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ALLOY STEEL HAVING HIGH STRENGTH
AT ELEVATED TEMPERATURE

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cible Steel Company of America, New York,
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This invention pertains to improvements in alloy steels possessing high strength at elevated temperatures, and provides a forgeable, ferritic and precipitation hardening steel of this type, of relatively low cost by reason of its low total alloy content, and which is characterized in possessing in the precipitation hardened condition, high strength and good mechanical properties at both room and elevated temperatures ranging up to about 1200° F.

The steel of the invention contains as essential constituents, small amounts of vanadium, boron, chromium and metal of the group molybdenum and tungsten, with molybdenum preferred. Man- ganese and silicon are also ordinarily present in small amounts.

There has long been a need for a relatively low cost, low alloy steel which has high strength at temperatures up to about 1100° F. for use in the steam power industry for tubes, flanges, bolts, studs, etc., and more recently for gas turbine parts such as wheels and buckets. The available ferritic steels of relatively low cost are limited for high temperature service to temperatures about 950° to 1000° F., since at higher temperatures they become quite weak. For parts subjected to ap- preciable stress at temperatures above about 1000° F. it is necessary therefore to use the more expensive, relatively high alloy, austenitic steels such as Types 302 and 316, or even more expen- sive "superalloys" 16-25-6 or 19-9DL, the general compositions of which are:

Type	Analysis %										
	C	Mn	Si	Ni	Cr	W	Mo	Cb	Ti	N	Bal
302.....	.10	1.5	.60	9.0	18.0	---	---	---	---	---	Fe
316.....	.10	1.5	.60	13.0	17.0	---	2.5	---	---	---	Fe
16-25-6.....	.10	1.5	.90	25.0	16.0	---	6.0	---	---	.15	Fe
19-9DL.....	.30	1.0	.70	9.0	19.0	1.3	1.3	0.4	0.3	---	Fe

Recently it has been reported by G. F. Com- stock (The Iron Age June 16, 1949, pages 90 and 91) that low carbon ferritic steels containing titanium (or columbium) and boron have very high strength at 1000 and 1100° F. For example, a steel containing:

Analysis, Per Cent						
C	Mn	Si	Cr	Ti	B	Bal
.06	.41	.29	2.82	.30	.025	Fe

after being treated by an air cool from 2100° F.

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and a temper at 1100° F., had a 1000 hour, stress-rupture strength at 1100° F. of 30,000 pounds per square inch (p. s. i.).

Another steel suggested by Comstock which analysed

Bar	C	Mn	Si	Cr	Mo	Ti	B
2144	.08	.64	.53	2.47	.83	.82	.029

was found on test to have the stress-rupture prop- erties shown in Table I below.

Now I have discovered that a steel of the fol- lowing composition has an extraordinary strength at 1100° F.

Carbon	.03 to .30%
Manganese	.20 to 2.00%
Silicon	.10 to 2.00%
Chromium	1.00 to 6.00%
Vanadium	0.15 to 2.00%
Tungsten and Molybdenum	0.30 to 3.00%
Boron	.005 to 0.10%
Balance	Iron

This steel after being air cooled from 2100° F. and tempered at about 1100° to 1200° F. has a 1000 hour, stress-rupture strength at 1100° F. of over 50,000 p. s. i., as shown by the test results set forth below in Table I comparing the above Com- stock analysis of Bar 2144 with a steel of the fol- lowing analysis in accordance with the present invention, viz.:

Bar	Analysis %							
	C	Mn	Si	Cr	V	Mo	B	Bal
2146.....	.08	.45	.32	2.35	.28	.90	.019	Fe

TABLE I—TIME TO RUPTURE AT 1100° F. OF COMSTOCK STEEL AND STEEL OF THIS INVENTION

All samples air cooled from 2100° F. and tem- pered at 1100 to 1200° F.

Bar	Type	Time to Rupture with Stress of—	
		50,000 p. s. i.	40,000 p. s. i.
2144	Comstock Steel.....	Hours 281	Hours 704
2146	This Invention.....	Hours 1225	over 2,750

Thus it is clear that the steel of this invention is far superior to the Comstock steel in strength at 1100° F. Indeed the strength of the steel of this invention is even better than that of the superalloy 19-9DL at 1100° F. as reported by Robinson in "High Temperature Bolting Materials (Project No. 16)" ASTM, 1948. Furthermore when the steel of this invention was tested at 1100° F. by the relaxation procedure described by E. L. Robinson in "The Resistance to Relaxation of Materials at High Temperature," Trans. ASME, August 1939, it was found that after an initial stress of 30,000 p. s. i., the residual stress calculated by the Robinson formula was 25,300 p. s. i. after 100 hours; 21,100 p. s. i. after 1000 hours; and 17,600 p. s. i. after 10,000 hours. Finally, this steel not only has outstanding strength at 1100° F., but as heat treated by the method mentioned above, has excellent room temperature mechanical properties as shown in Table II below.

TABLE II—ROOM TEMPERATURE TENSILE PROPERTIES OF STEEL OF THIS INVENTION

[Test pieces austenitized at 2100° F., air cooled and tempered as indicated.]

Bar	Tempered	Tensile, p. s. i.	0.2% Yield, p. s. i.	El. in 2 in., Per Cent	Red. Area, Per Cent
2146---	1100° F.—2 hr.-----	160,000	130,000	13.7	42.4
2146---	1200° F.—2 hr.-----	157,000	126,000	14.6	45.6

The Comstock steel referred to above has relatively poor room temperature properties because it does not harden appreciably. The austenitic steels, such as those given above, also have relatively low yield strengths at room temperature as is well known because of the non-hardening character of these steels. The steel of this invention is therefore superior to known steels because of the combination of both good room temperature strength and excellent elevated temperature strength at least up to about 1100° F.

Without being bound to any particular theory as to specific alloy additions and effects thereof in producing the highly desirable properties in this steel, it is my opinion that the high hardenability of the steel is dependent on the combination of vanadium, boron, chromium, and molybdenum and/or tungsten, especially molybdenum, in the analysis. It is because of the presence in the steel of the combination of boron, chromium and molybdenum and/or tungsten, that the steel has sufficient hardenability so that it develops practically a martensitic structure when air cooled from 2100° F. in at least a ½ in. section. As to the vanadium addition, the precipitation of vanadium-molybdenum-chromium and/or vanadium-tungsten-chromium carbides, and also of a boron compound during subsequent tempering at temperatures up to about 1100° F., gives the steel its resistance to softening at room temperature and its extra-ordinary high temperature strength. The effect of the vanadium is well illustrated in Table III below.

TABLE III—COMPARISON OF ROOM TEMPERATURE HARDNESS OF STEELS WITH-OUT AND WITH VANADIUM

Bar	C	Mn	Si	Cr	V	Mo	B
2143-----	.08	.40	.29	2.21	-----	.93	.011
2146-----	.08	.45	.32	2.35	.28	.90	.019

Test pieces air cooled to room temperature from 2100° F. then tempered as indicated.

Rockwell "C" Hardness

Bar	As Air Hardened	Tempered At			
		1100° F.	1200° F.	1250° F.	1300° F.
2143-----	31	30	25.5	9.5	7
2146-----	33	35.5	34.5	31	24.5

Obviously there is precipitation hardening at 1100° and 1200° F. in the steel containing vanadium, whereas the steel having no vanadium begins to soften at the 1100° F. temper and softens quite rapidly at the higher temperatures. The tremendous effect of the precipitation at 1100° F. in the vanadium steel is evidenced by the fact that when the steels were treated by an air cool from 2100° F. and a temper at 1100° F., and

each was then subjected to a stress of 40,000 p. s. i. at 1100° F., the steel without vanadium (Bar 2143) ruptured in 125 hours whereas the steel with vanadium (Bar 2146) did not rupture even after 2700 hours under the same test conditions.

Vanadium has a very strong tendency to form carbide in steel. In the annealed condition, and generally in the as rolled condition also, the vanadium is present in the steel as sizeable particles of carbide. In order for the vanadium to be effective in developing high temperature strength, it is necessary for it to be dissolved in the austenite of the steel, retained in solution by the fairly rapid cooling from the austenitizing temperature, and then precipitated as very fine particles of carbide during the subsequent tempering at about 1100° F. If the carbon content of the steel is high and if the vanadium content is less than about 3 to 5 times the carbon content, it is difficult to get the vanadium to dissolve in the austenite even at temperatures as high as 2100° F., and higher. Therefore, the carbon in the steel of the invention should not exceed about 0.3%, and is preferably held well below this figure as evidenced by the preferred range of analysis given above. The vanadium should be maintained at a level at least about 3 to 5 times the carbon content. The broad range for the carbon content in the steel of this invention is about 0.03 to 0.30%, while the corresponding range of vanadium is from about 0.15 to 2.00%. The higher the carbon content in the steel, the greater should be the ratio of V to C. Vanadium is limited on the high side to about 2% for purposes of economy.

Since the steel of this invention is designed for elevated temperature service, chromium is included in the composition to provide, in addition to the effects above noted, resistance to scaling. About 1% of chromium is adequate for scaling resistance up to about 1000° F. For service above

that temperature, the steel should contain more chromium. However, since the creep resistance of steel decreases with increasing chromium content, as is well known, the chromium in this steel is limited on the high side to about 6%.

Metal of the group tungsten and molybdenum, particularly the latter, is required in the steel for its strengthening effect at elevated temperatures, and for the beneficial effect such additions have in counteracting temper brittleness. In order to minimize the expense of manufacturing, the metal of this group is limited to about 3.0%. While molybdenum is the preferred addition, tungsten may be substituted for part or all of the molybdenum in steel of this type, but generally tungsten is not employed, because it is less effective in developing high temperature strength of the steel, and it is more expensive.

The effect of boron in strengthening the steel at elevated temperatures particularly around 1100° F. is very great, and only a small quantity, that is, about .01 to .03% is ordinarily required, although as little as .005% or as much as 0.10% may effectively be employed. Although it is possible to forge steels containing larger amounts of boron than 0.10%, particularly if the carbon in the steel is below about 0.10%, it is generally necessary to control the hot working temperatures quite carefully for the satisfactory forging of steels containing boron over about 0.10%, and this type of control limits the production rate and hence increases the cost of the steel. For this reason I limit the boron on the high side, in the steel of this invention to 0.10%.

Manganese is desired in the steel for its deoxidizing and desulfurizing effects and also for its beneficial effect on the hardenability of the steel. For these purposes additions of about 0.20 to 2.00% manganese are employed in the steel of this invention.

Silicon is required in the steel for thorough deoxidation and in addition when present in larger amounts this element provides improved oxidation resistance of the steel. For these purposes additions of about 0.10 to 2.00% are employed in the steel of this invention.

Aluminum, titanium, and zirconium may also be used in aggregate amount up to about 0.5% for the purpose of thoroughly deoxidizing the steel.

A preferred range of analysis for the steel of the present invention is as follows:

Carbon	0.05 to 0.15%
Manganese	0.30 to 1.00%
Silicon	0.15 to 0.80%
Chromium	2.00 to 3.00%
Vanadium	0.20 to 0.50%
Molybdenum	0.50 to 1.00%
Boron	0.01 to 0.03%
Balance	Iron

What is claimed is:

1. A forgeable, ferritic, alloy steel of high hardenability, and which as air cooled from about 2100° F. in sections up to about 1 inch in diameter, attains a hardness of at least Rockwell "C" 25, and which on being so hardened and thereafter tempered at about 1100 to 1200° F., is characterized in possessing high strength at both room and elevated temperatures, and in having a 1000 hour, stress-rupture value at 1100° F. of at least 40,000 pounds per square inch, said steel having substantially the following composition: 0.03 to 0.3% carbon; 0.15 to 2% vanadium, the minimum vanadium content being from about 3 to 5 times the carbon content; 1 to 6% chromium;

0.3 to 3% of metal of the group molybdenum and tungsten; 0.005 to 0.1% boron; 0.2 to 2% manganese; 0.1 to 2% silicon; up to about 5% in aggregate of other elements which do not impair the aforesaid properties of the steel; and the balance iron.

2. A forgeable, ferritic, alloy steel of high hardenability, and which as air cooled from about 2100° F. in sections up to about 1 inch in diameter, attains a hardness of at least Rockwell "C" 25, and which on being so hardened and thereafter tempered at about 1100 to 1200° F., is characterized in possessing high strength at both room and elevated temperatures and in having a 1000 hour, stress-rupture value at 1100° F. of at least 40,000 pounds per square inch, said steel having substantially the following composition: 0.03 to 0.3% carbon; 0.15 to 2% vanadium, the minimum vanadium content being from about 3 to 5 times the carbon content; 1 to 6% chromium; 0.3 to 3% of metal of the group molybdenum and tungsten, molybdenum being present as an essential constituent and in an amount exceeding the tungsten; 0.005 to 0.1% boron; 0.2 to 2% manganese; 0.1 to 2% silicon; up to about 5% in aggregate of other elements which do not impair the aforesaid properties of the steel; and the balance iron.

3. A forgeable, ferritic, alloy steel of high hardenability, and which as air cooled from about 2100° F. in sections up to about 1 inch in diameter, attains a hardness of at least Rockwell "C" 25, and which on being so hardened and thereafter tempered at about 1100 to 1200° F., is characterized in possessing high strength at both room and elevated temperatures and in having a 1000 hour, stress-rupture value at 1100° F. of at least 40,000 pounds per square inch, said steel having substantially the following composition: 0.05 to 0.15% carbon; 0.2 to 0.5% vanadium, the minimum vanadium content being from about 3 to 5 times the carbon content; 2 to 3% chromium; 0.5 to 1% molybdenum; 0.01 to 0.03% boron; 0.3 to 1% manganese; 0.15 to 0.8% silicon; and the balance iron.

4. A hardened and tempered alloy steel characterized in having a hardness of at least Rockwell "C" 25 and a 1000 hour, stress-rupture value at 1100° F. of at least 40,000 pounds per square inch, said steel having substantially the following composition: 0.03 to 0.3% carbon; 0.15 to 2% vanadium, the minimum vanadium content being from about 3 to 5 times the carbon content; 1 to 6% chromium; 0.3 to 3% of metal of the group molybdenum and tungsten; 0.005 to 0.1% boron; 0.2 to 2% manganese; 0.1 to 2% silicon; up to about 5% in aggregate of other elements which do not impair the aforesaid properties of the steel; and the balance iron.

5. A hardened and tempered alloy steel characterized in having a hardness of at least Rockwell "C" 25 and a 1000 hour, stress-rupture value at 1100° F. of at least 40,000 pounds per square inch, said steel having substantially the following composition: 0.03 to 0.3% carbon; 0.15 to 2% vanadium, the minimum vanadium content being from about 3 to 5 times the carbon content; 1 to 6% chromium; 0.3 to 3% of metal of the group molybdenum and tungsten, molybdenum being present as essential constituent and in an amount exceeding tungsten; 0.005 to 0.1% boron; 0.2 to 2% manganese; 0.1 to 2% silicon; and the balance iron.

6. A hardened and tempered alloy steel characterized in having a hardness of at least Rock-

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well "C" 25 and a 1000 hour, stress-rupture value at 1100° F. of at least 40,000 pounds per square inch, said steel having substantially the following composition: 0.05 to 0.15% carbon; 0.2 to 0.5% vanadium, the minimum vanadium content being from about 3 to 5 times the carbon content; 2 to 3% chromium; 0.5 to 1% molybdenum; 0.01 to 0.03% boron; 0.3 to 1% manganese; 0.15 to 0.8% silicon; and the balance iron.

7. A forgeable, ferritic, precipitation hardenable alloy steel of high hardenability, and which as air cooled from about 2100° F. in sections up to about 1 inch in diameter, attains a hardness of at least Rockwell "C" 25, and which on being so hardened and thereafter tempered at about 1100 to 1200° F., is characterized in possessing high strength at both room and elevated temperatures, and in having a 1000 hour, stress-rupture

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value at 1100° F. of at least 40,000 pounds per square inch, said steel having substantially the following composition: 0.03 to 0.3% carbon; 0.15 to 2% vanadium, the minimum vanadium content being from about 3 to 5 times the carbon content; 1 to 6% chromium; 0.3 to 3% of metal of the group molybdenum and tungsten; 0.005 to 0.1% boron; 0.2 to 2% manganese; 0.1 to 2% silicon; and the balance iron.

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REFERENCES CITED

The following references are of record in the file of this patent:

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