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PROCESS OF NITROGENIZATION

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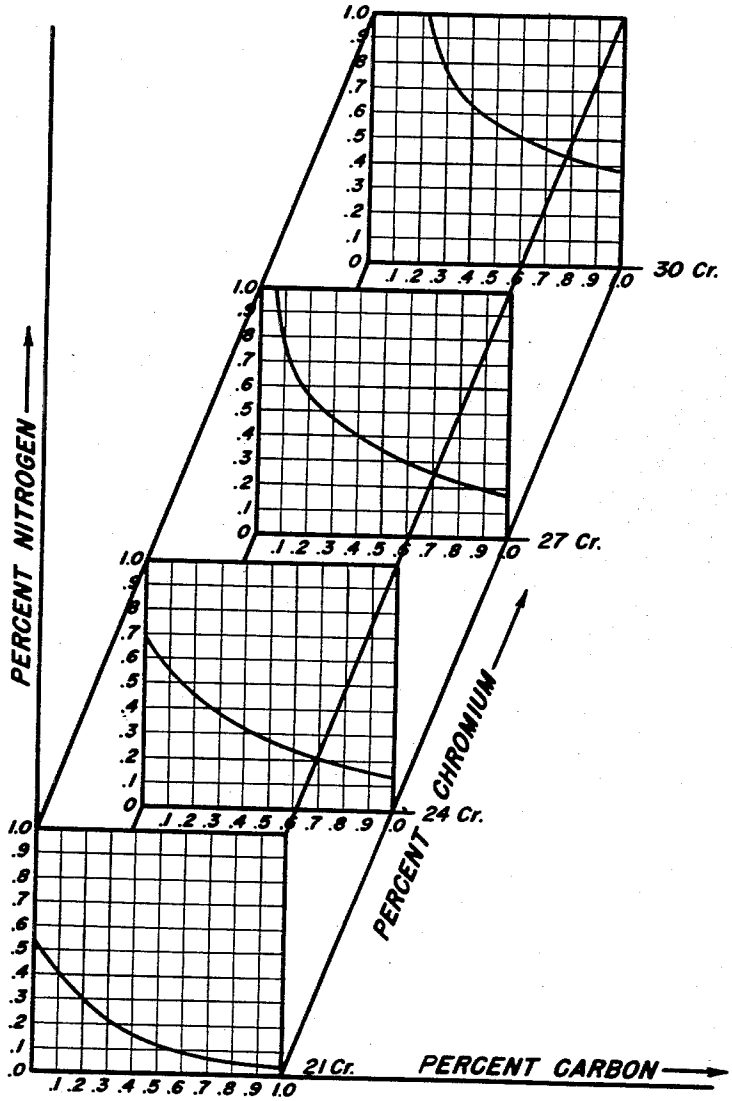

INVENTORS:
James K. Stanley
George F. Tisinai
BY Arthur G. Gilkes
ATTORNEY

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PROCESS OF NITROGENIZATION

James K. Stanley, Chicago, Ill., and George F. Tisinai, Highland, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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Our invention relates to means for the production of stable austenitic stainless steels without depending upon nickel as an essential alloying element.

The chrome alloy stainless steels are normally ferritic or martensitic in structure. Although austenitic iron-chromium-nickel and iron-manganese-carbon alloys are well known, so far as we know, it has not been possible to produce completely austenitic steels without the use of nickel or manganese. These alloys have useful, distinctive properties including a high degree of oxidation and corrosion resistance but their cost and the strategic significance of nickel and manganese have stimulated a great deal of research by investigators, both here and abroad, in an effort to produce austenitic alloys by other means.

The iron-chromium-carbon system, for example, has been studied extensively. Ordinarily carbon-free iron-chromium alloys containing more than 13% chromium are ferritic at all temperatures. Below 13% chromium the austenitic field exists above 1550° F. Carbon additions will expand the austenite field up to about 21% chromium at temperatures above 1550° F. With increased chromium content above 21%, the single phase austenite field is eliminated. Krivobok and Grossman, Trans. Am. Soc. Steel Treat., v. 18 (1930), pp. 760–807, have reported production of an essentially austenitic structure in a steel containing as high as 21% chromium by addition of 0.62% carbon. On the other hand, their work with 28% and 33% chromium alloys of variable carbon content (up to 0.70%) resulted in only minor amounts of austenite.

The effect of nitrogen on the structure of iron and chromium alloys also has been extensively investigated. The most significant work appears to be that of Colbeck and Garner, J. Iron and Steel Inst., v. 193 (1939), pp. 99–135, who have reported the production of 24% chromium alloys containing as much as 60% austenite and of 27% chromium alloys containing as much as 50% austenite. See also B. G. Bandel, Archiv f. d. Eisenhuttenwesen, vol. 11, pp. 139–144, 1937, wherein the partial austenitization of a number of chromium alloys by addition of nitrogen is reported. A completely austenitic structure, however, has not been realized for high chromium alloys, insofar as we are aware, except for the single non-reproducible example reported by Krivobok and Grossman, supra, without the use of upwards of about 4% nickel.

According to our invention, a process is provided for converting ferritic iron-chromium-carbon alloys to completely austenitic alloys by subjecting the ferritic alloy to the action of a dry nitrogen-supplying gas at elevated temperature. The ferritic alloy should contain at least 21 weight percent chromium and 0.1 to 1.0 percent carbon. A temperature in the range of about 2000 to 2400° F. should be provided to effect conversion, and the period of contact of gas and metal should be sufficient to incorporate from about 0.3 to about 1.0 weight percent nitrogen in the alloy to be converted. After the desired extent of conversion is obtained, the alloy is rapidly cooled to a temperature below about 800° F.

In our research in this field, we have found that there is a critical relationship between carbon and nitrogen affecting austenitization, a relationship which prior investigators appear to have overlooked, perhaps because of the unexpectedness of cooperation in this respect between these minor constituents or perhaps because of the confusing fact that nearly all steels contain some concentration of carbon as a constituent impurity. We have also found that the rate of nitrogen absorption is increased significantly by increasing the carbon content up to about 0.5% carbon. With a low carbon alloy, e.g. about 0.1% carbon, the rate of nitrogen absorption is low. The concentration of nitrogen at the boundary between an austenitic layer and a ferritic layer apparently must be relatively high for rapid extension of the austenite structure. As carbon content is increased to about 0.5%, the induction period that may be encountered in austenization as an incident to this problem is appreciably reduced.

In investigating the new alloys, we have discovered that completely austenitic alloys can be produced when the proportions of carbon and nitrogen are adjusted to a critical relationship for a particular chromium content, apparently through some synergistic action. A hyperbolic relationship exists between carbon and nitrogen in the chromium alloy steels which appears to be responsible for stabilization of an austenitic structure. The higher the carbon content, the lower is the nitrogen content necessary to make the resulting alloy completely austenitic. Conversely, the lower the carbon content, the higher is the amount of nitrogen that is required to make the alloy completely austenitic. As the amount of chromium in the alloy is increased, larger amounts of carbon and nitrogen appear to be required for a stable austenitic structure. At the higher chromium contents, e.g. say 27 to 33% chromium, the stable austenite field becomes smaller although useful alloys of stable austenitic structure containing co-existing chromium carbide may be formed over a field of broader range.

The new iron-chromium-carbon-nitrogen alloys have valuable corrosion-resistant properties, including oxidation resistance at elevated temperatures at least up to 900° F. and also above 2000° F., of a type associated with austenitic nickel- and manganese-containing chrome alloys. In other respects, however, the new austenitic alloys appear to be quite distinctive in properties such as tensile and yield strength, work-hardening and the like.

Although the relationship between carbon and nitrogen appears to have some general application to chrome alloy steels, alloys of less than about 21% chromium content appear to lack the distinctive corrosion resistance and stability of the austenitic structure of the new alloys. For example, a 21% chromium steel, even though of substantially austenitic structure, is borderline in oxidation resistance at 2000° F. Also, with chromium contents substantially above 33%, impracticably high nitrogen contents are required to avoid restriction of the austenite field to the vanishing point although the two phase field of austenite plus carbide may have general usefulness. The alloys treated may be pure, but as in conventional alloy production, they normally contain minor or non-detrimental amounts of constituent elements such as sulfur, phorphorus, manganese and silicon.

The invention also may be applied to treatment of alloys containing nickel but in insufficient amount to provide an austenitic structure. The mechanism by which the carbon and nitrogen combination functions however appears to be fundamentally different from that of a metal such as nickel. Both the carbon and nitrogen dis-

solve interstitially between atoms, whereas the larger nickel atoms take the place of other metal atoms.

In the practice of the invention, we prefer to operate with a carbon content above about 0.15, advantageously in the range of 0.3 to 1.0%. The austenitic structure then is obtained by incorporating sufficient nitrogen at elevated temperature to provide a nitrogen content of about 0.5 to 1%, with the higher chromium alloys demanding nitrogen contents in the upper portion of the range.

The critical amount of nitrogen for a given carbon content at representative levels of chromium content is indicated in the accompanying drawing. The drawing is a simplified representation of a quaternary phase diagram based on the preparation and analysis of numerous samples of iron-chromium-carbon-nitrogen alloys.

The drawing illustrates the approximate limits of the austenite field in the iron-chromium-carbon-nitrogen system for four different chromium levels. Each panel represents a constant chromium content, the ordinates are percent nitrogen and the abscissas are percent carbon. The diagram applies to alloys cooled rapidly from above 2200° F. All of the alloys above the curved lines are ferrite-free, while the alloys below the curved lines contain ferrite. Thus, the drawing indicates the boundaries between the combined austenile (γ) and the austenite plus carbide ($\gamma+c$) fields, above the lines and the combined austenite plus ferrite ($\gamma+\alpha$) and the austenite plus ferrite plus carbide ($\gamma+\alpha+c$) fields, below the lines. It will be noted that the boundaries resemble the hyperbolic form; i.e. a hyperbolic relation appears to exist between the content of carbon and nitrogen which is responsible for the stable austenitic structure. The hyperbolic boundary shifts upward systematically as the chromium content is increased so that greater amounts of carbon and nitrogen are required to obtain the austenitic structure. Thus, from the 3-dimensional diagram of the drawing it may be seen that a curved surface exists which separates the upper austenitic field from austenite containing ferrite.

In its broader aspects, the invention may be practiced to produce the austenitic alloys falling within the areas represented as above the curved lines of the drawing separating the combined austenite and austenite plus carbide fields from the combined austenite plus ferrite and austenite plus ferrite plus carbide fields. Although alloys in the austenite plus ferrite field having a predominantly austenitic structure may have engineering usefulness, the presence of more than about 15 to 20% ferrite will result in the loss of high strength and the loss of the nonmagnetic nature, and possibly in the loss of general corrosion resistance by formation of a two-phase structure. The presence of small amounts of ferrite however may lower the susceptibility of the austenite toward intergranular brittleness, may favor the resistance of the alloy to corrosion under stress, and may be useful to prevent weld cracking in the event the alloys are welded.

The invention may be practiced by controlled addition of carbon and nitrogen to a high chromium steel, or to a mixture of the components thereof, and treatment of the resulting steel at a temperature above 2000°–2400° F. followed by rapid cooling to a temperature below 800° F. For example, an iron-chromium-carbon alloy, containing the desired percent carbon, say 0.1% or higher, can be made in any conventional way. The resulting alloy then can be nitrogenized by the direct addition of nitrogen from a nitrogen atmosphere at a temperature above 2000° F., preferably at about 2250° F. The nitrogen is absorbed by the alloy and produces a case of austenite. The rate of penetration of the nitrogen in a concentration sufficient to form the austenitic case is a function of the carbon content and the nitrogen pressure, and is increased by each. By exposing the alloy to be austenitized to the nitrogen atmosphere for sufficient time, the cross sectional thickness of the alloy can be completely penetrated and converted to the completely austenitic state.

Another method of directly introducing nitrogen by means of solid-gas reaction adapts conventional nitriding, i.e. introduction of nitrogen from a partially dissociated ammonia gas atmosphere at about 800–1300° F. In contrast to conventional nitriding, however, the iron-chromium-carbon alloys for austenitization are treated at elevated temperature, preferably about 1000 to 1200° F. and then are homogenized, or heat treated, above 2000° F,. preferably at about 2200 to 2300° F., in either vacuum or a protective atmosphere, for example, nitrogen, argon, or helium gas.

The use of nitriding has the advantage that the rate of conversion of ferrite to austenite in depth is faster because more nitrogen can be introduced at the lower temperature level of the two-stage process. On the other hand, the presence of hydrogen in the homogenizing gas in excess of about 1% is harmful, resulting in decarburization.

A small proportion of hydrogen below 1% in the nitrogen gas is advantageous in simplifying de-oxidation and dehydration of the treating gas. There is always some residual oxygen in commercial nitrogen. It may be desirable therefore to add enough hydrogen, but below 1% of the nitrogen, to the feed gas to combine with the residual oxygen. The resulting gas stream is passed over a catalyst, e.g. platinized asbestos, to cause the hydrogen and water to form water vapor and thereupon is dried by passage in contact with a dessicant, e.g. activated alumina.

In heat treatment, the alloy is cooled from about 2200° F. to below about 800 to 900° F. rapidly enough to prevent transformation of the austenitic structure to the ferritic structure. Although the change in structure from austenitic to ferrite is sluggish, some decomposition of austenite may occur on slow cooling as by air cooling of large sections. Quenching or rapid cooling therefore is desirable. A partially decomposed austenite, however, can be converted to an all austenite structure by reheating to 2200° F. followed by rapid cooling. Also, since the austenitic grain size may be undesirably large, it can be refined to improve mechanical properties by decomposing the alloys to ferrite, carbides and nitrides by heating to temperatures within the range of about 900° to 1700° F. followed by reaustenitizing for short periods of time at 2200° to 2300° F.

Data illustrating application of the invention on a test scale follow: The addition of nitrogen to the starting ferritic alloys was accomplished by passing purified nitrogen (approx. 1 atm. pressure) over the alloys for 20 hours at 2200° F. In certain instances, a nitrogenizing time of 72 hours also was employed. From previous experiments, it was known that 20 hours at 2200° F. was a sufficiently long time for the nitrogen to penetrate through a ⅛"×⅛" cross section of a 27% Cr–0.3% C alloy and convert it to the completely austenitic state. Since it was believed that oxide formation on the surface interfered with the diffusion of nitrogen into such alloys, pains were taken to eliminate an oxidizing potential from the atmosphere. Tank nitrogen was passed through containers of "Drierite" and magnesium perchlorate to remove most of the moisture, and then through calcium chips at 1100° F. to remove oxygen and residual moisture. The gas was passed through an Inconel tube which contained the samples at 2200° F. All equipment joints were sealed with glyptal paint. When the system was working properly, the dew point of the nitrogen gas was less than —80° F. and samples furnace-cooled in nitrogen after a 20 hr. treatment at 2200° F. did not contain a trace of oxide. The alloys were furnace-cooled in the dry nitrogen, or, after modification of the apparatus, the samples were pulled into the cold zone of the furnace while still being protected by dry nitrogen.

To illustrate the results obtained by the above procedure, a ferritic steel sample of ⅛" x ⅛" x 3" was supported in the furnace at one end, with the longest dimen-

sion parallel to the length of the furnace tube. The sample was analyzed after one hour, 5 hours, and 20 hours. After 20 hours, the structure of the sample was completely austenitic throughout. The analysis follows: Si, 0.61%; Mn, 0.51%; S, 0.017%; P, 0.024%; C, 0.27%; Ni, 0.18%, Cr, 27.50%; N, 0.483%.

The rate of austenitization of a ferritic steel can be increased by increasing the pressure of nitrogen. For example, a sample of 27% Cr–0.3% C was austenitized to a depth of about 1/64 inch in free flowing nitrogen after one hour at 2200° F., but to about 1/32 inch in a nitrogen pressurized bomb (estimated as 2 to 3 atmospheres) after ½ hour at 2200° F. The pressure for commercial operation suitably is within the range of approximately one to four atmospheres.

Also, in the commercial practice of the invention, it may be advantageous to retreat the austenitized alloys to refine grain structure in order to improve mechanical properties.

Control of grain size is important in obtaining desired mechanical properties, such as yield strength, tensile strength, and impact resistance, as is well known. The new series of Fe—Cr—C—N-alloys has a transformation range which can be used to obtain grain refinement and to change the hardness significantly. The austenitic alloys prepared by nitrogenizing may have an extremely coarse grain structure. The austenitic coating prepared by nitriding and annealing will have a variable grain size ranging from moderate at the surface to very large at the ferrite junction. In service where only the factor of corrosion is concerned, it may not be necessary to refine the grain size. However, there are instances, particularly for structural use, where improved physicals may be desirable.

To refine grain structure according to the invention, the treated steels (after nitrogen adsorption, heat treatment and cooling) are heated at a temperature which will decompose austenite to ferrite, carbides, and nitrides. A temperature of 1600° F. is recommended for a 27% chromium steel and 1400° F. for a 21% chromium steel. After decomposition, the steels are reheated at a temperature above 2000° F. preferably, between 2200° F. and 2300° F. for about one hour and are cooled rapidly. One hour at the elevated temperature generally is sufficient to dissolve virtually all the carbides and nitrides without causing excessive grain growth. The decomposition can be accomplished in some cases by controlled furnace cooling of the austenitized alloy so as to avoid the intermediate reheating step.

We claim:

1. A process for converting ferritic iron-chromium-carbon alloys to austenitic alloys substantially free of ferrite without incorporating austenitizing amounts of metals effective therefor, such as nickel, manganese, and the like which comprises subjecting a ferritic alloy consisting essentially of about 21% to 33% chromium and 0.1 to 1.0% carbon, the balance being iron except for incidental impurities, to an atmosphere of dry molecular nitrogen at a temperature in the range of from about 2000° F. to 2400° F., maintaining said alloy in said atmosphere at said temperature for a period of time sufficient to incorporate nitrogen in the alloy to be converted in an amount in the range of 0.3 to about 1.0% and sufficient to maintain the relative proportions of nitrogen to carbon for any particular chromium content above the line in the phase diagram of the accompanying drawing, and thereafter cooling the alloy rapidly to a temperature below about 800° F.

2. The process of claim 1 wherein the carbon content is in the range of about 0.3 to 1.0% and the nitrogen is in the range of about 0.5 to 1.0%.

3. The process of claim 1 wherein a pressure of nitrogen exceeding atmospheric is provided.

4. A two-stage process for converting ferritic iron-chromium-carbon alloys to austenitic alloys substantially free of ferrite without incorporating austenitizing amounts of metals effective therefor, such as nickel, manganese, and the like which comprises subjecting a ferritic alloy consisting essentially of about 21% to 33% chromium and 0.1 to 1.0% carbon, the balance being iron except for incidental impurities, to the action of dry partially dissociated ammonia gas at a temperature of about 800° to 1300° F., thereafter heating in an inert atmosphere to a temperature in the range of about 2000° to 2400° F. for a period of time sufficient to incorporate nitrogen in the alloy to be converted in an amount in the range of 0.3 to about 1.0% and sufficient to maintain the relative proportions of nitrogen to carbon for any particular chromium content above the line in the phase diagram of the accompanying drawing, and thereafter cooling the alloy rapidly to a temperature below about 800° F.

5. A process for converting ferritic iron-chromium-carbon alloys to austenitic alloys substantially free of ferrite without incorporating austenitizing amounts of metals effective therefor, such as nickel, manganese, and the like which comprises subjecting a ferritic alloy consisting essentially of about 21% to 33% chromium and 0.1 to 1.0% carbon, the balance being iron except for incidental impurities, to an atmosphere of dry molecular nitrogen at a temperature in the range of from about 2000° F. to 2400° F., maintaining said alloy in said atmosphere at said temperature for a period of time sufficient to incorporate nitrogen homogeneously in the alloy to be converted in an amount in the range of 0.3 to about 1.0% and sufficient to maintain the relative proportions of nitrogen to carbon for any particular chromium content above the line in the phase diagram of the accompanying drawing, cooling the austenitized alloy and holding at a temperature in the range of about 900° to 1700° F. to decompose the austenitic structure, thereupon raising the temperature to about 2000° to 2400° F. to reconvert to the austenitic structure, and thereafter cooling rapidly to a tempertaure below about 800° F.

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