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HIGH TEMPERATURE ALLOY STEEL WITH IMPROVED ROOM TEMPERATURE PROPERTIES

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6 Claims. (Cl. 75—125)

This invention relates to stainless steel of the type generally identified as 12.00% chromium steel (i.e., containing about 9.00% to 16.00% chromium), and more particularly to such a steel and articles made therefrom capable of being age hardened, having good corrosion resistance and stress rupture life at elevated temperatures as well as good ductility and tensile strength at room temperature.

In our co-pending application, Serial No. 639,644, filed February 12, 1957, now Patent No. 2,875,042, and assigned to the assignee of the present application, we have set forth a 12.00% chromium alloy steel which is especially well suited for fashioning parts which are subjected to high stress at elevated temperatures. Because such parts as turbine blades, buckets, bolts, etc., are operated at temperatures from 800° F. to 1400° F. or higher after warm-up, it is necessary that they have good corrosion resistance at such temperatures as well as as high a stress rupture life as possible in order to withstand the pressures to which they are subjected. The parts should not become embrittled, but should be ductile and retain their ductility under operating conditions for long periods of time. To facilitate their fabrication, the alloy from which the parts are made should be capable of being annealed and, from the point of view of the overall cost of the turbine or the like in which they are incorporated, such parts should have a temperature coefficient which matches well with those other parts of the turbine which are not required to bear the same high stresses.

Very often the parts are subjected to full operating pressures, as at the start of an operating cycle, when they are at room temperature or below. Hitherto it had not been considered feasible to provide an alloy steel of relatively low alloy content which combined to a high degree both the desired high temperature properties and good ductility and tensile strength at room temperature or below. We have found that a relatively inexpensive alloy steel may be provided which has both exceptional high temperature properties and outstanding ductility and tensile strength at room temperatures.

It is, therefore, a principal object of this invention to provide an age hardenable, inexpensive stainless alloy steel of the 12.00% chromium class which is not only characterized by high ductility, stress rupture strength and resistance to corrosion at elevated temperatures, but also is characterized by having exceptional ductility and tensile strength at room temperature.

A generally accepted figure of merit for alloy steels of this class is a capability of being able to withstand a load of 25,000 p.s.i. at 1200° F. for at least 100 hours. Our present composition has been found to be capable of withstanding substantially greater loads for longer periods at that temperature, and this high stress rupture life at an elevated temperature, together with the aforementioned high and low temperature properties, as well as other advantageous characteristics are achieved by incorporating in a 12.00% chromium steel (i.e., about 9.00% to 16.00% chromium), certain proportions of molybdenum or tungsten, about 4.5% to 6.00%, copper, about 0.6 to 4.5% and cobalt, about 1% to 9%. By proper adjustment and control of this composition a product is provided which, after age hardening, has excellent stress rupture characteristics at elevated temperatures, about 1200° F., which is of relatively low cost to manufacture, and which can be annealed soft enough for easy machining. Such an alloy is readily machinable when annealed but can be easily aged to a Rockwell C hardness of 25 or higher. This composition has a minimum stress rupture life of more than 100 hours when subjected to a load of 35,000 p.s.i. at 1200° F. and may be able to withstand such stress for as long as 300 hours or more. This same composition demonstrates a remarkable degree of room temperature ductility, having a minimum elongation of about 10% in its as-aged condition.

The composition which has been found to be capable of producing these results is as follows:

Carbon	0.15% maximum.
Manganese	1.00% maximum.
Silicon	1.00% maximum.
Chromium	9% to 16%.
Molybdenum and/or Tungsten	4.5% to 6.0%.
Copper	0.6% to 4.5%.
Cobalt	1% to 9%.

Balance substantially all iron except for incidental impurities in such steels.

In order to maintain the cost of the composition as low as possible I preferably do not add other elements; however, such elements as nickel, phosphorus, titanium, vanadium, and boron, as well as others may be added to the composition when desired. As will be pointed out more fully hereinafter, this composition provides the desired high temperature and room temperature properties to a unique degree.

Copper and cobalt work together to provide the most outstanding results when molybdenum is present in amounts greater than about 5.35%, that is to say, greater than from 5.30% to 5.40%. When the molybdenum content ranges from about 4.5% to 5.35%, copper in the absence of cobalt, provides an advantageous improvement in ductility as compared to the ductility of 12% chromium steels of low alloy content. However, above about 5.35%, copper alone is ineffective to provide the desired improvement in room temperature ductility and good high temperature stress rupture strength. With the molybdenum content above about 5.35%, but not greater than about 6%, cobalt, in the absence of copper, is effective to provide a composition having improved room temperature ductility and good high temperature stress rupture strength.

Examination of the microstructure of our composition shows that it is not a single-base structure. However, unlike known compositions wherein generally a two-phase microstructure with both ferrite and martensite indicate that the metal has undesirable properties, in the case of the present composition, the two-phase microstructure does not detrimentally affect the composition. Normally, the ferrite is soft compared to the martensite and this difference in the properties of the two results in a product of undesirably inferior strength. In our composition, after it has been heat treated, the ferrite becomes age hardened and the martensite becomes tempered so that the two approach each other in hardness with the result that they are substantially equal in hardness. Consequently, our two-phase martensite-ferrite composition with about 10% to 50% martensite, is free of the weakness which has hitherto been characteristic of such two-phase compositions.

Excessive carbon detracts from the hot strength of our composition, having a tendency to form austenite and carbides; the austenite in turn forming martensite. Good results are achieved with up to about 0.15% carbon although somewhat less carbon, up to about 0.10% is preferred to provide the most outstanding stress rupture properties.

Manganese and silicon are present in keeping with good melting practice and to insure good hot workability. Manganese and silicon each in amounts of up to about 1.0% are present in sufficient quantity to provide the desired degree of de-oxidation during melting and hot workability.

Because such instrumentalities as turbine blades, buckets, bolts and the like are subjected to a corrosive atmosphere during operation, a minimum amount of about 9.00% chromium is included in the composition. When present in amounts above about 16%, chromium adversely affects the room temperature ductility.

Molybdenum and tungsten, either separately or together, affect the microstructure and in turn the physical properties of such compositions. The amounts of molybdenum and/or tungsten required to provide the required minimum as aged hardness essential in the products for which such compositions as the present one are generally intended, have hitherto resulted in compositions having such poor room temperature ductility as seriously to impair their usefulness. We have found that by including carefully controlled amounts of copper and cobalt, the resulting composition not only has the required as-aged hardness but also enhanced stress rupture properties as well as exceptional room temperature ductility.

In our composition as little as 4.5% molybdenum and tungsten, either separately or together, these two elements being equivalent in our composition in about one-to-one relation by weight, is sufficient to provide the desired properties when from about 0.6% to 4.5% copper is used. Above about 6%, molybdenum and/or tungsten adversely affect the room temperature ductility of the composition.

The following examples of our composition, unless otherwise indicated, were processed as follows: The heats were cast into 1⅛ inch square ingots weighing 800 grams each and forged to a ½ inch square bar. The bars were solution treated by heating for one hour at 1950° F., followed by oil quenching, and were then aged at 1200° F., for 16 hours. As is customary, percent concentrations of elements in the examples and throughout this specification refer to percent by weight.

Example I.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.028
Manganese	0.3
Silicon	0.3
Chromium	8.7
Molybdenum	4.92
Copper	2.20
Iron	Balance

The alloy, after solution treating and in its thus annealed condition had a Rockwell C hardness of 22/24 and an as-aged hardness of Rockwell C 29/30. Tests conducted at room temperature on the as-aged specimen showed an ultimate tensile strength of 144,000 p.s.i. with a 13% elongation in a one inch gauge length and a 36.6% reduction in area. At 1200° F., the alloy had an 81.7 hour life when subjected to 35,000 p.s.i. and a 6.2 hour life under a load of 40,000 p.s.i.

Example II.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.04
Manganese	0.4
Silicon	0.1
Chromium	11.7
Molybdenum	5.1
Copper	1.3
Iron	Balance

This product had a Rockwell C hardness of 22/23 in its as-annealed condition and an as-aged hardness of Rockwell C 29/30. When tested in its as-aged condition at room temperature, it showed an ultimate tensile strength of 141,200 p.s.i. with a 13.6% elongation in a one inch gauge length and a 28.5% reduction of area. At 1200° F., the test bar had a life of 164 hours under a load of 35,000 p.s.i.

Example III.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.028
Manganese	0.4
Silicon	0.3
Chromium	11.9
Molybdenum	5.04
Copper	2.83
Iron	Balance

In its annealed condition this product had a Rockwell C hardness of 28/30 and an as-aged hardness of Rockwell C 35. At room temperature, in its as-aged condition, it demonstrated an ultimate tensile strength of 173,100 p.s.i. with an 11.2% elongation in a one inch gauge length and a 26.5% reduction of area. At 1200° F. the test bar had a life of 215.2 hours under a load of 35,000 p.s.i. and a life of 150.9 hours under a load of 40,000 p.s.i.

Example IV.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.034
Manganese	0.3
Silicon	0.3
Chromium	11.8
Molybdenum	5.0
Copper	4.02
Iron	Balance

The alloy, in its annealed condition, had a hardness of Rockwell C 31/33 and an as-aged hardness of Rockwell C 35. At room temperature this alloy demonstrated an ultimate tensile strength of 163,200 p.s.i. with a 14.6% elongation in a one inch gauge length and a percent reduction of area of 33.4%. At 1200° F. and under a load of 35,000 p.s.i. this alloy had a stress rupture life of 177 hours and under a load of 40,000 p.s.i. a stress rupture life of 72.8 hours.

Examples I–IV demonstrate that the usual adverse effect of increasing amounts of molybdenum from 4.5% upon the room temperature ductility and strength of a 12% chromium steel is counteracted by the copper additions of the present invention. It has also been found that in the narrow range of from about 5.35% to 6% molybdenum additions of cobalt in amounts ranging from about 1% to 9% also improves the room temperature ductivity and strength of such a composition.

The following two examples are illustrative of this effect of cobalt on 12% chromium steels containing molybdenum in the approximate amounts stated.

Example V.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.036
Manganese	0.4
Silicon	0.2
Chromium	11.7
Molybdenum	5.7
Cobalt	4.41
Iron	Balance

This alloy had, in its annealed condition, a Rockwell C hardness of 23/25 and an as-aged hardness of Rockwell C 32/33. The alloy demonstrated an ultimate tensile strength of 161,400 p.s.i. with 14.4% elongation in a one inch gauge length and a 37.6% reduction of area. Stress rupture tests at 1200° F. showed a life of 111 hours under a load of 35,000 p.s.i. and a life of 46.5 hours under a load of 40,000 p.s.i.

Example VI.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.044
Manganese	0.4
Silicon	0.2
Chromium	11.7
Molybdenum	5.65
Cobalt	6.93
Iron	Balance

The product when tested had a Rockwell C hardness of 23/33 in its as-annealed condition and an as-aged hardness of Rockwell C 37/38. At rom temperature the alloy demonstrated an ultimate tensile strength of 183,200 p.s.i. with a 15.6% elongation in a one inch gauge length and a 43.2% reduction in area. At 1200° F. the alloy demonstrated a stress rupture life of 260.1 hours under a load of 35,000 p.s.i. and a life of 121 hours under a load of 40,000 p.s.i.

Both copper and cobalt together are preferred particularly with the greater additions of molybdenum. The following examples illustrate the enhanced room temperature ductility and strength, as well as the good high temperature properties obtainable.

Example VII.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.038
Manganese	0.4
Silicon	0.3
Chromium	11.4
Molybdenum	5.74
Copper	2.16
Cobalt	1.00
Iron	Balance

This alloy had a Rockwell C hardness of 25/27 in its annealed condition and a Rockwell C hardness of 34/35 in its as-aged condition. The aged composition, when tested at room temperature, had an ultimate tensile strength of 165,800 p.s.i. with a 10% elongation in a one inch gauge length and a 25.4% reduction of area. When tested at 1200° F. the test bar had a stress rupture life of 263.8 hours under a load of 35,000 p.s.i. and a life of 69.1 hours under a load of 40,000 p.s.i.

Example VIII.—An alloy was prepared having the following analysis:

	Percent
Carbon	0.034
Manganese	0.4
Silicon	0.3
Chromium	11.6
Molybdenum	5.74
Copper	2.14
Cobalt	1.96
Iron	Balance

When tested, the product showed an as-annealed hardness of Rockwell C 25/26 and an as-aged hardness of Rockwell C 34/35. Under room temperature conditions the product had an ultimate tensile strength of 167,800 p.s.i. with a 10.6% elongation in a one inch gauge length and a 26.8% reduction in area. When tested at 1200° F. the alloy had a stress rupture life of 352.4 hours under a load of 35,000 p.s.i. and a life of 140 hours under a load of 40,000 p.s.i.

Example IX.—An alloy was prepared with the following analysis:

	Percent
Carbon	0.032
Manganese	0.5
Silicon	0.4
Chromium	11.3
Molybdenum	5.76
Copper	2.2
Cobalt	2.92
Iron	Balance

This alloy demonstrated in its annealed condition a Rockwell C hardness of 31/32 and in its as-aged condition a hardness of Rockwell C 36. The aged specimen had an ultimate tensile strength of 175,200 p.s.i. at room temperature with a 12% elongation in a one inch gauge length and a 30% reduction of area. When tested at 1200° F. the alloy had a stress rupture life of 386.7 hours when subjected to a load of 35,000 p.s.i and a life of 124.5 hours when subjected to a load of 40,000 p.s.i.

Example X.—An alloy was prepared with the following analysis:

	Percent
Carbon	0.034
Manganese	0.5
Silicon	0.4
Chromium	11.7
Molybdenum	5.65
Copper	2.18
Cobalt	3.93
Iron	Balance

As annealed, this alloy had a hardness of Rockwell C 29/31 and an as-aged hardness of Rockwell C 37/38. At room temperature the aged specimen demonstrated an ultimate tensile strength of 180,800 p.s.i. with a 13.2% elongation in a one inch gauge length and a 30.8% reduction of area. When tested at 1200° F. the specimen had a life of 269.1 hours under a load of 35,000 p.s.i. and a life of 140 hours under a load of 40,000 p.s.i.

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

What is claimed is:

1. A steel alloy capable of being age-hardened and in its age-hardened condition having good corrosion resistance and stress rupture life at elevated temperatures as well as good ductility and tensile strength at room temperature, said alloy containing up to about 0.15% carbon, silicon and manganese each in an amount not more than 1%, about 9% to 16% chromium, about 4.5% to 5.35% of an element selected from the class consisting of molybdenum and tungsten, about 0.6% to 4.5% copper, and the remainder substantially iron.

2. A steel alloy capable of being age-hardened and in its age-hardened condition having good corrosion resistance and stress rupture life at elevated temperatures as well as good ductility and tensile strength at room temperature, said alloy containing up to about 0.15% carbon, silicon and manganese each in an amount not more than 1%, about 9% to 16% chromium, about 5.35% to 6% of an element selected from the class consisting of molybdenum and tungsten, about 1% to 9% cobalt, and the remainder substantially iron.

3. A steel alloy capable of being age-hardened to show a double phase ferritic-martensitic microstructure with the martensitic phase ranging from about 10% to 50% wherein as the composition age-hardens the ferrite becomes age-hardened and the martensite becomes tempered to a condition of substantially equal hardness, said alloy in its age-hardened condition having good corrosion resistance and stress rupture life at elevated temperatures as well as good ductility and tensile strength at room temperature, said alloy containing up to about 0.15% carbon, silicon and manganese each in an amount not more than 1%, about 9% to 16% chromium, about 4.5% to 5.35% of an element selected from the class consisting of molybdenum and tungsten, about 0.6% to about 4.5% copper, and the remainder being substantially iron.

4. A steel alloy capable of being age-hardened to show a double phase ferritic-martensitic microstructure with the martensitic phase ranging from about 10% to 50%

wherein as the composition age-hardens the ferrite becomes age-hardened and the martensite becomes tempered to a condition of substantially equal hardness, said alloy in its age-hardened condition having good corrosion resistance and stress rupture life at elevated temperatures as well as good ductility and tensile strength at room temperature, said alloy containing up to about 0.15% carbon, silicon and manganese each in an amount not more than 1%, about 9% to 16% chromium, about 5.35% to 6% of an element selected from the class consisting of molybdenum and tungsten, about 1% to 9% cobalt, and the balance substantially iron.

5. A steel alloy capable of being age-hardened and in its age-hardened condition having good corrosion resistance and stress rupture life at elevated temperatures as well as good ductility and tensile strength at room temperature, said alloy containing up to about 0.15% carbon, silicon and manganese each in an amount not more than 1%, about 9% to 16% chromium, about 5.35% to 6% of an element selected from the class consisting of molybdenum and tungsten, about 0.6% to 4.5% copper, about 1% to 9% cobalt, and the remainder substantially iron.

6. A steel alloy capable of being age-hardened to show a double phase ferritic-martensitic microstructure with the martensitic phase ranging from about 10% to 50% wherein as the composition age-hardens the ferrite becomes age-hardened and the martensite becomes tempered to a condition of substantially equal hardness, said alloy in its age-hardened condition having good corrosion resistance and stress rupture life at elevated temperatures as well as good ductility and tensile strength at room temperature, said alloy containing up to about 0.15% carbon, silicon and manganese each in an amount not more than 1%, about 9% to 16% chromium, about 5.35% to 6% of an element selected from the class consisting of molybdenum and tungsten, about 0.6% to 4.5% copper, about 1% to 9% cobalt, and the balance substantially iron.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,932,568 April 12, 1960

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 51, for "single-base" read -- single-phase --; column 4, line 54, for "ductivity" read -- ductility --; column 5, line 12, for "23/33" read -- 29/33 --.

Signed and sealed this 4th day of April 1961.

(SEAL)

Attest: ERNEST W. SWIDER

XXXXXXXXXX

Attesting Officer

ARTHUR W. CROCKER

Acting Commissioner of Patents