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(54) **DUPLEX STAINLESS STEELS**

DUPLEXEDELSTAHL

ACIERS INOXYDABLES DUPLEX

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Description

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates generally to duplex stainless steels. In particular, the present invention relates to duplex stainless steels that can be an economical alternative to certain known duplex stainless steels, while also providing improved corrosion resistance relative to certain austenitic stainless steels, such as the Type 304, 316 and 317 austenitic stainless steels. The present invention is also directed to a method of manufacturing the duplex stainless steels of the invention. The duplex stainless steels of the present invention find application in, for example, corrosive environments and into articles of manufacture, such as, for example, strip, bar, plate, sheet, castings, pipe or tube.

DESCRIPTION OF THE INVENTION BACKGROUND

[0002] Duplex stainless steels are alloys that contain a microstructure consisting of a mixture of austenite and ferrite phases. Generally, they exhibit certain characteristics of both phases, along with relatively higher strength and ductility. Various duplex stainless steels have been proposed, some of which are described in U.S. Patent Nos. 3,650,709, 4,340,432, 4,798,635, 4,828,630, 5,238,508, 5,298,093, 5,624,504, and 6,096,441 as well as JP-A 10 102 206.

[0003] Early duplex alloys had moderate resistance to general corrosion and chloride stress corrosion cracking, but suffered a substantial loss of properties when used in the as-welded condition. Presently, one of the most widely used second-generation duplex stainless steels is available under the trademark AL 2205 (UNS S31803 and/or 32205) from Allegheny Ludlum Corporation, Pittsburgh, Pennsylvania. This duplex stainless steel is a nominal 22% chromium, 5.5% nickel, 3% molybdenum, and 0.16% nitrogen alloy that provides corrosion resistance in many environments that is superior to the Type 304, 316 and 317 austenitic stainless steels (Unless otherwise noted all percentages herein are weight percentages of total alloy weight). AL 2205, which is a nitrogen-enhanced duplex stainless steel that imparts the metallurgical benefits of nitrogen to improve corrosion performance and as-welded properties, also exhibits a yield strength that is more than double that of conventional austenitic stainless steels. This duplex stainless steel is often used in the form of welded pipe or tubular components, as well as a formed and welded sheet product in environments where resistance to general corrosion and chloride stress corrosion cracking ("SCC") is important. The increased strength creates opportunities for reduction in tube wall thickness and resists handling damage.

[0004] As just indicated, AL 2205 has been widely accepted by tube and pipe end users, particularly as a low cost replacement to Type 316 stainless steel when SCC is a concern. This is due, in large part, to the fact that AL 2205 is significantly more resistant to crevice corrosion than the Type 316 and Type 317 austenitic stainless steels. This superior resistance to chloride-ion crevice corrosion is illustrated in the table below, which shows the results of ASTM Procedure G48B using a 10% ferric chloride solution. The 10% ferric chloride solution referred to is by weight for the hexahydrate salt and is equivalent to an approximately 6% by weight solution of the anhydrous ferric chloride salt.

Crevice Corrosion Data in 10% Ferric Chloride	
Alloy	**Temperature of Onset of Crevice Corrosion**
Type 316	27°F (-3°C)
Type 317	35°F (2°C)
AL 2205	68°F (20°C)

[0005] However, the extraordinary corrosion resistance (and other properties) of AL 2205 may be greater than is required in some applications. In certain SCC applications, while AL 2205 would provide an acceptable technical solution, it may not be an economical replacement alloy for Type 304 stainless steel. The higher cost of AL 2205 is due primarily to the amounts of the alloying elements nickel (nominal 5.5%) and molybdenum (nominal 3%). Thus, it is desirable to provide a weldable, formable duplex stainless steel that has g-eater corrosion resistance than the Type 304. Type 316 or Type 317 austenitic stainless steels and may have a lower production cost than the commonly used AL 2205 duplex stainless steel.

SUMMARY OF THE INVENTION

[0006] The invention provides a ferritic-austenitic stainless steel in accordance with claim 1 of the appended claims.

[0007] The present invention relates to a duplex stainless steel exhibiting corrosion resistance and having reduced amounts of the alloying elements nickel and molybdenum relative to other duplex stainless steels, including AL 2205.

[0008] According to the present invenion, the duplex stainless steel comprises, in weight percent up to 0.06 percent carbon; 15 percent to 25 percent chromium; 1 percent to less than 2.5 percent nickel; up to 3.75 percent manganese; greater than 0.12 percent to 0.35 percent nitrogen; up to 2 percent silicon; up to 1.5 percent molybdenum; up to 0.5 percent copper; up to 0.2 percent cobalt; up to 0.05 percent phosphorus; up to 0.005 percent sulphur, 0.001 percent to 0.0035 percent bunion; iron and incidental impurities. According to the present invention, the duplex stainless steel comprises, in weight percent, up to 0.06 percent carbon; 17 percent to less than 20 percent chromium; 1 percent to less than 2,5 percent nickel; up to 3.75 percent manganese; greater than 0.12 percent up to 0.35 percent nitrogen; up to 2 percent silicon; up to 1.5 percent molybdenum; up to 0.5 percent copper, up to 0.2 percent cobalt; up to 0.05 percent phosphorous; up to 0.005 percent sulfur, 0.001 percent to 0.0035 percent boron; iron and incidental impurities.

[0009] The present invention also relates to articles of manufacture such as, for example, strip, bar, plate, sheet, castings, tubing, or piping fabricated from or including the duplex stainless steels of the present invention. The articles formed of the duplex stainless steels of the present invention may be particularly advantageous when intended for service in chloride containing environments. Furthermore, the present invention relates to methods for making duplex stainless steels. In particular, according to the method of the present invention, a duplex stainless steel having a chemistry as previously described is provided and is subject to processing, including solution annealing and cooling. The steel may be further processed to an article of manufacture or into any other desired form.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The present invention relates to duplex stainless steels characterized by including reduced amounts of the alloying elements nickel and molybdenum relative to certain known duplex stainless steels, including AL 2205. In particular, the duplex stainless steel of the present invention contains, in weight percent: less than 2.5 percent nickel and up to 1.5 percent molybdenum.

[0011] Another embodiments of the present invention are those according to the dependent claims 2 to 7.

[0012] The duplex stainless steels of the present invention include the austenite and ferrite phases, preferably each in the range of between 20% and 80% by volume in the annealed condition. Embodiments of the duplex stainless steels are weldable, formable materials that may exhibit greater corrosion resistance than the Type 304, 316 and 317 austenitic stainless steels. In addition to the above elemental ranges, the duplex stainless steels of the present invention may include various other alloying elements and additives as are known in the art. Embodiments of the duplex stainless steels of the invention may be less costly to produce than the commonly used AL 2205 alloy and certain other duplex stainless steels, because of a lower content of alloying elements, particularly nickel and molybdenum. Nevertheless, an enhanced level of corrosion resistance over the Type 304, 316 and 317 austenitic stainless steels is expected from the duplex stainless steels of the present invention. Moreover, the duplex stainless steels of the present invention provide a stable austenite phase (with respect to deformation incluced martensite) and the desired level of corrosion resistance. Below, the nickel and molybdenum content of certain embodiments of the present invention are compared to AL 2205.

Amounts of Alloying Elements Ni and Mo (In Weight Percent)		
Alloying Element	**AL 2205**	**Present Invention**
Ni	5.5% nominal	1% - less than 2.5%
Mo	3% nominal	up to 1.5%

[0013] Despite an expected lower cost of production as compared to the current cost of AL 2205, it is expected that the duplex stainless steels of the present invention will exhibit pitting/crevice corrosion resistance that is significantly greater than the Type 304, 316 and 317 austentic stainless steels. It is expected, however, that the steels of the present invention will have reduced corrosion resistance, but greater stretch formability than AL 2205 due to the lower content of nickel and molybdenum in the steels of the present invention. Thus, the duplex stainless steel of the present invention may be particularly advantageous as a lower cost alternative to AL 2205 in less demanding applications in which AL 2205 is now used.

[0014] According to various embodiment of the present invention, the duplex stainless steel may comprise, in weight percent, up to 0.03% C, at least 17% Cr, at least 1.5% Ni, up to 2% Mn, up to 1% Si, 1% to 1.5% Mo, and 0.001% to 0.0035% B. Thus, depending on the particular embodiment of the present invention employed as a result of the corrosion resistance requirements of the particular application, the duplex stainless steel of the present invention may be less costly to produce than AL 2205 and other duplex stainless steels.

[0015] The present invention also relates to articles of manufacture such as, for example, strip, bar, plate, sheet, casings, tubing, and piping composed of or including the duplex stainless steels of the present invention. According to one embodiment of the present invention, the article of manufacture is composed of or includes a duplex stainless steel comprising, in weight percent up to 0.06 percent carbon; 15 percent to 25 percent chromium; 1 percent to less than 2.5 percent nickel; up to 3.75 percent manganese; greater than 0.12 percent up to 0.35 percent nitrogen; up to 2 percent silicon; up to 1.5 percent molybdenum; up to 0.5 percent copper; up to 0.2 percent cobalt; up to 0.05 percent phosphorous; up to 0.005 percent sulfur; 0.001 percent to 0.0035 percent boron; iron and incidental impurities. According to yet another embodiment of the present invention, the article of manufacture is composed of or includes a duplex stainless steel comprising, in weight percent up to 0.06 percent carbon; 17 percent to less than 205 percent chromium, 1 percent to less than 2,5 percent nickel; up to 3.75 percent manganese; greater than 0.12 percent up to 0.35 percent nitrogen; up to 2 percent silicon; up to 1.5 percent molybdenum; up to 0.5 percent copper; up to 0.2 percent cobalt; up to 0.05 percent phosphorous; up to 0.005 percent sulfur, 0.001 percent to 0.0035 percent boron; iron and incidental impurities.

[0016] In addition, the present invention relates to a method for making the claimed duplex stainless steel. The duplex stainless steel is subsequently solution annealed and then cooled.

[0017] According to the method of the present invention, a duplex stainless steel is provided comprising, in weight percent: up to 0.06 percent carbon; 15 percent to 25 percent chromium; 1 percent to less than 2.5 percent nickel; up to 3.75 percent manganese; greater than 0.12 percent up to 0.35 percent nitrogen; up to 2 percent silicon; up to 1.5 percent molybdenum; up to 0.5 percent copper, up to 0.2 percent cobalt; up to 0.05 percent phosphorous; up to 0.005 percent sulfur, 0.001 percent to 0.0035 percent boron; iron and incidental impurities is provided. The duplex stainless steel is solution subsequently annealed and cooled. According to yet another embodiment of the method of the present invention, a duplex stainless steel is provided comprising, in weight percent: up to 0.06 percent carbon; 17 percent to less than 20 percent chromium; 1 percent to less than 2.5 percent nickel; up to 3.75 percent manganese; greater than 0.12 percent to 0.35 percent nitrogen; up to 2 percent silicon; up to 1.5 percent molybdenum; up to 0.5 percent copper; up to 0.2 percent cobalt; up to 0.05 percent phosphorus; up to 0.005 percent sulphur; 0.001 percent to 0.0035 percent boron; iron and incidental impurities is provided. The steel is subsequently solution annealed, and cooled.

[0018] In any of the above methods, other processing techniques and steps known to those in the art may be used. For example, the steels may be further processed using known techniques to provide an article of manufacture, such as those mentioned above, or into any other desired form.

[0019] It is to be understood that the present description illustrates aspects of the invention relevant to a clear understanding of the invention. Certain aspects of the invention that would be apparent to those of ordinary skill in the art and that, therefore, would not facilitate a better understanding of the invention have not been presented in order to simplify the present description. Although the present invention has been described in connection with only certain embodiments, those of ordinary skill in the art will, upon considering the foregoing description, recognize that many embodiments, modifications, and variations of the invention may be made within the scope of claims.

Claims

1. A ferritic-austenitic duplex stainless steel comprising, in weight percent:

up to 0.06 percent carbon;
15 to 25 percent chromium;
1 to less than 2.5 percent nickel;
up to 3.75 percent manganese;
greater than 0.12 up to 0.35 percent nitrogen;
up to 2 percent silicon;
up to 1.5 percent molybdenum;
up to 0.5 percent copper,
up to 0.2 percent cobalt;
up to 0.05 percent phosphorus;
up to 0.005 percent sulphur;
0.001 to 0.0035 percent boron;
balance iron and incidental impurities.

2. The duplex stainless steel of claim 1 comprising, up to 0.03 percent carbon.

3. The duplex stainless steel of claim 1 or claim 2 comprising 17 to 20 percent chromium.

4. The duplex stainless steel of any one of the preceding claims comprising 1.5 to less than 2.5 percent nickel.

5. The duplex stainless steel of any one of the preceding claims comprising greater than 0.12 up to 0.20 percent nitrogen.

6. The duplex stainless steel of any one of the preceding claims comprising up to 1 percent silicon.

7. The duplex stainless steel of any one of the preceding claims comprising 1 to 1.5 percent molybdenum.

8. An article of manufacture including a duplex stainless steel in accordance with any one of the preceding claims.

9. The article of claim 8 a wherein the article is selected from the group consisting of strip, bar, plate, sheet, casting, tubing and piping.

10. A method for making a ferritic-austenitic duplex stainless steel, the process comprising:

providing a ferritic-austenitic stainless steel in accordance with any one or claims 1 to 7;
solution annealing the steel; and
cooling the steel.

Patentansprüche

1. Ferritisch-austenitischer nichtrostender Duplexstahl, umfassend - in Gew.- %:

bis zu 0,06 % Kohlenstoff,
15 bis 25 % Chrom,
1 bis weniger als 2,5 % Nickel,
bis zu 3,75 % Mangan,
mehr als 0,12 und bis zu 0,35 % Stickstoff,
bis zu 2 % Silicium,
bis zu 1,5 % Molybdän,
bis zu 0,5 % Kupfer,
bis zu 0,2 % Cobalt,
bis zu 0,05 % Phosphor,
bis zu 0,005 % Schwefel,
0,001 bis 0,0035 % Bor,
als Rest Eisen und beiläufige Verunreinigungen.

2. Nichtrostender Duplexstahl nach Anspruch 1, der bis zu 0,03 % Kohlenstoff umfasst.

3. Nichtrostender Duplexstahl nach Anspruch 1 oder Anspruch 2, der 17 bis 20 % Chrom umfasst.

4. Nichtrostender Duplexstahl nach einem der vorhergehenden Ansprüche, der 1,5 bis weniger als 2,5 % Nickel umfasst.

5. Nichtrostender Duplexstahl nach einem der vorhergehenden Ansprüche, der mehr als 0,12 und bis zu 0,20 % Stickstoff umfasst.

6. Nichtrostender Duplexstahl nach einem der vorhergehenden Ansprüche, der bis zu 1 % Silicium umfasst.

7. Nichtrostender Duplexstahl nach einem der vorhergehenden Ansprüche, der 1 bis 1,5 % Molybdän umfasst.

8. Produktgegenstand, der einen nichtrostenden Duplexstahl gemäß einem der vorhergehenden Ansprüche umfasst.

9. Gegenstand nach Anspruch 8, wobei der Gegenstand aus der Gruppe von Bandstahl, Stangen, Blech, Feinblech, Gussteilen, Rohrsträngen und Rohrmaterial ausgewählt ist.

10. Verfahren zur Herstellung eines ferritisch-austenitischen nichtrostenden Duplexstahls,

wobei das Verfahren:

Bereitstellen eines ferritisch-austenitischen nichtrostenden Stahls gemäß einem der Ansprüche 1 bis 7,
Lösungsglühen des Stahls und
Abkühlen des Stahls umfasst.

Revendications

1. Acier inoxydable duplex ferritique-austénitique comprenant, en pourcentage massique:

jusqu'à 0,06 pour cent de carbone ;
15 à 25 pour cent de chrome ;
1 à moins de 2,5 pour cent de nickel ;
jusqu'à 3,75 pour cent de manganèse ;
plus de 0,12 et jusqu'à 0,35 pour cent d'azote ;
jusqu'à 2 pour cent de silicium ;
jusqu'à 1,5 pour cent de molybdène ;
jusqu'à 0,5 pour cent de cuivre ;
jusqu'à 0,2 pour cent de cobalt ;
jusqu'à 0,05 pour cent de phosphore ;
jusqu'à 0,005 pour cent de soufre ;
0,001 à 0,0035 pour cent de bore ;
le reste étant du fer et des impuretés inévitables.

2. Acier inoxydable duplex selon la revendication 1, comprenant jusqu'à 0,03 pour cent de carbone.

3. Acier inoxydable duplex selon la revendication 1 ou la revendication 2, comprenant de 17 à 20 pour cent de chrome.

4. Acier inoxydable duplex selon l'une quelconque des revendications précédentes, comprenant 1,5 à moins de 2,5 pour cent de nickel.

5. Acier inoxydable duplex selon l'une quelconque des revendications précédentes, comprenant plus de 0,12 jusqu'à 0,20 pour cent d'azote.

6. Acier inoxydable duplex selon l'une quelconque des revendications précédentes, comprenant jusqu'à 1 pour cent de silicium.

7. Acier inoxydable duplex selon l'une quelconque des revendications précédentes, comprenant 1 à 1,5 pour cent de molybdène.

8. Article de fabrication incluant un acier inoxydable duplex en conformité avec l'une quelconque des revendications précédentes.

9. Article selon la revendication 8, dans lequel l'article est choisi dans le groupe constitué par une bande, une barre, une plaque, une feuille, une pièce coulée, un tubage et une pièce de tuyauterie.

10. Procédé de fabrication d'un acier inoxydable duplex ferritique-austénitique, le procédé comprenant :

la fourniture d'un acier inoxydable ferritique-austénitique en conformité avec l'une quelconque des revendications 1 à 7 ;
le recuit de mise en solution de l'acier ; et
le refroidissement de l'acier.

REFERENCES CITED IN THE DESCRIPTION

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