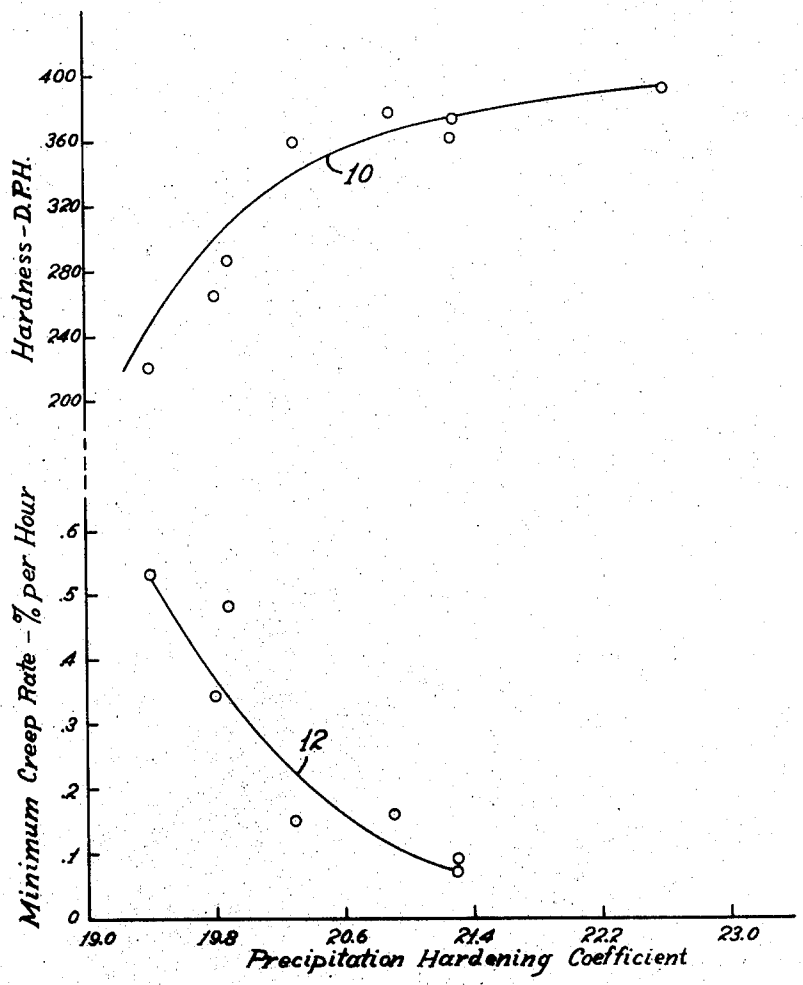
July 12, 1949. H. SCOTT ET AL 2,475,642

MECHANICAL ELEMENT WHICH IS TO BE SUBJECTED TO HIGH TEMPERATURES

Filed Sept. 29, 1944



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Patented July 12, 1949 2,475,642

UNITED STATES PATENT OFFICE

2,475,642

MECHANICAL ELEMENT WHICH IS TO BE SUBJECTED TO HIGH TEMPERATURES

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Application September 29, 1944, Serial No. 556,385

2 Claims. (Cl. 148—32.5)

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This invention relates to alloys, and in particular to alloys having high strength and oxidation resistance at room and elevated temperatures.

At the present time there are a number of alloys available which are known to the trade as heat resistant alloys. The known alloys, however, usually have one or more disadvantages in that the strength at elevated temperatures is insufficient for many modern applications or the oxidation resistance is poor, or the alloy cannot be forged. Among the known heat resistance alloys, the iron-nickel-chromium alloys have been generally considered as superior alloys, the chromium imparting oxidation resistance while the nickel tends to maintain the alloys austenitic, that is, having a face-center-cubic crystal structure.

The known austenitic iron-nickel-chromium alloys, however, do not have high strength or creep resistance at elevated temperatures in excess of 1200° F., the strength rapidly diminishing as the temperature is raised. None of the commercially available austenitic iron-nickel-chromium wrought alloys have the characteristic of being resistant to creep and rupture at temperatures of 1500° F. or higher under stresses of 10,000 to 15,000 pounds per square inch for periods of time in excess of 1000 hours.

An object of this invention is to provide a precipitation hardened austenitic alloy which is resistant to creep at elevated temperatures.

Another object of this invention is to provide an austenitic alloy containing nickel, cobalt, chromium, molybdenum and tungsten which can be formed as by machining or forging to a predetermined shape and precipitation hardened to impart thereto resistance to creep at elevated temperatures.

A more specific object of this invention is to provide a low carbon alloy containing nickel, cobalt, chromium, molybdenum, tungsten, manganese and silicon so balanced that the alloy can be precipitation hardened to a hardness in excess of 300 DPH while imparting thereto resistance to creep at elevated temperatures.

Other objects of this invention will become apparent from the following description when taken in conjunction with the accompanying drawing, the single figure of which is a graph, the curves of which illustrate the relation of a precipitation hardening coefficient for the alloys of this invention to the hardness and creep rate obtained with the alloys.

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We have found that alloys of the heat resistant type can be produced having oxidation resistance, high strength and resistance to creep at elevated temperatures of 1500° F. and higher, the latter characteristics being imparted to the alloys by a precipitation hardening treatment. The alloys contemplated within the scope of this invention, in general, are low carbon alloys containing balanced amounts of nickel, cobalt, chromium, molybdenum, tungsten, manganese and silicon, the alloys being precipitation hardened by solution treating them at a high temperature and thereafter ageing them at a somewhat lower temperature to give the alloys high strength at elevated temperatures.

In particular, the heat treatment which has been found to be suitable for developing the characteristics of the alloys of this invention comprises quenching them from a solution temperature between 2200° F. and 2375° F. at which they are soaked for a period of time of 0.5 to 4 hours and ageing them at a temperature between 1500° F. and 1700° F. Generally, the period of time of ageing the alloy depends upon the treatment. Practically, however, the ageing temperature for any particular alloy is usually selected to produce maximum hardness in a particular time. Thus a time of 40 to 50 hours at an ageing temperature of 1550° F. or a time of 20 hours at an ageing temperature of 1600° F. is satisfactory for developing the characteristics of the alloys of the present invention.

The proportions of the constituents of the alloy may be varied over wide ranges in a predetermined manner as long as the alloying constituents are balanced as will be explained in full hereinafter. In general, the alloy composition may range from 15% to 35% by weight of nickel, 20% to 40% by weight of cobalt, 17% to 22% by weight of chromium, 3% to 15% by weight of molybdenum, 1% to 9% by weight of tungsten, 0.5% to 3% by weight of manganese, 0.1% to 0.7% by weight of silicon, not over 0.20% by weight of carbon and the balance iron with not more than 0.5% by weight of the usual contaminants such as impurities and deoxidizers.

It is preferred to maintain the carbon content

of the alloy at less than 0.20% and preferably lower than 0.12%. This is because carbon has been found to form carbides with chromium, molybdenum and tungsten and thereby lowers the oxidation resistance of the resulting alloy, the carbon having the further disadvantage of detracting or interferring with the precipitation of the precipitation hardening compounds to lower the resulting hardness of the alloys.

In the alloys of this invention, the nickel and cobalt contents are interrelated cooperating to control the solid solution hardening of the alloy, the lower limit of 20% cobalt being utilized for increasing the ductility of the alloy and improving its forgeability. It has been found that by substituting cobalt for nickel, a reduction in the amount of the hardener elements necessary for obtaining maximum strength as will be evident hereinafter, is obtained with an accompanying increase in forgeability. Where the lower limit of at least 20% cobalt is utilized, it is necessary to employ at least 15% nickel in order to maintain the alloy austenitic.

The chromium is primarily utilized for imparting corrosion and oxidation resistance to the alloy, it being found that not less than 17% chromium is necessary in the present alloy for giving the required corrosion and oxidation resistance to the alloy which will permit its use at temperatures of 1500° F. and higher. As the chromium content is increased beyond 20%, the nickel and cobalt contents also have to be increased to maintain solution hardness requirements as will be apparent from the relation of the alloying elements in maintaining a balanced relation as given hereinafter and it is therefore preferred to utilize not over 22% chromium in the present alloy.

In order to insure that the present alloy is susceptible to a precipitation hardening treatment from 3% to 15% of molybdenum and from 1% to 9% of tungsten are utilized, it being found that these elements when properly balanced within the ranges given, together with a proper balance of the other alloying constituents, as will be explained more fully hereinafter, are very active precipitation hardening agents in the resulting austenitic alloy. While molybdenum and tungsten constitute the active precipitation hardening agents, it has also been found that the other alloying elements have a definite effect on the characteristics of the alloy, and that the relation or balance of the alloying constituents in the alloy must be rigidly controlled, as will be explained hereinafter.

In introducing the elements, nickel, cobalt, chromium, molybdenum and tungsten, pure metals may be used if so desired, or the ferro-alloy form of the alloying constituents may be used. Care should be exercised, however, in order not to exceed 25% iron as a maximum in the alloy if the ferro-alloys are employed whereas if commercially pure nickel, cobalt, chromium, molybdenum and tungsten is employed only that amount of iron, amounting to a few tenths of a percent, which is present in such metals, is present in the resulting alloy. Manganese within the range given hereinbefore is utilized for improving the forgeability of the resulting alloy.

Through numerous experiments and tests, we have found that all alloys within the range given hereinbefore will not have the characteristics required by commercial applications. On the basis of our work, we have established that in order to obtain adequate solid solution hardness that only those alloys within the range given hereinbefore whose alloying constituents have the relation that

$$(1) \quad \%Ni+0.5(\%Co)=30 \text{ to } 47.5$$

and

$$(2) \quad \%Mo+0.75(\%W)=10 \text{ to } 15$$

are satisfactory.

We have further established that in order to respond in satisfactory degree to the precipitation hardening treatment referred to hereinbefore, the alloying constituents must be so balanced as to have the relation that

$$(3) \quad \%Mo+0.8(\%Cr)+0.75(\%W+\%Mn)+1.2(\%Si)-0.25(\%Ni)-0.125(\%Co)=19 \text{ to } 24$$

We have found that when a value lower than 19 is obtained when the alloying constituents within the ranges given are substituted in the foregoing equation, the alloys will lack hardenability and if the value of the alloying constituents when substituted in Equation 3 give a value greater than 24, the alloys are deficient in forgeability. For convenience the quantity calculated by substituting the values of the alloying constituents in the foregoing equation is termed the "precipitation hardening coefficient" or "PHC" since such quantity has been found to vary directly with the aged hardness of the alloys within the range of the composition given hereinbefore. From Equation 3 it is seen that molybdenum, chromium, tungsten, manganese and silicon, having a positive sign, act to increase the precipitation hardening coefficient and hardness, whereas the nickel and cobalt act to decrease the precipitation hardening coefficient and hardness.

We have found that the solution hardener content of the alloy has a definite effect in imparting high strength to the alloy, rendering the alloy suitable for use at temperatures of 1500° F. or higher. On the basis of our investigations we have derived an empirical equation termed for convenience the "coefficient for solution hardening" or "SHC" which the alloying constituents of our alloys must satisfy in order to have adequate creep strength. This relation among the alloying constituents is set forth in the following equation:

$$(4) \quad 1/2[\%Mo-0.8(\%Cr)-0.75(\%Mn-\%W)-1.2(\%Si)+0.25(\%Ni)+0.125(\%Co)]+7=7 \text{ to } 12.5$$

Even when satisfying the requirements of Equations 3 and 4, the alloys of this invention will not have adequate creep resistance unless they are heat treated to produce a grain size at least as coarse as No. 2 ASTM and a minimum hardness of 300 DPH. When the alloy has a composition within the range given hereinbefore so that the alloying constituents satisfy the relations given by the equations for the precipitation hardening coefficient and the coefficient for solution hardening and are heat treated by quenching and ageing them within the ranges given, it has been found that the characteristics of the alloys can be readily duplicated for the different alloys satisfying the conditions established.

Referring to the following table there are listed a number of alloys having compositions within the range given hereinbefore, together with the numerical value obtained by substituting the value of the alloying constituents in Equations 1, 2, 3 and 4 given hereinbefore.

Table I

Alloy No.	Composition, Wgt. Per Cent								Value of Equations			
	Ni	Co	Cr	Mo	W	Mn	Si	C	1	2	3	4
4610	30.2	20.3	20.7	7.6	4.3	2.00	0.4	0.1	40.4	10.8	19.2	8.2
4645	20.3	30.4	19.4	6.2	4.4	0.52	0.19	0.08	35.5	9.5	16.8	8.1
4651	20.3	30.5	19.9	6.0	4.2	0.95	0.20	0.1	35.6	9.1	17.1	7.5
4668	20.2	30.2	19.6	6.2	4.2	1.06	0.20	0.1	35.3	9.3	17.2	7.7
4669	20.3	20.8	20.1	6.8	3.1	2.09	0.20	0.1	30.7	9.1	19.3	6.4
4671	15.4	24.9	20.0	7.3	3.0	2.10	0.20	0.1	27.9	9.6	20.4	6.4
M269	30.0	20.6	20.1	6.3	4.9	2.00	0.40	0.1	40.3	10.0	18.0	8.0
M270	30.0	20.6	20.4	7.1	4.8	2.00	0.40	0.1	40.3	10.7	19.9	7.7
M284	20.0	30.1	20.2	8.3	3.8	1.97	0.25	0.11	35.6	11.2	20.3	8.0
M405	20.0	30.0	20.1	8.0	3.8	1.94	0.11	0.08	35.0	10.9	19.9	7.9
M406	20.1	30.1	20.0	8.2	3.7	2.00	0.10	0.06	35.2	11.0	19.8	8.1
M440	20.1	30.3	20.1	8.2	3.5	1.61	0.12	0.03	35.3	10.8	19.4	8.1
M465	20.2	30.2	20.7	8.2	3.2	1.68	0.14	0.03	35.3	10.6	19.8	7.7
M481	20.3	30.4	20.4	8.1	3.6	1.88	0.20	0.04	35.5	10.8	19.9	7.8
M492	20.1	29.6	20.8	8.3	3.8	1.95	0.30	0.08	35.9	11.2	20.9	7.7
M519	20.7	31.1	21.1	8.5	4.5	1.68	0.20	0.05	35.3	11.9	21.3	8.2
M537	20.9	30.8	20.8	8.5	4.7	1.95	0.20	0.04	36.3	12.0	21.3	8.3
M538	20.6	29.3	20.9	9.2	5.0	1.80	0.25	0.05	35.3	13.0	22.6	8.7

As will be noted, a number of the alloys given in the foregoing table fail to meet one or more of the relations established by the empirical equations given hereinbefore. In the foregoing table it is, of course, understood that the balance of each of the alloys listed constitutes iron with less than 0.5% of the deoxidizers, such as aluminum, titanium, vanadium and calcium and impurities such as phosphorus, sulphur, arsenic, tin and copper.

Referring to the following table, the heat treatment applied to the alloys listed in Table I is recorded together with the values of the hardness as solution treated and hardness as aged obtained on the different alloys.

Table II

Alloy No.	Solution Treatment			Ageing Treatment		
	Temp., ° F.	Time, Hrs.	DPH	Temp., ° F.	Time, Hrs.	DPH
4610	2,280	0.5	183	1,650	128	278
4645	2,200	4.0	180	1,600	64	232
4651	2,200	4.0	183	1,600	64	233
4668	2,200	4.0	191	1,600	128	260
4669	2,200	4.0	173	1,600	128	272
4671	2,200	4.0	180	1,600	128	298
M269	2,280	0.5	183	1,650	98	265
M270	2,280	0.5	178	1,650	100	280
M284	2,350	4.0	200	1,500	240	358
M405	2,350	4.0	202	1,500	240	327
M406	2,350	4.0	198	1,500	240	315
M440	2,350	4.0	175	1,500	240	220
M465	2,350	4.0	180	1,500	240	265
M481	2,350	4.0	218	1,500	240	284
M492	2,350	4.0	233	1,500	240	377
M519	2,350	4.0	199	1,500	240	371
M537	2,350	4.0	209	1,500	240	361

From an examination of Tables I and II, it is apparent that only those alloys which satisfy the relation set forth by the empirical Equations 1, 2, 3 and 4 will have a minimum hardness of 300 DPH such as is required in the preferred alloys of this invention.

The alloys listed in Table I and falling within the range of 19.5% to 21.5% by weight of nickel, 29% to 31.5% by weight of cobalt, 19.5% to 21.5% by weight of chromium, 8% to 9.5% by weight of molybdenum, 3% to 5% by weight of tungsten, 1.5% to 2.2% by weight of manganese, 0.1% to 0.4% by weight of silicon, less than 0.20% by weight of carbon and the balance iron with not more than 0.5% by weight of impurities when precipitation hardened as given hereinbefore is of particular value for use in turbine blades or the like, as such alloys are exceptionally resistant to creep at elevated temperatures of 1500° F. or higher. Referring to the following table, there is given the results of creep rupture tests at 1500° F. under a load of 20,000 pounds per square inch for certain of the alloys identified by composition in Table I.

Table III

Alloy No.	Rupture Time, Hrs.	Elongation, Per Cent	Minimum Creep Rate, Per Cent per Hr.	Time to 1.0% Strain, Hrs.
M284	47.6	31.3	0.15	4.0
M440	20.0	16.6	0.53	1.3
M465	40.0	27.0	0.34	3.7
M481	25.5	35.2	0.48	1.5
M492	49.6	36.0	0.16	5.9
M519	71.3	26.9	0.09	8.8
M537	105.0	20.9	0.07	11.0

By referring to Table II it is apparent that alloys M284, M492, M519 and M537 which have a hardness in excess of 300 DPH gives far superior creep resistance over that obtained on alloys M440, M465 and M481 which have DPH values lower than 300. However, by properly selecting the proper heat treatment within the range given hereinbefore, the hardness of the latter alloys can be raised to values over 300 DPH and creep resistance values comparable to those obtained on alloys such as M492 can be obtained.

The results of the creep rupture tests given in Table III are based on alloys of approximately the same matrix composition, the content of the hardener elements, however, varying over a considerable range as shown by the values of the precipitation hardening coefficient listed for Equation 3 in Table I. The effect of the precipitation hardening coefficient on the hardness and on the creep rate after a standard heat treatment is clearly shown by curves 10 and 12 respectively, of the drawing, these curves respectively illustrating that an increase in the precipitation hardening coefficient as given by Equation 3 results in an increase in the hardness and a decrease in the creep rate at 20,000 pounds per square inch at 1500° F.

As a specific example of the creep rate obtained with an alloy of this invention, an alloy having a composition of 19.98% nickel, 30.1% cobalt, 20.23% chromium, 8.32% molybdenum, 3.75% tungsten, 1.97% manganese, 0.25% silicon, 0.11% carbon and the balance iron with not more than 0.5% impurities was cast into a 6" square ingot weighing 270 pounds. It was found that the alloy thus cast was readily fabricated having excellent forgeability and good oxidation resistance in air up to 2100° F. while

being machinable. When this alloy was subjected to a precipitation hardening heat treatment consisting of a solution treatment for 4 hours at 2350° F. and then quenched in oil and thereafter aged for 240 hours at 1500° F., a hardness of 370 DPH was obtained. The outstanding creep and rupture properties for this alloy are listed in the following table:

Table IV

Test Temp., °F.	Test Load, p. s. i.	Minimum Creep Rate, per cent per Hr.	Rupture Time, Hrs.	Rupture Strain, per cent	Time to 1.0% Strain, Hrs.
1,500	20,000	0.19	49	28.2	4.0
1,500	16,000	.017	348	23.0	58
1,500	12,500	.000044	4,769+	------	4,769+
1,500	8,000	.000011	------	------	------
1,600	9,400	----------	2,000	------	1,000
1,500	14,000	----------	2,100	------	1,000
1,350	19,500	----------	7,600	------	1,000

As an example of the tensile strength obtained with alloys of this invention at different temperatures ranging between room temperature and 1600° F., the following table lists the tensile properties obtained on the alloy M537 identified in the foregoing tables and gives the heat treatment identified therewith in Table II.

Table V

Spec. No.	Test Temp., °F.	Initial Hardness, DPH	Yield Point, p. s. i.	Ultimate Strength, p. s. i.	Elongation, per cent	Red in. Area, per cent
A	70	334	87,000	131,000	3	3
B	1,000	346	77,000	113,400	9	9
C	1,200	343	72,000	111,600	11	12
D	1,350	336	59,000	87,700	20	19
E	1,500	351	47,000	69,400	30	32
F	1,600	338	41,000	48,400	33	29

The specimens A through F identified in Table V were of 0.200" in diameter over a 1" gage length and were stabilized for 20 hours at 1350° F. for the tests at 1350° F. or lower and for 20 hours at test temperature for the tests at 1500° F. and 1600° F.

The alloys of this invention are austenitic, that is, they have a face-centered-cubic crystal structure and have exceptional corrosion resistance and high strength and creep resistance at elevated temperatures. The alloys whose alloying constituents have a relation which will satisfy the formulas given hereinbefore and which have a DPH of 300 or greater and a grain size as coarse as at least No. 2 ASTM are particularly applicable for use in gas turbines where it is necessary to employ an alloy having relatively high tensile strength, low creep rate and a high degree of oxidation resistance. Further, the alloys of this invention are particularly adapted for use as parts of turbines where the temperature gradients range from the maximum down to as low as room temperature and where the turbine parts may be subjected to stresses which vary inversely with the temperature. Other uses of these alloys are as articles of manufacture such as bolts, springs or the like where high stresses at elevated temperatures may be encountered. These alloys are particularly useful as they may be readily formed to shape as by forging or mechanically working and thereafter subjected to the precipitation hardening treatment to impart the required characteristics thereto. Further, the alloys of this invention have unusual thermal stability at operating temperatures of 1500° F. or higher giving them unusually long life in industrial applications.

Although this invention has been described with reference to a particular embodiment thereof, it is, of course, not to be limited thereto except insofar as is necessitated by the scope of the appended claims.

We claim as our invention:

1. A mechanical element which is to be subjected to a temperature of 1500° F. and higher and considerable stress in normal use consisting of a precipitation hardened austenitic alloy composed of 15% to 35% nickel, 20% to 40% cobalt, 17% to 22% chromium, 3% to 15% molybdenum, 1% to 9% tungsten, 0.5% to 3% manganese, 0.1% to 0.7% silicon, less than 0.2% carbon, and the balance iron with less than 0.5% of impurities, which has been quenched from a solution temperature between 2200° F. and 2375° F., the solution temperature being maintained for a period of time of between 0.5 and 4 hours, and aged at a temperature between 1500° F. and 1700° F. for a period of time between 20 hours and 240 hours, the alloy having the relation among its alloying components that

$$\%Mo+0.8(\%Cr)+0.75(\%W+\%Mn)+1.2(\%Si)-0.25(\%Ni)-0.125(\%Co)=19 \text{ to } 24$$

the precipitation hardened alloy having a hardness in excess of 300 DPH.

2. A mechanical element which is to be subjected to a temperature of 1500° F. and higher and considerable stress in normal use consisting of a precipitation hardened austenitic alloy composed of 19.5% to 21.5% nickel, 29% to 31.5% cobalt, 19.5% to 21.5% chromium, 8% to 9.5% molybdenum, 3% to 5% tungsten, 1.5% to 2.2% manganese, 0.1% to 0.4% silicon, less than 0.20% carbon, and the balance iron with not more than 0.5% of impurities, which has been quenched from a solution temperature between 2200° F. and 2375° F., the solution temperature being maintained for a period of time of between 0.5 and 4 hours, and aged at a temperature between 1500° F. and 1700° F. for a period of time between 20 hours and 240 hours, the alloy having the relation among its alloying components that

$$\%Mo+0.8(\%Cr)+0.75(\%W+\%Mn)+1.2(\%Si)-0.25(\%Ni)-0.125(\%Co)=19 \text{ to } 24$$

the precipitation hardened alloy having a hardness in excess of 300 DPH.

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