US 20020144757A1

(19) United States

(12) Patent Application Publication

Craig et al.

(10) Pub. No.: US 2002/0144757 A1

(43) Pub. Date: Oct. 10, 2002

(54) **STAINLESS STEEL ALLOY WITH IMPROVED RADIOPAQUE CHARACTERISTICS**

(76) Inventors: **Charles Horace Craig**, Lakeside, CA (US); **Herbert R. Radisch**, San Diego, CA (US); **Thomas Trozera**, Del Mar, CA (US)

Correspondence Address:
Charles Horace Craig
9354 Harritt Road
Lakeside, CA 92040 (US)

(21) Appl. No.: **10/103,411**

(22) Filed: **Mar. 20, 2002**

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/612,157, filed on Jul. 7, 2000.

Publication Classification

(51) **Int. Cl.**[7] **C22C 38/38**; C22C 38/58

(52) **U.S. Cl.** **148/327**; 420/57

(57) **ABSTRACT**

The present invention is directed towards an austenitic, stainless steel series 300 alloy having improved radiopaque characteristics. The modified stainless steel alloy consists essentially of, in weight percent, about

C	Mn	Si	P	S
≦0.030	≦2.000	≦0.750	≦0.023	≦0.010
Cr	Mo	Ni	Fe	"X"
12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

whereby variable "X" could be comprised from a group consisting of Gold, Osmium, Palladium, Platinum, Rhenium, Tantalum, Tungsten or Iridium. The alloy provides a unique combination of strength, ductility, corrosion resistance, and other mechanical properties which also has improved radiopaque characteristics.

STAINLESS STEEL ALLOY WITH IMPROVED RADIOPAQUE CHARACTERISTICS

PRIOR APPLICATIONS

[0001] This application is a continuation-in-part of application Ser. No. 09/612,157 filed on Jul. 7, 2000. It was disclosed in the application that this inventions is an austenitic steel alloy having radiopaque characteristics.

BACKGROUND OF THE INVENTION

[0002] This invention relates to an austenitic steel alloy, and in particular to such an alloy and an article made therefrom in which the elements are closely controlled to provide a unique combination of high tensile strength, ductility, good resistance to stress cracking and corrosion, and have improved radiopaque characteristics.

[0003] Austenite generally does not exist at room temperature in plain-carbon and low-alloy steels, other than as small amounts of retained austenite that did not transform during rapid cooling. However, in certain high-alloy steels, such as the austenitic stainless steels and Hadfield austenitic manganese steel, austenite is the dominant microstructure. In these steels, sufficient quantities of alloying elements that stabilize austenite at room temperature are present (e.g., manganese and nickel). The crystal structure of austenite is face-centered cubic (fcc) as compared to ferrite, which has a body centered cubic (bcc) lattice. An fcc alloy has certain desirable characteristics; for example, it has low-temperature toughness, excellent weldability, and is nonmagnetic. Because of their high alloy content, austenitic steels are usually corrosion resistant. Disadvantages of the austenitic steels are their relative high costs, their susceptibility to stress-corrosion cracking (certain austenitic steels), the fact that they cannot be strengthened other than by cold working, and interstitial solid-solution strengthening.

[0004] The austenitic stainless steels (e.g., type 301, 302, 303, 304, 305, 308, 309, 310, 314, 316, 317, 321, 330, 347, 348, and 384) generally contain from 6 to 22% nickel to stabilize the austenite microstructure at room temperature. They also contain other alloying elements, such as chromium (16 to 26%) for corrosion resistance, and smaller amounts of manganese and molybdenum. The widely used type 304 stainless steel contains 18 to 20% Cr and 8 to 10.5% Ni, and is also called 18-8 stainless steel. The yield strength of annealed type 304 stainless steel is typically 290 MPa (40 ksi), with a tensile strength of about 580 MPa (84 ksi). However, both yield and tensile strength can be substantially increased by cold working. However, the increase in strength is offset by a substantial decrease in ductility, for example, from about 55% elongation in the annealed condition to about 25% elongation after cold working.

[0005] Some austenitic stainless steels (type 200, 201, 202, and 205) employ interstitial solid-solution strengthening with nitrogen addition. Austenite, like ferrite, can be strengthened by interstitial elements such as carbon and nitrogen. However, carbon is usually excluded because of the deleterious effect associated with precipitation of chromium carbides on austenite grain boundaries (a process called sensitization). These chromium carbides deplete the grain-boundary regions of chromium, and the denuded boundaries are extremely susceptible to corrosion. Such steels can be desensitized by heating to high temperature to dissolve the carbides and place the chromium back into solution in the austenite. Nitrogen, on the other hand, is soluble in austenite and is added for strengthening. To prevent nitrogen from forming deleterious nitrides, manganese is added to lower the activity of nitrogen in the austenite, as well as to stabilize the austenite. For example, type 201 stainless steel has composition ranges of 5.5 to 7.5% Mn, 16 to 18% Cr, 3.5 to 5.5% Ni, and 0.25% N. The other type 2xx series of steels contain from 0.25 to 0.40% N.

[0006] Another important austenitic steel is austenitic manganese steel. Developed by Sir Robert Hadfield in the late 1890s, these steels remain austenitic after water quenching and have considerable strength and toughness. A typical Hadfield manganese steel contains 10 to 14% Mn, 0.95 to 1.4% C, and 0.3 to 1% Si. Solution annealing is necessary to suppress the formation of iron carbides. The carbon must be in solid solution to stabilize the austenite. When completely austenitic, these steels can be work hardened to provide higher hardness and wear resistance. A work-hardened Hadfield manganese steel has excellent resistance to abrasive wear under heavy loading. Because of this characteristic, these steels are ideal forjaw crushers and other crushing and grinding components in the mining industry. Also, Hadfield manganese steels have long been used for railway frogs (components used at the junction point of two railroad lines).

[0007] AISI Types 304L, 316L, 321 and 347 stainless steels are austenitic, chromium-nickel and chromium-nickel-molybdenum stainless steels having the following compositions in weight percent:

	Type 304 L wt. %	Type 316 L wt. %	Type 321 wt. %	Type 347 wt. %
C	0.03 max	0.03 max	0.08 max	0.08 max
Mn	2.00 max	2.00 max	2.00 max	2.00 max
Si	1.00 max	1.00 max	1.00 max	1.00 max
P	0.045 max	0.045 max	0.045 max	0.045 max
S	0.03 max	0.03 max	0.03 max	0.03 max
Cr	18.0–20.0	16.0–18.0	17.0–19.0	17.0–19.0
Ni	8.0–12.0	10.–14.0	9.0–12.0	9.0–13.0
N	0.10 max	0.10 max	0.10 max	—
Mo	—	2.0–3.0	—	—
Fe	Bal.	Bal.	Bal.	Bal.

Source: METALS HANDBOOK RTM. Desk Edition; Chapt. 15, pages 2–3; (1985). The AMS standards for these alloys restrict copper to not more than 0.75%.

[0008] The above-listed chromium-nickel and chromium-nickel-molybdenum stainless steels are known to be useful for applications which require good non-magnetic behavior, in combination with good corrosion resistance. One disadvantage of the series 300 stainless steels is their poor radiopacity. For example, a stent made from standard 300 series stainless steel can not be sufficiently radiopaque for clinical observation due to the thin cross-section of the struts. Therefore, this present invention alloy can be useful in clinical observations because it can be radiopaque in these cross-sections. There continues to be a demand for improved chromium-nickel and chromium-nickel-molybdenum stainless steels, particularly for these alloys having increased radiopaque characteristics.

[0009] Given the foregoing, it would be highly desirable to have an austenitic stainless steel that provides better radiopacity than is provided by the known austenitic stainless steels.

SUMMARY OF THE INVENTION

[0010] The invention generally relates to an austenitic 300 series stainless steel alloy that provides better radiopacity than is provided by the known austenitic stainless steels. One application for the present invention is to use the austenitic stainless steel alloy with increased radiopacity for fabricating intravascular stents. In this clinical setting, the interventionalist uses angiographic and fluoroscopic techniques that employ X-rays and materials that are radiopaque to the X-rays to visualize the location or placement of the particular device within the human vasculature. Typically stents are fabricated from a variety of stainless steels, with the 316 series representing a large percentage of the stainless steel used to fabricate currently marketed stents. The typical composition of 316 series stainless steel is shown in Table I.

TABLE I

	Component (%)								
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774

[0011] While the 300 series of stainless steel has several characteristics, such as strength, flexibility, fatigue resistance, biocompatibility, etc. rendering it a good material to make an intravascular stent, one significant disadvantage of 316 series stainless steel, as well as other 300 series of stainless steel, is that they have relatively low radiopaque qualities and therefore not readably visual under fluoroscopic observation. A need has arisen to modify the stainless steel composition so it has radiopaque properties while at the same time, maintaining those characteristics which render it as a material of choice for fabricating stents.

[0012] Modified stainless steel of the 300 series for increasing radiopaque characteristic could be produced by creating alloys containing varying amounts of elements that have dense mass and radiopaque characteristics. The chemical make-up of standard series 300 stainless steel, using series 316 as an example, along with the possible chemical ranges of various such alloys are shown on the following Table.

TABLE II

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	X
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 300A	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	000–3.000	10.000–18.000	46.185–74.000	2.000–10.000

Variable "X" could be comprised of or a combination of Au, Os, Pd, Pt, Re, Ta, W or Ir.

[0013] Other features and advantages of the present invention will become more apparent from the following detailed description of the invention.

[0014] It is an object of the present invention to provide an austenitic 300 series stainless steel alloy that provides better radiopacity than is provided by the known austenitic stainless steels.

[0015] It is another object of the present invention to provide a stent or prosthesis which can be readily delivered to, expanded and embedded into an obstruction or vessel wall with relatively high radiopaque characteristics for fluoroscopy during all phases of the interventional procedure.

[0016] Another object of the present invention is to provide a material which has superior properties, including radiopacity, for fabricating any stent design or format.

DETAILED DESCRIPTION

[0017] The alloy according to the present invention comprises a stainless steel series 300 compound used to fabricate a stent which replaces a portion of the iron or molybdenum component of the 300 series with one or combination of several elements containing radiopaque properties. Examples of such elements are gold (Au), osmium (Os), palladium (Pd), platinum (Pt), rhenium (Re), tantalum (Ta), tungsten (W) or iridium (Ir). This group consists of elements with dense masses. The dense mass provides these materials with improved absorption of X-rays thus providing improved radiopaque characteristics. By including one or more of these elements in a series 300 stainless steel, thereby creating the present invention alloy, X-rays employed in angiogram procedures or cineograms allow the visualization of certain devices, such as a stent, during all phases of a standard clinical procedure. The alloy for fabricating stents contains a range of 2.0 to 10.0 percent of one or more of these radiopaque elements, with a preferred range of 4.0 to 5.0 percent. Replacing too much of the radiopaque element with the iron or molybdenum component could possible decrease the beneficial qualities of 300 series stainless steel for manufacturing stents without contributing significantly improved radiopaque characteristics. It is anticipated that various combinations of the radiopaque elements can be used to replace the iron or molybdenum component without adversely affecting the ability to form austenite.

[0018] The foregoing, as well as additional objects and advantages of the present invention, achieved in a series 300 stainless steel alloy, is compared with standard 316 stainless steel and summarized in Tables III through XI below, containing in weight percent, about:

TABLE III

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	X
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 300A	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

Where variable "X" could be comprised of or a combination of Au, Os, Pd, Pt, Re, Ta, W or Ir.

[0019]

TABLE IV

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	Au
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0020]

TABLE V

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	Os
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0021]

TABLE VI

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	Pd
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0022]

TABLE VII

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	Pt
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0023]

TABLE VIII

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	Re
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0024]

TABLE IX

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	Ta
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0025]

TABLE X

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	W
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0026]

TABLE XI

	Component (%)									
	C	Mn	Si	P	S	Cr	Mo	Ni	Fe	Ir
Standard 316	0.020	1.760	0.470	0.014	0.002	17.490	2.790	14.680	62.774	0.000
Modified 316B	≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

[0027] The alloy for fabricating a series 300 stainless steel with improved radiopaque properties can contain up to 0.03% of carbon. The carbon element contributes to good hardness capability and high tensile strength by combining with other elements such as chromium and molybdenum to form carbides during heat treatment. However, too much carbon adversely affects the fracture toughness of this alloy.

[0028] Chromium contributes to the good hardenability corrosion resistance and hardness capability of this alloy and benefits the desired low ductile-brittle transition temperature of the alloy. Therefore, at least about 12%, and preferably at least about 17.5% chromium is present. Above about 20% chromium the alloy is susceptible to rapid overaging such that the unique combination of high tensile strength and high fracture toughness is not attainable.

[0029] Nickel contributes to the hardenability of this alloy such that the alloy can be hardened with or without rapid quenching techniques. Nickel benefits the fracture toughness and stress corrosion cracking resistance provided by this alloy and contributes to the desired low ductile-to-brittle transition temperature. Accordingly, at least about 10.0%, and preferably at least about 14.7% nickel is present. Above about 18% nickel, the fracture toughness and impact toughness of the alloy can be adversely affected because the solubility of carbon in the alloy is reduced which may result in carbide precipitation in the grain boundaries when the alloy is cooled at a slow rate, such as when air cooled following forging.

[0030] Molybdenum is present in this alloy because it benefits the desired low ductile brittle transition temperature of the alloy. Above about 3% molybdenum the fracture toughness of the alloy is adversely affected. Preferably, molybdenum is limited to not more than about 1.2%. However, the entire portion of the molybdenum can be replaced with certain radiopaque elements such as Ta without adversely affecting the desired characteristics of the alloy.

[0031] The alloy for fabricating a series 300 stainless steel stent with radiopaque properties can also contain up to 2.0% manganese. Manganese is partly depended upon to maintain the austenitic, nonmagnetic character of the alloy. Manganese also plays a role, in part, providing resistance to corrosive attack.

[0032] The balance of the alloy according to the present invention is essentially iron except for the usual impurities found in commercial grades of alloys intended for similar service or use. The levels of such elements must be controlled so as not to adversely affect the desired properties of this alloy. For example, phosphorus is limited to not more than about 0.008% and sulfur is limited to not more 0.004%. In addition, the alloy for fabricating a series 300 stainless steel alloy with radiopaque properties can contain up to 0.75% silicon. Furthermore, the alloy for fabricating a series 300 stainless steel stent with radiopaque properties can contain up to 0.023% and 0.002% phosphorus and sulfur, respectively, without affecting the desirable properties.

[0033] No special techniques are required in melting, casting, or working the alloy of the present invention. Arc melting followed by argon-oxygen decarburization is the preferred method of melting and refining, but other practices can be used. In addition, this alloy can be made using powder metallurgy techniques, if desired. This alloy is also suitable for continuous casting techniques.

[0034] The alloy of the present invention can be formed into a variety of shapes for a wide variety of uses and lends itself to the formation of billets, bars, rod, wire, strip, plate, or sheet using conventional practices.

[0035] The alloy according to the present invention can be useful in a variety of applications requiring high strength and radiopaque characteristics, for example, to fabricate stents of other medical applications.

[0036] It is apparent from the foregoing description and the accompanying examples, that the alloy according to the present invention provides a unique combination of tensile strength and radiopaque characteristics not provided by known series 300 stainless steel alloys. This alloy is well suited to applications where high strength, biocompatibility and radiopacity are required.

[0037] The terms and expressions which have been employed herein are used as terms of description and not of limitation. There is no intention in the use of such terms and expressions to exclude any equivalents of the features described or any portions thereof. It is recognized, however, that various modifications are possible within the scope of the invention claimed.

[0038] While the invention has been illustrated and described herein in terms of its use as an intravascular stent, it will be apparent to those skilled in the art that the stent can be used in other instances such as to expand prostate urethras in cases of prostate hyperplasia. Other modifications and improvements may be made without departing from the scope of the invention.

[0039] Other modifications and improvements can be made to the invention without departing from the scope thereof.

[0040] The alloy of the present invention is readily melted using conventional and/or vacuum melting techniques. For best results, as when additional refining is desired, a multiple melting practice is preferred. The preferred practice is to melt a heat in a vacuum induction furnace (VIM) and cast the heat in the form of an electrode. The electrode is then remelted in a vacuum arc furnace (VAR) and recast into one or more ingots.

[0041] The alloy can be prepared from heats which can be melted under argon cover and cast as ingots. The ingots can be maintained at a temperature range of 2100-2300 degree F. (1149-1260 degree C.) for 2 hours and then pressed into billets. The billets may be ground to remove surface defects and the ends cut off. The billets can then be hot rolled to form intermediate bars with an intermediate diameter. The intermediate bars are hot rolled to a diameter of 0.7187 in. (1.82 cm) from a temperature range of 2100-2300.degree. F. (1 149-1260.degree. C.). The round bars are straightened and then turned to a final diameter or alternately, sheets are rolled to the desired diameter with optional intermediate anneals are required. All of the bars or sheets can be pointed, solution annealed, water quenched, and acid cleaned to remove surface scale.

[0042] To evaluate improved radiopacity of the present invention, stents can be fabricated from the present invention alloy and testing in animal studies utilizing standard angiography equipment. The stent fabricated from the alloy can be deployed in an animal model with other FDA approved stents with know radiopacity characteristics.

[0043] The terms and expressions that have been employed herein are used as terms of description and not of limitation. There is no intention in the use of such terms and expressions to exclude any equivalents of the features described or any portions thereof. It is recognized, however, that various modifications are possible within the scope of the invention claimed.

We claim:

1. A modified series 300 stainless steel alloy which provides increased radiopaque characteristics over standard 300 stainless steel.

2. A steel alloy as recited in claim 1, wherein said alloy is used for fabricating intravascular stents.

3. A steel alloy as recited in claim 1, wherein said steel alloy consisting essentially of, in weight percent, about

C	Mn	Si	P	S	Cr	Mo	Ni	Fe	"X"
≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

whereby variable "x" could be comprised from a group consisting of Ir.

4. A steel alloy as recited in claim 3, wherein a portion of Iridium replaces a portion of Iron.

5. A steel alloy as recited in claim 3, wherein a portion of Iridium replaces a portion of Molybdenum.

6. A steel alloy as recited in claim 3, wherein a portion of Iridium replaces a portion of both Iron and Molybdenum.

7. A modified series 300 stainless steel alloy which provides increased radiopaque characteristics over standard 300 stainless steel, said alloy consisting essentially of, in weight percent, about

C	Mn	Si	P	S	Cr	Mo	Ni	Ir
≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	2.000–3.000	10.000–18.000	2.000–10.000

and the balance is essentially iron.

8. A modified series 300 stainless steel alloy which provides increased radiopaque characteristics over standard 300 stainless steel, said alloy consisting essentially of, in weight percent, about

C	Mn	Si	P	S	Cr	Mo	Ni	Ir
≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	2.000–10.000

and the balance is essentially iron.

9. A modified series 300 stainless steel alloy which provides increased radiopaque characteristics over standard 300 stainless steel, said alloy consisting essentially of, in weight percent, about

C	Mn	Si	P	S	Cr	Mo	Ni	Fe	"X"
≦0.030	≦2.000	≦0.750	≦0.023	≦0.010	12.000–20.000	0.00–3.000	10.000–18.000	46.185–74.000	2.000–10.000

whereby variable "X" could be comprised from a group consisting of Gold, Osmium, Palladium, Platinum, Rhenium, Tantalum, Tungsten or Iridium.

* * * * *