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ALLOY STEEL AND METHOD OF MAKING THE SAME

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This invention relates to the production of alloys which are not only capable of resisting the action of hot corrosive gases but are also hard at ordinary temperatures and retain a very considerable degree of hardness even at red heat.

More particularly, the invention relates to a method of heat treating a certain group of alloys having desirable heat and corrosion resisting qualities but low hardness to convert them into alloys having far greater hardness and do this without sacrificing the other good qualities of the initial alloys.

Both the method of heat treatment and the resultant product are new and are included within my invention.

This application is a continuation in part of my applications Serial Nos. 76,900 filed December 21, 1925 and 163,315 filed January 24, 1927.

Ordinary straight carbon steel has three properties, inter alia, which render its use for such purposes as automobile poppet valves disadvantageous:

(1) Low hot oxidation resistance,

(2) Loss of hardness when heated and cooled comparatively slowly.

(3) The $\underline{Ac_3}$ point is too low with medium carbon resulting in the valves being soft under one set of conditions and hard under another set of conditions and this change in physical condition produces warpage, fatigue cracks due to local break-down of crystalline structure, etc.

Oxidation or scaling by hot gases may be reduced by the use of chromium, nickel and silicon. These three ingredients separately or together, greatly affect the change points and the stability of the constituents of steel at varying temperatures.

In ordinary carbon steel the constituent or structure stable at high temperatures is austenite—relatively soft. As such steel is cooled slowly, it changes first into the hard martensite and then into much softer constituents or structures such as troostite, sorbite and pearlite. The austenitic form may be retained in part by cooling the hot austenitic steel exceedingly rapidly by quenching in ice water for example. Even with this rapid cooling, a large part of the austenite is converted into martensite. The change of martensite into troostite, etc., may however, be prevented by quenching.

As either or both chromium and nickel are added the austenitic structure becomes more and more stable with increasing percentages of these metals and, for example, with 20% of Ni and 15% Cr the alloy is substantially wholly austenitic irrespective of any kind of heat treatment. Another change as progressive additions of nickel and chromium are added, starting with zero nickel and chromium, is in the proportion of the normal low temperature constituents or structures, such as troostite, which are formed when the alloys are heated to say 1500° F. or below and cooled slowly. With a straight carbon steel, the hard martensite disappears almost entirely so that by such heat treatment, the hardness will drop to around 25 to 30 scleroscope.

With say 8% nickel and 12% chromium, sufficient of the martensite will be converted into such softer constituents by such heat treatment to give a scleroscopic hardness of around 48–55, and may be subsequently rehardened to about 58–62 scleroscope. The 48–55 alloy is soft enough to drill or machine, and at the same time, hard enough to withstand wear and abrasion to a marked degree. This advantageous result is only obtained with a 8–12 nickel-chromium alloy, if prior to heat treating at 1500° F. or below, the alloy has been specially heat treated to convert the alloy from the normal austenitic form into the martensitic form. If this special heat treatment is omitted the normally austenitic alloy when subjected to vibratory or other conditions such as are produced in drilling or sawing, is converted into hard martensite (not the machinable martensite-troostite mixture above referred to) which prevents further sawing or drilling.

With 8–12 nickel-chromium steel, the rate of transition of austenite into martensite is so slow that to convert the soft austenitic structure into the hard martensitic structure, you have to cool exceedingly slowly and ordinary air cooling is far too quick to accomplish this purpose. Even slow cooling without a preceding "soak" is insufficient to bring about complete change. Preferably, such an alloy is heated to 1600° to 1650° F. and held at that temperature for two to six hours, then it is allowed to cool 50° F. per hour to 1350° F. after which the alloy may be allowed to cool in the air. This gives a martensitic or martensitic-troostitic, etc., structure.

In other words, the transition of austenite into martensite and martensite into troostite, etc., are both inhibited by the addition of nickel and/or chromium until, especially when both nickel and chromium are used, the austenitic alloy is only converted into martensite form by a special heat treatment forming part of this invention.

Hardness tests have been made with an alloy of the following composition:

	Per cent		
Chromium	11.5	to	13.00
Nickel	7	to	8
Silicon	2	to	3
Carbon	.25	to	.35
Manganese	under		.50
Sulphur	under		.03
Phosphorus	under		.03

Such an alloy (which constitutes my preferred composition) when cast or after forging at high temperature and air cooling, is in the soft austenitic form and has a hardness of about 30 scleroscope.

When the alloy in austenitic form is reheated to a given temperature held at that temperature for eight minutes and then allowed to cool in air, the following results of such heat treating were obtained:

Temperature to which steel was reheated	Scleroscopic hardness
800° F.	30
1000° F.	30
1250° F.	30
1450° F.	30
1550° F.	31
1650° F.	34
1750° F.	34
1850° F.	34
1950° F.	30

When, however, the same steel was allowed to "soak" for four hours at 1650° F. and then allowed to cool, 50° F. per hour, to 1350° F. and finally air cooled from that temperature, it had a scleroscopic hardness of 61. This high hardness indicates the production of the martensitic structure from the previous austenitic form.

When this martensitic alloy was given similar heat treatments as those above given for the austenitic alloy, viz: reheat to a given temperature, hold at that temperature for eight minutes but quenching in oil instead of allowing to cool in air, the following results were obtained:—

Temperature to which steel was reheated	Scleroscopic hardness
950° F.	61
1050° F.	56
1150° F.	55
1250° F.	55
1350° F.	61
1450° F.	60
1550° F.	61
1650° F.	54
1700° F.	42

The drop in hardness when the temperature of reheating exceeds 1550° F. or thereabouts indicates the beginning of the conversion of the alloy into the soft austenitic form. The table shows, however, that heating and cooling the alloy up to 1500° F. does not greatly reduce its hardness, thereby making it an exceptionally valuable alloy for making such articles as internal combustion engine exhaust valves.

On the other hand, there is sufficient softening by heat treatment around 1150° to 1250° F. (which is more marked if the alloy is air cooled when the hardness will be around 50–52 scleroscope) to allow drilling and other operations required in the making of valves and other articles from the alloy.

The alloy in its austenitic form is peculiar in that it may be turned in a lathe without change of structure, but when drilled or sawn, rapidly turns into the martensitic form. Hence, turning operations are performed while the alloy is in its austenitic form. Then before drilling, it is converted into the martensitic-troostitic or somewhat similar forms by heating to 1150° to 1250° F. and cooling in air. The alloys are then in as soft a condition as they can be placed, so long as austenite is not formed.

The production of maximum softness in an 8–12 nickel-chromium alloy of non-austenitic structure may be attained in one or two operations. Preferably, the alloy is converted as above described by a "soak" at 1600° to 1650° F. followed by slow cooling to 1350° F. and then subsequently heated to around 1250° F. and cooled in air or quenched in oil, although in some cases the conversion may be brought about by the slow cooling continued to 1250° F. or lower, depending on the "lag" in structural change and air cooled or oil quenched at that temperature. In either of these ways the hardness is reduced.

While my preferred procedure is a long "soak" followed by slow cooling, I have found that the same results are obtained by a series of heat treatments, each of usual duration. The following table gives the hardness of an alloy of the above mentioned composition after a series of 10 heat treatments consisting of heating to 1450° F. and quenching in oil:—

No. of heat treatment	Hardness	
	Scleroscope	Brinell
1	32	172
2	37	182
3	40	189
4	43.2	210
5	42	205
6	43	205
7	44	238
8	47	260
9	56	279
10	57	316

In short, with alloys of the type in question, the normal austenitic form can be broken down into martensitic and other forms by extended heat treatment either in a single operation or spread over a number of such operations.

Now the alloys that are capable of being converted into martensitic forms by the ordinary heat treatment are in the martensitic form usually readily converted into troostitic, etc., forms, although with nickel-chromium alloys having considerably lower nickel and/or chromium content the change from the martensitic into softer forms takes place very slowly, requiring a soak at say 1250° F. for some hours followed by a slow cool.

These last-mentioned alloys are, however, martensitic after any ordinary heat treatment which precludes the possibility of machining while in a soft austenitic form.

My invention is broader than the specific chromium nickel silicon carbon iron alloys of its present embodiment, and includes all alloys of iron and added metals which are always austenitic under ordinary heat treatment but may be converted by prolonged heat treatment into martensitic or martensitic-troostitic form.

Further, my invention not only includes non-austenitic alloys having the above characteristics, but also the method of heat treatment by which an otherwise austenitic structure is converted into martensitic or martensitic-troostitic structure.

Broadly, this treatment consists in prolonging the normal times of heat treatment of alloys of this character. The preferred method of treating an alloy of my preferred composition consists in "soaking" for six hours at 1600° F. followed by slow cooling (50° per hour) for five hours or eleven hours in all. With alloys of different composition the required change in structure may be brought about by soaking for a shorter time, say 1, 2, or 4 hours, and the whole treatment may in some cases, even take longer than 11 hours to produce the desired results.

As above indicated the preferred method of heat treatment consists of (1) a "soak" at a constant temperature followed by (2) a slow cool (50° to 75° F. per hour) to allow for variations in transformation points with variations in the composition of the alloys. In some cases it may be possible, however, to eliminate the second step by carefully determining the temperature at which the first step should be carried out to suit the particular alloy being treated. The possibility of such change in procedure depends on the "lag" in change of form with temperature.

My present preferred specific means of securing a non-austenitic alloy having the desired characteristics is by means of additions of chromium, nickel and silicon. Using these added elements the proportions may vary over a considerable range.

In the first place, so far as the transition of austenite into martensite and martensite into troostite, etc., are concerned, chromium and nickel are largely interchangeable but the sum of these two elements should not greatly exceed 21.5% or be much lower than 16.5%. Above 21.5% the tendency is to produce alloys which, even with prolonged heat treatment cannot be converted into martensitic form. With proportions much below 16.5% it is difficult to form austenite and hence to make the alloy readily machinable. When lowered still further the tendency is to produce troostitic or similar structure when annealed from 1500° F. In other words the martensitic form is not sufficiently stable to prevent softening of the valve or the like during use.

While nickel and chromium are interchangeable so far as the transition from one form or structure to another is concerned, a different suituation is presented when the surface stability or resistance to oxidation by hot gases or the like is considered. Nickel tends to lower the surface stability noticeably with chromium below 9%, and to a much lesser degree above 9%, while chromium increases the surface stability. Nickel, however, has a desirable characteristic in that it increases the "red-hardness" of the alloy while chromium in large proportions has relatively little red-hardness.

To obtain the surface stability required by a valve together with great red-hardness it is desirable to add silicon to obtain the desired surface stability. Silicon does not appreciably affect the red-hardness. Hence, where a high degree of both red-hardness and surface stability are required high silicon should accompany high nickel. Low silicon may be used with low nickel although no serious disadvantageous results arise when high silicon is used with low nickel. For example, the following compositions may be given:

(1)	Chromium	12%
	Nickel	8%
	Silicon	2%
	Iron and carbon	Balance.
(2)	Chromium	8%
	Nickel	12%
	Silicon	4%
	Iron and carbon	Balance.

In general, the alloys should fall within the following limits:

Chromium	5 to 20%	13 to 21.5% (Chromium and Nickel combined)
Nickel	0 to 14%	
Silicon		1.5 to 5 %
Carbon		.10 to .75%
Iron		Balance.

Preferably, the limits are somewhat more restricted such as:

Chromium	8 to 16%	16.5 to 21.5% (Chromium and Nickel combined)
Nickel	4 to 12%	
Silicon		2 to 4 %
Carbon		.20 to .40%
Iron		Balance.

As indicated other alloying substances than chromium, nickel and silicon may be used in place of one or more of these constituents, either wholly or in part, which are capable of producing non-austenitic alloys having the above defined physical characteristics.

On the other hand, it is ordinarily desirable to avoid certain elements or keep them within small limits. In my preferred formula I have given such limits for manganese, sulphur and phosphorus.

I am aware that numerous changes in my methods for heat treating normally austenitic alloys may be made without departing from the spirit of my invention, and I do not desire to limit the patent otherwise than as necessitated by the prior art.

I claim as my invention:

1. The method of heat treating an austenitic alloy consisting principally of iron and about 11.5 to 13.0% chromium, about 7 to 8% nickel, about 2 to 3% silicon and about 0.25 to 0.35% carbon, including heating from two to six hours at about 1600 to 1650° F. and then slowly cooling to render such alloy martensitic and hard.

2. An alloy having a martensitic structure and consisting principally of chromium, nickel, silicon, carbon and iron, in which the combined chromium-nickel content is between about 13.5 and 21.5% and the chromium is not substantially less than 5% or substantially greater than 20%, silicon about 1.5 to 5%, the silicon being high with nickel high and carbon about 0.15 to 0.75%.

3. An alloy having a martensitic structure and consisting principally of chromium, nickel, silicon, carbon and iron, in which the chromium is between 11.5 and 13%, the nickel between 7 and 8%, the silicon between 2 and 3% and the carbon between 0.20 and 0.40%.

4. An alloy having a martensitic structure and consisting principally of iron, chromium, nickel, silicon and carbon in which the chromium is between about 5 and 20% and the nickel between about 4 and 12%, with a combined chromium nickel content not substantially less than 16.5%.

5. An alloy as in claim 4 in which the silicon is between about 1.5 and 5.0%, the silicon being high with nickel high.

6. A method of heat treating ferrous alloys of nickel and chromium wherein the combined chromium-nickel content is between 15.0 and 21.5%, and the chromium is not substantially less than 5% or substantially greater than 20%, which comprises heating the alloys at a temperature of between 1600° and 1700° F. for a period of from two to six hours, cooling the alloys to approximately 1300° F. at a rate of approximately 50° F. per hour, and air cooling the alloys from that temperature.

7. A valve for an internal combustion engine composed of an alloy as in claim 2.

8. A valve for an internal combustion engine composed of an alloy as in claim 4.

9. The method of heat treating normally austenitic alloy consisting principally of chromium, nickel, silicon, carbon and iron, in which the combined chromium, nickel content is between about 15.0 and 21.5% and the chromium is not substantially less than 5% or substantially greater than 20%, including heating the alloys to from about 1250° to 1700° F. for a period of about 2 to 11 hours and slowly cooling the alloys to render the same martensitic.

10. The method as in claim 9 in which the alloy is heated for a period of from about 2 to 6 hours and then slowly cooled at a rate not substantially in excess of 75° F. per hour for about 4 hours.

11. The method of heat treating normally austenitic alloys consisting principally of chromium, nickel, silicon, carbon and iron, in which the combined chromium-nickel content is between about 15.0 and 21.5% and the chromium is not substantially less than 5% or substantially greater than 20% including heating the alloys to from about 1600° to 1650° F. for a period of from about 2 to 6 hours and slowly cooling the alloy to render the same hard and martensitic.

In testimony whereof I have hereunto subscribed my name.

RICHARD E. BISSELL.