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HIGH TEMPERATURE HIGH STRENGTH ALLOYS

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This invention pertains to a forgeable alloy steel having high strength at high temperatures, and more particularly to an alloy steel of this character which is characterized by high resistance to rupture under stress at temperatures up to about 1500° F.

The invention provides a new and improved corrosion- and oxidation-resistant, forgeable alloy steel of this type, having a 100-hour stress-to-rupture value at 1500° F. of at least 15,000 pounds per square inch (p. s. i.), and ranging upward therefrom to about 20,000 p. s. i., and which achieves this result without necessity for cobalt, columbium or titanium additions. In fact, the alloy steel of the present invention contains, in its preferred embodiment, no cobalt, although it optionally may include small amounts of columbium, up to about 1%, or titanium, up to about 2%.

The new forgeable alloy steel of the invention is a precipitation or age-hardening, austenitic alloy steel, containing as essential constituents: about 20 to 30% nickel; about 16 to 22% chromium; about 3 to 15% each of tungsten and molybdenum, the sum of these two elements being, however, held within limits of about 10 to 20%. Within the limits aforesaid, the chromium content in the steel is always less than the nickel content, for maintaining the austenitic structure and for avoiding the formation of delta ferrite. Carbon is present in the steel for purposes of stabilizing the austenitic structure, ranging from effective amounts up to about 0.3%, the upper limit being required for retention of forgeability of the steel. Manganese and silicon are both present in the steel in usual amounts ranging up to about 2% for manganese and up to about 1% for silicon. As above stated, the steel may contain either or both titanium and columbium in small amounts, titanium up to about 2% and columbium up to about 1%, although neither of these elements is required for achievement of the stress-to-rupture values aforesaid. On the same basis, vanadium may be present in the steel up to about 3%. Also, as above stated, cobalt is not an essential constituent of the steel and is ordinarily not present.

A preferred range of analysis of steel in accordance with the present invention is the following: carbon about 0.1 to 0.2%; nickel about 22 to 30%; chromium about 16 to 22%; tungsten and molybdenum, 3 to 8% each, with the sum of the two limited, however, to about 10 to 16%; manganese about 1 to 2%; silicon about 0.2 to 0.5%; and the balance substantially iron, except for optional

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additions of small amounts of any or all of vanadium, titanium and columbium, each within limits as above stated.

The alloy steels of the invention are precipitation hardening and are customarily employed in the precipitation or age-hardened condition. The optimum solution treatment consists in heating to a temperature close to the solidus of the steel, viz., about 2250° F. or higher, and then cooling fairly rapidly. For elevated temperature service it is customary to age the steel at about the temperatures encountered in service.

The alloys available at present for high temperature service are inadequate because those that do not contain appreciable amounts of cobalt and columbium are limited to service at temperatures no higher than about 1300° F.; whereas those that can withstand high stresses at temperatures over 1300° F. contain large amounts of the strategic elements, cobalt and columbium. Since the latter are in short supply and would not be readily available in time of war, it is desirable to have alloys of high strength which are serviceable at temperatures at least up to 1500° F., and which contain little, or none, of these elements.

Of those steels free from appreciable amounts of cobalt and columbium which are in use at present, most have to be given some special forging treatment in order to develop the maximum high temperature strength properties in the steel. This is a hardship in the fabrication of articles made from these steels because of the need of special control of temperature; limitation of size; and unusual risk of damage to forgings, and to forging equipment.

It is the object of this invention to provide forgeable alloy steels containing no cobalt, and only small amounts of columbium, that is, less than about 1%, which have high strength at 1500° F. It is a further object of this invention to provide steels which develop their high temperature strength properties by heat treatment rather than by special forging practice.

The steels of this invention are balanced in composition so that they will be substantially austenitic in structure since it is well known that austenite is much stronger than ferrite at high temperatures. The element most effective in establishing a stable austenitic structure in steel is nickel and therefore the steels of this invention contain upwards of 20% nickel. The upper limit of nickel is set at about 30% because the precipitation hardening reaction in the steels of this invention becomes less effective as the nickel exceeds this amount.

Since the steel to be useful at temperatures as high as 1500° F. must be resistant to oxidation, an addition of upwards of 16% chromium is made for this purpose. Chromium is also effective in improving the high temperature strength of the steel but amounts over about 22% cause the steel of this invention to be very difficult to forge, and therefore the upper limit of chromium is set at about 22%. Furthermore the chromium in the steel is always less than the nickel to maintain the austenitic structure in the steel and avoid the formation of delta ferrite.

Carbon is present in the steel for the purposes of stabilizing the austenitic structure, and contributing to the strength of the steel at high temperatures; but the carbon is limited to about 0.30%, because when the high-temperature, strength-giving elements, tungsten and molybdenum, are present in the steel in proper amounts, the steel becomes very difficult to forge when the carbon is present in amounts over about 0.30%.

Manganese and silicon are both present in the steel in usual amounts for the purposes of deoxidation of the steel and improving the forgeability. Manganese is useful up to about 2.0% and silicon up to about 1.0%.

As is well known, a steel that is merely austenitic in structure is not capable of supporting much stress at temperatures as high as 1500° F. For example Table 1 shows the stress values which cause rupture in 100 hours for three of the well known austenitic steels, Type 302 (18–8); Type 316 (18–13–3); and Type 310 (25–20). Along with these are shown values published by Grant, Frederickson, and Taylor in March 18 and April 8, 1948 issues of Iron Age for some modern high strength alloys.

TABLE I

Stress to cause rupture in 100 hours at 1500° F., for various known alloys

Grade	Analysis per cent										Bal.	Stress to Rupture (p. s. i.)
	C	Cr	Ni	Co	Mo	W	Cb	Ti	Cu	N		
302	0.1	18	8								Fe	6,000
316	0.1 (max.)	18	13		3						Fe	7,500
310	0.25	25	20								Fe	9,000
19-9-DL	0.30	19	9		1.25	1.25	0.40	0.35			Fe	13,000
16-25-6	0.1	16	25		6					0.1	Fe	14,000
GT 45	0.08	17.3	13.8		2.9		0.45	0.30	3.1		Fe	15,000
S 495	0.50	15	20		4.0	4.0	4.0				Fe	18,000
N 155	0.15	20	20	20	3	2.5	1.0			0.12	Fe	20,000
S 590	0.45	20	20	20	4.0	4.0	4.0				Fe	20,000
S 816	0.45	20	20	45	4.0	4.0	4.0				Fe	28,000

NOTE: Manganese 2% max. in all of the above alloys.

It will be noted that of those alloys which have values of stress over 15,000 p. s. i. for a 100 hour rupture time at 1500° F., S 495 contains 4% columbium; N 155 and S 590 contain 20% cobalt plus 1% and 4% columbium, respectively; and S 816 contains 45% cobalt plus 4% columbium. It is evident from these data and others published in the Iron Age article referred to above, that known alloys which will withstand a stress of more than 15,000 p. s. i. at 1500° F. for 100 hours must have appreciable amounts of either cobalt, or columbium (or tantalum) or both, in their composition.

The steels of this invention, on the other hand, have stress values over 15,000 p. s. i., and as high as 20,000 p. s. i. for a rupture time of 100 hours at 1500° F., and these steels contain no cobalt, and although they may contain columbium up to about 1%, their high stress values are not dependent to any large degree on the presence of columbium in the steel. The high strength of these steels is dependent on the presence of sizable amounts of tungsten, or molybdenum, and preferably a mixture of the two.

That the amount of tungsten and molybdenum required is critical is indicated in Table II below, which shows the time-to-rupture for a series of steels at 1500° F. under a stress of 22,000 p. s. i. Since these are precipitation hardening steels, they were solution treated at 2300 to 2350° F., followed by an air cool, and then aged at 1500° F. for about 15 hours prior to being tested.

TABLE II

Time-to-rupture at 1500° F. with stress of 22,000 p. s. i.

All steels contain .10/.20 C; 1.0/2.0 Mn; .10/1.0 Si; 22.0/30.0 Ni; and 17.0/21.0 Cr in addition to W and Mo indicated below.
All steels prior to being tested were solution treated at 2250/2350° F; and aged at 1500° F for about 15 hours.

Steel	W	Mo	W plus Mo	Hours to Rupture
GO 1				0.2
GO 2	2.5		2.5	0.3
GO 3	4.3		4.3	0.2
GO 4	6.2		6.2	1
GO 5	6.2	1.3	7.5	2
GT 1		8.4	8.4	8
GO 6	6.2	3.3	9.5	6
GT 2	3.0	7.1	10.1	11
GT 16	10.2	0.2	10.4	10
GT 4	5.4	5.5	10.9	25
GT 3	6.5	5.8	12.3	31
GT 6	8.5	4.2	12.7	30
GT 17	10.3	2.9	13.2	21
GT 20	13.2	0.3	13.5	19
GT 5	8.7	5.4	14.1	35
GT 24	14.5	0.2	14.7	30
GT 18	10.7	4.8	15.5	39
GT 21	13.2	2.8	16.0	27
GT 19	10.4	6.7	17.1	36
GT 22	13.1	4.9	18.0	39
GT 25	15.5	3.0	18.5	23

The data of Table II indicate that a minimum of about 10% of tungsten plus molybdenum is required for the steel to have any appreciable life under these test conditions. On the other hand, although there is some further increase in life as the sum of tungsten plus molybdenum increases from about 10 to about 20%, the magnitude of change is by no means as great as it is from 0 to about 10% of these two elements. Furthermore, the forgeability of the steel definitely deteriorates as the sum of tungsten and molybdenum approaches 20%. It is desirable therefore that the steel contain from about 10 to 20% of tungsten plus molybdenum with a minimum of about 3% for either element, and a maximum of about 15% of either.

These alloys are precipitation hardening and the optimum solution treatment consists of heating to a temperature close to the solidus of the steel, about 2250° F. or higher, and then cooling fairly rapidly, air cooling being suitable for relatively small sections. The effect of aging at several temperatures on the room temperature hard-

nesses of these steels is shown in Table III. For elevated temperature service it is customary to age the steel at about the temperatures encountered in service.

TABLE III

Effect of aging treatment on room temperature hardness

All steels contain about .10/.20 C; 1.0/2.0 Mn; .10/1.0 Si; 25/30 Ni; 17/21 Cr; besides W and Mo.
All samples solution treated at 2350° F, water quenched then aged at indicated temperatures for times shown.

Steel	W	Mo	S. T.[1]	Rockwell C Hardness								
				[2] 1300° F.			[2] 1400° F.			[2] 1500° F.		
				[3] 4	[3] 16	[3] 64	[3] 4	[3] 16	[3] 64	[3] 4	[3] 16	[3] 64
8705	5.6	5.3	11	23	30	38	28	35	36	28	33	33
8708	5.3	9.9	18	34	44	47	41	44	45	41	41	41
8706	11.2	5.0	17	17	36	44	38	42	43	40	40	41

[1] S. T.—hardness as solution treated.
[2] Aging temperature.
[3] Aging time, hrs.

Some stress rupture values at 1500° F. of steels of this invention are shown in Table IV.

TABLE IV

Stress rupture values of alloys of invention at 1500° F.

All test pieces solution treated at 2,300–2,350° F. and aged for 16 hours at 1,500° F.

Steel	C	Mn	Si	Ni	Cr	W	Mo	V	Cb	Ti	Stress to Rupture (p. s. i.) at 1,500° F.	
											in 100 hrs.	in 1,000 hrs.[1]
GO 6	.09	1.2	.25	26.6	18.8	6.2	3.3	------	------	------	14,000	11,500
GT 2	.11	1.3	.15	27.5	18.8	3.0	7.1	------	------	------	18,000	14,300
GT 4	.12	1.5	.30	27.5	18.1	5.3	5.4	------	------	------	18,000	14,500
GT 3	.11	1.4	.15	27.5	19.1	6.5	5.8	------	------	------	20,000	16,000
GT 6	.09	1.5	.30	27.9	18.0	8.4	4.2	------	------	------	19,000	15,500
GT 5	.11	1.5	.30	27.5	17.8	8.6	5.4	------	------	------	19,000	14,500
GT 12	.12	1.3	.40	22.8	19.5	7.0	5.3	------	------	------	20,500	17,000
GT 13	.13	1.3	.45	25.4	19.3	7.1	5.4	------	------	------	19,500	15,000
GT 10	.29	1.3	.45	27.7	19.3	6.9	5.3	------	------	------	20,000	16,000
GT 7	.16	1.3	.30	27.7	18.4	6.6	5.7	1.0	------	------	19,000	15,500
GT 29	.15	1.3	.35	26.4	19.0	5.9	5.7	------	------	0.24	20,000	17,000
GT 30	.15	1.3	.35	26.2	18.2	5.8	5.8	------	0.74	------	18,500	16,000
GT 31	.14	1.4	.45	26.5	18.9	6.1	5.4	------	------	0.72	19,500	17,000
GT 32	.17	1.5	.35	28.5	19.7	6.3	5.8	------	0.41	0.25	20,000	17,500

[1] Extrapolated from log-log plots of stress vs. time-to-rupture values.

It will be noted that steel GO 6, which contains a sum of tungsten plus molybdenum less than 10%, has a 100-hour stress-rupture value under 15,000 p. s. i., whereas all the other steels with values of the sum of tungsten and molybdenum over 10% have 100-hour values at 1500° F. well over 15,000 p. s. i. It will be noted also that the steels having a sum of tungsten and molybdenum over 10% have 100 hours stress rupture values at 1500° F. equal to, or better than, those of all the alloys listed in Table I, with the exception of S 816, which contains as much as 45% and 4% of cobalt and columbium, respectively. It will also be noted that although additions of V, Cb, and Ti in the steels of this invention in amounts up to about 1% do not much affect the 100-hour rupture value at 1500° F., they generally do improve the 1000-hour value at 1500° F., therefore these additions are useful for improving the long time life of the steel of this invention under stress at 1500° F.

The steels of this invention also have excellent stress-rupture values at temperatures under 1500° F, as shown in Table V.

TABLE V

Stress rupture properties of GT 3 steel at 1200° and 1350° F.

Samples solution treated at 2300° F. and aged at 1400° F. for 15 hours.

Stress p. s. i. to Cause Rupture			
at 1200° F.		at 1350° F.	
100 hr.	1000 hr.	100 hr.	1000 hr.
50,000	40,000	32,000	26,000

What I claim is:

1. A forgeable, austenitic, alloy steel, characterized in having a 100-hour stress-to-rupture value at 1500° F. of at least 15,000 pounds per square inch (p. s. i.), said steel containing: about 20 to 30% nickel and about 16 to 22% chromium, the chromium content being less than the nickel content; about 3 to 15% each of tungsten and molybdenum, the combined content of these two elements being about 10 to 20%; carbon from an effective amount up to about 0.3%; manganese up to about 2%; silicon up to about 1%; vanadium up to about 3% titanium up to about 2%; columbium up to about 1%; and the balance iron.

2. An age-hardened alloy steel, characterized in having a 100-hour stress-to-rupture value at 1500° F. of at least 15,000 p. s. i., said steel containing: about 20 to 30% nickel and about 16 to 22% chromium, the chromium content being less than the nickel content; about 3 to 15% each of tungsten and molybdenum, the combined content of these two elements being about 10 to 20%; carbon from an effective amount up to about 0.3%; manganese up to about 2%; silicon up to about 1%; titanium up to about 2%; columbium up to about 1%; vanadium up to about 3% and the balance iron.

3. A substantially cobalt free, austenitic and forgeable alloy steel, characterized in having a 100-hour stress-to-rupture at 1500° F. of at least 15,000 p. s. i., said steel containing: about 20 to 30% nickel and about 16 to 22% chromium, the chromium content being less than the nickel content; about 3 to 15% each of tungsten and

molybdenum, the combined content of these two elements being about 10 to 20%; carbon from an effective amount up to about 0.3%; up to about 1% columbium; up to about 10% in aggregate of other elements which do not impair the high strength, high temperature characteristics of the steel, and the balance iron.

4. A substantially cobalt free, age-hardened alloy steel, characterized in having a 100-hour stress-to-rupture value at 1500° F. of at least 15,000 p. s. i., said steel containing: about 20 to 30% nickel and about 16 to 22% chromium, the chromium content being less than the nickel content; about 3 to 15% each of tungsten and molybdenum, the combined content of these two elements being about 10 to 20%; carbon from an effective amount up to about 0.3%; up to about 1% columbium, up to about 10% in aggregate of other elements which do not impair the high strength, high temperature characteristics of the steel, and the balance iron.

5. A forgeable alloy steel, characterized in having a 100-hour stress-to-rupture at 1500° F. of at least 15,000 p. s. i., said steel containing: about 22 to 30% nickel; about 16 to 22% chromium; about 3 to 8% each of tungsten and molybdenum, the combined content of these two elements being about 10 to 16%; about 1 to 2% manganese; about 0.2 to 0.5% silicon; about 0.1 to 0.2% carbon; and the balance substantially all iron.

6. An age-hardened alloy steel, characterized in having a 100-hour stress-to-rupture value at 1500° F. of at least 15,000 p. s. i., said steel containing: about 22 to 30% nickel; about 16 to 22% chromium; about 3 to 8% each of tungsten and molybdenum, the combined content of these two elements being about 10 to 16%; about 1 to 2% manganese; about 0.2 to 0.5% silicon; about 0.1 to 0.2% carbon; and the balance substantially all iron.

PETER PAYSON.

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