits Brinell hardness (HB) and Charpy V-notch impact energy at -40°C (CVN) such that CVN (ft-lb) + (0.4 x HB) is about 160 or greater.

[**0007a**] According to a particular embodiment, there is provided a dual-phase ferritic-martensitic stainless steel comprising, by weight: 11.5% to 12% chromium; 0.8% to 1.5% manganese; 0.75% to 1.5% nickel; 0% to 0.5% silicon; 0% to 0.2% molybdenum; 0% to 0.0025% boron; iron: and impurities; wherein the steel has a Brinell hardness (HB) of 300 HB or greater and Charpy V-notch impact energy at -40°C (CVN) of 50 ft-lb or greater, ~~such that~~ and wherein CVN (ft-lb) + (0.4 x HB) is 160 or greater.

BRIEF DESCRIPTION OF THE DRAWING

[0008] Features and advantages of the stainless steels and articles of manufacture described herein may be better understood by reference to the accompanying drawing in which:

[0009] Figure 1 is a graph plotting Brinell hardness and Charpy V-notch impact energy of non-limiting embodiments of stainless steels according to the present disclosure in comparison to certain conventional steels.

[0010] The reader will appreciate the foregoing details, as well as others, upon considering the following detailed description of certain non-limiting embodiments of stainless steels and articles of manufacture according to the present disclosure. The reader also may comprehend certain of such additional details upon making or using the stainless steels and articles of manufacture described herein.

DETAILED DESCRIPTION OF CERTAIN NON-LIMITING EMBODIMENTS

[0011] In the present description of non-limiting embodiments and in the claims, other than in the operating examples or where otherwise indicated, all numbers expressing quantities or characteristics of ingredients, alloys, and articles, processing conditions, and the like are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, any numerical parameters set forth in the following description and the attached claims are approximations that may vary depending upon the desired properties one seeks to obtain in the stainless steels and articles of manufacture according to the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the

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claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0012] Any patent, publication, or other disclosure material, in whole or in part, that is said to be incorporated by reference herein is incorporated herein only to the extent that the incorporated material does not conflict with existing definitions, statements, or other disclosure material set forth in this disclosure. As such, and to the extent necessary, the disclosure as set forth herein supersedes any conflicting material incorporated herein by reference. Any material, or portion thereof, that is said to be incorporated by reference herein, but which conflicts with existing definitions, statements, or other disclosure material set forth herein is only incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material.

[0013] The present disclosure, in part, is directed to cost-effective dual-phase ferritic-martensitic stainless steels having advantageous hardness and which are suitable for use in various applications requiring abrasion resistance and/or wear resistance. In particular, certain embodiments of dual-phase ferritic-martensitic stainless steels according to the present disclosure comprise, by weight, about 11.5% to about 12% Cr, about 0.8% to about 1.5% Mn, about 0.75% to about 1.5% Ni, 0% to about 0.5% Si, 0% to about 0.2% Mo, 0% to about 0.0025% B, Fe, and impurities. In certain embodiments, the stainless steels exhibit Brinell hardness (HB) and Charpy V-notch impact energy at -40°C (CVN) such that the following is satisfied: CVN (ft-lb) + (0.4 × HB) is about 160 or greater.

[0014] Cr may be provided in the alloys of the present disclosure to impart corrosion resistance. A Cr content of about 11.5% (by weight) or more may be required to provide adequate corrosion resistance. On the other hand, excessive Cr may undesirably (1) stabilize the ferrite phase and/or (2) embrittling phases such as the sigma phase. Accordingly, certain embodiments of the stainless steels according to the present disclosure include a Cr content of about 11.5% to about 12%, by weight.

[0015] Mn may be provided in the alloys of the present disclosure to improve work hardenability. A Mn content of about 0.8% (by weight) or more may be required to achieve the desired work hardening effects. On the other hand, excessive Mn may undesirably segregate during processing of the stainless steels. Accordingly, certain embodiments of the stainless steels according to the present disclosure include a Mn content of about 0.8% to about 1.5%, by weight. In certain other embodiments, the Mn content of the stainless steels may be about 1.0% to about 1.5%, by weight. In certain embodiments of the stainless steels according to the present disclosure, the addition of Mn in combination with the addition of other alloying elements can advantageously affect work hardenability such that the steels attain a hardness of about 450 HB or greater.

[0016] Ni may be provided in the alloys of the present disclosure to help stabilize the martensitic phase of the dual-phase (martensitic-ferritic) alloys. A Ni content of about 0.75% by weight or more may be required to provide a material including higher levels of martensite than in Duracorr® 300 stainless steel. Without intending to be bound to any theory, the nickel content of the alloys may promote hardness of the alloys' martensite phase by stabilizing austenite formation during heat treatment, allowing more time for carbon diffusion. On the other hand, due to the high cost of Ni, it may be desirable to limit the Ni content. Accordingly, some embodiments of the steels according to the present disclosure include a Ni content of about 0.75% to about 1.5% (by weight) to provide a cost-effective dual-phase stainless steel with high hardness levels up to about 350 HB, in combination with higher toughness than is typical of Duracorr® 300 stainless steel. In further embodiments, the Ni content of stainless steels according to the present disclosure may be about 1.0% to about 1.5%, by weight.

[0017] In certain embodiments of the stainless steels according to the present disclosure, the level of Si may be limited to (1) destabilize the ferritic phase of the dual-phase stainless steels and/or (2) avoid embrittling phases such as the sigma phase. Accordingly, certain embodiments of the steels according to the present disclosure include 0% to no more than about 0.5% Si, by weight.

[0018] In certain embodiments of the stainless steels according to the present disclosure, the level of Mo may be limited to (1) destabilize the ferritic phase of the dual-phase stainless steels and/or (2) avoid embrittling phases such as the sigma phase. Accordingly, certain embodiments of the steels according to the present disclosure include 0% to no more than about 0.2% Mo, by weight. In certain other embodiments of the steels according to the present disclosure, the Mo concentration is 0% to no more than about 0.1%, by weight

[0019] B may be provided in the dual-phase stainless steels of the present disclosure to improve martensite hardness. Certain embodiments of the steels according to the present disclosure include 0% to about 0.0025% B, by weight. In certain embodiments of the steels, the B content may be about 0.002% to about 0.0025%, by weight.

[0020] Incidental elements and impurities in the disclosed alloys may include, for example, one or more of C, N, P, and S. In certain embodiment of the stainless steels according to the present disclosure, the total content of these elements is no more than 0.1%, by weight. In certain embodiments, C may be present in the steels disclosed herein in an amount no more than 0.025%, by weight. In certain embodiments, S may be present in the steels disclosed herein in an amount no more than 0.01%, by weight. In certain embodiments, N may be present in the steels disclosed herein in an amount no more than 0.03%, by weight. Incidental levels of various metallic elements also may be present in embodiments of alloys according to the present disclosure. For example, certain non-limiting embodiments of alloys according to the present disclosure may include up to 0.25% copper (Cu), by weight.

[0021] According to certain non-limiting embodiments, dual-phase ferritic-martensitic stainless steels according to the present disclosure comprise by weight: about 11.5% to about 12% Cr; about 1.0% to about 1.5% Mn; about 1.0% to about 1.5% Ni; 0% to about 0.5% Si; 0% to about 0.1% Mo; 0% to about 0.0025% B; 0% to about 0.025% C; 0% to about 0.01% S; 0% to about 0.03% N, Fe, and impurities. In certain embodiments, the stainless steels further comprise P. In certain embodiments, the total concentration of C, N, P, and S is no greater than about 0.1%, by weight. In certain embodiments, the concentration of B in the steels is about 0.002% to about 0.0025%, by weight. In certain embodiments, the steels include no more than 0.25% Cu, by weight.

[0022] According to certain non-limiting embodiments, dual-phase ferritic-martensitic stainless steels according to the present disclosure consist essentially of, by weight: about 11.5% to about 12% chromium; about 0.8% to about 1.5% manganese; about 0.75% to about 1.5% nickel; 0% to about 0.5% silicon; 0% to about 0.2% molybdenum; 0% to about 0.0025% boron; 0% to about 0.025% carbon; 0% to about 0.01% sulfur; 0% to about 0.03% nitrogen; optionally at least one of copper and phosphorus; iron; and impurities.

[0023] According to certain non-limiting embodiments, dual-phase ferritic-martensitic stainless steels according to the present disclosure consist essentially of, by weight: about 11.5% to about 12% chromium; about 1.0% to about 1.5% manganese; about 1.0% to about 1.5% nickel; 0% to about 0.5% silicon; 0% to about 0.1% molybdenum; 0% to about 0.0025% boron; 0% to about 0.025% carbon; 0% to about 0.01% sulfur; 0% to about 0.03% nitrogen; optionally at least one of copper and phosphorus; iron; and impurities.

[0024] According to certain non-limiting embodiments, dual-phase ferritic-martensitic stainless steels according to the present disclosure consist of, by weight: about 11.5% to about 12% chromium; about 0.8% to about 1.5% manganese; about 0.75% to about 1.5% nickel; 0% to about 0.5% silicon; 0% to about 0.2% molybdenum; 0% to about 0.0025% boron; 0% to about 0.025% carbon; 0% to about 0.01% sulfur; 0% to about 0.03% nitrogen; optionally at least one of copper and phosphorus; iron; and impurities.

[0025] According to certain non-limiting embodiments, dual-phase ferritic-martensitic stainless steels according to the present disclosure consist of, by weight: about 11.5% to about 12% chromium; about 1.0% to about 1.5% manganese; about 1.0% to about 1.5% nickel; 0% to about 0.5% silicon; 0% to about 0.1% molybdenum; 0% to about 0.0025% boron; 0% to about 0.025% carbon; 0% to about 0.01% sulfur; 0% to about 0.03% nitrogen; optionally at least one of copper and phosphorus; iron; and impurities.

[0026] For a given steel, hardness is generally inversely related to toughness. In the present disclosure, Brinell hardness (HB) is the primary measure of hardness, and Charpy V-notch impact energy at -40°C (CVN) is the primary measure of toughness. Referring to Fig. 1, for certain embodiments of the steels according to the present disclosure, CVN (ft-lb) + (0.4 × HB) of the steels is about 160 or greater. In certain embodiments of the steels according to the present disclosure, hardness is about 300 HB or greater, and CVN is about 50 ft-lb or greater. In certain embodiments, the steels according to the present disclosure have an in-service work hardenability up to a hardness of about 450 HB or greater.

EXAMPLES

[0027] Table 1 includes the compositions and certain properties of an embodiment of the dual-phase ferritic-martensitic stainless steels according to the present disclosure and of conventional ATI 412™ stainless steel and conventional Duracorr® 300 stainless steel. Heats of the three alloys listed in Table 1 were melted into slabs weighing about 15,000 lb and rolled at a temperature of about 1950 °F to produce material about 6 mm thick. Following the rolling process, the steels were annealed at 766°C or 843°C, for 15 minutes, and air cooled.

[0028] The mechanical properties of the experimental steel embodiment listed in Table 1 were measured and compared to those of the two listed conventional steels. The Brinell hardness and CVN at -40°C (ft-lb) are shown in Table 1 for the three alloys. The tensile tests were conducted according to the American Society for Testing and Materials (ASTM) standard A370 at room temperature, using a tungsten carbide ball indenter, on samples measuring about 5 cm in gauge length and about 0.5 cm in thickness. The Charpy tests were conducted according to ASTM standard A370 and E23 at about -40°C on transverse samples measuring about 10 mm × 2.5 mm. Because these samples are considered subsize per ASTM-A370, the measured impact energy was converted to standard size specimen values in Table 1.

[0029] As shown by the experimental results in Table 1, the experimental steel sample of the present disclosure exhibited very favorable hardness and toughness (CVN impact energy) relative to the conventional alloys. This was particularly unexpected and surprising. Commercially available alloys providing comparable hardness and toughness typically are carbon steels, which would not withstand corrosive environments.

[0030] In certain possible non-limiting embodiments, dual-phase stainless steels according to the present disclosure are prepared using conventional stainless steel production practices including, for example, melting of starting materials in an electric furnace, decarburization via AOD, and casting to an ingot. Ingots may be cast, for example, by continuous casting or ingot pouring. In certain embodiments, the cast material may be heat treated (austenitized) or sold as-rolled.

Table 1

	Embodiment of Present Steel		Conventional Steels		
wt%			ATI 412™ Alloy		Duracorr® Alloy
C	0.022		0.01–0.025		0–0.025
Mn	0.89		0.8–1		0–1.5
P	0.027		0–0.04		0–0.04
S	0.0014		0–0.004		0–0.015
Si	0.44		0.45–0.75		0–0.7
Cr	11.92		11.5–12		11–12.5
Ni	0.97		0.3–0.75		0–1
N	0.023		0–0.03		0–0.03
Mo	0.091		0–0.2		0.2–0.35
Cu	0.17		0.25		0
B	0.0003		0		0
Annealing temperature	As-rolled	843°C	766°C	843°C	—
Brinell hardness	340	322	177	258	260–360
CVN at -40°C (ft-lb)	26–34	56–62	65–90	7–49	15
CVN (ft-lb)+(0.4×HB)	162–170	185–191	136–161	111–152	119–159

[0031] The potential uses of alloys according to the present disclosure are numerous. As described and evidenced above, the dual-phase stainless steels described herein are capable of being used in many applications where abrasion resistance and/or wear resistance is important. Articles of manufacture for which the steels according to the present disclosure would be particularly advantageous include, for example, parts and equipment used in oil sands extraction and parts and equipment used in sugar processing. Other applications for the stainless steels accoring to the present disclosure will be readily apprent to ordinarily skill practitioners. Those having ordinary skill may readily manufacture these and other articles of manufacture from the stainless steels according to the present disclosure using conventional manufacturing techniques.

[0032] Although the foregoing description has necessarily presented only a limited number of embodiments, those of ordinary skill in the relevant art will appreciate that various changes in the alloys and article and other details of the examples that have been described and illustrated herein may be made by those skilled in the art, and all such modifications will remain within the principle and scope of the present disclosure as expressed herein and in the appended claims. For example, although the present disclosure has necessarily only presented a limited number of embodiments of stainless steels according to the present disclosure, and also has necessarily only discussed a limited number of articles of manufacture including the stainless steels, it will be understood that the present disclosure and associated claims are not so limited. Those having ordinary skill will readily identify additional steel compositions and may produce additional articles of manufacture along the lines and within the spirit of the necessarily limited number of embodiments discussed herein. It is understood, therefore, that the present invention is not limited to the particular embodiments disclosed or incorporated herein, but is intended to cover modifications that are within the principle and scope of the invention, as defined by the claims. It will also be appreciated by those skilled in the art that changes could be made to the embodiments above without departing from the broad inventive concept thereof.

Claims:

1. A dual-phase ferritic-martensitic stainless steel comprising, by weight:

11.5% to 12% chromium;

0.8% to 1.5% manganese;

0.75% to 1.5% nickel;

0% to 0.5% silicon;

0% to 0.2% molybdenum;

0% to 0.0025% boron;

iron: and

impurities;

wherein the steel has a Brinell hardness (HB) of 300 HB or greater and Charpy V-notch impact energy at -40°C (CVN) of 50 ft-lb or greater, and wherein CVN (ft-lb) + (0.4 x HB) is 160 or greater.

2. The dual-phase ferritic-martensitic stainless steel of claim 1, wherein molybdenum content is 0% to 0.1%.

3. The dual-phase ferritic-martensitic stainless steel of claim 1 or 2, wherein nickel content is 1.0% to 1.5%.

4. The dual-phase ferritic-martensitic stainless steel of any one of the previous claims, wherein manganese content is 1.0% to 1.5%.

5. The dual-phase ferritic-martensitic stainless steel of any one of the previous claims, wherein boron content is 0.002% to 0.0025%.

6. The dual-phase ferritic-martensitic stainless steel of any one of the previous claims, wherein the steel has work hardenability up to a hardness of 450 HB or greater.

7. The dual-phase ferritic-martensitic stainless steel of any one of the previous claims comprising, by weight:

11.5% to 12% chromium;

1.0% to 1.5% manganese;

1.0% to 1.5% nickel;

0% to 0.5% silicon;

0% to 0.1% molybdenum;

0% to 0.0025% boron;

0% to 0.025% carbon;

0% to 0.01% sulfur;

0% to 0.03% nitrogen;

iron; and

impurities.

8. The dual-phase ferritic-martensitic stainless steel of any one of the previous claims, further comprising at least one of copper and phosphorus.

9. The dual-phase ferritic-martensitic stainless steel of claim 8, wherein the total concentration of carbon, nitrogen, phosphorus, and sulfur present is no greater than 0.1%, by weight.

10. The dual-phase ferritic-martensitic stainless steel of claim 8 or 9, wherein boron content is 0.002% to 0.0025%.

11. The dual-phase ferritic-martensitic stainless steel of claim 1, consisting of, by weight:

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11.5% to 12% chromium;

0.8% to 1.5% manganese;

0.75% to 1.5% nickel;

0% to 0.5% silicon;

0% to 0.2% molybdenum;

0% to 0.0025% boron;

0% to 0.025% carbon;

0% to 0.01% sulfur;

0% to 0.03% nitrogen;

optionally at least one of copper and phosphorus;

iron; and

impurities.

12. The dual-phase ferritic-martensitic stainless steel of claim 1, consisting of, by weight:

11.5% to 12% chromium;

1.0% to 1.5% manganese;

1.0% to 1.5% nickel;

0% to 0.5% silicon;

0% to 0.1% molybdenum;

0% to 0.0025% boron;

0% to 0.025% carbon;

0% to 0.01% sulfur;

0% to 0.03% nitrogen;

optionally at least one of copper and phosphorus;

iron; and

impurities.

13. The dual-phase ferritic-martensitic stainless steel of any one of the previous claims, wherein CVN (ft-lb) + (0.4 x HB) is 162 or greater.

14. The dual-phase ferritic-martensitic stainless steel of any one of the previous claims, wherein CVN (ft-lb) + (0.4 x HB) is 185 or greater.

15. An article of manufacture including a dual-phase stainless steel as recited in any one of the previous claims.

16. The article of manufacture of claim 15, wherein the article of manufacture is selected from parts and equipment used in oil sands extraction and parts and equipment used in sugar processing.

FIG.1