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HARDENING ALLOY STEELS

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This invention relates to improvements in surface-hardening or case-hardening alloy steels by nitrogenization, by subjecting the alloy steel in a heated state to the action of ammonia gas or other substance which gives off nitrogen.

It is known that a limited number of alloy steels, such as those containing carbon, aluminium and separately or in any desired combination silicon, manganese, nickel, chromium, molybdenum, tungsten, vanadium, titanium or zirconium can be case-hardened to an extraordinary hardness, without appreciable distortion, by nitrogenization at a temperature not exceeding about 580 degrees Cent., the element which causes the alloy steel to become case-hardened being disseminated throughout the mass of the alloy steel.

It is also known that a limited number of alloy steels, such as those containing aluminium and vanadium can be case-hardened to an extraordinary hardness by nitrogenization at a temperature not exceeding about 580° C., the element which causes the alloy steel to become case-hardened, instead of being disseminated throughout the mass of the alloy steel, being concentrated in the surface layer. In the known methods the hardening element has been alloyed with the surface of the alloy steel by a high heat-treatment, which is separate from and is followed by the nitrogenization heat-treatment. The known alloying heat-treatment, besides being uneconomical, is of disadvantage in being liable to distort the shape of manufactured articles to be case hardened.

The present invention prevents distortion of the basis metal by applying the element (which acts as an agent in the hardening process) as a coating to the surface of the alloy steel, by a cold process.

The improved process enables a specially tough and tenacious case to be obtained, and generally enables a high value of hardness and a greater depth of case to be obtained than with the known process.

The present invention possesses the economical advantage of avoiding the necessity of excessive heat-treatment of the basis metal prior to nitrogenization, while allowing the core of the basis metal to be of a character best suited for special purposes of strength, etc., without regard to suitability for nitrogenization.

In carrying out the invention, there is applied to the surface of the alloy steel to be case-hardened while cold a film or coating of copper, silver, platinum, arsenic or cobalt, or any combination thereof, the coating being porous and thin enough to permit penetration of nitrogen to the alloy steel and serving as a nitride promoting agent to aid or cause the surface layer of the alloy steel to take up nitrogen and to become exceptionally hard when heated; the alloy steel is heated; and the heated coated alloy steel is subjected to the action of nitrogen or a substance which gives off nitrogen. Some metals are not suitable as coatings for the purpose of the present invention, for example, nickel, cadmium, zinc and tin.

The most suitable temperature to which the coated alloy steel should be heated varies according to the alloy steel, but generally speaking lies within the range 450 to 650 degrees Cent.

Immediately prior to receiving the coating, the alloy steel preferably is cleaned.

The coating can be produced on the alloy steel by any convenient method such as electro-deposition, or spraying, or chemical displacement from an aqueous solution. When the coating is sprayed on, it may be thicker than when it is electro-deposited. In any event, the coating must be thin enough to permit penetration of the nitrogen to the alloy steel. When the coating is sprayed on a coating of the order of 0.0015 inch in thickness is suitable. When the coating is electro-deposited, or obtained by chemical displacement from an aqueous solution, a coating of the order of 0.00001 inch in thickness is suitable. It is believed that the coating, for example when electro-deposited, tends to prevent decarburization, which is of importance in obtaining a highly tenacious layer.

The invention is applicable, for example, to chromium steels, nickel-chromium steels, nickel-chromium-tungsten steels, aluminium-chromium steels, aluminium-chromium-mo-

lybdenum steels, high manganese steels, chromium-nickel-manganese steels, silicon-chromium steels and chromium-molybdenum steels. Alloy steels containing from about 1 to 20 per cent of chromium can be treated.

By the described process a case having a thickness of the order of 0.005 inch to 0.03 inch may be obtained, according, inter alia, to the nature of the alloy steel treated, and the duration and temperature of treatment.

As an example of the use of a copper coating:—An alloy steel containing about 14 per cent of nickel, about 14 per cent of chromium, about 2 per cent of tungsten and about 0.36 per cent of carbon is cleaned by immersion for a few minutes in dilute sulphuric acid, washed in water, plated with copper electrolytically, and subjected to treatment at a temperature of about 550 degrees Cent. for about 90 hours in a current of ammonia gas. The ammonia gas may conveniently be obtained, for example, from liquid ammonia.

As another example of the use of a copper coating:—An alloy steel containing about 8 per cent of nickel, about 20 per cent of chromium and about 0.12 per cent of carbon is cleaned by immersion for a few minutes in dilute sulphuric acid, washed in water, plated with copper electrolytically, and subjected to treatment at a temperature of about 500 degrees Cent. for about 90 hours in a current of ammonia gas.

As a further example of the use of a copper coating:—An alloy steel containing about 5 per cent of manganese, about 12 per cent of nickel, about 3.5 per cent of chromium and about 0.5 per cent of carbon is cleaned by immersion for a few minutes in dilute sulphuric acid, washed in water, plated with copper electrolytically, and subjected to treatment at a temperature of about 550 degrees Cent. for about 90 hours in a current of ammonia gas.

As another example of the use of a copper coating:—An alloy steel containing about 1 per cent of chromium, about 0.2 per cent of molybdenum, about 0.4 per cent of manganese and about 0.3 per cent of carbon is cleaned by immersion for a few minutes in dilute sulphuric acid, washed in water, plated with copper electrolytically and subjected to treatment at a temperature of about 550 degrees Cent. for about 90 hours in a current of ammonia gas. The increase of hardness so obtained with the low chromium steel is somewhat less than that obtained with the high chromium steels above mentioned.

As an example of the use of a sprayed coating, a steel containing about 14 per cent of nickel, about 14 per cent of chromium, about 2 per cent of tungsten and about 0.36 per cent of carbon is given a sprayed coating of copper, and is afterwards subjected to treatment at a temperature of about 550 degrees Cent. for about 90 hours in a current of ammonia gas.

By way of comparing the already known process with the present process, the following examples may be mentioned:—Experiments, carried out at a temperature of about 500 degrees Cent. have shown that when applied to steel containing about 0.14 per cent of carbon, about 8 per cent of nickel, and about 17 per cent of chromium, the already known process gives no commercially useful increase in hardness; whereas the improved process using a copper coating gives a considerably increased hardness, at least equal to and in some cases greater than that given by the known process on steel containing about 0.45 per cent of carbon, about 1.77 per cent of chromium, about 0.31 per cent of molybdenum and about 1.32 per cent of aluminium. Further, when ordinary stainless steel (containing about 0.25 per cent of carbon, up to about 0.3 per cent of nickel and about 13 per cent of chromium) is subjected to treatment at a temperature of about 500 degrees Cent. in a current of ammonia gas, a higher value of hardness and a greater depth of case can be obtained where a coating of copper or other suitable metal or metalloid is present according to the improved process, than can be obtained without said coating according to the known process, under conditions otherwise similar.

As an example of the use of a silver coating:—A steel containing about 13 per cent of chromium, about 0.25 per cent of carbon and up to about 0.3 per cent of nickel may be coated with silver, for example by electro-deposition or by spraying, and then subjected to treatment at a temperature of about 500 degrees Cent. for about 90 hours in a current of ammonia gas.

As another example of the use of a silver coating:—An alloy steel containing about 13 per cent of manganese and about 1.0 per cent of carbon may be coated with silver, for example by electro-deposition, and then subjected to treatment at a temperature of about 500 degrees Cent. for about 90 hours in a current of ammonia gas.

As an example of the use of a platinum coating:—an alloy steel containing about 8 per cent of nickel, about 17 per cent of chromium and about 0.14 per cent of carbon; or about 2 per cent of nickel, about 18 per cent of chromium and about 0.2 per cent of carbon; may be coated with platinum, for instance by electro-deposition, and then subjected to treatment at a temperature of about 500 degrees Cent. for about 90 hours in a current of ammonia gas.

As an example of the use of an arsenic coating:—An alloy steel containing about 8 per cent of nickel, about 18 per cent of chromium and 0.14 per cent of carbon may be coated

with arsenic, for example by electro-deposition or by immersion in a suitable solution, and then subjected to treatment at a temperature of about 500 degrees Cent. for about 90 hours in a current of ammonia gas. A suitable solution for use when steel is to be coated with arsenic by ordinary immersion consists of 6 grams arsenic trioxide in 100 cc. concentrated hydrochloric acid, the bath being worked at about 60 degrees Cent. The article is immersed in the bath for about 2 minutes. When it is desired to deposit the coating electrolytically an electrolyte consisting of an aqueous solution containing about 4 per cent of arsenic trioxide and about 10 per cent of sodium cyanide may be employed.

As an example of the use of a cobalt coating, an alloy steel containing about 8 per cent of nickel, about 20 per cent of chromium and about 0.12 per cent of carbon may be coated with cobalt, for instance by electro-deposition, and then subjected to treatment at a temperature of about 500 degrees Cent. for about 90 hours in a current of ammonia gas.

Although 90 hours has been referred to as the duration of treatment in the above examples, the duration of treatment may be considerably reduced, say to not less than 4 hours, depending upon the thickness of case required.

In general, the alloy steel to be treated may be cleaned by immersion for a few minutes in dilute sulphuric acid and washing in water.

When using ammonia gas, which gives off nitrogen in a highly active state, the amount of dissociation of the gas should preferably be restricted within limits, say to about 20 to 40 per cent dissociation. The gas should preferably be supplied in a dry state for example by being passed through a tube containing quicklime.

The apparatus for carrying out the improved process may consist of a heated chamber, in which the articles of alloy steel after being coated are supported or suspended in such a manner as to permit of free circulation of the gas around the articles, means for regulating the temperature of the chamber, means for regulating the flow of ammonia gas into the chamber, and means for leading the gaseous mixture off from the chamber.

In any of the above examples, after being heated to the suitable temperature for a few of the above mentioned hours in the ammonia gas, the coated alloy steel may be allowed to cool to ordinary temperature without being removed from the current of ammonia gas. The thus treated specimen may then be re-heated to about the same temperature for the remainder of the above-mentioned hours in the current of ammonia gas.

Instead of using ammonia gas as above referred to, other substances liberating nitrogen may be employed.

What we claim is:—

1. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold with a porous, thin, adherent film of a nitride promoting agent of the group consisting of copper, silver, platinum, arsenic, cobalt, which permits penetration of nitrogen to the alloy steel.

2. Process for hardening the surface of an alloy steel consisting in applying to the surface while cold a porous, thin, adherent film of a nitride promoting agent of the group consisting of copper, silver, platinum, arsenic, cobalt, which permits penetration of nitrogen to the alloy steel, heating the coated alloy steel, and subjecting the coated and heated alloy steel to the action of nitrogen or a substance which gives off nitrogen.

3. Process for hardening the surface of an alloy steel containing from about 1 to 20 per cent of chromium, consisting in subjecting it to nitrogenization after coating it while cold with a porous, thin, adherent film of a nitride promoting agent of the group consisting of copper, silver, platinum, arsenic, cobalt, which permits penetration of nitrogen to the alloy steel.

4. Process for hardening the surface of an alloy steel containing a high percentage of manganese consisting in subjecting it to nitrogenization after coating it while cold with a porous, thin, adherent film of a nitride promoting agent of the group consisting of copper, silver, platinum, arsenic, cobalt, which permits penetration of nitrogen to the alloy steel.

5. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold with a porous coating of copper which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

6. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold with a porous coating of silver which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

7. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold with a porous coating of arsenic which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

8. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold by electrodeposition with a porous coating of copper which is thin enough to

permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

9. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold by electrodeposition with a porous coating of silver which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

10. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold by electrodeposition with a porous coating of arsenic which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

11. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold by spraying with a porous coating of copper which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

12. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold by chemical displacement by immersion in an aqueous solution of a copper salt with a porous coating of copper which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process.

13. Case-hardening articles made of an alloy steel by coating them while cold with a porous film of copper which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process, and subjecting the coated articles to treatment at a temperature of about 450° to 650° Cent. for about four to ninety hours in the presence of a substance which gives off nitrogen.

14. Case-hardening articles made of an alloy steel by coating them while cold with a porous film of copper which is thin enough to permit penetration of nitrogen to the alloy steel and acts as a nitride promoting agent in the hardening process, subjecting the coated articles to treatment at a temperature of about 450° to 650° Cent. for some hours in the presence of a substance which gives off nitrogen, allowing the articles to cool to ordinary temperatures without being removed from the presence of the substance which gives off nitrogen, and reheating the articles to about 450° to 650° Cent. for some hours.

15. Case-hardening an alloy steel by subjecting it to nitrogenization after coating it while cold with a layer of a nitride promoting agent of the group consisting of copper, silver, platinum, arsenic, cobalt, which is in a condition which permits penetration of nitrogen to the alloy steel.

Signed at London, England, this 6th day of November, 1930.

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