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METHOD OF IMPROVING THE HIGH-TEMPERATURE STRENGTH OF AUSTENITIC STEELS

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7 Claims. (Cl. 148—12)

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This invention relates to iron base alloys for use at elevated temperatures and refers more particularly to methods for rendering iron base alloys of relatively low total alloy content suitable for use at high temperatures.

Austenitic-chromium-nickel steels for instance of the 18% chromium, 8% nickel type and the 25% chromium, 20% nickel type have been used in the past for the fabrication of articles to be exposed to elevated temperatures. Sometimes these steels have been modified by the addition to them of "hardeners" such as molybdenum or tungsten or both, with or without such carbide-forming elements as columbium or titanium or both, and the steels containing such additional elements have improved properties, making them more suitable for use at high temperatures than the unmodified steels.

However, for certain applications where considerable mechanical stress is applied at high temperatures, a typical example being a disc to which impeller blades of a gas turbine are attached, the conventional chromium-nickel steels whether or not modified by the presence of additional elements have not proved entirely satisfactory. Moreover, although the beneficial effect on strength of cold working such steels is well recognized, this effect is lost when the cold-worked articles are exposed to elevated temperatures.

In contrast to the conventional austenitic steels, the so-called "super alloys" which contain relatively large quantities of cobalt in addition to chromium and nickel and one or more of the elements molybdenum, tungsten, columbium, tantalum and titanium, and which have the required strength to recommend them for use in the fabrication of blades and other parts of gas turbines which are subjected to most severe conditions of stress and temperature, are fully capable of withstanding the less rigorous conditions in which the austenitic steels have been used, their use for such purposes is uneconomical and wasteful of strategic materials. There is accordingly a need for alloys combining good workability with greater strength at high temperatures than conventional austenitic steels and containing less strategic materials than the super alloys.

It is the principal object of this invention to fulfill this need. More specifically it is an object of the invention to provide a method for improving the high temperature strength of austenitic steels containing at least 50% iron.

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The invention by means of which this object is achieved is based on the discovery that chromium steels containing in addition to 10% to 30% chromium, sufficient nickel or manganese or mixtures thereof to render them substantially fully austenitic and containing at least 50% iron, retain at elevated temperatures the improved strength gained by cold working within certain temperature ranges of a small proportion of boron is added to the steels. The critical working step in the method of the invention is conducted at a temperature below the recrystallization temperature of the steel and is consequently cold working, but since it is conducted at an elevated temperature it will be referred to herein as "hot cold-working" to differentiate from conventional cold working methods conducted at ordinary room temperatures. In the method of the invention it is applied to steels which have initially been hot worked in conventional manner. The invention includes a method of raising the temperature to which austenitic chromium steels containing at least 50% iron may be heated without destroying the beneficial effects attained by hot cold-working such steels, which method comprises the steps of incorporating in the steels 0.005% to less than 0.1% boron and working the boron-containing steels at an elevated temperature above 1000° F. but below their recrystallization temperature.

In general the method of the invention is applicable to steels containing 10% to 30% chromium, at least 50% iron and sufficient nickel or manganese or both to render the steels substantially completely austenitic at room temperatures. Steels containing for example 4% to 40% nickel and 0.25% to 20% manganese in addition to the chromium and iron contents already specified are amenable to treatment by the method of the invention. Such steels preferably also contain one or more of the elements molybdenum, tungsten, columbium, tantalum, vanadium and titanium. Suitable proportions for those elements are 0.1% to 7.5% molybdenum, 0.1% to 15% tungsten and an aggregate of 0.1% to 5% of columbium, tantalum, vanadium or titanium, the content of any single one of columbium, tantalum, vanadium or titanium not exceeding 2%. Such steels conventionally contain up to 1% silicon and up to 0.5% carbon but preferably the carbon content should not exceed 0.25%. Nitrogen may be present up to 0.2% and copper up to 5%. The aggregate of elements other than chromium, nickel, manganese and iron should not exceed 15% of the alloy.

Considerable experimental work has demonstrated conclusively that although steels within the composition ranges just disclosed are considerably strengthened by hot cold-working, the improvement in strength gained by hot cold-working is not retained if the steels are later exposed to elevated temperatures of the order of 1300° F. to 1400° F. nor does the addition of 0.005% to less than 0.1% boron to such steels of itself give the desired improvement in strength at these temperatures. Surprisingly, however, steels within these ranges of composition but also containing 0.005% to less than 0.1% boron not only benefit by hot cold-working, but the added strength gained by the hot cold-working operation is retained at elevated temperatures as high as 1400° F.

The hot cold-working step of the method of the invention is of extreme importance and must be conducted with care, otherwise poor results will be obtained. Apparently, steels within the composition ranges above discussed depend on some form of precipitation hardening induced to a certain extent by cold working to gain high temperature strength. Accordingly the condition of the metal prior to the hot cold-working step is a matter of importance and the amount of hot cold-working applied is also very important. If the working operation is too drastic there is a tendency for the precipitate to coagulate rapidly during service and such coagulation of the precipitate lessens the strength of the steel. Further, severe cold-working lowers the temperature to which the steel can be later exposed without loss of strength.

The optimum treatment for a given steel varies somewhat with composition and must be determined empirically. In general, however, the most satisfactory results are obtainable if the steel is hot worked in a normal manner (that is, worked at a temperature above the recrystallization temperature) and is then subjected to a solution heat treatment, for example being heated one hour at 2000° F. to 2100° F. and then cooled in still air. The solution heat treatment renders the grain size uniform and dissolves the precipitated phases, thus homogenizing the structure. The steel is then reduced about 10% to 40% in section at a temperature of about 1500° F. for example by rolling, drop forging or hot pressing. Such a treatment effectively strengthens all alloys within the composition ranges above discussed at temperatures up to about 1350° F. to 1400° F.

Another procedure which produces good results if carefully controlled, omits the solution heat treatment. In this procedure the steel is hot worked in the normal manner and is then reduced in section about 10% to 40% by working in the falling temperature range of 1900° F. to 1200° F. Although as indicated good results can be obtained by this procedure the problem of control is quite difficult, and it is ordinarily safer to follow the preferred procedure including a solution heat treatment between the hot working operation and the hot cold-working operation.

In the following tables specific test data for steels of several different compositions are illustrated. The various samples were treated in the different ways indicated in the tables.

TABLE I

Tests of 18% chromium–13% nickel steels containing molybdenum and columbium

Alloy No.	Composition—Remainder Iron							
	Per Cent Cr	Per Cent Ni	Per Cent Mn	Per Cent Si	Per Cent Mo	Per Cent Cb	Per Cent C	Per Cent B
1	18.5	13	1.5	0.4	2.3	0.75	0.07	Nil
2	18.5	13	1.5	0.3	2.4	1	0.085	0.0054
3	18.5	13	1.5	0.3	2.4	1	0.075	0.009

Tests at 1350° F.

Alloy No.	Condition	Stress, p. s. i.	Time to Fracture, Hrs.	Per Cent Elong.	Per Cent R. A.	Stress to Produce Failure in 1000 hrs.[1]
1	1	25,000	65.5	8	5	12,000
1	1	20,000	140.5	6	3	----------
1	1	15,000	441.5	6	4	----------
2	1	40,000	9.3	24	32	22,000
2	1	35,000	100	14	32	----------
2	1	30,000	337	10	16	----------
2	1	20,000	1,445	14	12	----------
3	1	40,000	51.5	18	42	29,000
3	1	35,000	217	17	37	----------
3	1	30,000	593	12	26	----------
3	1	20,000	[2] 2,232	----------	----------	----------

[1] Calculated from results of tests at given stresses.
[2] Test discontinued before failure of specimen.

Tests at room temperature

Alloy No.	Condition	Yield Strength 0.2% offset, p. s. i.	Tensile Strength, p. s. i.	Per Cent Elong.	Per Cent R. A.
1	1	69,300	94,800	40	64
2	1	74,600	99,000	35	56
3	1	75,000	101,900	35	62

Condition 1.—Forged at initial temperature of 2050° F., reheated to 2050° F., reduced about 28% in cross-sectional area by forging, finishing at 1475° to 1550° F. Heated 1 hour at 1650° F. and cooled in air.

It will be seen from the data given in Table I that the strength of the boron-containing steels tested was materially greater at 1350° F. than that of the steel containing no boron although both types of steel had been hot cold-worked and the principal difference in composition was in the presence or absence of boron. Further, it is evident from the room temperature tests that the ductility of the steels, as measured by the percentage elongation ("per cent elong.") and percentage reduction of area ("per cent R. A.") at the point of failure, was not materially decreased by the presence of the small quantities of boron used.

Other tests on steels similar to those listed in Table I were made and showed that in steels containing tungsten as a replacement for molybdenum and columbium or either of them the presence of boron produced an effect of the same order of magnitude as in the steels of Table I.

In Table II below similar test results obtained on steels containing 12% chromium and 15% nickel as well as the other elements there listed are set forth. For conciseness, room temperature data are omitted, but again it was evident from such data that the small quantities of boron used did not materially lessen the ductility of the steels. Also in Table II results of tests made at 1350° F. are limited, for conciseness only, to tests conducted only at one selected stress for each of the alloys tested after different working and heat treatments.

TABLE II

Tests of 12% chromium–15% nickel steel

Alloy No.	Composition—Remainder Iron								
	Per Cent Cr	Per Cent Ni	Per Cent Mn	Per Cent Si	Per Cent Mo	Per Cent W	Per Cent Ti	Per Cent C	Per Cent B
4	12.5	15	1.5	0.4	2.4	Nil	0.7	0.07	0.01
5	12	15	1.5	0.4	2.4	Nil	0.7	0.07	0.01
6	12	15	1.5	0.4	2.4	Nil	0.7	0.06	0.01
7	12	15	1	0.4	2.4	0.5	0.7	0.1	0.01
8	12	15	1	0.4	1.2	1	0.7	0.06	0.01
9	12	15	1.5	0.4	2	Nil	0.5	0.07	0.01

Tests at 1350° F.

Alloy No.	Condition	Stress, p. s. i.	Hrs. to Failure	Per Cent Elong.	Per Cent R. A.	Calculated[1] Stress to cause Failure in 1000 hrs.
4	1	35,000	373	21	68	33,000
5	2	35,000	66	23	70	26,500
5	3	25,000	218.4	30	72	22,000
6	4	27,000	171.3	40	70	23,000
6	5	30,000	106.5	30	68	20,000
7	6	25,000	66.3	28	60	19,000
7	7	25,000	109.6	46	48	21,000
8	6	35,000	209	19	55	31,000
8	7	35,000	278.6	33	51	32,500
9	7	40,000	195	22	50	34,500
9	6	30,000	463.3	34	63	29,500

[1] Calculated from results obtained at selected stresses applied at 1350° F.

The specimens listed in Table II were tested after seven different combinations of working and heat treatment had been applied to the different specimens. These "conditions" of the specimen referred to in the table are as follows:

Condition 1.—Forged at 2050° F., reheated to 2050° F.; reduced about 28% by forging, finishing at 1475° to 1550° F., heated 1 hour at 1650° F. and cooled in air.

Condition 2.—Hot-worked at initial temperature of 2050° F.; reheated to 1450° F. to 1650° F.; reduced about 12% by rolling in 5 passes, finishing at 1200° to 1300° F.; heated 1 hour at 1650° F. and cooled in air.

Condition 3.—Hot-worked at initial temperature of 2050° F.; reheated to 1450° F.; reduced about 15% by rolling; reheated to 1450° F.; reduced about 21% by rolling; heated 2 hours at 1500° F. and cooled in air.

Condition 4.—Hot-worked at initial temperature of 2050° F.; reheated to 1650° F. and reduced about 12% by rolling in 5 passes, finishing at about 1380° F.; heated 1 hour at 1650° F. and cooled in air.

Condition 5.—Hot-worked at initial temperature of 2050° F.; reheated to 1650° F. and reduced about 11% by rolling; reheated to 1650° F. and reduced about 21% by rolling, finishing at about 1380° F.; heated 2 hours at 1500° F. and cooled in air.

Condition 6.—Hot-worked at initial temperature of 2050° F.; reduced about 20% by rolling at 1500° F.; heated 2 hours at 1500° F. and cooled in air.

Condition 7.—Hot-worked at initial temperature of 2050° F.; reheated 1 hour at 2100° F. and air-cooled, reduced about 20% by rolling at 1500° F.; heated 2 hours at 1500° F. and cooled in air.

As will be seen from consideration of the data of Table III below, the invention is applicable to steels containing up to 20% manganese in addition to chromium, nickel and the other elements listed in the table. As in Table II, room temperature data are omitted for conciseness in Table III, but room temperature tests showed an improvement in strength in the boron-containing, hot cold-worked steels over boron-free steels without sacrifice of ductility.

TABLE III

Tests of steels containing 12% to 19.7% chromium and varying proportions of nickel and manganese

Alloy No.	Composition—Remainder Iron									
	Per Cent Cr	Per Cent Ni	Per Cent Mn	Per Cent Si	Per Cent Mo	Per Cent W	Per Cent Cb	Per Cent Ti	Per Cent C	Per Cent B
10	18.5	8	13	0.4	2.3	Nil	Nil	0.6	0.12	0.1
11	12.5	4.25	20	0.4	2.4	Nil	Nil	0.7	0.1	0.01
12	12.5	8	13	0.35	2.25	Nil	Nil	0.6	0.11	0.1
13	12	8	12	0.4	2.4	Nil	Nil	0.7	0.15	0.0018
14	12.5	11.5	6.5	0.4	2.4	Nil	Nil	0.7	0.1	0.01
15	12	12	6	0.4	2.3	Nil	Nil	0.6	0.1	0.015

TABLE III—Continued

Tests at 1350° F.

Alloy No.	Condition	Stress, p. s. i.	Hrs. to failure	Per Cent Elong.	Per Cent R. A.	Calculated [1] Stress to cause Failure in 1000 hrs.
10	1	25,000	95	35	35	21,000
11	1	25,000	117	17	25	20,000
12	1	35,000	174	25	58	30,000
13	1	25,000	205	17	36	21,000
14	1	35,000	292	20	56	32,000
15	1	25,000	91	34	55	22,000
15	2	30,000	332	31	66	27,000

[1] Calculated from results obtained at selected stresses applied at 1350° F.

The specimens listed in Table III had been subjected to two different treatments, these conditions being as follows:

Condition 1.—Forged at an initial temperature of 2050° F.; reheated to 2050° F. and reduced about 28% by forging, finishing at about 1475° F. to 1550° F.; heated 1 hour at 1650° F. and cooled in air.

Condition 2.—Hot-rolled at an initial temperature of 2050° F.; reheated to 1500° F. and reduced about 35% by rolling; reheated 1 hour at 1500° F. and cooled in air.

The data reported in Tables I, II, and III as well as many other tests show that the invention significantly improves the high-temperature strength of austenitic steels of lower alloy content than the super alloys making such steels suitable for use in the fabrication of parts for gas turbines and other devices where resistance to mechanical stress at high temperature is necessary. Moreover, the invention does not materially decrease the workability of weldability of the steels. It is applicable not only to steels of the specific compositions listed in the tables but is generally applicable to chromium steels made austenitic by nickel or manganese or both containing at least 50% iron.

In the practice of the invention a steel containing boron as well as chromium, nickel, manganese within the limits set forth which is to be used for the fabrication of articles for use at high temperatures is worked in the manner described. Following working all that may be necessary to finish fabrication is machining or other cold-forming operation. In other words, the hot-cold worked material may be in the form of a semi-finished article.

I claim:

1. The method of improving the high-temperature strength of austenitic chromium steels containing at least 50% iron, 10% to 30% chromium, up to 0.5% carbon and at least one element selected from the group consisting of nickel and manganese in a quantity at least sufficient to render said steels substantially completely austenitic which method comprises incorporating 0.005% to less than 0.1% boron in such steels and working them at an elevated temperature above 1000° F. but below their recrystallization temperature reducing said steels about 10% to 40% by such working.

2. The method of improving the high-temperature strength of austenitic chromium steels containing at least 50% iron, 10% to 30% chromium, up to 0.5% carbon and at least one element selected from the group consisting of nickel and manganese in a quantity sufficient to render said steels substantially completely austenitic, which method comprises incorporating 0.005% to less than 0.1% boron in such steels and working them in the temperature range of 1200° F. to 1900° F. but below their recrystallization temperature, reducing said steels about 10% to 40% by such working.

3. The method of improving the high-temperature strength of austenitic chromium steels containing at least 50% iron, 10% to 30% chromium, up to 0.5% carbon and at least one element selected from the group consisting of nickel and manganese in a quantity sufficient to render said steels substantially completely austenitic, which method comprises incorporating 0.005% to less than 0.1% boron in such steels, hot working them, subjecting them to a solution heat treatment, and then working such steels in the temperature range 1200° F. to 1900° F. but below their recrystallization temperature reducing said steels about 10% to 40% in said second working.

4. The method of improving the high-temperature strength of austenitic chromium steels containing at least 50% iron, 10% to 30% chromium, up to 0.5% carbon and at least one element selected from the group consisting of nickel and manganese in a quantity sufficient to render said steels substantially completely austenitic, which method comprises incorporating 0.005% to less than 0.1% boron in such steels, hot-working them, subjecting them to a solution heat treatment, and then working such steels at a temperature of about 1500° F., reducing such steels 10% to 40% in said second working.

5. The method of improving the high-temperature strength of austenitic chromium steels containing at least 50% iron, 10% to 30% chromium, up to 0.5% carbon and at least one element selected from the group consisting of nickel and manganese in a quantity sufficient to render said steels substantially completely austenitic, which method comprises incorporating 0.005% to less than 0.1% boron in said steels, hot working them and then further working such steels in the falling temperature range 1900° F. to 1200° F. reducing said steels about 10% to 40% in said second working.

6. The method of improving the high-temperature strength of austenitic chromium steels containing at least 50% iron, 10% to 30% chromium, up to 0.5% carbon and at least one element selected from the group consisting of nickel and manganese in a quantity sufficient to render said steels substantially completely austenitic, up to 7.5% molybdenum, up to 15% tungsten, up to 5% in the aggregate but not more than 2% of any one of at least one element selected from the group consisting of columbium, tantalum, vanadium, and titanium, the remainder iron and incidental impurities, which method comprises incorporating 0.005% to less than 0.1% boron in said steels,

hot-working them and then further working such steels in the falling temperature range 1900° F. to 1200° F. reducing said steels about 10% to 40% in said second working.

7. The method of improving the high-temperature strength of austenitic chromium steels containing at least 50% iron, 10% to 30% chromium, up to 0.5% carbon and at least one element selected from the group consisting of nickel and manganese in a quantity sufficient to render said steels substantially completely austenitic, up to 7.5% molybdenum, up to 15% tungsten, up to 5% in the aggregate but not more than 2% of any one of at least one element selected from the group consisting of columbium, tantalum, vanadium, and titanium, the remainder iron and incidental impurities, which method comprises incorporating 0.005% to less than 0.1% boron in said steels,

hot-working them, subjecting them to a solution heat treatment, and then further working such steels in the temperature range 1200° F. to 1900° F. but below their recrystallization temperature, reducing such steels 10% to 40% in said second working.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,107,014	Sachse	Feb. 1, 1938
2,432,618	Franks et al.	Dec. 16, 1947
2,432,619	Franks et al.	Dec. 16, 1947

Certificate of Correction

Patent No. 2,562,854

WILLIAM O. BINDER

July 31, 1951

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 11, for "of a" read *if a*; line 44, for "those" read *these*; column 7, line 38, for "workability of" read *workability or*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of October, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.