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HARDENED ALLOY STEEL AND PROCESS OF HARDENING SAME

Francis B. Foley, Philadelphia, Pa.

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This application is a continuation in part of an application filed by me December 20, 1930, Serial No. 503,762.

In the art of ferrous metallurgy it is well known to harden steels, capable of hardening, by a process of heating them above the so-called critical temperature A_{c1} , at which the material acquires the capacity to harden, and then hardening by a sudden cooling. If the material be of very high carbon, and the quenching sufficiently rapid, or if the material contains sufficient alloys to make it wholly or partially austenitic on less drastic quenching, it is well known that an increase of hardness may be obtained on material so quenched by a drawing or tempering at a temperature much below the temperature of hardening but sufficiently high to permit of the decomposition of austenite into martensite without causing the decomposition of the martensite into the softer phases of troostite or sorbite. Certain compositions readily made austenitic require for successful hardening in this manner a long continued heating at a moderate temperature, and such a process is known in the art.

I have discovered another way of hardening certain alloy steels, provided they contain both nickel and aluminum, which consists in heating the steel to a temperature which will cause absorption of the nickel and aluminum (presumably as the compound NiAl) in ferrite, cooling at a rate which will prevent the NiAl from precipitating, that is, so as to retain nickel and aluminum in solid solution, then reheating to a temperature high enough to cause precipitation of the microscopic or ultra-microscopic particles of the dissolved nickel and aluminum but not high enough to permit rapid re-solution of the nickel and aluminum, and then so cooling as to cause the nickel and aluminum to form a crystalline phase with greatly increased hardness.

A remarkable feature of the process is that the initial heating, as well as the subsequent heating, may be to a temperature below, and even very decidedly below, the A_{c1} point of the metal. Such a treatment applied to the usual steels of commerce would result in about the softest possible condition, but applied to the steels to which I have discovered it to be applicable, it may result in an increase of hardness as great as 150 to 200 points on the Brinell scale of hardness. Nickel-aluminum steels containing too little carbon to show much increase in hardness by the usual methods of quenching from above the critical temperature may, by my method, be made to show a great increase in hardness.

An example of the type of alloy steel which is susceptible to this new treatment is one containing C 0.07%, Mn 0.41%, Si 0.16%, Ni 5.10%, Al 2.36% with low phosphorus and sulphur. Such a steel is not appreciably hardened by quenching from temperatures above its A_{c1} , which may be in excess of 1700 degrees F., and is softened by quenching from below its critical temperature. In my process this steel may be heated to a temperature (say 1300° F.) much below its critical temperature and held at that temperature for the time required to cause solution of the NiAl and then cooled at a rate which will prevent the NiAl from precipitating during cooling. The steel, having the nickel and aluminum in solution in the ferrite, has been actually softened and has a hardness of but 207 Brinell scale. The steel may now be heated to a temperature of about 1050° F. and held at that temperature until the NiAl is precipitated and then cooled. Nickel and aluminum will be found to have combined to form a new crystalline phase resulting in an increase of hardness of the steel to 409 Brinell scale.

While I cite the above example of the application of this method of hardening to a steel otherwise relatively unhardenable, I have found that it may be applied to steels which are hardenable by the well known methods of hardening steel and which contain other alloying elements besides those producing the phase or compound involved in the hardening which is the subject of this discovery. An example of such a steel and a description of a specific procedure which will effect its hardening are given hereinafter.

It is impossible to specify any particular ranges of temperature within which the steel may be successively heated. The possible ranges of temperature vary widely with different compositions. Nickel lowers the critical temperature while aluminum raises the critical temperature to a substantially greater degree than it is lowered by the nickel. For example, in the specific composition above specified, the aluminum increases the critical temperature by about 330° F.

Even with a particular composition, the ranges within which the steel may be successively heated are very wide ranges. In the case of a steel having the composition above specified the first heating may be to any temperature below the critical and above about 1050° F. If, however, the temperature of heating be relatively high the duration of heating may be short, since a short time will be required to dissolve the NiAl, and the cooling must be sufficiently rapid to re-

tain the NiAl in solid solution. If the temperature be relatively low, the duration of heating must be correspondingly long in order to dissolve the NiAl. In all cases, however, rapid cooling is preferred so as to insure the retention of the nickel and aluminum in solid solution; and in the case of large masses, rapid cooling may be necessary in practically all cases.

The range within which the temperature of the second heating may be carried is distinctly below that of the first heating, although the upper limit of the second heating range may somewhat overlap the lower limit of the first heating range. In the case of the second heating, as of the first, time, as well as temperature, is a factor. If the second heating be to within the lower part of the permissive temperature range for the first heating, say to a permissive maximum of about 1250° F.; in the case of the composition specified, the precipitation of NiAl will be very rapid and the time of heating must be short and the cooling must be rapid, as otherwise there will be re-solution of the NiAl. The lower the temperature of the second heating, the longer must the steel be maintained at that temperature and the slower the permissive rate of cooling; cooling in the furnace being permissive if the second heating is not too high a temperature. Unless the second heating is to within the upper zone of the permitted temperature range, the cooling may proceed at any rate. Another factor that affects the time of heating and cooling is the factor of mass. It is usually desirable to cool large masses rapidly. Theoretically, there is no lower limit for the temperature range of the second heating, but practically the heating should not be to a temperature below about 700° F., since below that temperature the time of heating would be impracticably long. In general, it may be stated that the only temperature requisite for the second heating, other than that it must be with a range whose upper limit is from three hundred to five hundred degrees F. below the critical, is that it must be high enough to cause precipitation of NiAl but not so high as to permit rapid re-solution of the NiAl.

In the case of the composition specified the practical procedure would be to heat to between 1050° and 1700° F., preferably in the neighborhood of 1300° F. and cool by quenching, if the mass be large, or by quenching or air cooling, if the mass be small, and then heat to within the range 700° to 1250° F., preferably in the neighborhood of 1050° F. and cool preferably by quenching or in the air if the mass be large, or in the air if the mass be small.

It is not prohibited, in the first heat treatment, with compositions similar to that above specified, to heat to substantially above the critical temperature, but such high heating will result in no appreciable additional hardening and is distinctly disadvantageous, since it increases the cost, deteriorates the heat treating furnaces, and increases the difficulty, especially in the case of large masses, of cooling sufficiently rapidly to prevent the NiAl from precipitating during cooling. Even when the composition is such as to enable a somewhat increased hardness to be obtained by heating to above the critical temperature, it may be desirable to avoid it, since it is desirable, in this treatment, to take advantage of the softening effect produced by heating to and cooling from below the critical temperature, thereby facilitating the machining, the subse-

quent tempering heat being too low to cause any alteration of the finished surfaces.

In the case, however, of steels containing, besides nickel and aluminum, other alloying elements which render the steel distinctly hardenable by well known methods of hardening steel, it may be advantageous, although it is not necessary, in the case of such compositions, to precede the two heat treatments hereinbefore described by heating to above the Ac₁ and then cooling rapidly. Such a steel, for example, may contain, in addition to nickel and aluminum, chromium in such proportions that rapid cooling from well above its critical temperature renders it austenitic and consequently soft. Reheating such a steel to a proper temperature below its critical temperature hardens it somewhat by a conversion of the austenite to martensite. It is not, however, fully hardened if an element, such as aluminum, is present. In this latter case another reheating to a lower temperature followed by a cooling, normally in air, will result in a further increase in hardness due to the precipitation of the nickel aluminum phase. An example of such an alloy steel is one containing: C 0.66%, Mn 0.63%, Si 0.88%, Ni 2.83%, Cr 11.30%, Al 3.47%, having a critical temperature of about 1750 degrees F. Rapidly cooled from 2100 degrees F., this steel has a hardness of 201 Brinell and is practically non-magnetic. Reheating to 1400 degrees F. and cooling rapidly increases the hardness to 352 Brinell and renders the steel magnetic, due to the conversion of the non-magnetic austenite to martensite. A second reheating to 1100 degrees F. permits of the liberation of the nickel-aluminum phase from the martensite with a further increase of the hardness to 467 Brinell. Reheating to 1100 degrees for 1 hour immediately following the quenching from 2100 degrees F. does not increase the hardness of the austenite above 201 Brinell. It is necessary first to convert the austenite to martensite from which the nickel-aluminum phase is readily liberated by the low temperature treatment.

The process is not limited in its application to nickel-aluminum steel containing the other constituents enumerated in the above examples, nor is the process inapplicable to steel containing still other constituents which it may be desirable to add, in minor proportions, to secure the well known effects which such constituents produce in steel. It is believed that the process is applicable to most alloy steels containing any percentages of aluminum between .5 and 10% and of nickel between .5 and 20%. It is believed, however, that if the compound NiAl is formed, which is presumed but not conclusively demonstrable, such compound comprises by weight two parts of nickel and one part of aluminum, the excess aluminum or nickel, as the case may be, not entering into the described process of solution and precipitation. The maximum permissive percentage of nickel is limited by the amount which would render the steel permanently austenitic, which in no composition would be over 25%. In some compositions, the nickel, in much lower proportions, would render the steel permanently austenitic. For example, if the composition contains as high as about 18% of chromium, the process would not be operative if the nickel content were above about 8%.

I have also discovered that the process is applicable to the hardening of alloy steels in which the nickel is replaced, in whole or in part, by molybdenum and (or) copper. In each case a

compound forms, which is soluble above a certain temperature and is insoluble below that temperature, and the steel itself is in the Alpha form. Thus, aluminum and molybdenum, and aluminum and copper, both cause substantial precipitation hardening, although in a less degree than aluminum and nickel; the advantages of the process, when applied to nickel-aluminum steel, being distinctly more pronounced than when applied to copper-aluminum and molybdenum-aluminum steel. While, of course, nickel, copper and molybdenum are not equivalent so far as concerns the qualities which they impart to the steel, they should be understood as equivalents so far as concerns the herein described process of hardening.

Except in the case of those compositions, such as contain a substantial proportion of chromium, or high carbon, which are distinctly hardenable by well known methods of hardening steel, the hardened low carbon nickel-chromium alloy steels herein described are compositions heretofore unknown in the art and are distinguishable from other hardened alloy steels of similar composition by their comparatively great hardness. Known methods of hardening steel, when applied to these alloys, will not produce a hardness in excess of about 280 on the Brinell scale, whereas my improved low carbon nickel-aluminum steel may have a hardness on the Brinell scale substantially in excess of 400.

It is known in the art that the hardness or strength and toughness of ferrous alloys containing substantial percentages of berillium may be brought, by suitable heat treatment, to very favorable values. So far as I know, only such iron-berillium alloys are comparable in quality to compositions embodying my invention. The percentage of berillium required in such ferrous alloys is usually about four per cent. and may be as high as thirteen per cent. Such compositions have obviously no commercial utility, since the cost of berillium is over one hundred times that of nickel or aluminum, making the ferrous alloy prohibitive in cost. My improved composition contains no berillium and must not contain it in any appreciable proportion.

Having now fully described my invention, what I claim and desire to protect by Letters Patent is:

1. The process of hardening alloy steel containing substantial but minor proportions of nickel and aluminum not exceeding a combined percentage of 30% which comprises heating the steel to such temperature below its A_{c1} as will cause the solution of the nickel and aluminum in ferrite and cooling at such rate as will retain the nickel and aluminum in solid solution, and then reheating to a temperature at least 300° F. below its A_{c1} and cooling, the time and temperature of reheating and rate of cooling being

such as will cause nickel and aluminum to form and retain a new crystalline phase imparting greatly increased hardness.

2. The process of hardening alloy steel containing substantial but minor proportions of nickel and aluminum not exceeding a combined percentage of 30% which comprises heating the steel to such temperature below its A_{c1} and for such time as will cause the solution of the nickel and aluminum in ferrite and cooling at such rate as will retain the nickel and aluminum in solid solution, and then reheating to such temperature below the temperature of the first heating and for such time as will effect precipitation of nickel and aluminum, and cooling, whereby the nickel and aluminum form a new crystalline phase imparting greatly increased hardness.

3. The process of hardening alloy steel containing substantial but minor proportions of nickel and aluminum not exceeding a combined percentage of 30% which comprises first so heating the steel to within a temperature range of $50-500^{\circ}$ F. below its A_{c1} for such time and followed by so cooling that the nickel and aluminum will be in solid solution and the steel will be relatively soft and machinable, and then so heating the steel to within a temperature range of $400-1000^{\circ}$ F. below its A_{c1} and so cooling as to precipitate nickel and aluminum and cause them to form and retain a new crystalline phase and produce a steel having greatly increased hardness.

4. The process of hardening alloy steel containing substantial but minor proportions of nickel and aluminum in which the nickel ranges from .5 to 20% and the aluminum ranges from .5 to 10%, which comprises heating the steel to a temperature range of $50-500^{\circ}$ F. below its A_{c1} for such time as will cause the solution of nickel and aluminum in ferrite, then cooling at such rate as to retain the nickel and aluminum in said solution and produce a soft machinable steel, then reheating the steel to within a temperature range of $400-1000^{\circ}$ F. below its A_{c1} and high enough to cause precipitation of nickel and aluminum but not high enough to cause their rapid re-solution and then so cooling as to cause the nickel and aluminum to retain the new crystalline phase imparting greatly increased hardness.

5. A heat treated low carbon substantially berillium-free steel containing, in addition to manganese and silicon in proportions usual in alloy steel, and as the chief alloying ingredients, nickel .5 to 20% and aluminum .5 to 10%, in which effective portions of nickel and aluminum are precipitated from solution thereof in ferrite and in crystalline phase, the balance being substantially iron, said steel having a hardness not less than 320 on the Brinell scale.

FRANCIS B. FOLEY.