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ALLOY STEEL

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This invention relates to alloy steel and more particularly to austenitic, chromium-nickel steel which is age hardenable to a substantial extent as well as products and articles made therefrom.

Alloy steels having good high temperature properties are available and for many applications austenitic, stainless steels containing chromium and nickel as well as varying amounts of other elements are preferred due to their ability to withstand stress and corrosive atmosphere at temperatures above 1200° F. Such steels are characterized by substantially less hardness at somewhat lower temperatures so that at temperatures of about 800° F. or less, martensitic steels are more desirable from the standpoint of hardness. In practice this often results in an article being manufactured as a composite of two different steels. An apt illustration of this is found in the manufacture of valves for internal combustion engines wherein the heads of the exhaust valves may operate at temperatures varying from 1200° F. to 1500° F. or higher while the remote ends of the valve stems may be at substantially lower temperatures well below 1000° F. In order to meet the requirements of such operating conditions, the valve head has been fabricated from austenitic steel and the stem from martensitic steel, the two parts being welded together. In this way, the required hardness of the valve stem at the lower temperature is provided while high hot hardness and corrosion resistance of the valve head is provided by the austenite. In addition to being costly, the necessity for forming a bond between the two parts and their differing compositions introduces problems and disadvantages which I have found may be completely avoided.

Thus, an important object of this invention is the provision of an austenitic alloy steel as well as articles made therefrom having improved hardness at temperatures below 1000° F. and having good hardness at elevated temperatures ranging from 1200° to 1500° F. or higher.

The value and usefulness of an alloy steel is determined to a large extent by its workability. That is to say, no matter how desirable other properties of the composition may be, if products cannot be formed therefrom on a commercial basis, its usefulness is seriously curtailed. Alloy steels have been improved over a long period of years to such an extent that compositions presently available have such high as hot worked hardnesses that a further increase in such hardness adversely affects forming or machining and necessitates the use of expensive high temperature annealing before the metal may be satisfactorily worked. This is far short of the desired property of being readily machinable.

While cumulative additions of such elements as carbon tend to improve some properties of the steel including the hardness, above a critical amount of carbon, difficulty in forming and machining is encountered. Thus, it has been necessary to limit the carbon content and accept lower hardness properties in order to maintain the working properties of the composition within a feasible range. Even after aging or precipitation hardening, the hardness values attained with alloys having such lim-

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ited carbon content leaves much to be desired and have resulted in the use of composite structures as was pointed out hereinabove in connection with engine valves.

Known practices for accomplishing age hardening of austenitic alloy steels involves a solution treatment at relatively high temperature followed by aging at a lower temperature. For example, the steel may be given a solution treatment at about 1900° F. to about 2300° F. Then, after working, the part is again heated at about 1200° to 1500° F. for a sufficient length of time for hardening to take place. In general, the high temperature solution treatments were essential to the aging process and had to be utilized even though undesirable grain growth and impairment of ductility resulted. Furthermore, such treatments materially increase the cost of the material and products made therefrom.

It is, therefore, another object of this invention to provide austenitic, chromium-nickel alloy steel and articles made therefrom having substantially improved hardness which may be aged or precipitation hardened directly from the hot worked structure by a heat treatment at temperatures below about 1500° F. without requiring preliminary, higher temperature treatments.

I have found that low carbon, i. e., from about .10% to .3%, austenitic chromium-nickel steels with controlled additions of both phosphorus and copper may be readily hot worked and then aged to hardnesses heretofore considered characteristic of or attainable only in high carbon steels but without the detrimental effects of the higher carbon content. My improved alloys are also characterized by improved tensile and stress rupture strengths to the extent that they compare well with alloys containing cobalt, molybdenum, columbium or tungsten for improving the strength thereof. While I do not wish to exclude the possibility of adding such elements to my alloys in order to enhance still further certain properties thereof, it should be clearly understood that my present alloys have substantially improved properties as compared to lean alloys heretofore available. The hardness of my compositions may be improved further by an addition of small amounts of boron.

Stainless steels contain sufficient chromium to provide corrosion resistance at low and elevated temperatures. Ordinarily such steels contain a minimum of about 12% chromium and may contain as much as 30% or more. For applications in which high resistance to corrosive atmospheres at elevated temperatures is required, I prefer about 17% to 22% chromium.

Austenitic stainless steels contain a minimum of about 3% nickel and may contain as much as 35% or even more. In practice, some of the nickel content may be replaced by up to about 8% manganese. Such alloys often contain varying amounts of silicon, sulphur and nitrogen although usually up to a maximum of about 1% silicon, about .03% sulphur or within normal melting limits and between .15% to about .35% or more nitrogen.

I attain a marked improvement in such alloys by carefully controlled additions of both phosphorus and copper. My alloys not only have good high temperature properties including enhanced resistance to creep and stress rupture, but also are readily hardenable by aging to such a degree that even though the alloys are austenitic, they may be utilized where high hardness below 1000° F. is required. The present alloys are readily machined, and products are readily formed therefrom which on being age hardened are advantageously used where high hardness over a wide temperature range is required. I readily attain hardnesses ranging from 30 to 40 or more on the Rockwell C scale (R_c) and hardness of 48 R_c have been obtained. Below .10% carbon, the hardness of the alloy

as hot worked is so low that even after aging, desired hardness is not obtainable. Consequently, I include a minimum of .10% carbon and preferably no less than .15% for optimum aging properties. It is important to note that the improvements in my alloys are attained with a maximum of .3% carbon while preferably only up to .25% carbon is present. My compositions may be readily aged to hardness hitherto considered characteristic of carbon contents above 0.3%, while avoiding the hot working difficulties associated with such large carbon contents.

While it has been generally understood that no appreciable hardness through aging could be obtained with less than .3% carbon in austenitic, stainless alloys, I have found that with additions of .15% to .40% phosphorus together with .50% to 3% copper not only are the hardnesses obtainable by aging improved, but also the aging may be carried out without first subjecting the alloy to a high temperature solution treatment. Such alloys may be readily hot worked and machined and may then be subjected to an aging or precipitation treatment at about 1200° F. to about 1500° F. to provide enhanced hardnesses. In some instances, it may be desirable to subject the alloys to a solution treatment at about 1950° F. to about 2250° F. For example, when I desire to increase further room temperature tensile and yield strengths I may solution treat at about 2100° F. and then age at 1200° F. to 1300° F. for from 8 hours to as long as may be required to attain the desired properties. However, an important advantage of my compositions resides in the fact that such high temperature solution treatment is not necessary as a preliminary step before the aging or precipitation treatment at the lower temperature.

Table I presents data which indicates the significant improvement in physical properties characteristic of my compositions even when they are aged from their as hot worked condition without first being subjected to a high temperature solution treatment. The data set forth was obtained from samples the base compositions of which were similar but including differing amounts of phosphorus and copper. Composition #1 contained about 21.08% chromium, 12.11% nickel, 1.36% manganese, 0.20% carbon, 0.47% silicon, 0.008% sulphur, 0.20% nitrogen, 0.195% phosphorus and 1.62% copper. Composition #2 contained about 21.00% chromium, 11.99% nickel, 1.54% manganese, 0.20% carbon, 0.46% silicon, 0.009% sulphur, 0.19% nitrogen, 0.244% phosphorus and 1.03% copper. In both compositions the remainder was substantially iron. The samples were hot rolled, aged at 1200° F. for 16 hours and tested at room temperature.

Table I

Composition	0.2% Yld. Str., p. s. i.	Ten. Str., p. s. i.	Percent Elong., 2 inches	Percent Red. of Area
#1-----	79,000	129,500	31.8	43.9
#2-----	98,500	140,250	27.8	42.1

The actual changes in the alloy which occur during the aging process are not clearly understood at this time. However, I have found from experiments which I have conducted that a small amount of age or precipitation hardening is attainable with the foregoing compositions as the phosphorus content is increased from about .15% with only residual amounts of copper. The hardnesses attained were well below those attainable with carbon contents above .3% and in the neighborhood of .5% carbon. I have also found that copper additions in the absence of an effective amount of phosphorus, about .1%, have little or no effect upon the age hardening properties of the alloys. Excessive amounts of either or both of phosphorus and copper adversely affect other desired properties of the compositions. For example, in the case of phosphorus above about .4%, the compositions have poor

hot working properties, and even with as little as .34% some forging difficulties may be encountered in some instances. Additions of copper greater than about 3% also adversely affect the forgeability of the compositions. Consequently, I more specifically prefer to use approximately 0.20% to 0.30% phosphorus and 0.75% to 2% copper. Within these ranges of my compositions, the good aging properties of high carbon alloys, i. e., above .3% carbon, are attained together with good resistance to creep, rupture under stress and hardness at high temperatures as well as the highly desired properties of being readily hot worked and machined.

I have also found that some further increase in the low temperature hardness of my compositions containing phosphorus and copper may be had by adding small amounts of boron thereto. An increase of from 2 to 4 points R_c may be obtained with additions of from about 0.002% to about 0.010% boron. Larger amounts of boron, about 0.13% to 0.25%, have an adverse effect and the resulting hardness as aged is less than that obtainable in the absence of boron.

Products such as valves for internal combustion engines are illustrative of a class of articles which are markedly improved when made of my present alloy steel. The rigorous conditions under which such parts are used particularly require a combination of exceptionally good high and low temperature properties. For such products, I preferably use compositions containing not less than 0.15% to about 0.25% carbon, about 8% to 22% nickel and manganese combined, about 0.20% to 0.30% phosphorus, about 17% to 22% chromium, about 0.75% to 2% copper and the remainder substantially iron. Such compositions usually contain silicon and sulphur in small amounts as well as some nitrogen, the last being important since it improves the hot hardness and room temperature strength of the alloys. It should be noted that a sufficient amount of nickel and manganese either separately or combined is included to provide an austenite free of the undesired ferrite or martensite.

I provide austenitic, chromium-phosphorus-copper stainless steel having the preferred composition noted above by producing a melt in a conventional steel making furnace in accordance with well known melting processes. The resulting ingots may be cogged or bloomed or otherwise formed into billets or bars from which various products as, for example, valves, may be made by suitable forming and machining operations. After the part has been worked and the machining accomplished where necessary, I heat the steel at about 1200° F. to 1300° F. Aging may also be carried out at somewhat higher temperatures, about 1400° F. to 1500° F., but maximum hardness is attainable at about 1200° F. to 1300° F. For most purposes, the hardnesses attained in the first 8 to 16 hours of this heat treatment are sufficient. A solution treatment before the steel is aged is not necessary with my compositions. In the absence of the phosphorus and copper contents pointed out above, such a solution treatment is essential and no appreciable age or precipitation hardening is attainable unless the steel is first solution treated. Austenitic stainless steel alloys illustrative of my invention are set forth in Table II.

Table II

Heat	C	Mn	Si	P	S	Cr	Ni	Cu	N	B
A-----	.25	4.88	.57	.250	.009	21.72	4.45	1.10	.26	.007
B-----	.21	1.47	.42	.181	.007	20.84	12.06	.65	.18	-----
C-----	.19	1.45	.42	.198	.008	21.00	12.18	2.48	.19	-----
D-----	.17	1.41	.43	.203	.007	21.19	12.15	1.29	.18	-----
E-----	.18	1.43	.43	.214	.008	21.36	12.55	1.76	.18	-----
F-----	.18	1.43	.43	.289	.008	21.36	12.55	1.76	.18	-----
G-----	.21	1.47	.42	.324	.007	20.84	12.06	.65	.18	-----
H-----	.21	1.53	.44	.361	.007	20.93	12.26	3.06	.18	-----
I-----	.19	1.45	.42	.375	.008	21.00	12.18	2.48	.19	-----

NOTE.—Such elements as molybdenum if present were in residual amounts only, well below normal melting limits.

To show the ease with which my compositions may be aged, multiple specimens from each of the heats in Table II were prepared. The hardness as forged was found. One set of specimens, including at least two from each heat, was then aged as forged at 1200° or 1300° F. for 16 hours. A second set, also including at least two specimens from each heat, was then annealed at a solution treating temperature of 2100° F. These specimens were held for one hour at heat and water quenched. Aging was then carried out at 1200° F. or 1300° F. for 16 hours. Rockwell hardnesses as determined by test are set out in Table III as averages for each heat. The percentages of phosphorus and copper have been repeated for ready reference.

Table III

Heat	Percent P	Percent Cu	R _e As forged	R _e As forged, Aged 1,200° F.	R _H W. T. 2,100° F.	R _e W. T. 2,100° F., Aged 1,200° F.
A ¹	0.25	1.10	32	41	22(R _e)	40.5
B	0.181	0.65	28	35.5	95	30
C	0.198	2.48	25.5	35	98.5	28
D	0.203	1.29	25.5	33	92.5	29
E	0.214	1.78	26.5	34	92	31
F	0.280	1.78	29.5	36	92.5	38.5
G	0.324	0.65	26	37.5	93.5	39
H	0.361	3.06	30.5	38.5	90.5	41.5
I	0.375	2.48	32	39.5	91	39.5

¹ Aging of heat A was conducted at 1300° F.

From Table III is apparent that my compositions, particularly when aged from the as hot worked condition, provide a marked improvement in hardness as compared to comparable alloys hitherto available but not containing phosphorus and copper or phosphorus, copper and boron as indicated. It will be noted that in most instances, the as-forged, aged hardnesses compare favorably with the corresponding hardnesses obtained after the high temperature solution treatment. Of even greater significance is the fact that the hardnesses obtained by aging the alloy in its as-forged state, i. e., without first solution treating, are more than adequate and provide products having the desired hardnesses in addition to good resistance to creep and high tensile strength. Products of the foregoing compositions are especially suitable where good ductility as aged is an important consideration since the impairment of ductility in such materials which results from solution treating austenitic steel at high temperature is completely avoided.

Compositions containing nickel and manganese each in a range of about 4.5% to 6.5% are especially suitable for use in the manufacture of such articles as internal combustion engine valves, and such compositions are especially preferred for that purpose. Hardnesses well above 35 R_e are consistently obtained while hardnesses as high as 48 R_e have been obtained with longer aging treatments of from 32 to 48 hours. The optimum temperature for attaining maximum hardness is 1300° F. for compositions falling in this preferred range.

The hot hardness of my compositions is substantially improved. Tests were conducted on aged specimens at 1350° F. in an enclosed electrical resistance wound furnace in a still air atmosphere. A 10 mm. chromium carbide ball under a load of 2000 kg. applied for 15 seconds was used with the ball also at 1350° F. The Brinell hardnesses obtained show an improvement in hot hardness at 1350° F. of about 40 to 80 points as compared to comparable alloys which did not contain the additions of phosphorus and copper or phosphorus and copper together with boron in accordance with my present invention. Hot hardnesses well over 200 Brinell may be readily attained with my preferred compositions.

V-notch Charpy impact tests conducted at room temperature indicate that my compositions with phosphorus and copper compare well with comparable materials with-

out my phosphorus and copper content. The physical properties of my compositions as demonstrated by tensile tests conducted at room temperature show a marked improvement as was pointed out hereinabove, and, in particular, the improvement in ductility is outstanding.

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

I claim:

1. Austenitic chromium-nickel-phosphorus-copper stainless steel readily age hardenable to Rockwell C 30 and above containing from about 0.10% to not more than 0.30% carbon, about 0.15% to about 0.40% phosphorus, from about 0.5% to about 3% copper, about 12% to about 30% chromium, about 3% to about 35% nickel and manganese combined but no less than 3% nickel, and the remainder substantially iron.

2. Austenitic chromium-nickel-phosphorus-copper stainless steel readily age hardenable to Rockwell C 30 and above containing from about 0.10% to not more than 0.30% carbon, about 0.15% to about 0.40% phosphorus, from about 0.5% to about 3% copper, about 0.002% to about 0.010% boron, at least 0.15% nitrogen, about 12% to about 30% chromium, about 3% to about 35% nickel and manganese combined but no less than 3% nickel, and the remainder substantially iron.

3. Austenitic chromium-nickel-phosphorus-copper stainless steel characterized by being both readily machinable and readily age hardenable as hot worked to at least Rockwell C 30 and above by means of an aging or precipitation treatment at a temperature of about 1200° F. to about 1500° F. in the absence of a previous solution treatment at a substantially higher temperature, containing from about 0.15% to about 0.25% carbon, about 8% to about 22% manganese and nickel combined but no less than about 3% nickel, about 0.20% to about 0.30% phosphorus, about 17% to about 22% chromium, about 0.75% to about 2% copper, at least 0.15% nitrogen, and the remainder substantially iron.

4. Austenitic chromium-nickel-phosphorus-copper stainless steel characterized by being both readily machinable and readily age hardenable as hot worked to at least Rockwell C 35 and above by means of an aging or precipitation treatment at a temperature of about 1300° F. in the absence of a previous solution treatment at a substantially higher temperature, containing at least 0.15% to no more than 0.25% carbon, nickel and manganese each in a range from 4.5% to 6.5%, about 0.20% to about 0.30% phosphorus, about 0.75% to about 2% copper, at least 0.15% nitrogen, from about 20% to about 22% chromium, and the remainder being substantially iron.

5. Austenitic chromium-nickel-phosphorus-copper stainless steel characterized by being both readily machinable and readily age hardenable as hot worked to at least Rockwell C 35 and above by means of an aging or precipitation treatment at a temperature of about 1300° F. in the absence of a previous solution treatment at a substantially higher temperature, containing at least 0.15% to no more than 0.25% carbon, nickel and manganese each in a range from 4.5% to 6.5%, about 0.20% to about 0.30% phosphorus, about 0.75% to about 2% copper, at least 0.15% nitrogen, from about 20% to about 22% chromium, about 0.002% to about 0.010% boron and the remainder being substantially iron.

6. The method of age or precipitation hardening articles of austenitic stainless steel to Rockwell C 30 and above without a high temperature solution treatment, comprising forming the article of austenitic chromium-nickel-phosphorus-copper stainless steel containing about 0.15% to no more than 0.30% carbon, about 0.20% to

about 0.30% phosphorus and about 0.75% to about 2% copper, and then, without solution treating the article, aging the article at a temperature of about 1200° F. to about 1300° F. to a hardness of at least Rockwell C 30.

7. The method of age or precipitation hardening articles of austenitic stainless steel to Rockwell C 30 and above without a high temperature solution treatment, comprising hot working and forming the article of austenitic chromium-nickel-phosphorus-copper stainless steel containing about 0.10% to no more than 0.30% carbon, about 0.15% to about 0.40% phosphorus and about 0.5% to about 3% copper, and then, without solution treating, aging the article at a temperature of about 1200° F. to about 1300° F. to a hardness of at least Rockwell C 30.

8. Austenitic chromium-nickel-phosphorus-copper stainless steel articles age hardened to at least Rockwell C 30 containing approximately 12% to 30% chromium, 3% to 35% nickel and manganese combined but no less than 3% nickel, at least 0.10% to not more than 0.30% carbon, about 0.15% to 0.40% phosphorus, from 0.5% to about 3% copper, and the remainder substantially iron.

9. Austenitic chromium-nickel-phosphorus-copper stainless steel articles age hardened to at least Rockwell C 30 containing approximately 12% to 30% chromium, 3% to 35% nickel and manganese combined but no less than 3% nickel, at least 0.10% to not more than 0.30% carbon, about 0.15% to 0.40% phosphorus, from 0.5% to

about 3% copper, about 0.002% to about 0.010% boron, and the remainder substantially iron.

10. Austenitic chromium - nickel - phosphorus - copper stainless steel articles age hardened to at least Rockwell C 30 containing from about 0.15% to about 0.25% carbon, about 8% to about 22% manganese and nickel combined but no less than about 3% nickel, about 0.20% to about 0.30% phosphorus, about 17% to about 22% chromium, about 0.75% to about 2% copper, at least 0.15% nitrogen, and the remainder substantially iron.

11. Austenitic chromium - nickel - phosphorus - copper stainless steel articles age hardened to at least Rockwell C 35 containing from about 0.15% to about 0.25% carbon, nickel and manganese each in a range from 4.5% to 6.5%, about 0.20% to about 0.30% phosphorus, about 0.75% to about 2% copper, at least 0.15% nitrogen, from about 20% to about 22% chromium, and the remainder being substantially iron.

References Cited in the file of this patent

UNITED STATES PATENTS

1,972,241	Lorig	Sept. 4, 1934
2,528,497	Clarke	Nov. 7, 1950
2,686,116	Schempp et al.	Aug. 10, 1954

FOREIGN PATENTS

375,793	Great Britain	June 20, 1932
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