

**A CAST SHAPED ARTICLE MADE FROM
HIGH STRENGTH, PRECIPITATION-HARDENABLE
STAINLESS STEEL AND A PROCESS FOR MAKING SAME**



Field of the Invention

159159

[0001] This invention relates to shaped articles that are cast from a high strength precipitation-hardenable stainless steel and a process for making such articles. More particularly, the invention relates to a cast golf club head made from such an alloy.

Background of the Invention

[0002] In order to gain a competitive edge, golf club manufacturers demand progressively higher-strength, corrosion-resistant alloys which are air castable. Hitherto, precipitation-hardenable stainless steels have been used for such applications because they provide both high strength and hardness together with good corrosion resistance. For example, international application publication number WO 01/79576 describes a high-strength, martensitic precipitation-hardenable stainless steel that is suitable for air casting of shapes. In the context of that patent application, high-strength is defined as a room-temperature yield strength of at least about 190 ksi when the alloy is in the solution-treated-and-age-hardened condition. The alloy described in the published international application typically provides a yield strength of up to about 200 ksi and an ultimate tensile strength of up to about 210 ksi.

[0003] While varying combinations of higher strength, toughness, and corrosion resistance can be achieved by the known precipitation-hardenable stainless steel alloys, those alloys utilize highly reactive elements, such as titanium or aluminum which react with nickel to form a strengthening precipitate during an age-hardening heat treatment. However, titanium and aluminum have a strong affinity for oxygen and nitrogen. Therefore, alloys that employ those elements are unsuitable for air casting of shaped articles because of undesirable reactions with oxygen and nitrogen when the molten metal is exposed to the air. Efforts to isolate the molten metal from air such as by inert



gas shrouding have not provided adequate protection. Consequently, the economic benefits of air or non-vacuum melting and casting are not readily obtainable with such steels.

[0004] An age-hardenable stainless iron-base alloy has been sold under the tradename PYROMET X-23 by Carpenter Technology Corporation in wrought product forms. That alloy provides good notch tensile strength (i.e., NTS/UTS ≥ 1) in combination with good tensile ductility at an ultimate tensile strength of up to about 260 ksi. The PYROMET X-23 alloy was developed primarily for gun barrel applications because of its combination of high strength, toughness, corrosion resistance and thermal stability. In that context, thermal stability refers to the alloy's resistance to embrittlement at temperatures within the range of 700 to 1000°F. The PYROMET X-23 alloy has been manufactured typically as a single vacuum-melted (i.e., VIM) or double vacuum-melted (i.e., VIM/VAR) product.

Summary of the Invention

[0005] In accordance with the present invention, there is provided a shaped article which is manufactured by casting in air or under inert-gas shrouding at atmospheric pressure. The article according to this invention provides a superior combination of high strength, hardness, ductility, and corrosion resistance compared to the known air-castable stainless steels. A cast article in accordance with this invention is made from a high strength, castable, stainless steel alloy having the following broad, intermediate, and preferred weight percent ranges.

	<u>Broad</u>	<u>Intermediate</u>	<u>Preferred</u>
C	0.1 max.	0.025 max.	0.015 max.
Mn	2 max.	1 max.	0.5 max.
Si	1 max.	1 max.	0.5 max.
P	0.05 max.	0.04 max.	0.03 max.
S	0.05 max.	0.03 max.	0.01 max.
Cr	9-13	9.5-12	10.0-11.5
Ni	4-8	5-8	5.5-7.5
Mo	4-8	4-8	5-6
Co	8-16	8-16	9.5-13.5
N	0.1 max.	0.025 max.	0.015 max.

The balance of the alloy is essentially iron and the usual impurities found in commercial grades of age-hardenable stainless steels intended for similar use or service. In addition, the alloy may optionally contain up to about 1% niobium or niobium and/or tantalum. The alloy may also contain up to about 0.02% boron. A cast article, such as a golf club head, made from this alloy provides a yield strength of at least about 220 ksi together with good toughness and ductility.

[0006] The foregoing tabulation is provided as a convenient summary and is not intended thereby to restrict the lower and upper values of the ranges of the individual elements of the alloy of this invention for use in combination with each other, or to restrict the ranges of the elements for use solely in combination with each other. Thus, one or more of the element ranges of the broad composition can be used with one or more of the other ranges for the remaining elements in the intermediate or preferred compositional ranges. In addition, a minimum or maximum for an element of the broad, intermediate, or preferred range can be used with the maximum or minimum for that element from one of the other ranges.

[0007] Here and throughout this application, the term "percent" or the symbol "%" means percent by weight, unless otherwise indicated. Also, the term "yield strength" means the offset yield strength determined by the stress corresponding to the intersection of the stress-strain curve and a line parallel to the elastic part of the curve

offset by a strain of 0.2%.

[0008] In accordance with another aspect of this invention, there is provided a process for making a shaped article. The process includes the step of melting a stainless steel alloy having the composition in weight percent of any of the alloys set forth above. The molten alloy is cast into a mold to form a shaped article which is allowed to solidify. The shaped article is then heated at an elevated temperature for a time sufficient to substantially fully homogenize the composition and microstructure of the shaped article. The shaped article is then heat treated to develop the combination of strength and toughness desired for the use to which the shaped article will be put.

Detailed Description

[0009] Alloy compositions falling within the weight percent compositions set forth in the table above are particularly suited for air-cast golf club components. The alloy can economically achieve room-temperature ultimate tensile strengths of at least 220 ksi while retaining sufficient ductility and corrosion resistance for the golf-club application. Wrought forms of the subject alloy composition, including forgings, strip and tubular products, are also useful for golf club applications and are compatible with air-cast components. Articles of the invention also may find application for small parts unrelated to the golf industry such as firearm components.

[0010] An important aspect of this invention is the ability of the subject alloy compositions to respond to age hardening without the need for highly reactive elements such as titanium or aluminum. Age-hardenable stainless steels containing aluminum and/or titanium achieve high strength through the precipitation of Ni-Al or Ni-Ti compounds within a low-carbon martensitic matrix. In contrast, the alloy described in this application is age hardened through the precipitation of a Co/Mo/Cr-rich intermetallic compound known as "R" phase. Because of the absence of highly reactive elements, the alloy used in this invention exhibits a reduced tendency to form oxide and/or nitride compounds in the alloy matrix. Further, the alloy used in this invention is less susceptible to other compositional changes such as decarburization, when the

molten metal is exposed to air during remelting and casting.

[0011] The alloy used in the cast article according to this invention contains at least about 9%, better yet at least about 9.5%, and preferably at least about 10.0% chromium to provide adequate resistance to corrosion under oxidizing conditions, including atmospheric exposure. While increased chromium levels may provide additional corrosion resistance, too much chromium adversely affects the toughness and phase stability of the alloy. Chromium adversely affects phase stability because it promotes the formation of ferrite and an excessive amount of retained austenite. Therefore, chromium is limited to not more than about 13%, better yet to not more than about 12%, and preferably to not more than about 11.5%.

[0012] Cobalt serves multiple purposes in the alloy used in this invention. For example, cobalt promotes the formation of austenite and benefits the toughness of the alloy. Cobalt also participates in age-hardening through the precipitation of "R" phase. To achieve those benefits the alloy contains at least about 8%, and preferably at least about 9.5% cobalt. Too much cobalt stabilizes the austenite in this alloy, such that a full martensitic transformation during quenching is inhibited, thereby preventing the alloy from achieving the very high strength and hardness of which it is capable. Increasing cobalt content also significantly adds to the cost of the alloy without any further significant benefit. For these reasons, cobalt is limited to not more than about 16% and preferably to not more than about 13.5% in the alloy.

[0013] Nickel, like cobalt, promotes austenite formation and benefits the toughness provided by the alloy. Therefore, the alloy used in a cast article according to this invention contains at least about 4%, better yet at least about 5%, and preferably at least about 5.5% nickel to achieve good toughness and ductility. However, nickel also has a strong effect on suppressing the austenite-to-martensite transformation on quenching. Therefore, nickel is limited to not more than about 8%, and preferably to not more than about 7.5%.

[0014] At least about 4%, and preferably at least about 5%, molybdenum is present in the steel alloy used in this invention because molybdenum contributes not only to

strength through its role in the formation of the "R" phase strengthening precipitate, but also because it benefits the toughness, ductility, and corrosion resistance of the alloy. On the other hand, the molybdenum content is limited to not more than about 8% and preferably to not more than about 6% because too much molybdenum leads to excessive retained austenite and promotes undesirable formation of ferrite in the alloy. All or part of the molybdenum can be replaced by an equivalent amount of tungsten. As is known to those skilled in the art, the amount of tungsten required to replace a given amount of molybdenum and provide an equivalent effect is in the proportion of approximately 2% tungsten for each 1% of molybdenum.

[0015] A small amount of silicon, for example, about 0.01 to 0.02%, may be present in the alloy used in this invention because it benefits the fluidity of the alloy during casting. Silicon is also beneficial as a deoxidizing agent. Because silicon is a ferrite forming element, its concentration, when present in the alloy, is limited to not more than about 1%, and preferably to not more than about 0.5%.

[0016] The alloy used in a cast article according to the present invention may optionally include up to about 1% niobium. Because niobium is far less reactive with oxygen and nitrogen than aluminum or titanium, the presence of niobium in the alloy does not compromise the castability of the alloy in air. Moreover, niobium benefits the strength of the alloy because it reacts with some of the nickel to form a nickel-niobium rich intermetallic compound that strengthens the martensitic matrix of the alloy. The amount of niobium that is used in the alloy is limited to the aforesaid amount because more than about 1% niobium in the alloy adversely affects the toughness and ductility of the alloy. Tantalum may be substituted for all or part of the niobium on a 2-for-1 weight percent basis.

[0017] The alloy used in the cast articles of this invention may also contain a small but effective amount of boron up to about 0.02% because boron benefits the hot workability and toughness of the alloy. Boron is also useful as a deoxidizing agent. Although hot-workability is not typically a concern with regard to cast articles, hot working operations may be employed to manufacture product forms that can be remelted for

casting articles according to this invention.

[0018] The balance of the alloy is essentially iron and the usual impurities found in commercial grades of precipitation-hardenable stainless steels intended for similar use or service. In this regard, carbon, nitrogen, manganese, phosphorus, and sulfur are inevitably present in the alloy used in this invention. However, the amounts of those elements are controlled because the presence of too much of them, either individually or in combination, adversely affects the strength and toughness provided by the alloy. Carbon and nitrogen are strong austenite stabilizing elements when present in the solid solution. Their presence in too great a concentration adversely affects the phase stability of the alloy. Also, carbon and nitrogen are likely to combine with chromium to form undesirable carbide, nitride, and carbonitride compounds. Therefore, carbon and nitrogen are each restricted to not more than about 0.1%, better yet to not more than about 0.025%, and preferably to not more than about 0.015% in the alloy.

[0019] Manganese is limited to not more than about 1% and preferably to not more than about 0.5%. Phosphorus is restricted to not more than about 0.050%, better yet to not more than about 0.040%, and preferably to not more than about 0.030%. Sulfur is limited to not more than about 0.05%, better yet to not more than about 0.030%, and preferably to not more than about 0.01% because it adversely affects the mechanical properties and corrosion resistance of the alloy. Other elements including copper, vanadium, zirconium, calcium, titanium, aluminum, and rare-earth metals can be present in the article at tramp levels or as residual amounts retained from alloying additions.

[0020] The alloy is readily prepared and cast into a mold to form a component such as a golf club head. It can be melted in air in the known ways or under an inert gas atmosphere. Although better results are obtained when the alloy is vacuum melted, as by vacuum induction melting (VIM), the added cost of VIM may not be warranted for golf club components. A relatively simple heat treatment of the cast component is used to bring out the unique properties of the alloy. Preferably, the cast article is heated at a temperature of about 2000-2300°F for about 1 to 4 hours to homogenize the alloy material. The cast article is then cooled in air from the homogenizing temperature.

After the homogenizing heat treatment, the cast article is solution annealed from about 1400°F to about 2000°F for a time sufficient to ensure substantially complete austenitizing of the alloy. At least about 30 minutes at temperature is sufficient for cast, shaped articles made in accordance with this invention. The cast article is rapidly cooled from the solution annealing temperature to room temperature, preferably by quenching in water, oil, or a polymer solution, to ensure optimum response to the age-hardening heat treatment that follows. Forced gas cooling has also been used successfully.

[0021] After the solution treatment, the cast article is age-hardened by heating at about 900°F to about 1100°F, preferably at about 950°F to about 1025°F for about 1 to 4 hours, and then cooled in air.

Example

[0022] As an example of an article according to the present invention, a small heat having the weight percent composition shown in Table 1 below.

Table 1

<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Co</u>	<u>Cu</u>	<u>B</u>	<u>N</u>
0.006	<0.01	<0.01	<0.005	<0.001	10.12	7.01	5.48	10.05	<0.01	0.003	0.002

The balance of the alloy is iron and the usual impurities. The example heat was melted under an argon shroud at atmospheric pressure. An evaluation of the mechanical properties of the example heat in the cast + heat-treated condition was performed. The results of the evaluation are set forth in Table 2 below.

Table 2

Heat Treatment*	0.2% YS (ksi)	UTS (ksi)	%Elong. (in 4D)	%R.A.	NTS (ksi)	NTS/UTS	Hardness (HRC)
A	230.0	245.7	13.4	51.6	351.7	1.43	49.5
B	233.6	253.1	13.2	48.5	346.7	1.37	50.0
C	222.8	253.4	14.1	54.2	324.3	1.28	49.0
D	214.2	249.7	14.7	52.4	321.6	1.29	48.0
E	201.6	242.8	16.4	54.5	297.6	1.23	47.5
F	192.0	236.0	15.5	51.1	284.5	1.21	47.0

*For the above testing, all specimens were homogenized + solution-annealed after casting as follows: Heat at 2100°F for 4 hours and then air cool; heat at 1700°F for 1 hour followed by water quench. Specimens were then age hardened utilizing different temperatures as follows:

Treatment A - 950F, 4 hours, air cool
 Treatment B - 975F, 4 hours, air cool
 Treatment C - 1000F, 4 hours, air cool
 Treatment D - 1025F, 4 hours, air cool
 Treatment E - 1050F, 4 hours, air cool
 Treatment F - 1075F, 4 hours, air cool

[0023] As the data in Table 2 show, a peak hardness of about HRC 50 is achieved upon aging the cast article at about 975°F. The results also reveal that non-vacuum cast specimens of the subject invention can achieve a yield strength well in excess of 220 ksi ultimate tensile strength with useful levels of ductility and notch tensile strength over a wide range of aging temperatures.

[0024] Castings made in accordance with this invention also respond to age hardening temperatures below about 950°F. However, such treatments are considered to be “underaging” heat treatments, that is, they result in the alloy developing less than the peak strength of which it is capable. Useful strength levels are still provided when this alloy is age-hardened at such “underaging” heat treatments. That feature makes the alloy of this invention “design compatible” with other precipitation-hardenable stainless steels that reach peak strength when aged at lower temperatures, such as about 900-950°F. This feature is advantageous in golf club head designs in which a face formed from wrought strip of one grade of precipitation-hardenable stainless steel is joined to a body of another precipitation-hardenable stainless steel alloy. When used for golf club

head designs that do not employ multiple materials, the alloy according to this invention is preferably age-hardened at the highest temperature capable of providing the prescribed or specified strength requirement.

[0025] The presence of a controlled amount of reverted austenite benefits the toughness and ductility provided by the alloy of this invention. Set forth in Table 3 below is the amount of austenite present in the samples of the alloy of Table 1 above. Heat treatment identifiers correspond to those specified in Table 2 above.

Table 3

Heat Treatment	Vol. % Austenite
Homogenized + Soln Annld	Trace (<1)
A	Trace (<1)
B	4
C	5
D	8
E	13
F	18

[0026] The data set forth in Table 3 shows that as the age-hardening temperature increases, the amount of austenite present in the age-hardened steel increases.

[0027] It is noteworthy that the mechanical properties described herein are achieved in spite of a somewhat coarse grain size (i.e., ASTM Grain Size No. 0-1), a condition which has been frequently encountered during the casting of golf club heads.

Furthermore, it is an additional feature of this invention that the use of a homogenizing heat treatment as described above, prior to the solution annealing treatment, provides several benefits to the cast component including improved strength capability, tensile ductility and uniformity of properties. To demonstrate the benefit of the homogenization heat treatment, a second example heat having the weight percent composition shown in Table 4 was prepared.

Table 4

C	Mn	Si	P	S	Cr	Ni	Mo	Co	Cu	B	N
0.002	<0.01	<0.01	<0.005	<0.001	10.09	6.98	5.48	10.96	<0.01	0.0020	0.005

The balance of the alloy was iron and the usual impurities.

Table 5

Heat Treatment	0.2% YS (ksi)	UTS (ksi)	% Elong. (in 4D)	% RA
A ¹	192.0	230.8	9.3	15.4
B ²	206.8	245.3	13.4	42.0

¹ Treatment A: Solution anneal at 1700°F for 1 hour, then water quenched + Aging at 1025°F for 4 hours, then air cooled.

² Treatment B: Homogenize at 2100°F for 4 hours, then air cool + Solution anneal at 1700°F for 1 hour, then water quenched + Aging at 1025°F for 4 hours, then air cooled.

[0028] The data in Table 5 show that the sample which received the homogenizing heat treatment prior to solution annealing achieved a significantly better combination of strength and ductility than the sample that was not homogenized.

[0029] The terms and expressions which have been employed herein are used as terms of description, not of limitation. There is no intention in the use of such terms and expressions of excluding any equivalents of the elements, features, or steps shown and described or portions thereof. However, it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A cast, shaped article that is made from a high strength, precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about

C	0.1 max.
Mn	2 max.
Si	1 max.
P	0.05 max.
S	0.05 max.
Cr	9-13
Ni	4-8
Mo	4-8
Co	8-16
N	0.1 max.

the balance being essentially iron and the usual impurities.

2. A shaped article as set forth in Claim 1 which provides a room temperature yield strength of at least about 220 ksi in the cast and heat treated condition.
3. A shaped article as set forth in Claim 1 in which the precipitation hardenable stainless steel alloy contains up to about 1% niobium.
4. A shaped article as set forth in Claim 1 in which the precipitation hardenable stainless steel alloy contains up to about 0.02% boron.
5. A shaped article as set forth in Claim 1 in which the precipitation hardenable stainless steel alloy consists essentially of, in weight percent, about

C	0.025 max.
Mn	1 max.
Si	1 max.
P	0.04 max.
S	0.03 max.
Cr	9.5-12
Ni	5-8
Mo	4-8
Co	8-16
N	0.025 max.

the balance being essentially iron and the usual impurities.

6. A shaped article as set forth in Claim 5 in which the precipitation hardenable stainless steel alloy contains up to about 1% niobium.

7. A shaped article as set forth in Claim 5 in which the precipitation hardenable stainless steel alloy contains up to about 0.02% boron.

8. A shaped article as set forth in Claim 1 in which the precipitation hardenable stainless steel alloy consists essentially of, in weight percent, about

C	0.015 max.
Mn	0.5 max.
Si	0.5 max.
P	0.03 max.
S	0.01 max.
Cr	10.0-11.5
Ni	5.5-7.5
Mo	5-6
Co	9.5-13.5
N	0.015 max.

the balance being essentially iron and the usual impurities.

9. A shaped article as set forth in Claim 8 in which the precipitation hardenable stainless steel alloy contains up to about 1% niobium.

10. A shaped article as set forth in Claim 8 in which the precipitation hardenable stainless steel alloy contains up to about 0.02% boron.

11. A process for making a shaped article, comprising the steps of:
melting a stainless steel alloy having the following composition in weight percent

C	0.1 max.
Mn	2 max.
Si	1 max.
P	0.05 max.
S	0.05 max.
Cr	9-13
Ni	4-8
Mo	4-8
Co	8-16
N	0.1 max.

the balance being essentially iron and the usual impurities;

casting the molten alloy into a mold to form a cast article;

allowing the cast article to solidify; and then

heat treating the cast article to age harden the cast article.

12. A process as set forth in Claim 11 wherein the molten alloy is cast in air.

13. A process as set forth in Claim 11 wherein the molten alloy is cast under an inert gas atmosphere.

14. A process as set forth in Claim 11 comprising the step of heat treating the cast article to substantially homogenize the composition and microstructure of the cast article, said homogenization heat treating being performed after the cast article has solidified, but before the cast article is age hardened.
15. A process as set forth in Claim 14 wherein the homogenization heat treating step comprises the step of heating the cast article at a homogenization temperature of about 2000 to 2300°F and then cooling the cast article.
16. A process as set forth in Claim 15 wherein the homogenization heat treating step comprises the step of heating the cast article for about 1 to 4 hours.
17. A process as set forth in Claim 15 comprising the step of cooling the cast article from the homogenization temperature to about room temperature.
18. A process as set forth in Claim 11 wherein the age hardening heat treating step comprises the steps of:
heating the cast article at an elevated temperature sufficient to substantially completely austenitize the stainless steel alloy;
rapidly cooling the cast article to about room temperature; and then
heating the cast article at a hardening temperature of about 900 to 1100°F.
19. A process as set forth in Claim 18 wherein the step of austenitizing the stainless steel alloy comprises heating the cast article at a temperature of about 1400 to 2000°F for at least 30 minutes.
20. A process as set forth in Claim 18 wherein the step of heating the austenitized alloy comprises the step of heating the austenitized alloy at a temperature of about 950 to 1025°F to provide a yield strength of at least about 220 ksi.

21. A process as set forth in Claim 18 or 20 wherein the austenitized alloy is heated for about 1 to 4 hours.

22. A golf club head made from a high strength, precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about

C	0.1 max.
Mn	2 max.
Si	1 max.
P	0.05 max.
S	0.05 max.
Cr	9-13
Ni	4-8
Mo	4-8
Co	8-16
N	0.1 max.

the balance being essentially iron and the usual impurities,

said golf club head having been formed by casting said alloy into a mold, solidifying the alloy, and then heat treating the alloy under conditions of temperature and time sufficient to provide a yield strength of at least about 220 ksi for said golf club head.