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AUSTENITIC FERROUS ALLOYS AND ARTICLES MADE THEREOF

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This invention relates to austenitic ferrous alloys and articles made therefrom, and more particularly corrosion resistant austenitic chromium-iron alloys for use at elevated temperatures, the object of the invention being to provide articles of such alloys which shall to a high degree resist corrosion and maintain their physical properties when used at elevated temperatures and exposed to the action of corroding substances.

Austenitic chromium-iron alloys, and especially chromium-nickel-iron alloys of the class containing 10 to 22 percent chromium and 7 to 15 percent nickel, with a low carbon content, usually not over about .15 percent and more generally of about .07 percent maximum, and sometimes containing also small quantities of additional elements such as molybdenum, silicon, vanadium, tungsten, and titanium, have come into quite extensive use for various purposes where resistance to corrosion combined with a comparatively great strength and a good degree of ductility and toughness is desirable. The invention has been made more especially with the idea of improving alloys of this general class, but applies to other austenitic ferrous alloys in which chromium is used to give corrosion resistance.

It has generally been considered that to develop the greatest corrosion resistance combined with a relatively high degree of ductility and toughness in these alloys, they should be treated by heating them to a temperature sufficient to obtain complete solubility of the carbon and then cooling at a rate sufficiently fast to retain the carbon in solid solution; and from 1100 to 1200 degrees C. has been generally accepted as the best temperature range for such treatment, the articles being preferably quenched in water. There seems to be no question but that the corrosion resistance, ductility, and toughness of these alloys are best after such treatment and will remain so at low temperatures.

It has been found, however, that when these alloys so treated have been used at elevated temperatures above 900 degrees F. the ductility of the metal becomes impaired to a substantial degree, even when the metal is not exposed to corrosive substances, and that the corrosion resistance of the metal is very greatly impaired, so much so that when exposed to corrosive attack the metal is liable to such deterioration in its physical structure as to be entirely unsuitable and dangerous to use under conditions of any considerable strain or sudden stress. Tubes of this material heat treated by quenching from the 1100 to 1200 degree C. range have been known to burst, after service at a temperature somewhat above 900 degrees F., under pressure well below what the tube should have withstood, and such bursting has taken place without warning, that is, without the bulging which in the case of ordinary carbon steel tubes under similar conditions serves as a warning that the tube is weakening and replacement necessary. And in place of a slight split in the tube such as finally results in a tube which is properly ductile, the bursting of the tubes referred to has been violent and destructive.

I have discovered that if these alloys are worked to produce a small grain size, and are then cooled, either quickly or slowly, from a temperature that is not much above and may even be within the upper limits of the range within which carbon precipitation occurs, the metal, while not quite so highly corrosion resistant and possibly not quite so ductile, at room temperature, as when quenched from a temperature between 1100 and 1200 degrees C., will still have a relatively high degree of corrosion resistance and will be only slightly less ductile at room temperature than when cooled from the higher temperature, and, in addition, will lose comparatively little of its corrosion resistance and ductility and strength as the result of exposure to elevated temperatures, even when long continued, such as have been found to greatly impair the ductility and practically destroy the corrosion resistance of these alloys when they have been quenched from the previously mentioned high temperatures. It apparently does not become subject to intergranular corrosion.

If articles made from these alloys are fabricated by hot rolling or other hot working, then the desired condition of the metal may be obtained by governing the finishing temperature so as to produce the desired fine grain in the metal. The finishing temperature for any working of the metal which involves substantial deformation should be above the temperature at which ductility is substantially reduced, while low enough to obtain the desired small grain size. It is usually desirable in the case of plain chromium-nickel-iron-carbon alloys of usual carbon content to work as much as possible down to near 1800 degrees F., although working to a somewhat lower temperature may be desirable for alloys containing some additions, such as those containing silicon or molybdenum. Usually, the finishing temperature should not be higher than about 1850 degrees F. Usually, with these alloys the desired conditioning of the metal

will be secured by cooling either quickly or slowly from a temperature only slightly above the temperature of recrystallization, that is, from a temperature of about 1800 degrees F., and preferably not substantially over 1850 degrees F.

The deterioration of these austenitic chromium-nickel-ferrous alloys which have been quenched from the generally accepted high heat treatment temperatures when used at elevated temperatures is, I believe, due to carbide precipitation in the grain boundaries. Carbide precipitation occurs in these alloys regardless of previous heat treatment when they are heated for sufficient time to temperatures between about 900 degrees F. as a minimum and about 1800 degrees F. as a maximum. At about 1800 degrees F., carbon (carbide particles) again starts to go into solution. This temperature range varies somewhat with variations in analysis of the alloy. With higher carbon or with substantial silicon, for example, the range extends somewhat above 1800 degrees F. and may extend somewhat below 900 degrees F.

When the grain size is small and the carbon content low, carbide precipitation does not seriously impair either the corrosion resistance or the ductility of the alloy; but if the grain size is large, then, even with relatively low carbon content, carbide precipitation has a very marked effect on the metal, resulting in lowering its ductility and large loss in corrosion resistance; and the higher the carbon content, the greater are these losses. The heat treating temperature used before the metal is placed in service determines the grain size and thus permanently establishes the physical properties and limitations of the metal when used at elevated temperatures. The range of temperature for which alloys of the class referred to are usually considered suitable for use within the carbon precipitation range is from about 900 degrees F. to about 1350 degrees F., and it is use within this range which causes the greatest loss of corrosion resistance, either during or after such use. Above about 1350 degrees F., and up to the upper limit of the carbon precipitation range, they are not generally used under conditions requiring maintenance of strength and ductility. Re-heating within this service range of 900 degrees to 1350 degrees F., or even considerably above 1350 degrees F., does not affect the grain size, and, therefore, does not change the relationship of the initial heat treatment temperature as to effect on physical properties.

Carefully conducted tests have shown that when an alloy of the class referred to which has been quenched from a temperature sufficiently high to completely absorb the carbon (for example, the generally accepted high heat treatment temperature of from 1100 to 1200 degrees C.) and which is thereby given a large grain structure, is exposed to corrosive attack after having been subjected in service to a temperature within a range corresponding approximately to said service range of about 900 degrees to 1350 degrees F., an intergranular corrosion takes place which is exceedingly detrimental, penetrating more or less deeply into the metal according to conditions and causing embrittlement of the metal and destroying its characteristics and usefulness. Small grain material, on the other hand, while it may show some corrosion loss under the same conditions after use at such elevated temperatures, does not lose coherence as does the large grained alloy, the corrosion being relatively slight and confined to the surface of the metal, and the characteristics of the metal remaining substantially unaffected. Similar results have been observed in actual use of these alloys.

The extensive tests which I have made on different austenitic chromium-nickel-iron alloys of the class referred to, and my observations of these alloys in use under various conditions, clearly establish that the value of the alloys for use at temperatures within the carbide precipitation range, and especially when exposed to corrosive attack, diminishes with increase in grain size and with increase in carbon content, and that to avoid large grain size in the alloys, heat treatment at the high temperatures most suitable when the alloys are intended for low temperature service should not be used. The grain size increases greatly when the alloys are heated above 1900 degrees F.

Tests which I have made in connection with this invention were made mostly on alloys containing approximately .06 percent carbon, 18 percent chromium, and 9 percent nickel, with small percentages in the neighborhood of .35 percent of manganese and silicon, but other tests show clearly that similar results follow with other alloys of the class referred to and with chromium-nickel-iron alloys containing higher percentages of the chromium and nickel and with other corrosion resistant chromium-iron alloys.

The explanation of the greatly improved corrosion resistance and retention of physical properties of the fine grained alloys when used at temperatures within the carbon precipitation range, and especially from about 900 to about 1350 degrees F., I believe to be as follows. With a given carbon content in the alloy, a certain quantity of carbide particles will precipitate when the temperatures prevailing in service are sufficiently high. The carbide particles are mostly chromium carbide, and the precipitation of these chromium carbide particles removes such an amount of chromium from the solid solution near the grain boundaries as to render these adjacent areas non-corrosion resistant. In coarse grained metal, the ratio of grain boundary extent to grains is relatively small, and even with a very low carbon content the carbide formation in the grain boundaries will usually substantially completely surround the grains and the removal of chromium from the solid solution will then render the area completely surrounding the grains non-corrosion resistant. The metal will then be subject, not only to surface corrosion, but to intergranular corrosion which may proceed to an extent sufficient to result in complete loss of usefulness of the metal. If the grain size is small, the ratio of boundaries to grains is relatively high, and with the amount of carbon in the alloy sufficiently low, the carbide precipitation resulting from the service temperature does not result in the grains being completely surrounded by the carbide particles, but the carbide particles are mostly separated and spaced widely apart so that the corrosion resistance is lowered locally only and general intergranular corrosion does not take place. With the grain size small, corrosion resistance, as stated, is somewhat lowered by the carbide precipitation, but corrosion is relatively slight and is confined substantially to the surface of the metal, and the metal does not suffer from intergranular corrosion, nor is the ductility of the metal seriously affected. When the grains are large, however, with a similar carbon content, the ductility is

substantially impaired even without any corrosion having taken place.

As the carbon content of the alloy increases, the desired grain size diminishes, that is, the ratio of boundary extent to amount of carbide particles must be maintained; otherwise, even very fine grained alloys may not retain their properties under elevated temperature service conditions and exposure to corrosion. The carbon content should, therefore, not be so high that with the small grain size which may be obtained in practice by treating the alloy as hereinbefore pointed out, the grain boundaries will become so filled with carbide particles as to destroy the corrosion resistance of the alloy when in service at elevated temperatures. In general, to retain corrosion resistance the carbon content should not exceed about .15 percent. In some cases, however, it may be desirable to exceed this amount somewhat. When the alloys contain substantial silicon, for example, the silicon tends to form delta iron, which entails a considerable loss in corrosion resistance, and a carbon content slightly higher than .15 percent might in some cases be desirable in order to retain the austenite phase.

A further advantage of the invention is that the treated alloys do not suffer appreciable loss in impact value on exposure to temperatures within the carbon precipitation range. It has been found that while austenitic iron chromium alloys quenched from a high temperature (1100° to 1200° C.) have a better impact value prior to subsequent heating than the same alloys treated according to the invention, they show a large loss of impact value on reheating, whereas the same alloys treated according to the invention maintain nearly their original impact value on being heated at elevated temperature. This is especially noticeable with the alloys of relatively high chromium and nickel content.

It is well known that certain elements such as vanadium, molybdenum and titanium when added to austenitic iron-base alloys in sufficient amounts tend to prevent grain growth. In practicing my new method, therefore, suitable additions of such elements to the alloy may sometimes be of advantage in aiding in securing and maintaining the desired small grain size in the alloy.

The term "elevated temperature" as used in the claims is to be understood as meaning a temperature within the range of about 900 degrees to about 1350 degrees F. The term "low carbon" as used in the claims means a carbon content of not over about .15 per cent. The meaning of the expressions "small grain" and "fine grain" as used in the claims will be clear from the foregoing description, but it may be pointed out that the terms are used as applied to austenitic alloys the grains of which under all corresponding conditions are larger than the grains of plain carbon steel and much larger than those of tool steel. As examples only, an alloy having grains of the order of .001 of an inch in diameter would be a small grain, or fine grain, alloy as the terms are used herein, but one having grains averaging .01 inch in diameter would not be.

It is recognized that on long continued exposure to temperatures within the carbon precipitation range austenitic alloys treated according to the invention may become partly magnetic.

What is claimed is:

1. An article made of low carbon austenitic iron-chromium-nickel alloy which is required to maintain ductility and resistance to corrosion and which is subjected to temperature within the range of 900 degrees to 1350 degrees F. during manufacture or use whereby carbon is precipitated, said alloy being hot worked down to a finishing temperature between 1650 degrees and 1900 degrees F. to produce a fine grain structure and then cooled, the alloy being in ductile condition and having such fine grain structure that when the carbon is precipitated in the form of carbide in the grain boundaries the carbide particles occupy only a minor portion of the extent of the boundaries, whereby the metal remains substantially resistant to intergranular corrosion.

2. An article of low carbon austenitic iron-chromium-nickel alloy which is required to maintain ductility and which is subjected to temperature within the range of 900 degrees to 1350 degrees F. during manufacture or use whereby carbon is precipitated, said alloy being hot worked down to a finishing temperature between 1650 degrees and 1900 degrees F. to produce a fine grain structure and then cooled, the alloy being in ductile condition and of such small grain size that when the carbon is precipitated in the form of carbide in the grain boundaries the carbide particles occupy only a minor portion of the extent of the boundaries, whereby the metal remains ductile.

3. An article of low carbon austenitic iron-chromium-nickel alloy which is required to maintain ductility and resistance to corrosion and which is subjected to temperature within the range of 900 degrees to 1350 degrees F. during manufacture or use whereby carbon is precipitated, said alloy being hot worked down to a finishing temperature between 1650 degrees and 1900 degrees F. to produce a fine grain structure and then cooled, the alloy being in ductile condition and of such small grain size that when the carbon is precipitated in the form of carbide in the grain boundaries the proportion of carbide particles to the extent of the grain boundaries is not sufficient to render the metal subject to intergranular corrosion.

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