United States Patent [19]

Lincoln et al.

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[54] **METHOD OF NITRIDING**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 243,824, April 13, 1972, abandoned.

[52] **U.S. Cl.** **148/16.6;** 148/31.5

[51] **Int. Cl.** **C23c 11/16**

[58] **Field of Search** 148/12.1, 16.6, 31.5

[56] **References Cited**

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[57] **ABSTRACT**

A process for the nitriding of ferrous work utilizing a carrier gas consisting essentially of nitrogen with controlled low quantities of hydrogen. A ductile, wear resistant, hardened part is obtained by nitriding with a carrier gas containing 2–4 percent hydrogen, the balance being nitrogen, to which ammonia gas is added in quantities sufficient to prevent more than 10 percent hydrogen being present. Additionally, the ferrous parts are treated over a relatively short period of time, thereby obtaining a thin iron nitride layer on the surface of the work.

1 Claim, 2 Drawing Figures

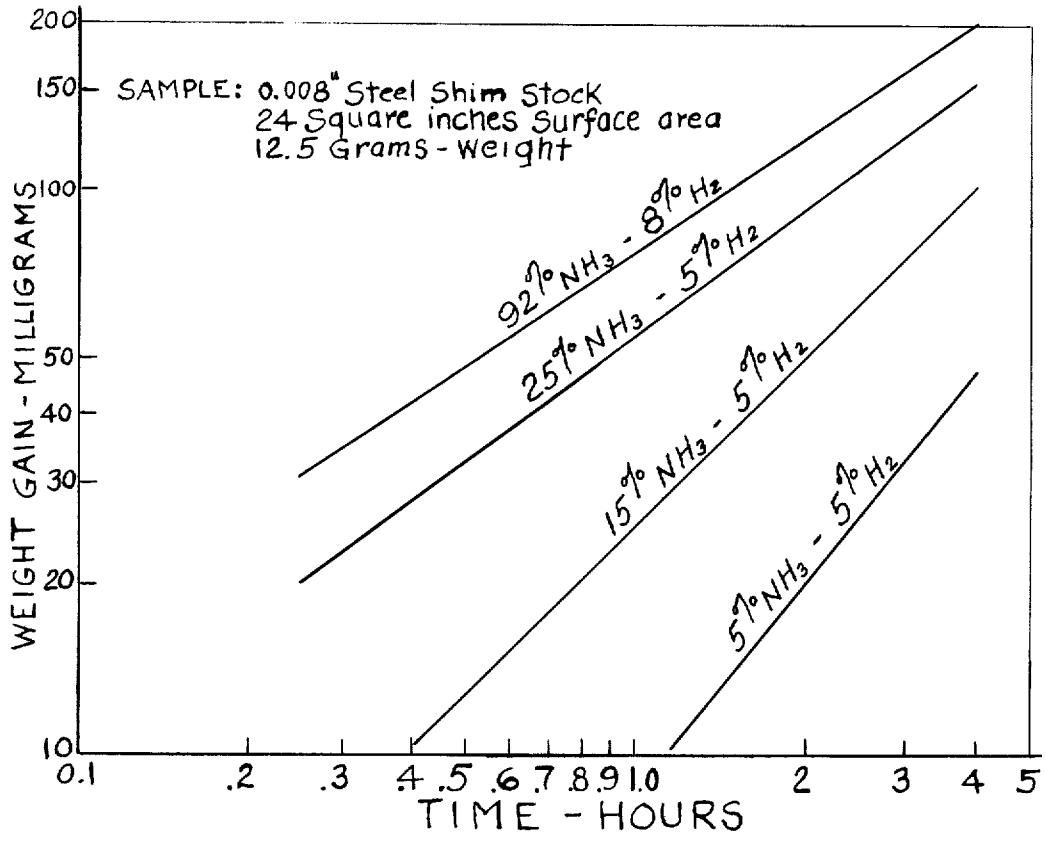

SAMPLE: 0.008" Steel Shim Stock
24 Square inches Surface area
12.5 Grams - Weight
92% NH3 - 8% H2
25% NH3 - 5% H2
15% NH3 - 5% H2
5% NH3 - 5% H2
WEIGHT GAIN - MILLIGRAMS
TIME - HOURS
200
150
100
50
40
30
20
10
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
2
3
4
5

Fig. 1.

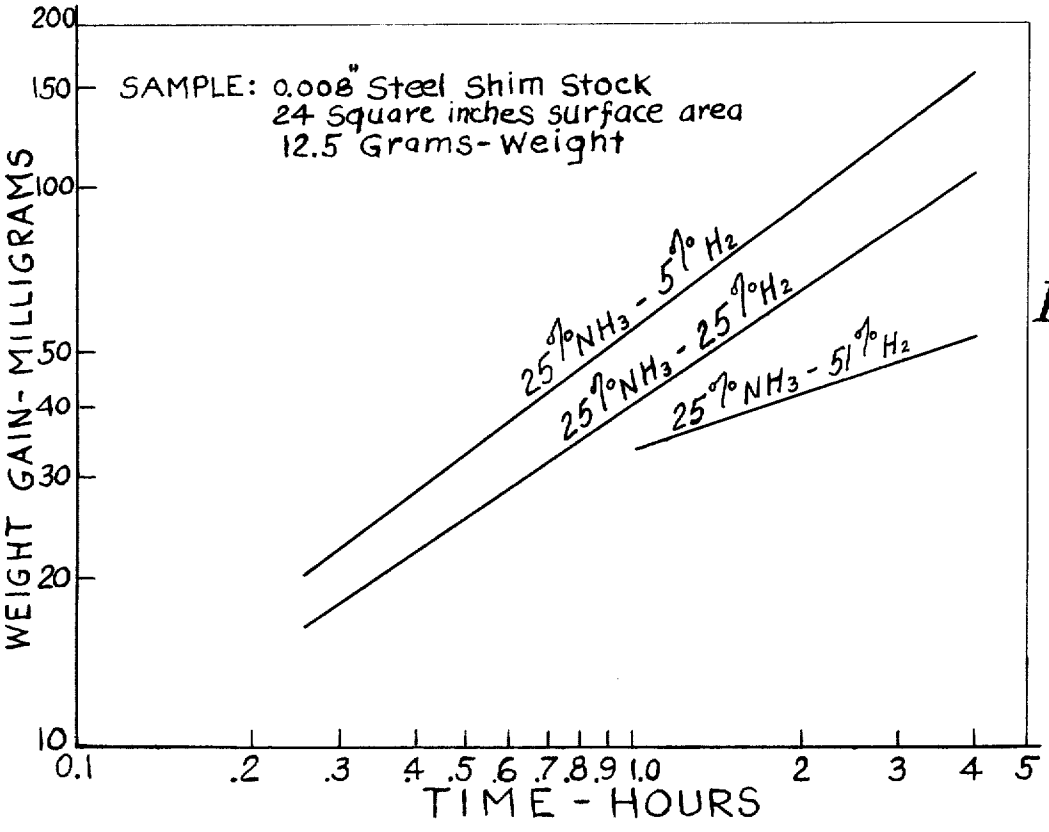

SAMPLE: 0.008" Steel Shim Stock
24 Square inches surface area
12.5 Grams - Weight
25% NH3 - 5% H2
25% NH3 - 25% H2
25% NH3 - 51% H2
WEIGHT GAIN - MILLIGRAMS
TIME - HOURS
200
150
100
50
40
30
20
10
0.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
2
3
4
5

Fig 2.

METHOD OF NITRIDING

This is a continuation-in-part of application Ser. No. 243,824, filed Apr. 13, 1972 now abandoned.

BACKGROUND OF THE INVENTION

Throughout the years, methods have been sought to improve the properties of ductility, hardness, high strength and durability in ferrous parts. One means of achieving these properties is to nitride the parts to produce a nitrogen compound layer on the surface of the ferrous parts and a nitrogen solution beneath the layer. Previous attempts have been made to nitride a ferrous workpiece through a method using a gaseous medium. These attempts have primarily concentrated on the cracking of ammonia to produce nascent nitrogen which will react with the metal to nitride the same. Mixtures of gases such as ammonia with hydrogen or endothermic gases have been suggested in the past and high percentages of ammonia, at least 50 percent, along with hydrogen in excess of 20 percent had been used in these processes. These prior processes have had certain shortcomings, the basic one being that the gaseous nitriding processes resulted in brittleness being imparted to the ferrous workpiece. Additionally, hydrogen gas is expensive to produce and the high percentages of hydrogen create a safety hazard.

In order to overcome the shortcomings of the gaseous processes, various investigators have turned to nitriding with a salt bath. This usually involves a form of cyanide and/or cyanate being used to nitride the metal. Although this has shown some success, the basic disadvantage is that the cyanide process is an inconvenient and hazardous method of accomplishing the nitriding process. Contamination of the salt bath is another problem associated with such a process. It obviously would be advantageous to provide a process for nitriding ferrous parts through a gaseous method which yields ductility, hardness and wear resistance.

It is therefore an object of this invention to provide a novel gaseous method of nitriding metal.

It is another object of this invention to nitride ferrous work using a gaseous medium which results in the work having ductility, hardness and high fatigue strength.

It is still another object of nitriding ferrous parts in a process which is safer to use than previous processes containing high quantities of hydrogen.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows the effects on rate of nitriding by maintaining the hydrogen constant and increasing the ammonia.

FIG. 2 shows the effects on the rate of nitriding by maintaining the ammonia constant and increasing the hydrogen.

SUMMARY OF THE INVENTION

A process using a gaseous medium has been found in which ferrous workpieces may be nitrided with the result that desirable properties are imparted to the workpieces. The gaseous medium includes a carrier gas consisting substantially of nitrogen but containing a relatively small amount of hydrogen into which is introduced relatively small quantities of ammonia gas, these quantities of ammonia ranging from 5–25 percent. The amount of hydrogen present in the carrier gas is preferably about 2–4 percent of the total carrier gas mixture. The process takes place at a temperature of approximately 1,000°F. ± 100° and the work is exposed to the gaseous atmosphere for a relatively short period of time, the average being approximately 4 hours. In this way, a relatively thin compound layer of iron nitride is formed on the surface of the work and the nitrogen solution penetrates sufficiently deep into the work to impart the desired property of increased fatigue strength.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The neutral or carrier gas in which the nitriding process takes place is first produced and introduced into a suitable furnace. Such a carrier gas consisting substantially of nitrogen with traces of CO and hydrogen may be produced exothermically by the reaction of air with methane or natural gas. The products of combustion are cooled, the CO_2 is removed, as by a molecular sieve, and the gas is dried to remove H_2O. The resulting carrier gas is approximately 95–97percent nitrogen, ½ to 1–½% CO and 2–4% H_2, and will be referred to in the balance of this specification as carrier gas. It will be appreciated that the carrier gas does not react in the nitriding process, but is the vehicle for exposing the workpieces to a desired quantity or density of ammonia gas. As such, another neutral gas, such as helium, may work equally as well as nitrogen in the carrier gas. It should be noted that the carrier gas is noncombustible because the amount of H_2 is below the combustion level, which level is about 4 percent. After the carrier gas has been introduced into the furnace, the ferrous parts to be treated are placed in the furnace and are heated to a temperature of about 1,000°F.

The parts are maintained at this temperature for a period of ½ to 10 hours. This is done by first mixing a given quantity of ammonia with carrier gas and then introducing the ammonia-carrier gas mixture into the furnace so as to maintain a given percentage of ammonia in the furnace. Next, ammonia is added to the carrier gas. The quantity of ammonia will vary depending upon the type of ferrous part being treated, the content varying from 5–25 percent of the furnace atmosphere. As the ammonia is added to the heat treating chamber, it reacts with the hot ferrous parts to form an iron nitride compound on the surface of the ferrous parts. A sufficient quantity of the gas mixture within the furnace is drawn off and new gas (ammonia-carrier gas mixture) is added to control the composition of the treating gas so that the hydrogen content in the furnace is at least 3 percent but does not exceed 10 percent. Lower amounts of hydrogen are recommended because the equation $Fe + xNH_3 \leftrightarrows Fe\ xN + H_2$ is reversible and larger amounts of H_2 cause the reaction to tend toward the left side of the equation thereby retarding the nitriding reaction. In addition, an atmosphere containing only 3–10 percent hydrogen is less hazardous, the combustion level being approximately 4% H_2, thereby reducing the hazard of explosions.

EXAMPLE I

Parts made of 1035 steel were placed in a furnace in which the carrier gas comprises 95–97% N_2 and 2–4% H_2 and heated to a temperature of 1,050°F. Ammonia in the amount of 12 percent was added to the carrier gas. The 1035 steel was treated for approximately 4 hours after which the treatment was discontinued. An X-ray diffraction pattern was conducted to determine the results achieved. It was found that a major portion

of the surface of the steel contained epsilon phase iron nitride, which is a solid solution of nitrogen and iron, and there were no traces of Fe_4N or ferrite. A compound layer of 0.0005 inch thickness was found to have formed on the surface of the parts.

EXAMPLE II

Other parts made of 1035 steel were heated to approximately 1,050°F. in a furnace containing the same carrier gas as in Example I, and into which ammonia in the amount of 17.2 percent was added. The treating was continued for 4 hours and the results by X-ray diffraction again showed that the major portion of the surface of the steel was epsilon phase iron nitride, there being no evidence of Fe_4N or ferrite.

EXAMPLE III

A sample of 4620 steel was nitrided in a furnace in which the carrier gas was the same as in Example I, and into which ammonia in the amount of 15 percent was added. Again the temperature of the heat treating was 1,050°F. and the time was for 4 hours. Once more it was found that the epsilon phase was evident and there were no traces of Fe_4N or ferrite.

Physical testing of these examples showed that they had achieved a surface hardness of over Rc 70 and that these samples were completely ductile. Thin shim stock which had been nitrided to produce a file hard surface could be flexed 180° without fracture. All samples were found to have a relatively thin, approximately 0.0005 inch, complex compound layer of various nitrides on the surface, and nitrogen in solution below this surface layer. The thin compound layer of complex nitrides gives increased wear resistance to the sample, particularly when it is porous free. The diffused region of nitrogen in solid solution will impart increased fatigue strength.

Increasing the amount of ammonia in the atmosphere, while holding the hydrogen constant, caused the sample to not only gain more weight, but at an increased rate as shown in FIG. 1. On the other hand, increasing the amount of hydrogen while holding the ammonia constant caused a marked decrease in the weight gain as shown in FIG. 2. These effects can be illustrated using the ammonia breakdown equation:

$$2NH_3\ (gas) \rightarrow \underline{2N}\ (\text{in iron}) + 3H_2\ (gas)$$

Ammonia in equilibrium with nitrogen in iron plus hydrogen gas.

As stated previously, increasing the ammonia would tend to shift the equation to the right, to form more nitrogen in iron; whereas, increasing the hydrogen would tend to shift the equation to the left, to form less nitrogen in iron, which is what was noted in weight gain tests using a recording balance. The magnitude and rate of these changes were demonstrated by these tests.

Determination of the effects of ammonia and hydrogen on the thickness and composition of the compound layer was made using microscopic techniques and X-ray diffraction techniques. As would be expected, higher ammonia contents produced a thicker compound layer; however, the porosity and brittleness were also increased. Using an atmosphere having between 15 percent and 25 percent ammonia, the compound layer was relatively pore-free. Increasing the hydrogen content at a constant ammonia decreased the compound layer thickness but its effect was not nearly as pronounced as noted with variations in ammonia. This effect was demonstrated by a test on shim stock of 1008 steel.

In the first run, the 1008 steel shim stock sample was heated to a temperature of 1,050°F. within a furnace containing a gas mixture of 92 percent NH_3 and 8% H_2. The treatment was maintained for 4 hours. The compound layer was examined and it was found to have 40 percent porosity.

A second run was made with similar 1008 steel samples under the same conditions as above with the exception that the gas mixture within the furnace contained 25.5% NH_3 and 4.9% H_2, the balance being nitrogen. The surface layer was found to have 15 percent porosity, which figure is at the threshold of acceptability.

One final run was made under the same conditions with the exception that the gas mixture within the furnace was 15% NH_3 and 5.6% H_2, the balance being nitrogen. No porosity was detected in these samples.

Another important observation was noted from these samples. The overall thickness of the samples was approximately 0.008 inch and this thickness did not appreciably change even with the high nitrogen compound layer samples. This indicates that the compound layer is not built up on the surface, but instead just alters the surface layer of iron to form iron nitride. Some growth will probably take place due to the addition of nitrogen into the steel, but its magnitude is not large enough to allow the change in thickness to be measured. This is important for at least two reasons: (1) Materials which are not homogeneous, such as cast irons, and have graphite flakes, or nodules, that extend all the way to the surface, will not form a complete compound layer, but will have fatigue strength increased even with the presence of stress risers. (2) Dimensional changes and distortions with nitrided parts are held to a minimum.

What is claimed is:

1. A process for nitriding ferrous parts to produce a thin compound layer of complex nitrides containing principally epsilon phase without the presence of Fe_4N comprising the steps of:

placing said parts in a furnace containing an atmosphere defined as a noncombustible carrier gas consisting essentially of 95–97 percent nitrogen, ½ to 1½ percent carbon monoxide and 2–4 percent hydrogen;

heating said parts to an approximate temperature of 1,000°F;

introducing ammonia gas to said carrier gas to form a nitriding atmosphere within the furnace, said nitriding atmosphere containing 5–25 percent ammonia gas by volume;

maintaining the hydrogen gas in said nitriding atmosphere at a value no greater than 10 percent by volume in said nitriding atmosphere by introducing additional quantities of carrier gas while withdrawing portions of said nitriding atmosphere; and

subjecting said parts to said nitriding atmosphere for a period between ½ to 10 hours until a compound layer of approximately 0.0005 inch thickness and composed principally of epsilon phase exists at the surface of said parts.

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