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FERROUS ALLOY

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For many years, alloy steels comprising substantial quantities of nickel and chromium have been known to possess certain valuable characteristics, but at the same time they are subject to certain defects; for example, where the alloy content is low, they show a tendency to scale at high temperatures, and as the nickel content goes up, they become increasingly difficult to machine though this difficulty is not directly proportioned to the nickel increase. In this application where I speak of an alloy containing substantial quantities of nickel and chromium, I mean an alloy which contains between 5% and 35% of nickel and between 5% and 25% of chromium.

The critical point of chromium steels is raised somewhat as the chromium content is increased. On the other hand, with nickel steels, the critical points both on heating and cooling are depressed as the nickel content is increased, and this is particularly true of the critical points on cooling. Steels high in nickel are generally Austenitic and non-magnetic even when very slowly cooled.

If a steel contains both chromium and nickel, the predominating element as to critical points is the nickel which tends to lower the critical points and also causes the change or reversibility on cooling to be very slow or sluggish and in some cases to disappear entirely, so that as the nickel content is increased, the alloy first becomes increasingly air-hardening and then with a still greater nickel content becomes Austenitic or non-magnetic. If the chromium content is increased with a given nickel content, there is a less rapid approach to the Austenitic condition than is the case where the chromium is constant and the nickel content progressively raised.

Steels containing substantial quantities of nickel and chromium that are just about in the complete Austenitic condition or are bordering thereon, are very hard to machine due to the wear-hard properties of the alloy which tend to form so-called mechanical Martensite. Even if the alloys are well on the Austenitic side, they are still difficult to machine (probably due to the same cause) even though the alloy may be soft as measured by the Brinell test or even by the file. The machining difficulties are a direct result of the lowering or disappearance of the critical point, which as stated results largely from the presence of the nickel in the alloy.

The nickel in the alloy imparts toughness, and where the nickel content is high adds resistance to acid attack (particularly in the case of dilute sulphuric or hydrochloric acid) and adds resistance to rust and surface sealing at high temperatures. If the nickel content is low, say under 5%, the nickel content actually causes the alloy to scale at high temperatures more than if the high chromium alloy were nickel free, and so unless the nickel is at least 5%, I prefer to have the alloy nickel free.

I have discovered that if aluminum within the ranges hereinafter set forth is added to these ferrous alloys comprising substantial quantities of nickel and chromium, the transformation points are raised and the aluminum appears in this respect to work against the nickel, thereby imparting to the alloy the property of ready machinability without substantially detracting from the desirable quality of toughness. If aluminum is added the alloys are no longer irreversible (except where the nickel content is very high) and can be well annealed by heating to a high temperature and slowly cooling. The correct temperature for each specific analysis can be readily determined by the usual method. The presence of the aluminum also imparts to the alloy a very high degree of resistance to oxidation at high temperatures and does not substantially detract from the alloy's usefulness as an acid resisting alloy or from its rust-resisting characteristics.

By including aluminum in a ferrous alloy comprising substantial quantities of nickel and chromium, I produce an alloy steel which is readily rolled or drawn, can be formed hot or cold, has very little tendency to seam or crack during hot mechanical operations, and which is adapted to form ingots and castings of great soundness. My new alloy steel is particularly valuable for wrought metal articles which are to have high mechanical strength and which demand resistance to surface deterioration at elevated temperatures, for in this respect they are greatly superior to articles of an alloy containing a like amount of chromium and nickel but without the aluminum content. Such articles also show high resistance to the attack of nitric, sulphuric and hydrochloric acids which is increasingly so as the chromium and nickel content is raised, though they are not particularly resistant to the action of hydrochloric acid. They have excellent rust-resisting qualities, and in addition they may readily be machined showing in this respect considerable superiority to articles made of an alloy of like chromium and nickel content but without aluminum.

The percentage of aluminum to be included in the alloy will vary somewhat, depending upon the percentage of the other constituents but should not be above 6%, for if more than 6% is

actually alloyed it causes the product to be brittle in the cast condition, or when it is heated as for forging, so that if the alloy contains more than 6% of aluminum it can be forged only with very great care and certainly not by the methods usually employed in the steel industry.

On the low end, it will be found that the aluminum should ordinarily constitute at least 1% of the whole, but if the chromium content is high and the nickel content low (under 8%) then as little as .3% of aluminum (included as an actual alloying metal as distinguished from entrapped aluminum oxide) will add materially to the heat resistance and machinability. As the nickel content is raised, more aluminum is desirable, but between 1% and 4% of aluminum will be found to meet most of the requirements for a commercial alloy of the type under discussion.

The aluminum content reduces the amount of hardness that can be produced in these alloys by heat treatment, although a hardness of about 500 to 600 Brinell can be obtained in alloys having less than about 17% chromium and nickel lower than 5% and aluminum less than about 3%. The higher the carbon the greater the hardness, particularly when the alloy is quenched from a high temperature, but in general the carbon content should be kept low, preferably below 1% and certainly under 1.5% and may be reduced to only a trace. Unless the alloy has a high nickel and chromium content, aluminum will prevent the formation on slow cooling, of the non-magnetic Austenitic structure and in the case of Martensitic or hardenable alloys will prevent maximum hardness being obtained, so that there may be maintained a desirable toughness and good physical properties when the alloy is tempered or drawn after quenching. In this connection, it may be stated that the aluminum-nickel-chromium alloys seem to be improved as to toughness if given a high draw after a very slow cool during the annealing treatment. This step, however, is not always necessary.

Even if the aluminum-chromium-nickel alloy steels of my invention are not cooled sufficiently slowly and are non-magnetic, they can be more readily machined than is the case with an alloy containing similar carbon, chromium and nickel contained in iron but without the aluminum, because in the case of my alloys the troublesome formation of surface hardening due to the rubbing of the tool on the alloy is not so apparent; in fact, my alloys, even when non-magnetic, can be readily cut with a reciprocating hack saw.

Silicon is usually present as an incident to the melting operation, but should be kept low, preferably under 1%, though this figure may for some purposes be allowed to rise to as high as 5%.

Other alloying elements may be added to give some special characteristics to the product and for this purpose it is preferable to use metals which have a high melting point or have a high melting point oxide which will not react with aluminum oxide in the presence of iron to form at high temperatures a readily detachable porous scale. Such metals include molybdenum, tungsten, vanadium, tantalum, uranium, cobalt and copper. Titanium and zirconium meet the other requirements but are difficult to incorporate and for that reason are not recommended. Manganese, although not adding to the scale resistance, appears to be useful in the alloy in moderate quantities, as it seems to assist in making the steel more readily rollable. Such additional ingredients as are used should be employed only in small percentages, as for example under 6% in the aggregate and in most cases under 2% for any one of them, as they may interfere with machinability and impart but little merit to the alloy.

Of the ingredients stated, I prefer to use copper with optional manganese, as copper readily enters into the aluminum carrier, which is hereafter described, lending itself quickly to the formation of a copper-aluminum alloy, or a copper-aluminum-iron alloy.

As has already been indicated, the alloys produced under this invention are in some cases Austenitic or non-magnetic and in other cases are magnetic. The magnetic or non-magnetic characteristic has its principal significance in indicating the crystalline structure or atomic arrangement. In ferrous alloys the magnetic condition indicates that the alloy is capable of being softened for machining by proper heat treatment and that the alloy probably exists in the alpha phase. In general, where ferrous alloys are magnetic, the carbides are found largely out of solution, and where non-magnetic the carbides are largely in solution. As has been pointed out, in some instances where my alloys are non-magnetic when cooled rapidly or even fairly slowly, they can be rendered magnetic and changed to the alpha phase by very slow cooling.

The alloy steel of the present invention is adapted for a large number of uses requiring resistance to surface deterioration together with marked toughness, good physical properties and machinability. Among numerous uses the following may be referred to solely for the purpose of illustration: turbine bucket blades, machinery parts, pump shafts, acid resisting apparatus, valves for internal combustion engines and valves for handling water or steam. My steel may also be used for articles and products formed from sheets, such as barrels, particularly those having a welded joint. This alloy is not very prone to material grain growth and when subjected to high temperatures for short periods the grain growth is almost negligible, so that the welding temperature will not materially injure the qualities of the sheet and if the added alloy used in the weld is of the same analysis, this likewise will generally be of small crystalline structure. Such a weld is not hard, and if reheated or annealed after welding, the welded joint will be tough. The alloy has a very pleasing color and will take a high polish.

The alloy made in accordance with this invention cannot readily be hardened, particularly when either the aluminum or nickel content is high. Double heat treatments, such as heating to a high temperature, and cooling, and subsequently reheating and cooling again, can be made use of. To give good machinability the steel should be subjected to a high drawing temperature, such as heating to above 1200 degrees F. and preferably to above 1600 degrees F. after which the steel is cooled, preferably slowly. Special heat treatments can be resorted to when the alloy, particularly in the middle ranges, is required to have some special physical property.

All of these alloys containing aluminum in excess of 2% should be cast at as low a temperature as possible, otherwise there is a tendency for the alloys to be of large crystal size and therefore annealing is desirable if the alloys are cast at ordinary temperatures, or temperatures higher than ordinary. The alloys should be forged at a rather high temperature, particularly in the initial stages.

The electric furnace is preferable for melting but not absolutely essential. I find that the most advantageous method of adding the aluminum (though this is not essential to the formation of the alloy) is by first preparing an alloy which is rich in aluminum (together with other ingredients which are to be included in the finished product) and adding such alloy to the bath after first preheating it. The bath is provided with the usual slag cover and the heated alloy is thrown violently on this so that it passes through the slag and down into the molten metal. On rising to the surface of the bath it remains under the slag blanket and its surface is thoroughly wetted by the slag and thereby protected against loss by oxidation on its upper surface. As it dissolves very rapidly in the bath there is substantially no loss of aluminum by oxidation.

Such preliminary alloy should contain sufficient ingredients other than aluminum substantially to raise the melting point and specific gravity, but at the same time it is advantageous that enough aluminum be present so that an undue amount of such preliminary alloy will not have to be handled. Thus, for ordinary commercial results I find it useful to have present about 50% of aluminum and the balance largely iron, with which may be included nickel, chromium, copper, manganese or other alloying ingredients, or other material such as lead, which will not enter into the final alloy, may be added. It is to be understood that the figure given is not in any way a limitation, for the aluminum content may be reduced as low as commensurate with the requirements of the final product and on the high side the aluminum percentage may be raised to 75% or higher, without substantial losses, but in general the aluminum content of this preliminary alloy should be between 25% and 75%.

The preliminary aluminum alloy may be made according to any of the known processes of making aluminum alloys, but I prefer to melt the aluminum with a fluid slag such as a chloride or fluoride slag in an electric furnace and then add the iron or other alloying ingredients. The heat from a previous charge will ordinarily be sufficient to melt the aluminum and the furnace can again be brought up to heat after the higher melting point elements are added. If the alloy thus formed is provided with a very fluid slag it may be poured down a trough under its slag blanket and allowed to run out on a pig bed. An alternative method is to heat the aluminum and other elements separately and then pour the higher melting point elements into the aluminum through the protective slag covering of the latter. If the ingredients are mixed in a crucible or vessel, the alloy can be poured into an ingot mold without much loss, for the distance the falling stream has to pass through the atmosphere is short, and ordinarily the temperature will be lower than where the mixture is made in the electric furnace. However, these operations are slow, and so undesirable for quantity production.

When it is desired to use this preliminary alloy rich in aluminum, such alloy in fairly large chunks is preheated to a temperature above 1000° F. and preferably to a good read or yellow heat. Apparently during this heating the alloy scales slightly and so has a coating of oxide on it which is rough and readily dissolved by the slag, or adhered to by the molten slag, so that the slag wets this alloy and keeps it submerged under the overlying slag. In fact, after the alloy has been added to the bath, the metal can be safely stirred while the aluminum addition is melting so as to insure good mixing. This method of operation reduces the aluminum losses to a minimum so that generally the calculated quantity of aluminum is found in the finished metal without loss and gives a final alloy of unusually even composition. Inasmuch as very little of the aluminum is oxidized, my method produces a metal practically free from alumina inclusions, whereas alloys made by adding aluminum directly to the metallic bath result in heavy losses of aluminum and give a relatively dirty ferrous alloy including substantial amounts of alumina. In the same way, if the aluminum is added in the ladle by pouring the ferrous alloy on to the aluminum in either solid condition or molten, a dirty steel results high in alumina inclusions and there is a heavy aluminum loss so that a consistent alloy content cannot be maintained between various constituents. I have also found that if the alloy rich in aluminum is added to the bath without being pre-heated, the resulting product is more apt to include alumina and show a loss of aluminum in the finished product than where the added alloy is pre-heated as stated.

For the purposes of illustration, I give a number of sample analyses of various alloys which may be roughly grouped in three categories. In these examples it is to be understood that the figures given represent parts per hundred.

The first group of alloys is as follows:

C..... .07 Cr..... 9. Ni..... 11. Al..... 3.	C..... .10 Cr..... 10. Ni..... 8. Al..... 3.	C..... .20 Cr..... 11. Ni..... 5. Al..... 1.	C..... .25 Cr..... 10. Ni..... 8. Al..... 2.
C..... .50 Cr..... 10. Ni..... 6. Al..... 2.	C..... .40 Cr..... 10. Ni..... 5. Al..... .5 Si..... .5 Mn..... .60	C..... .30 Cr..... 10. Ni..... 12. Al..... 2. Si..... .50 Mn..... .30	

The alloys were magnetic when cooled either fairly slowly or very slowly, were strong, tough and readily machinable. All of them forged very well without any evidence of a tendency to crack or split. Soaking up to a forging heat of about 2000° to 2300° F. is desirable.

The second group of alloys is as follows:

C..... .40 Cr..... 8. Ni..... 20. Al..... 2.50 Si..... .30 Mn..... .50	C..... .20 Cr..... 7. Ni..... 17. Al..... 6. Si..... .30 Mn..... .40	C..... .10 Cr..... 8. Ni..... 17. Al..... 1. Si..... .25 Mn..... .60	C..... .25 Cr..... 9. Ni..... 17. Al..... 2. Si..... .30 Mn..... .20
C..... .45 Cr..... 10. Ni..... 20. Al..... 3. Si..... .40 Mn..... .15	C..... .25 Cr..... 5. Ni..... 22. Al..... 3.0 Si..... .35 Mn..... .20	C..... .05 Cr..... 10. Ni..... 20. Al..... 2.4 Si..... .30 Mn..... .50	C..... .25 Cr..... 13. Ni..... 13. Al..... 4. Si..... .25 Mn..... .20
C..... .05 Cr..... 15. Ni..... 15. Al..... 3. Si..... .40 Mn..... .45	C..... .20 Cr..... 17. Ni..... 11. Al..... 3. Si..... .35 Mn..... .60		

These alloys were non-magnetic when cooled down moderately slowly from a temperature of about 1950° F. but when cooled very slowly from a like temperature were magnetic, quite soft, readily machinable and showed excellent physical properties and toughness. The example containing 6% aluminum, showed some tendency to crack or split in the corners when forged, and

required careful handling and frequent reheating. This trouble appears to be augmented with a higher nickel and chromium content; otherwise all of these examples forged readily.

The third group of alloys is as follows:

C ..... .30	C ..... .20	C ..... .40
Cr 11.50	Cr ..... 14.	Cr ..... 17.
Ni 29.50	Ni ..... 25.	Ni ..... 20.
Al 2.5	Al ..... 4.	Al ..... 3.
Si ..... .40	Si ..... .25	Si 1.5
Mn ..... .60	Mn ..... .30	Mn ..... .60

These alloys remained non-magnetic even though cooled very slowly from about 1950° F., yet they were soft, strong and very tough. They were readily machinable and forged extremely well.

It is to be understood that these examples are given primarily for the purposes of illustration and may be modified in many particulars without departing from the spirit of my invention.

In the foregoing analyses, the iron content is not included, but it is of course understood that subject to the additions of small quantities of high melting point elements approximately as stated above, and subject to the presence of small quantities of other elements such as the impurities found in steels, the balance is iron. Accordingly to cover this situation, I may state that in addition to the elements named in the analyses, the balance is substantially all iron.

What I claim is:

1. A ferrous alloy characterized by its malleability and machinability and resistance to hot oxidation in which silicon is present as a result of melting operations but the silicon does not exceed about 1% and the sum of the silicon and any manganese present is substantially below 3% which comprises chromium between about 5% and 25%, nickel between 5% and 35%, carbon not over 1.5% and under 1% for nickel not over 10% and aluminum between about .3% and 4.5% but in excess of the carbon the balance being substantially all iron.

2. An alloy as specified in claim 1, in which the nickel range is between 5% and 27% and the chromium range is between 5% and 20%.

3. An alloy as specified in claim 1 in which the nickel range is between 5% and 27% and the chromium range is between 5% and 20% and the sum of the nickel and chromium is over 20%.

4. An alloy as specified in claim 1, in which the nickel range is between 10% and 15% and the chromium range is between 12% and 17% and the sum of the aluminum and silicon is between 1.5% and 6%.

5. A ferrous alloy characterized by its resistance to oxidation at high temperatures and its forgeability and machinability, of substantially the following analysis: nickel between 11% and 35%, chromium between 5% and 25%, aluminum between .5 and 6%, silicon incident to the melting operation but less than about 1%, carbon under 1.5% and less than the aluminum, the balance being substantially all iron.

6. An alloy as specified in claim 5, in which the nickel is between 11% and 27% and the chromium is between 7% and 22%.

7. A ferrous alloy characterized by its resistance to oxidation at high temperatures and its forgeability and machinability, of substantially the following analysis: nickel between 5% and 18%, chromium between 5% and 17%, aluminum between .5% and 5%, carbon under 1½% and less than the aluminum, silicon incident to the melting operation but less than about 1% and the sum of the nickel, aluminum, carbon and silicon being in excess of the chromium the balance being substantially all iron.

8. A malleable steel valve element characterized by its forgeability and resistance to hot oxidation, of substantially the following analysis: nickel between about 11% and 25%, chromium between 5% and 17%, silicon incident to the melting operation but less than about 1% and aluminum between .5% and 5% and in excess of any carbon present, the balance being substantially all iron.

9. A malleable steel valve element characterized by its forgeability and resistance to hot oxidation, of substantially the following analysis: nickel between 5% and about 35%, chromium between about 5% and about 25%, aluminum between about .5% and 6%, silicon incident to the melting operation but less than about 1%, carbon not over 1½% and under 1% for nickel not over 10% and less than the aluminum, the balance being substantially all iron.

PERCY A. E. ARMSTRONG.

CERTIFICATE OF CORRECTION.

Patent No. 1,941,648. **January 2, 1934.**

PERCY A. E. ARMSTRONG.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 56, for "sealing" read scaling; and line 101, for "hydrochloric" read hydrofluoric; page 3, line 69, for "read" read red; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of January, A. D. 1934.

F. M. Hopkins

(Seal) **Acting Commissioner of Patents.**