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SINGLE PHASE AUSTENITIC ALLOY STEEL

Wesley R. Kegerise and Basil T. Lanphier, Reading, Pa., assignors to The Carpenter Steel Company, Reading, Pa., a corporation of New Jersey

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This invention relates to improved austenitic stainless steel alloys characterized by substantially enhanced stress rupture properties at elevated temperatures.

It has long been desired to increase the useful life and improve the performance of parts subjected to stresses and particularly parts subjected to stress at elevated temperatures. Internal combustion engine valves are commonly subjected to stresses in a corrosive atmosphere at elevated temperatures ranging from 1300° to 1500° F. or higher and are illustrative of parts the performance of which has hitherto left much to be desired. Common failings of such parts as valves are the occurrence of ruptures at high temperature and a tendency to neck down evidenced by elongation of the valve stem and narrowing thereof in a region adjoining the valve head. Warping and dishing of the valve head very often shortens the useful life of such parts.

We have found that the stress rupture properties of certain corrosion resistant austenitic steels commonly termed lean alloys, due to the absence of any effective quantity of such metals as cobalt, molybdenum, columbium or tungsten, may be markedly improved by the addition of copper so long as the carbon content is carefully controlled. This improvement is attained without detrimentally affecting other desired and necessary properties of the alloys such as their hot hardnesses and yield strengths, and even with some improvement therein.

It is, therefore, a principal object of this invention to provide austenitic steel alloys having substantially improved stress rupture properties especially well suited for use in making valves for internal combustion engines as well as other parts subjected to stresses under extreme conditions.

Another object is to provide austenitic steel alloys having substantially improved stress rupture properties as well as good yield strengths and hot hardnesses.

The general class of austenitic chromium-steel alloys with which our invention has been found effective consists of those steel alloys characterized by a chromium content of approximately 19.5% to 24% stabilized against transformation by the addition of about 8% to 13% nickel and manganese together. Preferably the content of nickel and manganese each ranges from 4.5% to 6.5%. The carbon content must be carefully controlled and while the copper is effective with carbon ranging from .15% to about .4%, the working conditions such as temperature and load should be considered in determining the optimum composition for a given application. As will be more specifically pointed out hereinafter our improved alloys may include such other constituents as may be desired to provide or enhance various properties such as machinability, greater hot or room temperature hardness or the like.

Further objects as well as advantages of this invention will be apparent from the following description.

The addition of limited amounts of copper to chromium-steel alloys having a limited range of carbon content has unexpectedly provided a substantial improvement in the stress rupture properties of such alloys and

the parts made therefrom. Alloys containing as little as .50% by weight copper are improved while the best results have been attained with a copper content ranging from about 1% to about 2%. As much as 3% copper may provide beneficial results but above that amount the properties are reduced and difficulty in forging may be encountered. The effectiveness of the copper in improving the alloys is restricted to a narrow range of carbon and its effect is most enhanced with a carbon content ranging from about .2% to about .4%. Above .45% carbon, the effect of copper is the reverse of that desired, that is, the alloy is less able to withstand stress and more readily ruptures. Below .15% carbon the copper does not appear to have any appreciable effect. With carbon contents slightly below .45% or of about .4%, the compositions are substantially improved when the maximum temperature to be encountered is about 1200° F., while at about 1350° F. or higher somewhat less carbon is desirable. As will be clearly shown, the copper cannot be replaced by additions of carbon and in the absence of copper, the compositions do not have the desired properties. Thus, our alloys preferably include from about .15% to less than .45% carbon, from about .50% to 3.0% copper, about 19.5% to 24% chromium, nickel and manganese together in amounts ranging from about 8% up to about 13%, a maximum of 1% silicon, usually about .03% phosphorous and sulphur or within normal melting limits, varying amounts of nitrogen but usually ranging from .15% to .35%, only residual amounts of molybdenum, and the balance substantially iron. In order to insure a stable, single phase, austenitic alloy, the nickel content should be a minimum of about 4% and preferably not less than 4.5%. With the minimum of about 4% nickel there is included about 4% manganese in order to provide the minimum combined nickel and manganese content of 8%. The preferred composition includes nickel and manganese each in a range from 4.5% to 6.5%. As will be pointed out, most outstanding results were obtained with a content of approximately 5% each of nickel and manganese.

To show the effect of copper, samples of varying composition and including amounts of copper varying from nil to about 3% were made up and tested as will be described. The composition of the samples is set forth in Table I, the balance thereof being substantially iron in accordance with standard commercial practices.

Table I

	C	Mn	Si	P	S	Cr	Ni	N	Cu
#0	.23	5.48	.44	.021	.016	21.36	4.85	.33	------
#1	.23	5.56	.44	.028	.013	21.18	5.18	.31	1.08
#2	.22	5.48	.44	.028	.013	21.01	5.21	.31	2.06
#3	.22	5.48	.44	.028	.013	20.96	5.27	.31	3.12

It is to be noted that apart from the variations in the copper content, 1, 2 and 3 are similar. For convenience these compositions have been designated 0, 1, 2, and 3 in correspondence with their approximate copper content.

In preparing the samples, 3 inch ingots were forged to bars ¾ inch to 1 inch square. Annealing tests were conducted on samples of each of numbers 0–3 using discs approximately ½ inch thick, specimens being water treated at 1900° F., 2100° F., and 2200° F. Hardnesses were measured both as annealed and as aged 32 hours at 1200° F. and aged 32 hours at 1400° F. The results obtained indicated that when annealed at temperatures of 2100° F. and 2200° F. some samples showed lower hardnesses with increasing copper content, while after aging the higher copper alloys had somewhat higher hardness.

An important characteristic of parts made from the

alloys of the present invention is their ability to withstand rupture under stress particularly at elevated temperatures. Tests were conducted at 1350° F. with loads as indicated in Table II. The specimens used were 4½ inches long with a 1 inch gage length and a gage diameter of .252 inch.

Table II

	30,000 p.s.i.			20,000 p.s.i.		
	Time [1]	Percent Elongation	Percent Reduction of area	Time [1]	Percent Elongation	Percent Reduction of Area
#0	15	44	50	110	38.0	50.0
#1	30	21	23.1	300	23	30.8
#2	52	16	21.2	354	18.8	22.0

[1] Time—Time in hours to rupture.

Referring to Table I, it will be noted that 0 contains nil or an ineffective amount of copper, i.e., less than .1% and serves as a basis of comparison for the remaining samples. From Table II it is apparent that an important and an unexpected improvement in the stress rupture properties at elevated temperatures is obtained with the addition of limited amounts of copper. As previously indicated the carbon content is critical and as will be more fully pointed out hereinafter, the carbon content of .22–.23% provides outstanding results at 1350° F. Specimens of composition #3 were not available at the time the tests for Table II and Table IV (below) were made.

To determine the effect of the addition of copper on the hot hardnesses of the alloys, hot Brinell hardness tests were conducted in an electrical resistance wound furnace in a still atmosphere using a 10 mm. chromium carbide ball under a 2000 kilogram load to make the indentations. All tests were conducted at 1350° F. with the ball also at that temperature. For comparative purposes the results in columns 1 and 2 of Table III were obtained from specimens water treated at 1900° F. to 1950° F. The results shown in columns 3 and 4 of Table III were obtained from specimens water treated at 2100° F. to 2200° F. The aging treatment was 16 hours at 1400° F.

Table III

	W.T. 1,900°/1,950° F.		W.T. 2,100°/2,200° F.	
	1—Annealed	2—Aged	3—Annealed	4—Aged
#0	131	124		
#1	124	124	124	131
#2	131	124	127	127
#3	131	131	124	134

From Table III is it apparent that copper does not adversely affect the hot hardness of the alloys and may be used to some advantage.

The test data included in the following table, Table IV, clearly shows that the yield and tensile strength of the alloys are not detrimentally affected by the addition of copper and, in the case of their yield strength, additions of copper may be used to good advantage. The .2% yield and tensile strength data are set out in Table IV as well as Brinell hardness data, all obtained at room temperature. Tests were conducted on specimens which had been water treated at 1950° F. and aged 16 hours at 1400° F.

Table IV

	.2% Yield Str., p.s.i.	Tensile Str., p.s.i.	Percent Elongation for 2 inches	Percent Reduction of area	Brinell Hardness
#0	77,500	131,200	36.8	43.3	248
#1	82,000	129,500	33.0	43.1	255
#2	81,300	128,800	30.0	41.0	255

The alloys of our present invention exhibit the usual characteristics with increasing carbon content with an important exception. Table V sets forth compositions which were used to determine the effect of variations of carbon, and from the data in Tables VI, VII and VIII it is apparent that while the yield and tensile strengths improve with increasing carbon, in the neighborhood of .4%, the effect of the copper on the stress rupture property diminishes. Furthermore, above .4% carbon and at temperatures as high as 1350° F., the stress rupture properties begin to be adversely affected. However, it will be noted that at 1200° F. the alloys show a pronounced improvement, more than 30%, even with a carbon content of about .4%. Tests which have been conducted on still other compositions indicate that above about .45% carbon the copper does not improve the stress rupture property and at temperatures of about 1350° F. the addition of copper has an adverse effect and such alloys show a reduction of their stress rupture property as compared to similar compositions containing no effective amount of copper.

In the following tables the compositions, for ready reference, are designated by their approximate copper and carbon contents.

Table V

	C	Mn	Si	P	S	Cr	Ni	N	Cu	Mo
#0—.2	.23	5.20	.44	.024	.009	21.35	5.28	.30	.08–.09	.10
#0—.3	.32	5.20	.44	.024	.009	21.35	5.28	.30	.08–.09	.10
#0—.4	.41	5.20	.44	.024	.009	21.35	5.28	.30	.08–.09	.10
#2—.2	.22	4.66	.42	.024	.007	21.28	5.38	.31	2.18	.07
#2—.3	.31	4.66	.42	.024	.007	21.28	5.38	.31	2.18	.07
#2—.4	.42	4.66	.42	.024	.007	21.28	5.38	.31	2.18	.07

Table VI

	.2% Yield Strength, p.s.i.		Tensile Strength, p.s.i.		Percent Elongation for 2 inches		Percent Reduction in Area	
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
#0—.2	73,700	70,000	126,250	124,000	37.5	48.8	45.7	63.0
#0—.3	78,700	77,500	136,500	134,000	34.4	38.9	35.7	53.4
#0—.4	85,600	85,000	145,750	145,000	23.2	33.8	20.6	40.3
#2—.2	72,500	66,200	125,000	120,500	37.5	48.7	44.5	66.4
#2—.3	85,000	87,800	135,250	133,500	24.0	30.6	24.4	41.3
#2—.4	-------	92,500	143,000	143,250	22.5	27.3	27.2	31.5

Table VII

	BHN		Rockwell-C	
	(A)	(B)	(A)	(B)
#0—.2	223	217	23	22
#0—.3	255	255	27	27.5
#0—.4	302	277	34	31
#2—.2	223	207	22	19
#2—.3	277	255	30.5	30
#2—.4	293	277	32	33.5

Table VIII

	Test Temperature, ° F.	Stress, p.s.i.	Percent Elongation in 1 inch	Percent Reduction of Area	Time,[1] Hours
#0—.2	1,200	50,000	10.8	13.8	11
	1,200	40,000	8.8	9.3	99
	1,350	30,000	14.0	16.7	28
	1,350	20,000	19.8	23.8	319
#0—.3	1,200	50,000	12.4	13.8	20
	1,200	40,000	13.4	16.7	184
	1,350	30,000	34.6	42.0	33
	1,350	20,000	36.2	38.3	331
#0—.4	1,200	50,000	26.4	26.8	23
	1,200	40,000	21.2	25.6	172
	1,350	30,000	32	38.3	37
	1,350	20,000	27.4	39.6	282
#2—.2	1,200	50,000	11.0	13.8	60
	1,200	40,000	5.4	6.3	165
	1,350	30,000	19.0	23.8	56
	1,350	20,000	34.8	34.6	469
#2—.3	1,200	50,000	16.8	21.0	55
	1,200	40,000	18.8	22.3	300
	1,350	30,000	24.4	26.8	49
	1,350	20,000	16.2	29.3	564
#2—.4	1,200	50,000	19.8	21.0	64
	1,200	40,000	21.4	21.0	280
	1,350	30,000	16.6	25.2	29
	1,350	20,000	31.8	31.9	280

[1] Time=Time to rupture.

In Tables VI and VII the columns designated (A) contain results from tests conducted on specimens which were water treated at 1950° F. for 1 hour and aged for 16 hours at 1400° F. and then cooled in air. In the columns designated (B) the specimens were water treated at 1950° F. for 1 hour, machined, and then tested. The various tests were carried out as previously described with the Brinell hardness test being made at 1350° F.

It should be noted that the nitrogen content is important affecting as it does the hot hardness of the alloy and its room temperature strength. In order to attain the desired properties the nitrogen content should be at least .15%. In some instances it may be desirable to increase the sulphur content for free machining.

While we have described our invention in connection with the improvement in the properties of engine valves constructed therefrom, it is to be understood that our alloys are also useful in the fabrication of other parts such as turbine blades, which are subjected to stress at elevated temperatures and in a corrosive atmosphere.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we 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.

We claim:

1. A stable, single phase austenitic stainless steel containing between 19.5% and 24% chromium, between 8% and 13% nickel and manganese with the percentage of nickel and manganese each being at least 4%, less than .4% but at least .15% carbon, between .5% and 3% copper, at least 15% nitrogen, the remainder being substantially iron, and characterized by an improvement of more than 30% in resistance to rupture under stress when subjected to a stress of 50,000 p.s.i. at a temperature of 1200° F. as compared to said composition in the absence of copper alloyed in the amount indicated and with more than .4% carbon.

2. A stable, single phase, austenitic stainless steel containing between 19.5% and 24% chromium, between 8% and 13% nickel and manganese with the percentage of nickel and manganese each not less than 4%, less than .4% but at least .15% carbon, between .5% and 3% copper, at least .15% nitrogen, a maximum of 1% silicon, about .03% phosphorous and sulphur, only residual amounts of molybdenum, the remainder substantially iron, and characterized by an improvement of more than 30% in resistance to rupture under stress when subjected to a stress of 50,000 p.s.i. at a temperature of 1200° F. as compared to said composition in the absence of copper alloyed in the amount indicated and with more than .4% carbon.

3. A stable, single phase, austenitic stainless steel containing chromium in a range from 20% to 23%, nickel and manganese each in a range from 4.5% to 6.5%, carbon in a range from .15% to less than .4%, copper in a range from 1% to 2.5%, nitrogen in a range from .15% to .35%, the remainder being substantially iron, and characterized by an improvement of more than 30% in resistance to rupture under stress when subjected to a stress of 50,000 p.s.i. at a temperature of 1200° F. as compared to said composition in the absence of copper alloyed in the amount indicated and with more than .4% carbon.

4. Austenitic chromium-nickel-copper stainless steel articles, the steel of said articles being a stable, single phase, austenite containing about 19.5% to 24% chromium, about 8% to 13% nickel and manganese combined with the percentage of nickel and manganese each being at least 4%, less than .4% but at least .15% carbon, between .5% and 3% copper, at least .15% nitrogen, the remainder being substantially iron, and characterized by an improvement of more than 30% in resistance to rupture under stress when subjected to a stress of 50,000 p.s.i. at a temperature of 1200° F. as compared to said composition in the absence of copper alloyed in the amount indicated and with more than .4% carbon.

5. Stress rupture resistant chromium-nickel-copper stainless steel articles, the steel of said articles being a stable, single phase, austenite comprising approximately 20% to 23% chromium, 4.5% to 6.5% each of nickel and manganese, .15% to less than .4% carbon, 1% to 2.5% copper, .15% to .35% nitrogen, about .03% each of phosphorous and sulphur, the remainder being substantially iron, and characterized by an improvement of more than 30% in resistance to rupture under stress when subjected to a stress of 50,000 p.s.i. at a temperature of 1200° F. as compared to said composition in the absence of copper alloyed in the amount indicated and with more than .4% carbon.

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