Patented Dec. 20, 1938

2,141,016

UNITED STATES PATENT OFFICE

2,141,016

ALLOY STEEL

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No Drawing. Application November 19, 1936, Serial No. 111,616

13 Claims. (Cl. 148—31)

This invention relates to improvements in heat, oxidation and corrosion resisting steels adapted for such uses as valves, valve seat inserts and related parts of internal combustion engines, high speed and other cutting, forming and shearing tools, hot work dies, die casting dies, and more generally for use in articles requiring great strength, hardness and resistance to corrosion, oxidation and scaling at elevated as well as at atmospheric temperatures.

This application is a continuation in part of my copending application Serial No. 83,451, filed June 4, 1936, which in turn is a continuation in part of my applications for Letters Patent Nos. 2,009,974 and 2,051,415.

In my patents aforesaid I have described a series of steels, having the properties above noted, containing about 18 to 35% chromium, about 1 to 10% of metal of the group consisting of nickel and manganese, and about 1 to 10% of metal of the group consisting of molybdenum, tungsten and silicon, characterized in undergoing a change in phase or in structure when maintained for a period—usually a matter of hours—at elevated temperature within the approximate range of 1200 to 1800° F., whereby they acquire outstanding and distinguishing characteristics as compared to known steels, and also as compared to the characteristics of these same steels prior to such heat treatment. Such steels when so treated acquire high hardness—up to "C" 65 Rockwell or more for some analyses—as compared to their hardness prior to such heat treatment and following usual rolling, forging or annealing operations. Elevated temperature measurements have shown that these steels actually harden at heat, their elevated temperature hardness being superior to that of known steels and their hardness on cooling being substantially independent of the rate of cooling. When so hardened these steels undergo no substantial reduction in hardness after heating to temperatures as high as 1400° or 1600° F. or even higher for some analyses, and this irrespective of the number, duration or temperature of individual heats.

Whereas according to the information of my patents aforesaid, at least one of the elements nickel and manganese and at least one of the elements molybdenum, tungsten and silicon in addition to chromium within the percentage limits noted, is required for imparting heat hardenability, my further investigations have established that straight chrome steels are susceptible to such hardening provided chromium is present in sufficient amount, i. e. in excess of about 35%; and also that steels containing about 18 to 35% chromium and which are thereby substantially non-heat hardenable on the basis of their chromium contents alone, can be rendered so by adding the above elements in the manner taught by my patents aforesaid, or by adding about 1 to 10% silicon, about 1 to 10% molybdenum or its equivalent tungsten, or about 1 to 15% of metal of the group comprising silicon, molybdenum and tungsten, as taught by this application. These latter steels differ from those of my patents aforesaid in that metal of the group consisting of nickel and manganese is not required for imparting heat hardenable properties of such steels.

It is shown in my patents aforesaid that heat hardenability of the steels therein described, increases with increasing content of the alloying elements other than carbon within the limits therein stated. The same is true of the steels constituting the subject matter of this application, as is shown by the following data:

Table I

Effect of chromium on hardenability of straight chrome steels. C .12%; other elements present in usual amounts.

Cr per cent	Hardness: Rockwell "C"	
	As rolled	After 16 hrs. at 1400° F.
30.6	16	17
36.9	21	40
40.7	24	65

For straight chrome-steels therefore, heat hardenability occurs only where chromium exceeds about 35%, but increases with increasing chromium above this amount.

Table II

Effect on hardenability of adding silicon to

chrome steel. C about .12%; Cr about 25%; elements other than Si present in usual amounts.

Si per cent	Hardness: Rockwell "C"	
	As rolled	After 16 hrs. at 1400° F.
3.8	26	26
4.6	24	43
5.4	31	48
6.9	41	58

Steels which contain insufficient chromium for heat hardening, may thus be rendered so hardenable by adding silicon in sufficient amount, the hardenability increasing with further increase of this element.

Table III

Effect on hardenability of adding molybdenum to chrome steel. C about .14; Cr about 30%; elements other than Mo present in usual amounts.

Mo per cent	Hardness: Rockwell "C"	
	As rolled	After 16 hrs. at 1400° F.
0	16	17
4.4	27	55

Heat hardenability may be thus imparted to an otherwise non-heat hardenable chrome steel by adding sufficient molybdenum.

Table IV

Effect on hardenability of adding molybdenum to chrome-silicon steels and of adding silicon to chrome-molybdenum steels. C about .15%; elements other than Cr, Si, Mo present in usual amounts.

Steel	Cr per cent	Si per cent	Mo per cent	Hardness: Rockwell "C"	
				As rolled	After 16 hrs. at 1400° F.
1	29.6	3.3	----	23	45
2	29.1	----	4.4	27	55
3	28.2	3.4	4.7	32	61
4	25.2	3.1	2.4	27	41
5	24.4	4.1	2.6	34	45
6	24.4	5.1	1.7	33	48
7	29.9	3.1	1.5	27	51
8	29.6	3.1	2.5	27	56
9	28.2	3.4	4.7	32	61

Comparison of the heat hardening for steel 3 with that of steels 1 and 2, shows that hardenability is enhanced by adding molybdenum to chrome-silicon steel, and also by adding silicon to chrome-molybdenum steel. The results for steels 4 to 6 inclusive, show that hardenability increases with increasing silicon keeping the chromium and molybdenum about constant. Similarly the results for steels 7 to 9 inclusive, show that hardenability increases with increasing molybdenum keeping the chromium and silicon about constant.

Table V

Effect on hardenability of varying the chromium content in steels containing either or both of silicon and molybdenum. C about .15%; elements other than Cr, Si and Mo present in usual amounts.

Cr	Si	Mo	Hardness: Rockwell "C"	
			As rolled	After 16 hrs. at 1400° F.
19.0	5.6	4.7	37	44
23.8	3.7	4.7	31	52
25.7	4.3	4.8	30	56
28.2	3.4	4.7	32	61
37.2	1.8	1.2	26	63
40.7	.9	0	24	65

Hardenability thus increases with increasing chromium.

Table VI

Effect of carbon on hardenability. Cr about 28.5%; Si about 4%; Mo about 1.7%; elements other than C present in usual amounts.

C per cent	Hardness: Rockwell "C"	
	As rolled	After 16 hrs. at 1400° F.
.10	29	50
.35	33	50
.54	33	49

Increasing the carbon content therefore does not increase hardenability.

The data of Tables I to VI inclusive, thus establish that: Chromium is the dominant element as regards hardenability, and if present in sufficient amount, i. e., in excess of about 35%, none of the other elements above referred to need be present, although additions thereof enhance hardenability. As the chromium content is decreased, other elements such as silicon, molybdenum and tungsten, must be added in increasing amounts for imparting a given hardenability, additions of such elements being requisite where the chromium is below about 35%. In general, hardenability increases with increasing additions of the individual alloying elements other than carbon, and hence with increase in the aggregate content of such elements.

I have observed, moreover, that the heat hardenable steels of this invention appear to satisfy a certain relationship whereby they may be differentiated on the basis of their chromium, silicon and molybdenum contents, from steels containing those elements which are not susceptible to such hardening in appreciable degree. This relationship may be formulated as follows: steels are heat hardenable when the sum comprising two-thirds the chromium content plus twice the silicon content plus the molybdenum content divided by twenty-five exceeds unity. Designating this as the "Hardenability Ratio" or more briefly as "H. R.", this relationship may be expressed more concisely as follows:

(1) For hardenability

$$\text{H. R.} = \frac{.67\text{Cr} + 2\text{Si} + \text{Mo}}{25} > 1.0$$

The data presented below embracing a wide range of analyses conform to this relationship and tend to substantiate it as a rule of general applicability to such steels.

Table VII

Steel	Analysis				Hardenability	Hardness: Rockwell "C"	
	C	Cr	Si	Mo	Ratio: H. R.	As rolled	After 16 hrs. at 1400° F.
CHROMIUM 18.0 TO 20.0 INCLUSIVE							
1	.11	19.0	5.6	4.7	1.15	37	44
2	.16	19.2	6.3	3.7	1.16	33	38
CHROMIUM 20.1 TO 22.0 INCLUSIVE							
3	.09	20.2	4.9	0	.93	25	26
4	.18	21.0	6.7	0	1.10	38	46
CHROMIUM 22.1 TO 24.0 INCLUSIVE							
5	.16	23.6	3.7	4.7	1.11	31	52
CHROMIUM 24.1 TO 26.0 INCLUSIVE							
6	.14	25.3	2.0	0	.84	15	14
7	.14	24.6	3.8	0	.96	26	26
8	.14	25.7	4.4	0	1.04	30	43
9	.12	25.6	4.6	0	1.05	24	43
10	.15	24.9	5.4	0	1.10	31	48
11	.14	24.3	1.0	4.8	.92	18	20
12	.11	25.7	2.0	1.7	.92	16	18
13	.12	25.2	3.1	2.4	1.02	27	41
14	.10	24.4	4.1	2.6	1.08	34	45
15	.13	25.7	4.3	4.8	1.22	30	56
16	.14	24.4	5.1	1.7	1.13	33	48
CHROMIUM 26.1 TO 28.0 INCLUSIVE							
17	.15	26.0	3.0	0	.94	22	19
18	.15	26.0	6.9	0	1.25	41	58
19	.14	26.3	2.7	2.5	1.02	26	34
20	.14	26.1	4.4	1.6	1.11	31	49
CHROMIUM 28.1 TO 30.0 INCLUSIVE							
21	.15	28.5	2.9	0	1.00	24	28
22	.16	29.6	3.3	0	1.05	23	45
23	.12	28.4	3.9	0	1.07	27	47
24	.18	29.1	.8	4.4	1.19	27	55
25	.15	29.9	3.1	1.5	1.11	27	51
26	.17	29.6	3.1	2.5	1.14	27	56
27	.18	28.2	3.4	4.7	1.22	32	61
28	.10	28.2	3.9	1.7	1.13	29	50
29	.54	29.0	4.0	1.6	1.16	33	49
30	.35	28.6	4.0	1.7	1.16	33	50
CHROMIUM 30.1 TO 33.0 INCLUSIVE							
31	.12	30.6	2.0	0	.98	16	17
32	.14	32.6	2.7	0	1.09	25	45
33	.10	31.0	4.7	0	1.20	25	58
34	.14	32.7	2.1	1.2	1.09	25	51
CHROMIUM OVER 33.0							
35	.12	36.9	1.3	0	1.09	21	40
36	.14	37.2	1.8	1.2	1.19	26	63
37	.12	40.7	.9	0	1.12	24	65

Referring to the data of Table VII, in every instance that the hardenability ratio is unity or less, the corresponding steel undergoes little or no increase in hardness after being heat treated; whereas in every instance that the ratio exceeds unity the hardness of the corresponding steel is greatly enhanced by heat treating. And generally speaking, the analyses which are susceptible to the greatest heat hardening are those for which the hardenability ratio is largest.

The data of Table VII embrace a wide range of compositions for steel containing chromium both with and without silicon, molybdenum or both; so that the above rule appears to be of general applicability as a criterion of hardenability for such steels. The data of the table, moreover, amplify those of Tables I to VI, inclusive, and lend further support to the conclusions derived therefrom as above stated.

As was the case with the steels of my patents aforesaid, heat hardening of the steels described herein is a function of time at temperature, and in general is more readily secured and to an increased degree if the steel is in the "as forged" or "as rolled" condition before hardening, as compared to hardening from the "as annealed" condition, as appears from:

Table VIII

Analysis				Pre-heat hardened condition	Rockwell "C" Hardness						
					Time: hrs. at 1400° F.						
C	Si	Cr	Mo		0	1	2	4	8	16	32
.16	3.30	34.90	----	As rolled	25	25	26	32	42	46	47
				1850° F. anneal	20	20	20	25	34	43	45
.12	3.10	25.22	2.43	As rolled	27	27	28	30	36	42	44
				1850° F. anneal	24	25	25	28	29	33	39

As heretofore stated, such steels after being heat hardened, undergo no substantial reduction in hardness after heating to temperatures as high as about 1400° F. or more, as shown by:

Table IX

C	Si	Cr	Mo	Rockwell "C" hardness						
				As heat hardened	After reheating 16 hours at—					
					600° F.	800° F.	1000° F.	1100° F.	1200° F.	1400° F.
.12	4.62	25.63	----	44	44	44	44	44	45	46
.16	3.39	35.04	----	46	46	46	46	46	47	47
.12	3.10	25.22	2.43	42	42	42	42	42	42	43

Steels in accordance with this invention have also been found highly resistant to the combustion products of both plain and special motor fuels for internal combustion engines, and hence are especially adapted for use as valves, valve seats and related parts of internal combustion engines.

As shown by the data contained in Table VIII, heat hardening of the steels above described is accomplished by maintaining the same at elevated temperature within the approximate range of 1200° to 1800° F., until a desired hardening has been imparted. It is immaterial in this connection whether the steel is held within this temperature range while cooling from some higher temperature, such as that of forging, extruding, etc., or is elevated to temperature within this range from some lower temperature for hardening. Also, it is not essential, although preferable, that hardening be effected at reasonably constant temperature within the hardening range; the temperature may be permitted to increase, decrease, or fluctuate during this treatment. All such modes of treatment are intended to be embraced in the appended claims by the recital of a steel "characterized in being hardened by heating within the approximate temperature range of 1200 to 1800° F."

Also reference to molybdenum in the claims is intended to include its equivalent, tungsten.

Although silicon is classified as a non-metal, or metalloid, by certain authorities, it nevertheless has the attributes of a metal in the steels of this invention, and is therefore so designated in the specification and claims herein.

What I claim is:

1. An alloy steel, characterized in being hardened by maintaining the same at temperature within the approximate range of 1200 to 1800° F. until hardened, and in thereafter undergoing no substantial reduction in hardness after heating to any temperature up to about 1400° F., said steel containing about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% of metal of the group consisting of silicon and molybdenum, the balance of said steel consisting principally of iron.

2. An article subjected to use to elevated temperatures at least a portion of which is made of a steel according to claim 1.

3. A cutting, forming or shearing tool at least a portion of which is made of a steel according to claim 1.

4. A valve or valve element for internal combustion engines at least a portion of which is made of a steel according to claim 1.

5. An alloy steel, characterized in being hardened in excess of "C" 32 Rockwell by maintaining the same at temperature within the approximate range of 1200 to 1800° F. until so hardened, said steel being so hardenable while in the as forged, rolled or annealed condition, the resulting hardness of said steel being substantially independent of the rate of cooling from the hardening temperature, and said steel thereafter undergoing no substantial reduction in hardness after heating to any temperature up to about 1400° F., said steel containing about 18 to 35% chromium, less than 1% of nickel and manganese, and about 1 to 15% of metal of the group consisting of silicon and molybdenum, the balance of said steel consisting principally of iron.

6. An alloy steel characterized in being hardened by maintaining the same at temperature within the approximate range of 1200 to 1800° F. until hardened, and in thereafter undergoing no substantial reduction in hardness after heating to any temperature up to about 1400° F., said steel containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% silicon, the balance of said steel consisting principally of iron.

7. An alloy steel characterized in being hardened by maintaining the same at temperature within the approximate range of 1200 to 1800° F. until hardened, and in thereafter undergoing no substantial reduction in hardness after heating to any temperature up to about 1400° F., said steel containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% molybdenum, the balance of said steel consisting principally of iron.

8. An alloy steel characterized in being hardened by maintaining the same at temperature within the approximate range of 1200 to 1800° F. until hardened, and in thereafter undergoing no substantial reduction in hardness after heating to any temperature up to about 1400° F., said steel containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% of metal of the group consisting of silicon and molybdenum, the percentage sum of the molybdenum content, twice the silicon content and two-thirds the chromium content divided by twenty-five exceeding unity, the balance of said steel consisting principally of iron.

9. A heat hardened alloy steel, hardened by maintaining the same at elevated temperature within the approximate range of 1200 to 1800° F. and characterized in undergoing no substantial reduction in hardness on subsequent heating to any temperature up to about 1400° F., said steel containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% of metal of the group consisting of silicon and molybdenum, the balance of said steel consisting principally of iron.

10. A heat hardened alloy steel, hardened by maintaining the same at elevated temperature within the approximate range of 1200 to 1800° F. and characterized in undergoing no substantial reduction in hardness on subsequent heating to any temperature up to about 1400° F., said steel having a hardness in excess of "C" 32 Rockwell and containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% of metal of the group consisting of silicon and molybdenum, the balance of said steel consisting principally of iron.

11. A heat hardened alloy steel, hardened by maintaining the same at elevated temperature within the approximate range of 1200 to 1800° F. and characterized in undergoing no substantial reduction in hardness on subsequent heating to any temperature up to about 1400° F., said steel containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% silicon, the balance of said steel consisting principally of iron.

12. A heat hardened alloy steel, hardened by maintaining the same at elevated temperature within the approximate range of 1200 to 1800° F. and characterized in undergoing no substantial reduction in hardness on subsequent heating to any temperature up to about 1400° F., said steel containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% molybdenum, the balance of said steel consisting principally of iron.

13. A heat hardened alloy steel, hardened by maintaining the same at elevated temperature within the approximate range of 1200 to 1800° F. and characterized in undergoing no substantial reduction in hardness on subsequent heating to any temperature up to about 1400° F., said steel containing: about 18 to 35% chromium, under 1% of nickel and manganese, and about 1 to 15% of metal of the group consisting of silicon and molybdenum, the percentage sum of the molybdenum content, twice the silicon content and two-thirds the chromium content divided by twenty-five exceeding unity, the balance of said steel consisting principally of iron.

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