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TITLE

Duplex Stainless Steels

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INVENTORS

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BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

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

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.

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

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increased strength creates opportunities for reduction in tube wall thickness and resists handling damage.

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)

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 greater 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

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. According to one embodiment of the present invention, the duplex stainless steel comprises, in weight percent, up to 0.06 percent carbon; 15 percent to less than 19 percent chromium; 1 percent to less than 3 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; up to 0.03 percent boron; iron and incidental impurities. According to another embodiment of the present invention, 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

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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 duplex stainless steel comprises, in weight percent, up to 0.06 percent carbon; 15 percent to less than 21.5 percent chromium; 1 percent to less than 3 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.

10 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

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 3 percent nickel and less than 1.5 percent molybdenum. According to one particular embodiment of the present invention, the duplex stainless steel comprises, in weight percent: up to 0.06 percent carbon; 15 percent to less than 19 percent chromium; 1 percent to less than 3 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; up to 0.03 percent boron; iron and incidental impurities. According to another embodiment of the present invention, the duplex stainless steel includes, 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 duplex stainless steel comprises, in weight percent: up to 0.06 percent carbon; 15 percent to less than 21.5 percent chromium; 1 to less than 3 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.

It will be understood that in the steel compositions just recited, carbon, manganese, silicon, molybdenum, copper, cobalt, phosphorus, sulfur and, in one embodiment only, boron, are optional components of the steel.

5 The duplex stainless steels of the present invention preferably include the austenite and ferrite phases, 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
10 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
15 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
20 deformation induced 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 3%
Mo	3% nominal	up to 1.5%

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

5 significantly greater than the Type 304, 316 and 317 austenitic 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

10 may be particularly advantageous as a lower cost alternative to AL 2205 in less demanding applications in which AL 2205 is now used.

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,

15 and/or 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.

The present invention also relates to articles of manufacture such as, for example, strip, bar, plate, sheet, castings, 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

5 manufacture is composed of or includes a duplex stainless steel comprising, in weight percent: up to 0.06 percent carbon; 15 percent to less than 19 percent chromium; 1 percent to less than 3 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

10 to 0.2 percent cobalt; up to 0.05 percent phosphorous; up to 0.005 percent sulfur; up to 0.03 percent boron; iron and incidental impurities. According to 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; 15 percent to 25 percent chromium; 1

15 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

20 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; 15 percent to less than 21.5 percent chromium; 1 percent to less than 3 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.

In addition, the present invention relates to a method for making
5 a duplex stainless steel including, in weight percent: less than 3 percent nickel and less than 1.5 percent molybdenum. According to one embodiment of 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 less than 19 percent chromium; 1 percent to less than 3 percent nickel; up to 3.75
10 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; up to 0.03 percent boron; iron and incidental impurities, is provided. The duplex stainless steel is subsequently solution annealed and then cooled.

15 According to 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; 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
20 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; 15 percent to less than 21.5 percent chromium; 1 percent to less than 3 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 steel is subsequently solution annealed, and cooled.

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.

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. All such variations and modifications of the invention are covered by the foregoing description and the following claims.

CLAIMS

1. A duplex stainless steel comprising, in weight percent: up to 0.06 percent carbon; 15 to less than 19 percent chromium; 1 to less than 3 percent nickel; greater than 2 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 phosphorous; up to 0.005 percent sulfur; up to 0.03 percent boron; iron and incidental impurities, **wherein the duplex stainless steel comprises ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.**
2. The duplex stainless steel of claim 1 comprising up to 0.03 percent carbon.
3. The duplex stainless steel of claim 1 comprising 17 to less than 19 percent chromium.
4. The duplex stainless steel of claim 1 comprising 1.5 to less than 2.75 percent nickel.
5. The duplex stainless steel of claim 1 comprising greater than 0.12 to 0.20 percent nitrogen.
6. The duplex stainless steel of claim 1 comprising up to 1 percent silicon.
7. The duplex stainless steel of claim 1 comprising 1 to 1.5 percent molybdenum.

8. The duplex stainless steel of claim 1 comprising 0.001 to 0.0035 percent boron.
9. An article of manufacture including a duplex stainless steel comprising, in weight percent: up to 0.06 percent carbon; 15 to less than 19 percent chromium; 1 to less than 3 percent nickel; greater than 2 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 phosphorous; up to 0.005 percent sulfur; up to 0.03 percent boron; iron and incidental impurities, **wherein the duplex stainless steel comprise ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.**
10. The article of claim 9 wherein the article is selected from the group consisting of strip, bar, plate, sheet, casting, tubing and piping.
11. A method for making a duplex stainless steel, the process comprising:
 - providing a duplex stainless steel comprising, in weight percent, up to 0.06 percent carbon, 15 to less than 19 percent chromium, 1 to less than 3 percent nickel, greater than 2 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 phosphorous, up to 0.005 percent sulfur, up to 0.03 percent boron, iron and incidental impurities;
 - solution annealing the steel; and
 - cooling the steel;**wherein the duplex stainless steel comprises ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.**

12. A 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; greater than 2 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 phosphorous; up to 0.005 percent sulfur; 0.001 to 0.0035 percent boron; iron and incidental impurities, **wherein the duplex stainless steel comprises ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.**
13. The duplex stainless steel of claim 12 comprising up to 0.03 percent carbon.
14. The duplex stainless steel of claim 12 comprising 17 to 20 percent chromium.
15. The duplex stainless steel of claim 12 comprising 1.5 to less than 2.5 percent nickel.
16. The duplex stainless steel of claim 12 comprising greater than 0.12 up to 0.20 percent nitrogen.
17. The duplex stainless steel of claim 12 comprising up to 1 percent silicon.
18. The duplex stainless steel of claim 12 comprising 1 to 1.5 percent molybdenum.
19. An article of manufacture including a 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 phosphorous; up to 0.005 percent sulfur; 0.001 to 0.0035 percent boron, iron and incidental impurities, **wherein the duplex stainless steel comprises ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.**

20. The article of claim 19 wherein said article is selected from the group consisting of strip, bar, plate, sheet, casting, tubing and piping.

21. A method for making a duplex stainless steel, the method comprising:
 providing a 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, greater than 2 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 phosphorous, up to 0.005 percent sulfur, 0.001 to 0.0035 percent boron, iron and incidental impurities;
 solution annealing the steel; and
 cooling the steel;

wherein the duplex stainless steel comprises ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.

22. A duplex stainless steel comprising, in weight percent: up to 0.06 percent carbon; 15 to less than 21.5 percent chromium; 1 to less than 3 percent nickel; greater than 2 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 phosphorous; up to 0.005 percent sulfur; 0.001 to 0.0035 percent boron; iron and incidental impurities, **wherein the duplex stainless steel comprise ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.**

23. The duplex stainless steel of claim 22 comprising up to 0.03 percent carbon.
24. The duplex stainless steel of claim 22 comprising 17 to 20 percent chromium.
25. The duplex stainless steel of claim 22 comprising 1.5 to 2.75 percent nickel.
26. The duplex stainless steel of claim 22 comprising greater than 0.12 up to 0.20 percent nitrogen.
27. The duplex stainless steel of claim 22 comprising up to 1 percent silicon.
28. The duplex stainless steel of claim 22 comprising 1 to 1.5 percent molybdenum.
29. An article of manufacture including a duplex stainless steel comprising, in weight percent: up to 0.06 percent carbon; 15 to 21.5 percent chromium; 1 to less than 3 percent nickel; greater than 2 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 phosphorous; up to 0.005 percent sulfur; 0.001 to 0.0035 percent boron; iron and incidental impurities, **wherein**

the duplex stainless steel comprises ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.

30. The article of claim 29 wherein said article is selected from the group consisting of strip, bar, plate, sheet, casting, tubing and piping.

31. A method for making a duplex stainless steel, the method comprising:
providing a duplex stainless steel comprising, in weight percent, up to 0.06 percent carbon, 15 to 21.5 percent chromium, 1 to less than 3 percent nickel, greater than 2 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 phosphorous, up to 0.005 percent sulfur, 0.001 to 0.0035 percent boron, iron and incidental impurities;
solution annealing the steel; and
cooling the steel;

wherein the duplex stainless steel comprises ferrite and austenite that is substantially stable with respect to deformation induced martensitic transformation.