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METHOD OF CASE HARDENING

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This invention relates to the case hardening of ferrous metals and more particularly to the case hardening of iron and steel articles by heating them in contact with the vapors of an organic compound.

Heretofore iron and steel articles have been case hardened by heating them in an atmosphere of hydrocarbon vapors, and certain alloy steels have been nitrided by heating them in an atmosphere of ammonia. Also, mixed carbon-nitrogen cases have been produced on steel articles by heating them in a mixture of carbon monoxide and ammonia for about 10 hours. It has also been proposed to produce a mixed carbon-nitrogen case on iron and steel articles by heating them in an atmosphere of the vapors of hydrocyanic acid. Although this method produces a satisfactory case in a relatively short time, it has not met with general approval because of the hazards involved in handling hydrocyanic acid, which is a highly volatile, poisonous and somewhat unstable substance.

An object of this invention is to provide an improved method for case hardening ferrous metals to produce a mixed carbon-nitrogen case. Other objects will be hereinafter apparent.

I have discovered that a satisfactory mixed carbon-nitrogen case can be produced on iron and steel articles within a relatively short time by heating them in an atmosphere of formamide vapor. The results obtained by my method are at least equal to those obtained by the use of hydrocyanic acid, and the desired case is produced in a much shorter time than by the use of a mixture of carbon monoxide and ammonia. Formamide is a substantially non-poisonous liquid, boiling at about 200° C. It is substantially non-corrosive to the ordinary metals of construction and may be transported and handled like any non-corrosive liquid.

I have further discovered that the case hardening action of formamide vapor is more or less affected by the catalytic properties of the materials of which the apparatus used for carrying out the process is constructed. For example, I have found that if the chamber in which the articles are case hardened is constructed of or lined with nickel or silica or materials containing substantial quantities of these elements, the results obtained are superior to those obtained in apparatus constructed of or lined with iron or ferrous alloys. I have further found that this advantageous catalytic effect of nickel tends to deteriorate with use, but that this catalytic activity can be regenerated by heating the nickel or nickel-containing surface at a temperature of about 1000° F. or higher for several hours in an atmosphere of ammonia. Nickel which has been treated in this manner is hereinafter referred to as nitrided nickel.

By way of illustration, one method of practicing my invention will be described. The steel articles to be case hardened are suspended in a closed chamber lined with nitrided nickel or siliceous brick, which chamber is provided with suitable inlet and outlet connections. After the air in the chamber has been displaced by passing therethrough a non-oxidizing, non-decarburizing gas; for example, nitrogen, vapors of a hydrocarbon or formamide, the container is placed in a furnace and heated to a temperature of 1500 to 1700° F. When the desired temperature has been reached, liquid formamide is introduced in a continuous small stream during the desired length of time of treating. During the introduction of the formamide, the pressure within the container preferably is maintained at about atmospheric pressure by the provision of a vent connection open to the air; however, higher pressures may be used, if desired. For best results, the formamide is added at least as rapidly as the carbon and nitrogen which it furnishes is taken up by the steel being treated. I prefer to maintain the minimum rate of formamide addition at a volume of liquid formamide equal to about 0.4% of the volume of the unoccupied chamber space per hour. After a period of one to four hours, depending upon the results desired, the flow of formamide is cut off, the container is cooled, and the work is removed.

Preferably the formamide is introduced in such a manner that the liquid will not directly contact with the work being treated. This may be arranged either by dropping or flowing the formamide onto the surface of the interior wall of the container or by having the work spaced sufficiently far from the point of introduction of the formamide so that the liquid is entirely vaporized before it contacts with the work.

In one method of carrying out my invention I supplement the case hardening effects of the formamide by the simultaneous addition of the vapors of an organic carburizing compound, preferably a non-nitrogenous organic compound. The effect of this is to increase the carburizing action in proportion to the nitriding action of the mixture used. Such carburizing material may be introduced simultaneously with the formamide by means of a separate inlet connection or, preferably, the carburizing material is first dissolved in the formamide and the solution introduced into the case hardening chamber. The latter method is usually preferable since it insures that the ratio of formamide to hydrogen-carbon compound will be essentially constant during the course of the process. Various volatile, non-nitrogenous carbon compounds or organic substances; e. g., hydrocarbons or vegetable oils, are well known in the art as having carburizing properties; and these are suitable for supplementing the action of formamide in accordance with my invention. If hydrocarbons are used, they must be added through a separate connection, since these are not sufficiently soluble in formamide. I prefer to use phenolic compounds; for example, phenol or cresol, since these are miscible in formamide within a wide range of proportions and are effective carburizing agents.

My invention is further illustrated by the following examples.

Example I

Bars of S. A. E. 1020 steel were suspended in a closed, nickel-lined chamber, provided with inlet and outlet connections, which chamber had previously been used for nitriding steel with ammonia at temperatures of 950 to 1200° F. The volume of the space in the chamber unoccupied by the steel bars was approximately 5 liters. The air in the chamber was displaced by passing therethrough a stream of oxygen-free nitrogen and the chamber then was placed in a furnace and heated until a thermocouple placed in the center of the container showed a temperature of 1650° F. During a period of one hour formamide was flowed into the container through a connection at the top at the rate of about 1 cc. per minute while the temperature was maintained at about 1650° F. The treating chamber was then removed from the furnace and cooled and the work removed therefrom. The case depth gradients; that is, the percentages of carbon and nitrogen introduced into the steel at various depths from the surface, were determined by placing one of the treated bars in a lathe and cutting successive peripheral layers of 0.003 inch in depth and analyzing the cuttings from each layer for carbon and nitrogen. The following results were obtained:

0.003 inch cuts	Percent carbon	Percent nitrogen
1st	1.50	0.60
2nd	0.97	0.45
3rd	0.91	0.40
4th	0.77	0.28
5th	0.61	0.15
6th	0.49	0.10
7th	0.38	0.06
8th	0.32	0.04
9th	0.21	0.03

The above procedure was repeated except that the rate of flow of the formamide was about 0.5 cc. per minute and the treatment was continued for two hours. The gradient analysis, which in this case was made with 0.004 inch cuts, gave the following results:

0.004 inch cuts	Percent carbon	Percent nitrogen
1st	1.29	0.70
2nd	1.01	0.50
3rd	0.84	0.38
4th	0.71	0.24
5th	0.53	0.15
6th	0.40	0.08
7th	0.36	0.04
8th	0.27	0.02

Example II

S. A. E. steel bars were case hardened by the procedure described in Example I, using a heating chamber having a new nickel lining. The inside volume of the chamber was 9.73 liters and the formamide was introduced at the rate of about 1 cc. per minute during a period of one hour, while the temperature was maintained at 1650° F. Microscopic examination of an etched cross-section of the treated bars showed the depth of the case to be about 0.009 inch.

The above described nickel-lined heating chamber was treated by maintaining an atmosphere of ammonia therein while it was heated to a temperature of about 1200° F. for a period of 8 hours. S. A. E. 1020 steel bars were then case hardened therein with formamide for a period of one hour by the above described procedure. Microscopic examination showed the resulting case depth to be 0.012 to 0.013 inch.

Example III

A disc of S. A. E. 1020 steel was suspended in a vertical silica tube, open at the lower end and having an internal diameter of about one inch, which was heated in a furnace at a temperature of 1650° F., while a mixture of about equal parts by weight of liquid formamide and phenol was introduced at the top of the tube at the rate of 0.5 cc. per minute during a period of one hour. The silica tube was open at the lower end. Microscopic examination of a polished and etched cross-section of the treated steel disc showed the case depth to be about 0.018 inch.

Example IV

The procedure described in Example III was repeated except that the silica tube was replaced by an iron tube of approximately the same inside diameter. The case depth as determined by microscopic examination was 0.012 to 0.013 inch.

Example V

A silica tube about 1 inch in diameter by 24 inches in length was arranged at an angle of about 5 to 10° from the vertical within a furnace. A disc of S. A. E. 1020 steel was suspended at about the mid-point of the tube and a formamide inlet tube was arranged at the top end in such manner that the inflowing liquid formamide would strike the side wall of the tube. The tube was heated to a temperature of about 1650° F., while formamide was introduced at a rate of about 0.5 cc. per minute for a period of 1 hour. Microscopic examination of a cross-section of the treated steel sample showed that a case depth of 0.025 inch had been obtained.

The temperatures suitable for carrying out my process are in general the same as those required for the ordinary case hardening processes, for instance, pack hardening, or hardening by means of a hydrocarbon gas, that is, from 1300 to 1800° F. I prefer to operate at temperatures between 1500 and 1700° F. The time of treatment required will depend upon the degree of case hardening desired. In general the depth of the case produced is proportional to the time and the temperature of the operation. Except in unusual cases, my process will produce satisfactory case hardening by treating the iron or steel for from 1 to 4 hours.

The formamide may be added either as a liquid or as a vapor. Methods for vaporizing formamide with little or no decomposition are known and I prefer to use these methods when vaporizing formamide outside the treating chamber in my process. Such preferred methods comprise spraying or flowing liquid formamide onto a surface maintained at a temperature above the boiling point of the formamide, whereby rapid or instantaneous vaporization is effected. I prefer to add the formamide in the liquid state since this avoids the necessity of providing a separate vaporizer. The formamide should be added substantially continuously since it is very quickly decomposed in contact with the hot surfaces of the treating chamber and the work. To obtain the best results the formamide should be added practically as fast as it gives up carbon and nitrogen to the steel. I have found that good results may be obtained by adding the liquid formamide continuously at a rate equivalent to 0.25 to 1.0% of the volume of the unoccupied space in the treating chamber per hour. If desired, the formamide may be applied at a higher rate; there is no disadvantage except waste in using a large excess of the formamide.

In practicing my invention it will sometimes be desirable to displace the air in the treating chamber before applying heat to the articles to be treated in order to prevent surface oxidation. This however is not essential, since a small amount of oxidation often is not objectionable. The air may be displaced by passing through the treating chamber a non-oxidizing, non-decarburizing gas or vapor, e. g., nitrogen, hydrocarbons or formamide. Preferably, I exclude from the chamber any substantial quantities of gases which tend to decarburize steel, e. g., carbon dioxide, hydrogen, oxygen or water vapor.

I claim:

1. A process for case hardening ferrous metal articles comprising heating said articles to case hardening temperatures in an atmosphere of formamide vapor.

2. A process for case hardening ferrous metal articles comprising heating said articles to a temperature of 1300° to 1800° F. in an atmosphere of formamide vapor.

3. A process for case hardening ferrous metal articles comprising heating said articles to a temperature of 1500° to 1700° F. in an atmosphere of formamide vapor for 1 to 4 hours.

4. A process for case hardening ferrous metal articles comprising subjecting said articles to vapors of formamide at case hardening temperatures in the presence of a catalyst.

5. A process for case hardening ferrous metal articles comprising subjecting said articles to vapors of formamide at a temperature of 1300° to 1800° F. in the presence of silica.

6. A process for case hardening ferrous metal articles comprising subjecting said articles to vapors of formamide at a temperature of 1300° to 1800° F. in the presence of nickel which has been heated in contact with ammonia to at least about 1000° F.

7. A process for case hardening ferrous metal articles comprising subjecting said articles to vapors of formamide and a non-nitrogenous carbon compound soluble in liquid formamide at a temperature of 1300° to 1800° F. in the presence of a catalyst.

8. A process for case hardening ferrous metal articles comprising subjecting said articles to vapors of formamide and a non-nitrogenous carbon compound soluble in liquid formamide at a temperature of 1500° to 1700° F. in the presence of silica.

9. A process for case hardening ferrous metal articles comprising subjecting said articles to vapors of formamide and a phenol at a temperature of 1500° to 1700° F. in the presence of silica.

10. A process for case hardening ferrous metal articles comprising subjecting said articles to vapors of formamide and a phenol at a temperature of 1500° to 1700° F. in the presence of nickel which has been heated in contact with ammonia to at least about 1000° F.

11. A process for case hardening ferrous metal articles comprising heating said articles to a temperature of 1500° to 1700° F. in an enclosed space and continuously vaporizing a solution of a phenol in liquid formamide in said space at the aforesaid temperature.

12. A process for case hardening ferrous metal articles comprising heating said articles to a temperature of 1300 to 1800° F. in an enclosed space and continuously vaporizing formamide in said space at the aforesaid temperature in the presence of a catalytic surface.

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