

EXPERIMENTS TO DETERMINE THE EFFECT OF

NITROGEN UPON NON-FERROUS METALS

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INTRODUCTION

As a result of ever increasing demand for metals which will stand up under severe working conditions as friction, corrosion, high temperatures, etc., metallurgists are striving by every conceivable alloying and case hardening method to produce metals which will meet the multiplicity of demands made by our present day machinery.

While they have been very successful in producing alloys of satisfactory hardness and utility, the machinist invariably encounters difficulty in machining such alloys, and, incidentally, the cost of such alloys is comparatively high. For these reasons, mainly, their use is restricted.

In 1913 a study was made of a section of a 1895 model--12 inch gun, and the following abstract from the nitriding symposium of the American Society for Steel Treatment transaction of 1929, explains the findings of the investigation of that period:

"There is a hard surface skin known as the 'white layer' formed in the bore of gun tubes during service.

"This layer seems to result from the effect of hot powder gases in contact with gun steel at high pressures. It is concluded from metallographic and X-ray diffraction evidence that this layer is the result of nitrification of the bore surface.

"The layer studied seemed to be largely austenitic. The Alpha and Gamma lattices of the iron crystals were found to

be enlarged by 0.5 and 0.6 per cent respectively. The Alpha lattice of the iron crystals in the case of nitrided chromium-Aluminum steels was found to be enlarged by 0.5 per cent.

"It is suggested that this enlargement is due to the absorption of nitrogen and that most of the hardness of the Fe-N solid solutions. It is pointed out that the austenitic case of the gun tube merits further study as a possible extension of nitriding to other steels for special services."

It is worthy of note that the members of the above mentioned investigation recognized possibilities of hardening metals by nitriding.

The growing interest manifested in the case hardening of special steels with ammonia gas to obtain extraordinary surface hardness without warping or distortion indicates that the evolution of these special metals represents one of the most important metallurgical developments in recent years.

The ammonia case hardening process which is termed "nitriding" consists in subjecting the machined and preferably heat treated article to the action of ammonia gas under certain conditions whereby remarkable surface hardness is imparted to the material without any further treatment. Remarkable wear-resisting properties together with retention of hardness at elevated temperatures and marked resistance to atmospheric water and salt water corrosion are to be obtained by this method.

The common method of case hardening involves a heat treatment after the carbonization of the material. Articles treated under this condition undergo warping or distortion and have less surface hardness than that obtained by nitriding.

Although the introduction of nitrogen into a metal through the medium of ammonia gas is not new, credit for the present practicability of the process is due to the thorough study of the problem by Dr. Adolph Fry of the Krupp Works in Germany, and to its further development by investigators in this country and abroad. They have succeeded in developing the process to a point where it is commercially acceptable in the treatment of steels and steel alloys.

NITRIDING OF STEELS

The value of nitriding of steel may be summed up as follows:

1. The nitriding process, if handled properly, gives surface hardness with practically no distortion.
2. The physical properties of the core material are not changed by nitriding.
3. The hardness and wear resistance are higher than those of any other steel testing process.
4. The hardness is not injured by tempering; temperatures were above 950° Fahrenheit.
5. Nitrided parts are free of internal stresses and, therefore, free from ageing effects (important for gages, crankshafts, etc.)
6. Nitrided parts are rust-resisting to a certain extent.
7. The process may be adapted to various applications having varying requirements. This is done by selecting a nitriding steel of the proper composition for each purpose.
8. The best results are obtained by quenching and tempering the raw material, and then carrying out the machining and nitriding operations.
9. Various nitriding agents have been tested in the past several years, not only ammonia gas but also cyanides, sulpho-cyanides, and so on. Some of them, such as sodium nitrate, failed to give surface hardness; whereas others

such as sodium potassium cyanide, gave good surface hardness but were less easy to handle than ammonia gas.

10. Circulation of gas by some means gives better and more uniform nitriding.

The following conditions should be avoided:

- A. Surface oxidation
- B. Foreign metals touching the part to be nitrided.
- C. Foreign substances in the ammonia, such as oil and water.

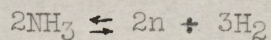
Since the author's experiments with non-Ferrous metals were based upon the methods and practices applied to the nitriding of steels, a brief discussion of the process will be made.

The commercial equipment required for the case hardening of articles with ammonia consist of a suitable furnace provided with automatic temperature control, a gas-tight container made of a material such as chrome-Fe, which will not be acted upon when exposed to ammonia at the nitriding temperature, a tank of ammonia provided with a suitable needle valve for controlling the flow of the gas inlet and outlet tubes, and finally a special pipette for determining the extent of the ammonia dissociation.

The part to be nitrided is placed in this furnace, and after the furnace has been tightly closed the gas is turned in and the heat is applied. The operation is very simple and it requires very little attention.

THEORY:

The ammonia gas decomposes to a certain extent into nitrogen and hydrogen according to the following reaction:



The nitrogen, which is very active at the moment of decomposition of the ammonia gas, undoubtedly combines to a certain extent with the iron and with the alloying elements in the steel to form nitrides. These nitrides, which are in solid solution or, more likely, in a fine state of dispersion in the case, impart extreme hardness to the surface of steel, a hardness which gradually decreases inwardly until it corresponds to that of the core.

The gas moisture leaving the furnace consists of hydrogen, nitrogen and undissociated ammonia.

EFFECT OF NITROGEN ON NON-FERROUS METALS

So far as the author has been able to determine, there has been no published results of experiments on the "Effects of Nitrogen on Non-Ferrous Metals."

One hesitates to attribute the non-existence of such material to the lack of research on this subject. A more logical explanation is that such investigations have not met with success in changing the physical characteristics as in the case of steel alloys.

In so far as such limited experiments are an indication, the following metals are affected in no way by nitrogen as applied by the steel nitriding process:

1. Copper,
2. Aluminum,
3. Nickel,
4. Silver,
5. Brass,
6. Lead.

EQUIPMENT:

1. Tank of Ammonia.
2. Empty receiving tank.
3. Ammonia Gage.
4. Piping.
5. Bunsen Burner.
6. Pan.
7. Heating Mediums. (Paraffin, Borax, etc.)
8. Pyrometer.
9. Miscellaneous.

The equipment was assembled as shown by accompanying drawing.

The material to be nitrided is inserted in the equipment at A, the plug is screwed in and ammonia gas is passed from the tank of ammonia over the metal into the low pressure tank. At the same time the metal is kept at a constant temperature by the heating medium which is kept boiling by a gas flame.

PROCEDURE:

Before starting the experiments on non-ferrous metals, it was first necessary to adjust and operate the equipment so that it successfully nitrided steel. A three inch piece of 3/4 inch tool steel was placed in the apparatus and the temperature was brought up to 950° Fahrenheit. Ammonia gas was passed over the sample under atmospheric pressure. This experiment was carried on for a period of eight hours. At the end of this period the piece was tested for hardness on the Brinell machine. There was no appreciable increase in hardness.

The experiment was repeated several times with a variation of temperature from 600° F. to 1000° F. and a variation in pressure from atmospheric to 60 pounds gage pressure. Six trials failed to produce any increase in hardness of the sample.

The equipment was taken apart and by means of graphite packing several small ammonia leaks in the pipe line were repaired. The above experiments were then repeated. This time a nitrided case was secured under the following conditions:

ORIGINAL : HARDNESS : BRINELL :	TIME OF : HEATING : HOURS :	AMMONIA : PRESSURE : POUNDS :	TEMP. : FAHREN : :	BRINELL : HARDNESS : :	COLOR OF CASE :
212	36	30	930	230	GRAY
212	29	60	900	220	"
212	8	30	900	212	"
212	48	10	930	235	BLUE

COPPER:

The equipment, after successfully nitriding steel, was considered servicable for nitriding purposes.

A 3 inch piece of large diameter copper wire was thoroughly cleansed and scraped and placed in the apparatus. Below is a tabulation of the experiments, giving the conditions and results of each,

ORIGINAL : HARDNESS : BRINELL :	TIME OF : HEATING : HOURS :	GAGE : AMMONIA : PRESSURE : POUNDS :	TEMP : FAHRE : :	BRINELL : HARDNESS : AFTER :	COLOR OF CASE :
42	8	9	600 ⁰	42	NO CHANGE
42	10	10	500	42	" "
42	15	10	600	42	" "
42	24	5	600	42	" "
42	30	30	810	36	NO CHANGE COPPER
42	48	20	650	42	ANNEALED NO CHANGE
42	48	5	500	42	" "
42	24	60	700	42	" "
42	24	30	600	42	" "

This series of tests seemed to indicate that copper and nitrogen do not unite directly to form a Cu-N solid solution~~as~~ in the case of iron. Such a solution may possibly exist, but another process must be devised for bringing about the union of the two.

ALUMINUM:

Aluminum seems to be a necessary element in steel alloys which gives the most favorable nitriding results, but as an independent metal no physical change resulted from the nitriding process. A series of six tests were carried out, each varying in time, temperature and pressure. No appreciable results were obtained.

NICKEL:

Messrs. V. O. Homerberg and J. P. Walsted, members of the faculty of Massachusetts Institute of Technology, carried on an exhaustive study of the nitriding process as applied to steel alloys for the Ludlum Steel Company and, in so doing, indirectly determined that nickel and tin cannot be nitrided in the ordinary manner. An abstract from this discussion is given:

"It frequently happens that threaded portions or other parts of articles must be protected from nitriding. Nickel plating to a depth of about 0.0005 has proved to be satisfactory. A coating of tin or tin solder is also an effective protective agent. Although tin melts at a temperature considerably lower than the nitriding temperature, a sufficient amount will adhere by surface tension to provide ample protection."

In spite of this discovery, there remained a possibility that nickel would behave differently when treated independently; however, the equipment was cast steel, which gave practically the same conditions which the above named authors found.

The tests were made on a pure nickel alloy, but a thorough examination failed to show any physical change.

SILVER:

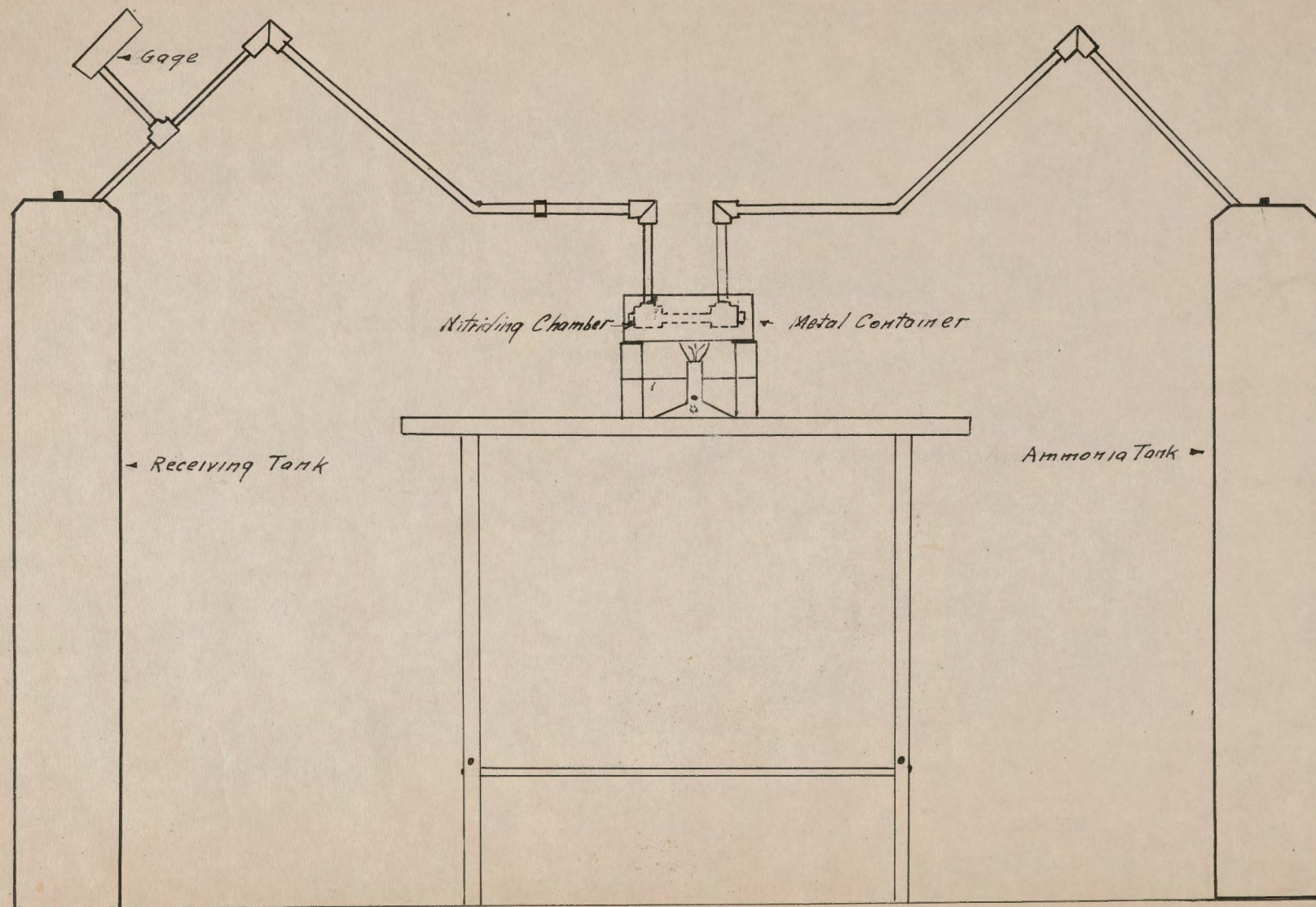
A piece of silver was treated in a similar way as the above metals. There was no change in hardness, but there was a change in the color from the characteristic silver luster to a dull dark color. This combination was only on the surface, however. While it could not be rubbed off, it could be scraped off easily. This coloration was the only observable change in the sample.

BRASS AND LEAD:

Brass and lead were subjected to the nitriding conditions but no results were obtained. It was necessary to treat lead at relatively low temperatures because of its low melting point.

CONCLUSIONS

Although these experiments were necessarily limited as to time and number, the complete failure of the non-ferrous metals to receive nitrogen under these experimental conditions seems to indicate that little should be expected along these lines.



NITRIDING EQUIPMENT

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APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrent its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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