

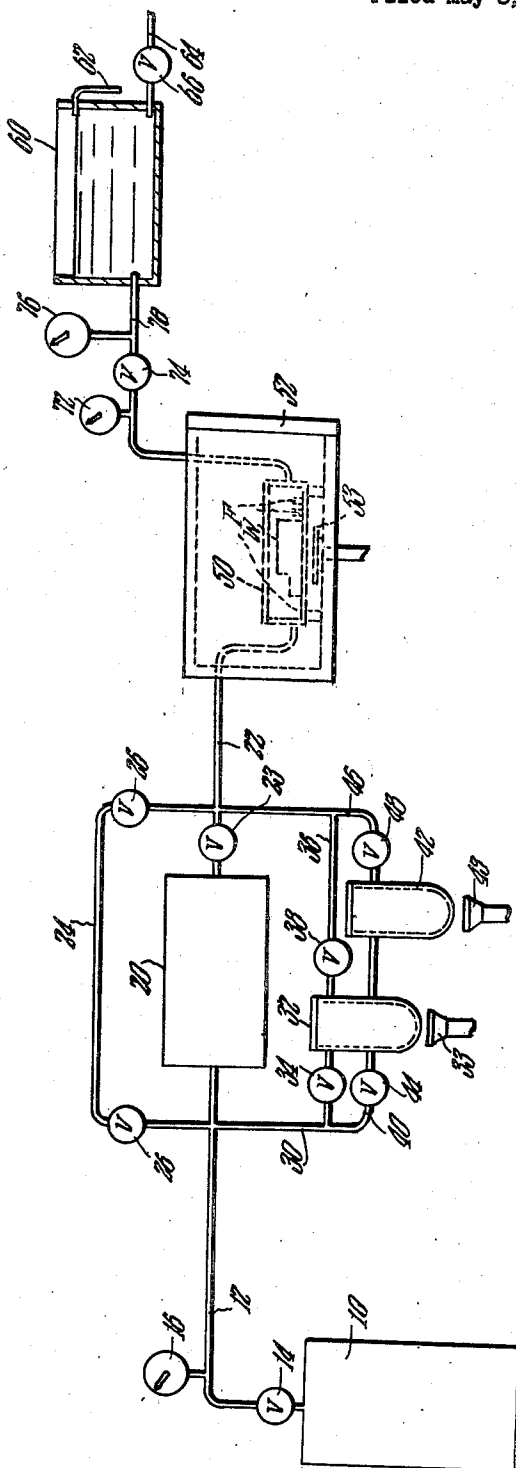
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METHOD OF DEPASSIFYING HIGH CHROMIUM STEELS PRIOR TO NITRIDING

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METHOD OF DEPASSIFYING HIGH CHROMIUM STEELS PRIOR TO NITRIDING

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My invention relates to new and useful improvements in the surface hardening of ferrous alloys and is directed particularly to an improved process for nitriding chromium-containing ferrous alloys including in particular the austenitic high chromium and high chromium-nickel stainless steels and rustless irons and to the resultant nitrided steel products and manufactures.

The products hereof offer improved qualities of high wear resistance, especially for applications where high surface hardness (even after heating at elevated temperatures of as high as 1100° F.), high resistance to corrosion, low tendency to seize or gall, minimum warpage or distortion, and improved fatigue resistance, are desiderata.

Hardening processes of the known prior art have comprised the heating of the work piece in contact with ammonia gas, usually at elevated temperatures in the range of 800–1100° F. for a predetermined period of time which may vary from as short as a few minutes to as great as one hundred or more hours, depending upon the specific results desired in each particular instance.

During this period of time, nitrogen, which is liberated by the decomposition of the ammonia, is absorbed by and forms nitrides with the iron and the alloying elements, such as aluminum, chromium, molybdenum, nickel, vanadium, and/or other nitride-hardening elements, present in the steel.

The nitrides of the alloying elements are precipitated at the nitriding temperature along the crystal planes of the iron resulting in the production of a hard, wear-resistant case.

As is well known, the nitrides, which are in a fine state of dispersion in the case, impart an extreme hardness to the surface of the steel, the changes associated with the formation of the alloy nitrides at the nitriding temperature accounting for the hardened case and the hardening gradually decreasing inwardly until it corresponds to that of the core.

At the lower temperatures of the range, between 800–900° F. a very hard case results but little penetration is offered so that the use of these temperatures is unsuited for valves, valve seats and the like, which are subjected to wear or more or less localized stresses.

For any given temperature within the range, the penetration may be increased by increasing the duration of the nitriding reaction but the increase of penetration is not commensurate with the increased time, i. e., the rate of penetration falls off rapidly after 15 to 20 hours.

As is also well known, the nitriding process has enjoyed wide commercial use heretofore but difficulties have been encountered in applying it to the high chromium-nickel ferrous alloy compositions. Unless these alloys are given a special preliminary treatment, a case either is not formed at all within any reasonable time of treatment or is too shallow or of too low a degree of hardness to accomplish the desired result.

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Ferrous alloy articles or work pieces to be hardened are usually machined to final shape and dimensions before being subjected to the nitriding treatment.

The chief difficulty in nitriding the high chromium ferrous alloys has been attributed to the presence on the surface of the alloy of an inert or passive film composed of chromium oxide. A characteristic quality of this surface oxide film is that it has a tendency to prevent the effects of the conventional nitriding treatment on the metal.

These alloys may be made more susceptible to nitriding by a depassifying treatment involving etching of the surfaces of the article to be nitrided with a hydrogen-liberating acid such as hydrochloric acid. While such treatment will accomplish the desired purpose, it involves the introduction of an additional step, not to mention the expense, in the preparation of the articles for nitriding. Too, it necessitates the introduction of the work piece into the nitriding furnace immediately following the depassifying treatment. Failure so to do will result in the oxide film re-forming upon exposure to air. Obviously, unless special precautions are taken, the results obtained with the use of such an acid are not uniformly dependable.

An electrolytic cleaning operation followed by a washing step immediately preceding the introduction of the work piece into the nitriding furnace has also been employed successfully. Here again, however, extra operations and increased costs are involved.

High chromium ferrous alloys have also been successfully nitrided with an initial reduction of the passive oxide layer by a treatment with hydrogen in the same furnace in which the nitriding is carried out. Such procedure has been found to give a satisfactory nitriding result, but necessitates additional equipment for cracking ammonia so as to furnish the hydrogen for the reduction of the oxide film.

In some prior art practices, it has been found necessary and/or desirable to roughen the surface of the work piece as by sandblasting or the like prior to the actual nitriding operation in order to achieve optimum nitriding results. For the obvious reason that such a practice destroys the oftentimes painstaking and careful machine work represented in the work piece, not to mention the sometimes spoilage of work where tolerances are an especially critical consideration, the procedure is undesirable. Furthermore, unless the initial cleaning procedure is followed with reasonable promptness by the nitriding operation, an oxide film forms anew on the metal. Too, the very shape or size of the work piece has made it difficult or impossible to subject the metal satisfactorily to the essential cleaning operation. Where sandblasting has been employed, a certain roughness is imparted to the metal, which roughness is frequently undesirable and objectionable as aforesaid. Same may not only spoil the appearance of the finished hardened product but also affect the utility thereof. The sandblasting or like treatment, when brought to bear upon small or delicate objects, might even result in obviously objectionable deformation or distortion.

A still further objection to the known and conventional nitriding procedures resides in the frequent obtainment of nitrided surfaces which lack uniformity of hardness and wear-resistance. This non-uniformity apparently is due to an inefficient or improper removal of the passive oxide film initially or is due to a reformation of the oxide subsequent to the cleaning operation and prior to the nitriding.

In this invention, I provide an economical and industrially practical process of nitriding stainless steel products

wherein the cleaning and surface hardening are achieved in a thoroughly satisfactory manner with a minimum of operational steps.

It is a principal object hereof to provide a method of nitriding alloy steel, especially stainless steel, which as a procedure is characterized by directness and simplicity, and ensures the obtainment of uniformly nitrided steel surfaces at greatly increased rates.

It is another object hereof to provide a nitriding process applicable to the various high-chromium ferrous alloys, including those of austenitic structure and in particular the stainless steels of the high-chromium and austenitic high chrome-nickel types, which is substantially free from the objections of the above cited prior art processes.

It is a further object to provide a thoroughly practical and highly effective method of removing the outermost oxide film from the metal directly as a part of the nitriding procedure and of rapidly and efficiently case-hardening the same in a nitrogenous atmosphere.

A further object hereof is to provide a nitriding process by which high chromium ferrous alloys may be satisfactorily nitrided with substantially no sacrifice of time and with only a moderate increase of cost as compared with the conventional nitriding process as it is applied to the low-chromium-aluminum nitriding steels.

Another object hereof is to provide a nitriding process applicable to high chromium ferrous alloys by which a nitride case of markedly increased depth can be obtained in a given nitriding cycle as compared with the results obtained by following any of the above referred to prior practices.

It is a still further object hereof to provide a durable, wear-resistant case-hardened chromium ferrous alloy product which individually possesses high surface hardness, which hardness moreover is uniform along the surface.

The nitriding treatment alone, by way of an atmosphere of a nitrogen liberating gas, fails to serve effectively to remove the oxide film from the metal so as to ensure the desirable formation of a uniformly hard nitrided case, resistant to wear and corrosion.

I introduce outside of or to the nitriding retort a substantial amount of a fluorocarbon so as to make available therein an abundance of gas upon the decomposition thereof. Said gas is directed to the vicinity of the steel and accomplishes the desired oxide film removal.

Subsequently, I introduce a nitrogenous atmosphere comprising such amounts of ammonia gas as to make available an abundance of free nitrogen in the vicinity of the steel for the completion of the nitriding process.

I have determined that the above itemized purposes and objects can be attained and high chromium ferrous alloys can be provided with a nitride case of good characteristic in a conventional nitriding furnace and within the normal range of nitriding temperatures, provided the preparation for nitriding is carried out in the presence of one of a group of fluorocarbons in close contact with the work piece surface to be nitrided.

The materials which have been found to give this beneficial result are those which have the capacity, upon being heated to predetermined elevated temperatures, of emitting gaseous derivatives of fluorine.

Preferably, the fluorocarbon employed is one whose range of decomposition is such that it become active at approximately the temperature at which the nitriding operation is carried out.

These gaseous derivatives etch the surface of the work piece within the retort just prior to the nitriding action. The etching action offers an improved or super active surface resulting in an accelerated nitriding rate.

The heart or real spirit of the invention resides in the sequential steps of making the surface of the work piece "active" while within the nitriding retort and nitriding immediately there-following without interruption.

A surface, so prepared, is thus activated so as to be

more receptive to the nitrogen within the retort than has heretofore been possible to achieve. Such activation constitutes the process of reducing the film of any oxide material upon the surface practically as an integral part of the nitriding process.

With this method, the work pieces may be prepared for the treatment in any of the conventional ways and it is unnecessary to introduce any special operation for depassifying the work piece surface so as to prepare same for the nitriding.

The invention consists in the combination of elements, composition of materials, and mixture of ingredients, and in the several operational steps, and in the relation of each of the same to one or more of the others, as described herein.

The invention, broadly defined, generally relates to the process of nitriding steels at an accelerated rate by means of a fluorine gas capable of activating the surfaces thereof so as to make same more receptive to the nitrogenous gas, same constituting a sequential step in the treating process. The invention further includes the nitrided articles of manufacture produced by said process.

As conducive to a clearer understanding of certain features of the invention, it may be noted at this point that stainless steel is defined as a low-carbon alloy metal which comprises from about 10 to approximately 35% chromium, with or without nickel, and with or without the supplemental addition of manganese, silicon, cobalt, copper, molybdenum, tungsten, vanadium, columbium, titanium, and/or sulphur, and a balance of substantially all iron.

The process of this invention is normally applied to steels of the austenitic stainless type although conceivably it can be used for the ferritic or martensitic steels as well.

Austenitic stainless steels, where the chromium is the predominating alloy addition to iron, varying from 16 to 26% in content, are generally envisioned for the purposes hereof. Particular reference will be made herein, by way of illustration only, to A. S. T. M. A276 Type 304 with an 0.08% carbon maximum in the popular 18 chromium-8 nickel steel. As another example, reference will also be made herein to A. S. T. M. A276 Type 410 stainless steel.

Austenitic steels have desirable characteristics in that they resist corrosion but the surface characteristics thereof are not such that wear is resisted and they cannot be hardened as may other steels. When parts made from austenitic steel are in contact with one another, or when a part made from austenitic steel is in contact with a part made from another steel, and when there is any relative movement of those parts, the austenitic steel has a tendency to scratch, score, seize and/or gall. For instance, when a valve or a seat of a valve is made from austenitic steel, the action of one part on another causes the austenitic steel to scratch, score, seize and/or gall so that the unit is rendered unfit for service, in spite of the fact that the steel still has retained its desirable ability to resist corrosion.

In this invention, austenitic steel is treated in such a way that it is hardened, or at least its surface is hardened, to the extent that it is definitely wear-resisting and does not tend to scratch, score, seize, or gall, while its resistance to corrosion and temperature is in no way impaired.

By means of this invention, I provide a method of treating steel of the austenitic class, and the ferritic and martensitic classes as well, whereby the treated steel has an improved hardened wear-resisting surface and also has new corrosion and temperature resisting characteristics. Such a steel is especially adapted for use under the more unfavorable conditions of elevated temperature and/or association with agents capable of bringing about excessive oxidation and corrosion.

Further, by means hereof, I provide an article of manufacture having a nitrided surface properly supported by an

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underlying core capable of withstanding extreme operating stress without such plastic deformation as will cause a cracking or failure otherwise of the hard nitrided case.

Usually the steel work piece is heated in a nitriding furnace subjected first to the action of a fluorine gas and then to an atmosphere of a nitrogenous medium such as ammonia gas under conditions whereby surface hardness is imparted to the material by the absorption of the nitrogen.

In the accompanying drawing, I have illustrated a complete example of a physical embodiment of the invention in which the steps are combined and arranged in accordance with one mode which I have devised for the practical application of the principles of the invention. It will be understood however that changes and alterations are contemplated and may be made in the procedures hereof and in the exemplifying drawing, all within the scope of the claims, and without departing from the principles of the invention.

In the drawing, the figure is a diagrammatic elevational view of an apparatus adapted for carrying out the novel method of the invention.

Referring now to the drawing more in detail, the novel apparatus and method of the invention will be fully described.

In this disclosure, I show, for illustration purposes, a complete example of a physical embodiment of the invention in which the steps are combined and arranged in accordance with one mode which I have devised for the practical application of the principles of the invention.

Means for supplying ammonia gas may include a supply source or tank such as 10 and the gas is conducted therefrom through a suitable conduit 12 having a valve means 14 and a pressure indicating means 16 provided therealong.

The conduit 12 connects directly to one side of a dissociation furnace 20, on the opposite side of which, a conduit 22 having a valve 23 therein leads away therefrom to a nitriding retort 50 which is disposed in a suitable electric, gas or oil fired batch-type metallurgical furnace 52.

A by-pass conduit 24, having one or more suitable valves 26 therealong may be provided to by-pass the furnace 20, if desired.

Another conduit 30 may be provided and communicates at one extremity with the conduit 12 and at its opposite extremity with a decomposing chamber 32. A valve 34 may be provided in the conduit 30.

On the opposite side of the chamber 32 and communicating therewith, a conduit 36 may be provided.

The opposite extremity of the conduit 36 communicates with the conduit 22. A valve member 38 may be provided in said conduit 36. A heating element 33 may be provided in conjunction with the decomposing chamber 32.

Additionally if desired, another conduit 40 connecting with conduit 30 and a decomposing chamber 42 substantially as shown, may be provided. A valve 44 may be provided in the conduit 40. On the opposite side of the decomposing chamber 42 and communicating therewith, a conduit 46 may be provided.

The opposite extremity of the conduit 46 communicates with the conduit 36, substantially as shown. A valve 48 may be provided in conjunction with the conduit 46. A heating element 43 may be provided in conjunction with the decomposing chamber 42.

The nitriding retort 50 receives the work piece being treated, and is heated by a heating element 53.

A water bath 60 may be provided including a water inlet 62 and a water outlet 64. Inlet 62 and/or outlet 64 may be provided with a valve means 66 if desired.

Leading from the retort 50 is a conduit 70 through which the exhaust products of the nitriding action may pass from the retort to the bath 60 for absorption therein.

The conduit 70 may be provided with a pressure indi-

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cating means 72, a valve means 74, and an indicating means 76 to show the volume (by percentage) of the dissociation of the ammonia gas in the retort 50.

The mechanical elements having been described, one method of applying the principles of the invention will not be defined in the following essential series of sequential steps.

For a continuous supply of the treating ammonia gas to the nitriding retort, I prefer to employ a tank of commercial anhydrous ammonia (represented by the source of supply 10) from which gaseous ammonia is conducted under a predetermined positive pressure through conduit 12 to the dissociation furnace 20 whereat the hydrogen and nitrogen constituents of the ammonia gas are dissociated. The control is maintained over the gas flow through the use of a pressure regulating valve 14.

The dissociation furnace 20 is heated to a temperature within the range of 1200-1600° F.

The decomposing chambers 32 and 42 may be employed if it is desired to decompose the fluorocarbon in an area other than with the nitriding retort.

Further, it is conceivable that it may be desired under certain circumstances to supplement the flow of the dissociated ammonia gas as it leaves the dissociation furnace 20 with the gaseous derivatives of the fluorocarbon from the decomposing chambers 32 and/or 42 so as to proceed through conduit 22 to the nitriding retort 50 simultaneously.

Conceivably, the fluorocarbon can be decomposed in the decomposing chambers 32 and/or 42 or in the nitriding retort 50, all as may be desired.

The work piece W to be treated is placed in the nitriding retort 50 and the quantity of polytetrafluoroethylene generally indicated by F in the drawing is placed either in the decomposing chambers 32 and/or 42 or in the nitriding retort 50.

The nitriding retort, after having been purged with NH₃ to remove atmosphere therefrom, is heated to a temperature of 900° F. which is maintained for a period of sixty minutes. Simultaneously therewith, the dissociation furnace is heated to 1300° F. Specific temperatures are indicated as preferred.

The entire piping system, dissociation furnace, nitriding, retort, etc. are purged with NH₃ before heating. The dissociation furnace is then heated to 1200-1600° F. with a small flow of NH₃ flowing thru the system. When the dissociation furnace reaches operating temperature, the NH₃ flow is adjusted to a flow of dissociated ammonia of 4 to 50 C. F./H. The nitriding retort is then heated to 950-1120° F. The fluorocarbon in the nitriding retort begins to decompose at approximately 500° F. The rate of decomposition is proportional to the temperature. At 500° F., the fluorocarbon decomposes slowly, at 900° F., rapidly. During the period of decomposition of the fluorocarbon, the nitriding retort is filled with an atmosphere of dissociated NH₃ plus gaseous decomposition products of the fluorocarbon. This atmosphere reduces the oxide film on the work surface and prepares it for nitriding.

When the fluorocarbon is completely decomposed (usually within the heating up period of the loaded nitriding retort) the dissociation furnace is shut off, valve 23 closed, valves 26 opened and the NH₃ flow adjusted so that the dissociation measured by instrument 76 is 5 to 20% (by volume).

The flow of NH₃ is maintained at this quantity for a period of 2 to 20 hours, depending on the case depth desired. A nitriding period of 15 hours will produce a case depth of approximately 5½ mils on the austenitic stainless steels and a case depth of approximately 11½ mils on the ferritic or martensitic stainless steels.

Under the influence of the heat within the retort, the C₂F₄ begins to decompose so that the work piece W is subjected to the action of the decomposing fluorocarbon,

the gas circulating around and on all sides of the work piece W.

The materials falling within the fluorocarbon classification which I have tested and found suitable for use in the present process are tetrafluoroethylene, trifluorochloroethylene resin, Freon and other fluorocarbons.

Each of these resins, when heated above 750° F., decompose slowly to yield a gaseous monomer together with small amounts of other gaseous derivatives of fluorine.

There is a wide latitude in the choice of the temperatures and times employed. The choice of these factors generally depends upon the retort, the time available, the metallurgical effects on the base metal, and related factors.

When the work piece W has thus been heated and subjected to the etching action of the gas of the fluorocarbon, it is then subjected to the action of the products of the ammonia gas. That is, the heated steel is put in contact with a source of active nitrogen at the specified temperature for periods ranging from a few minutes to 100 hours depending upon the steel being treated and the depth of case desired.

The ammonia gas is conducted to within the nitriding retort by means of the conduit 22. The gas circulates around and on all sides of the stainless steel work piece W and thence from the nitriding retort through gas outlet conduit 70 to suitable disposed means 60.

As treatment of the work pieces continues at nitriding temperatures in the presence of the fluorine gas, the oxide film is effectively removed from the surface of the article and due to the action of the nitrogenous gas, a hard nitrided core begins to form.

Over an extended period of continued treatment, the nitrided layer gradually increases to a useful thickness; usually a treatment period ranging from approximately 30 to 90 hours gives a thickness which is satisfactory for most articles, although I do not wish to be bound by such period.

The time of treatment will vary according to the size and shape of the steel, and to the particular results desired. The time treatment may vary from a few minutes to as much as 100 hours.

The rate of flow of the ammonia is adjusted so that the percentage dissociation of the exhaust gases is held at between substantially 15–50%.

The process of the present invention is equally applicable with other ammonia dissociation values. It may be employed, for example, in conjunction with the process disclosed in the patent of Carl F. Floe, #2,437,249, dated March 9, 1948, in which process the ammonia dissociation value is held relatively low in the earlier stage of the nitriding operation and thereafter is raised.

The heat is maintained at the stated temperature for a predetermined time following which the flow of the ammonia gas products is cut off.

An excess fluorine in the retort reacts with the ammonia gas to form a stable salt which is disposed of as a waste product.

As examples of the process employing C₂F₄ (polytetrafluoroethylene), test specimens of both A. S. T. M. A276 Type 304 stainless steel and A. S. T. M. A276 Type 410 stainless steel placed in the nitriding furnace along with pieces of the fluorocarbon. The retort was heated to 900° F. and the fluorocarbon was decomposed.

The ammonia gas, with a dissociation ranging from 5 to 20% was circulated into the retort.

As to the general metallography of the test specimens, they were found to have representative cases and interface structures for their respective material types. The case was found to be uniform in hardness and case depth for the section viewed. Photomicrographs, etched and unetched at 100×, for both materials, were prepared. The case depths, Rockwell 15 N surface hardness, and hardness traverse follow.

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Case Depth—Inches	Knoop Hardness Values—500 Gram Load
.001.....	Cracked
.002.....	1,058
.003.....	756
.004.....	363

(Upon removal from the furnace and after cooling, the test specimen was found to have a hardness of 88–89 on the Rockwell 15 N scale, as contrasted with its initial hardness of 77 on the same scale. Transverse sections of this specimen were prepared and examined microscopically and were found to have a nitride case of good characteristics extending to a depth of 0.003".)

A. I. S. I. Type 410—Sample #1344

Case Depth—Inches	Knoop Hardness Values—500 Gram Load
.001.....	Cracked
.002.....	1,058
.003.....	1,008.5
.004.....	1,008.5
.005.....	462.5
.006.....	347.5

(Upon removal from the furnace and after cooling, the test specimen was found to have a hardness of 91–92 on the Rockwell 15 N scale, as contrasted with its initial hardness of 77 on the same scale. Transverse sections of this specimen were prepared and examined microscopically and were found to have a nitride case of good characteristics extending to a depth of 0.0045").

It will be appreciated that the invention is not limited to the particular nitriding procedures disclosed herein. The disclosure is made by way of illustration and not of limitation. Those skilled in the art will also appreciate that the process is applicable to chromium-containing ferrous alloys of other compositions than those mentioned by way of example above including, among others, various stainless steels, rustless irons and high chromium cast irons, wherein various other alloying additions are present besides chromium or chromium and nickel. The duration of the treatment also may be changed in accordance with the requirements of the particular work to be processed.

Having thus described the invention and the best method of practicing the new process for preparing this steel without being limited to the order of steps of such process as herein recited, or to the proportions of parts employed therein, or to the precise ingredients named therein, it being evident that each of these steps has a considerable range of equivalents, and it being also evident that the order and proportions of the process may be carried out without departing from the scope and purposes hereof, what it is desired to claim and secure by Letters Patent of the United States is:

1. In a method of conditioning chromium steel for a nitriding treatment, the art which includes, heating the steel within a sufficiently high temperature range in the presence of the gaseous derivatives of a fluorocarbon and the removal of the chromium oxide film on the steel surface, and further heating the steel within a sufficiently high temperature range and for a sufficiently long period of time in a nitrogenous atmosphere.

2. The improvement in the nitride hardening of a high chromium ferrous alloy characterized by the presence on the surface thereof of a passive oxide film serving to inhibit penetration of nitrogen into said surface portions when such articles are heated in a nitrogenous atmosphere, comprising, heating the ferrous article directly and without a preliminary depassivating treatment at a nitriding temperature and in the presence of the gas of

a decomposing fluorocarbon, and continuing the heating treatment in the presence of a nitrogenous atmosphere.

3. The improvement in the nitride hardening of a high chromium ferrous alloy characterized by the presence on the surface thereof of a passive oxide film acting to inhibit penetration of nitrogen into said surface portions when such articles are heated in a nitrogenous atmosphere, comprising, heating the ferrous article directly and without a preliminary depassifying treatment at a temperature between 900 and 1100° F. initially in the

presence of the gases of a decomposing fluorocarbon and subsequently in the presence of a nitrogen-liberating gas.

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