# AMMONIA IN METALLURGY

by

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## ABSTRACT:

This report discusses the metallurgical uses of anhydrous ammonia in heat treating processes. Two basic uses are discussed - as a furnace atmosphere and in case hardening. The most important furnace atmosphere in competition with that derived from ammonia is commercial nitrogen which may be used with hydrogen or other additives. The choice of atmosphere depends on several factors which are discussed. Ammonia gas carbonitriding is clearly superior to liquid cyaniding as a case hardening treatment, though carburizing will remain preeminent.

## AMMONIA IN METALLURGY

## INTRODUCTION

Anhydrous ammonia is widely used in the metals processing industry; it plays two different roles. Ammonia is a source of a protective atmosphere during the heat treatment of metal. It is also a source of nitrogen for case hardening by carbonitriding or by nitriding. The specifications for metallurgical grade ammonia are quite tight: minimum ammonia content - 99.99%, maximum water content - 33 ppm by weight, maximum oil content - 2 ppm by weight .

This report briefly describes metallurgical heat treating processes, disucsses the use of ammonia in those processes and compares ammonia with other gases used in the industry. The report is in two sections. The first section deals with furnace atmospheres; the second with case hardening.

## PROTECTIVE ATMOSPHERES IN METAL FURNACES

A protective atmosphere is used in the furnace during most types of heat treatment of metals. The atmosphere is used to prevent surface oxidation or scaling of ferrous and nonferrous metals during heat treating, brazing or other operations in which metals are exposed to elevated temperatures. The atmosphere also maintains the carbon content of steel during the heat treatment.

### Heat Treating Processes

Heat treating is any heating and cooling process performed to alter metallurgical structure, mechanical properties or the residual stress state of a metal product. Definitions of some common heat treatments follow:

**Normalizing:** A heat treating process that may increase or decrease the strength and hardness of a given steel in a given product form depending on the thermal and mechanical history of the product. The treatment improves machinability and grain-structure, reduces residual stresses and ensures a uniform structure and hardness.

**Annealing:** A treatment that consists of heating to and holding the metal at a suitable temperature, followed by cooling at an appropriate rate. The treatment facilitates cold working or machining, improves mechanical and electrical properties and promotes dimensional stability.

**Tempering:** Previously hardened or normalized steel is heated and cooled to increase ductility and toughness.

**Brazing:** A process for joining metals in which a molten filler metal is drawn by capillary attraction into the space between adjacent surfaces of the parts to be joined.

**Sintering:** The agglomeration of loose or compressed powders by heating at a temperature below the melting point of the major constituents. The process increases strength, ductility and thermal and electrical conductivity.

**Decarburizing:** During some heat treatments, the carbon in steel can be removed by reaction with components of the the furnace atmosphere. Carbon dioxide is decarburizing according to the following equation:

$$(C) + CO_2 \longrightarrow 2CO$$

where (C) represents carbon dissoved in the steel. This reaction proceeds until the steel surface is completely free of carbon or until no carbon dioxide remains. Once the carbon has been completely removed from the steel, the carbon dioxide will oxidize the steel.

Hydrogen is decarburizing according to:

$$(C) + 4H \longrightarrow CH_4$$
$$\text{or}$$
$$(C) + 2H_2 \longrightarrow CH_4$$
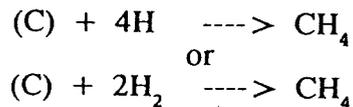
Water vapour combines with the carbon in steel according to:

$$(C) + H_2O \longrightarrow CO + H_2$$
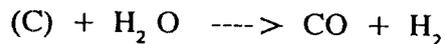
## Types of Furnace Atmospheres

The American Gas Association has classified the commercially important prepared atmospheres into groups based on the method of preparation or the original constituents. The chemical composition of these atmospheres is shown in Table 1.[2]

**Ammonia Base (Class 600)** This can consist of raw ammonia, dissociated ammonia or partially or completely combusted dissociated ammonia with regulated dew point. Only metallurgical grade ammonia can be used - containing less than 50 ppm water and less than 2 ppm oil.

**Dissociated Ammonia (Class 601)** This is a medium-cost furnace atmosphere which provides a dry, carbon-free source of reducing gas. The composition of the atmosphere is typically 75% hydrogen ($H_2$) and 25% nitrogen ($N_2$). This atmosphere is prepared by heating anhydrous ammonia in the presence of an iron or nickel catalyst. The decomposition occurs at approximately 900 to 980°C.

$$2NH_3 + \text{heat} \xrightarrow{\text{cat}} N_2 + 3H_2$$
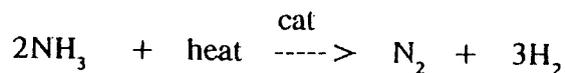
## TABLE 1

### Classification and Application of Principal Furnace Atmospheres[2]

| Class | Description | Common Application | Nominal Composition, vol % |  |  |  |  | Dew Point (°C) |
|---|---|---|---|---|---|---|---|---|
|  |  |  | $N_2$ | CO | $CO_2$ | $H_2$ | $CH_4$ |  |
| 101 | Lean exothermic | Oxide coating of steel | 86.8 | 1.5 | 10.5 | 1.2 | – | – |
| 102 | Rich exothermic | Bright annealing; copper brazing; sintering | 71.5 | 10.5 | 5.0 | 12.5 | 0.5 | – |
| 201 | Lean prepared nitrogen | Neutral heating | 97.1 | 1.7 | – | 1.2 | – | -40 |
| 202 | Rich prepared nitrogen | Annealing, brazing stainless steel | 75.3 | 11.0 | – | 13.2 | 0.5 | -40 |
| 301 | Lean endothermic | Clean hardening | 45.1 | 19.6 | 0.4 | 34.6 | 0.3 | -7 to +10 |
| 302 | Rich endothermic | Gas carburizing | 39.8 | 20.7 | – | 38.7 | 0.8 | -20 to -4 |
| 402 | Charcoal | Carburizing | 64.1 | 34.7 | – | 1.2 | – | -30 |
| 501 | Lean exothermic-endothermic | Clean hardening | 63.0 | 17.0 | – | 20.0 | – | -57 |
| 502 | Rich exothermic-endothermic | Gas carburizing | 60.0 | 19.0 | – | 21.0 | – | -46 |
| 601 | Dissociated ammonia | Brazing, sintering | 25.0 | – | – | 75.0 | – | -51 |
| 621 | Lean combusted ammonia | Neutral heating | 99.0 | – | – | 1.0 | – | – |
| 622 | Rich combusted ammonia | Sintering stainless powders | 80.0 | – | – | 20.0 | – | – |

**Fig. 1 : Simplified process schematic of ammonia dissociator system** [2]

Cooling water

Gas cooler

Heating chamber

Catalyst retort

Ammonia vapor

Vaporizer

Dissociated ammonia

Heat

Flowmeter

Anhydrous ammonia storage

Heat

Liquid ammonia

Ammonia dissociator



**Fig. 2 Exothermic gas generator system** [2]

Prepared exothermic atmosphere

Air  Fuel

Cooling water

Flowmeters

Combustion chamber

Gas cooler

Mixture pump

Burner

Trap  Drain

Drain

Exothermic gas generator

Refrigerant dryer

Desiccant dryer
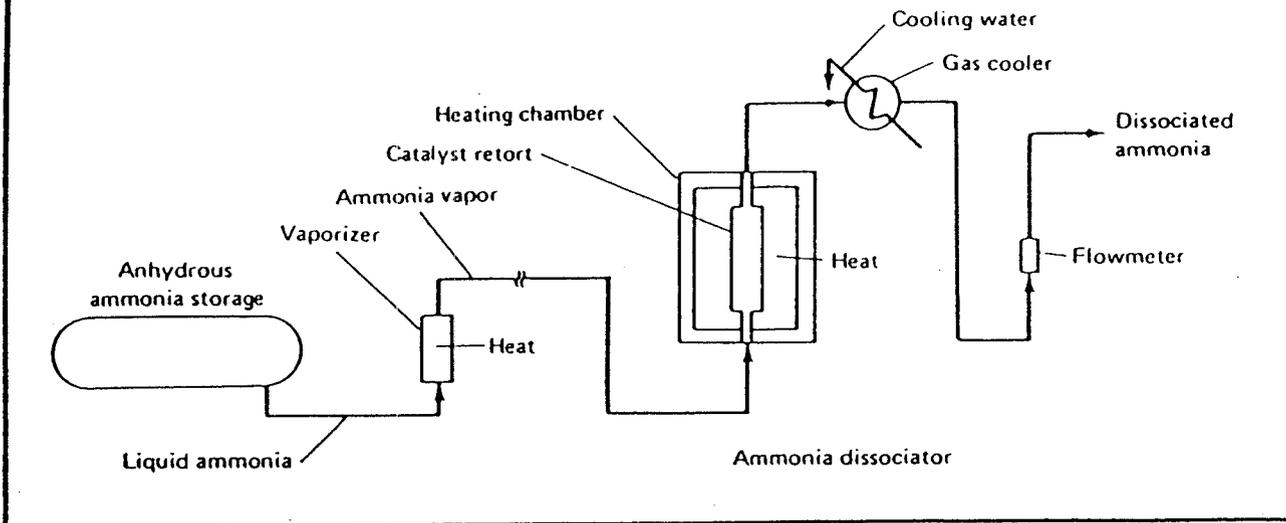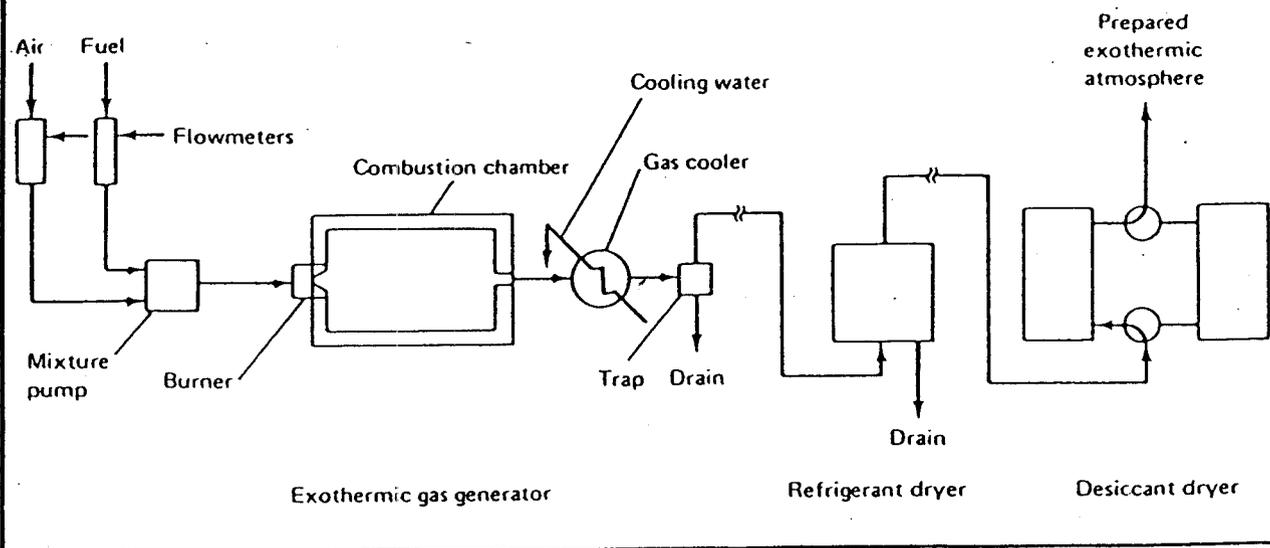
The basic ammonia dissociator consists of either an electrically heated or gas-fired chamber containing one or more catalyst-filled alloy retorts, followed by a water-cooled heat exchanger. Figure 1 shows a simplified process schematic of an ammonia dissociator. Operation is simple. To obtain the highest quality furnace atmosphere and to minimize possible dissociator maintenance, an oil-free metallurgical grade of dry anhydrous ammonia should be used. If usage requires, all traces of residual ammonia can be removed by passage through water, followed by drying. Unlike other prepared atmospheres which contain a substantial proportion of air, the entire furnace atmosphere is prepared from ammonia gas. Therefore this atmosphere is more expensive.

**Burned Ammonia** Dissociated ammonia can be partially or fully burned with air in a slightly modified exothermic gas generator to remove the hydrogen (forming water). Lean combusted ammonia (Class 621) is inert and nonflammable. It contains from 0.25 to 1.0% hydrogen and the remainder nitrogen. Rich combusted ammonia (Class 622) is a moderately reducing atmosphere, containing from 5 to 20% hydrogen and the balance nitrogen. The moisture content is removed by water cooling, followed by refrigeration and dessication as needed. These atmospheres are quite costly so use is restricted.

**Exothermic Base (Class 100)** This atmosphere is formed by partial or complete combustion of a gas/air mixture; water vapour may be removed to produce a desired dew point. Exothermic base is the most economical of the generated atmospheres. It is dependable, requires a minimum of generator maintenance and is suitable for a broad range of application. Figure 2 shows an exothermic gas generator system.

**Prepared Nitrogen Base (Class 200)** An exothermic base with the carbon dioxide and water vapour removed. The cost is relatively low and this base can be used in a variety of heat treating operations for low-carbon, medium-carbon and high-carbon steels. However, the equipment to produce the atmosphere is costly and requires more space, with a need for more exacting maintenance and process control. Figure 3 shows two different types of nitrogen base generators.

**Endothermic Base (Class 300)** Formed by the partial reaction of a mixture of fuel gas and air in an externally heated catalyst-filled chamber. This atmosphere is almost universally adaptable for protecting most production steels from oxidation and decarburization. It is relatively easy to produce and can be produced to consistently stable analyses. However, it cannot be used with stainless steel, because of the propensity of the gas for reacting with chromium. There is a tendency to precipitate soot at lower furnace temperatures. Figure 4 shows an endothermic gas generator.

**Commercial Nitrogen-Base Atmosphere** Industrial nitrogen gas is supplied from a storage tank and serves as a pure, dry, inert gas that provides efficient purging and blanketing. The nitrogen stream is often enriched with a reactive component, such as hydrogen, methane, propylene or methanol. There is a great deal of flexibility to control the composition of the atmosphere and the flow rate independently over a wide range to provide very different end use characteristics. There has been a significant shift to commercial nitrogen-base atmosphere systems since the late 1970's. Figure 5 shows a typical setup for commercial nitrogen gas. Figure 6 details the liquid nitrogen storage facility.

**Hydrogen Atmosphere** Commercially available hydrogen is 98% to 99.9% pure and is available in cylinders, banks of interconnected cylinders, trailers or tank cars. Very large amounts of hydrogen can be generated in-plant by decomposing ammonia or partially burning hydrocarbon fuels and purifying. Since hydrogen is readily absorbed by most common metals at elevated temperatures, its use can lead to serious embrittlement, especially in high-carbon steels.

**Charcoal Base (Class 400)** Formed by passing air through a bed of incandescent charcoal. This type of atmosphere is becoming obsolete; it is mainly used by small scale manufacturing plants that need a generator of low capital cost for intermittent operation.

**Exothermic-Endothermic Base (Class 500)** Formed by complete combustion of a mixture of fuel gas and air, followed by removal of the water vapour. Then the carbon dioxide is converted to carbon monoxide by reaction with fuel gas in an externally heated catalyst-filled chamber. This costly atmosphere is seldom used.

**Oxygen Atmosphere** Oxygen is essential for the heat treatment of certain precious metals and precious metal alloys.

**Inert Gases** Argon and helium are used during the heat treatment of certain specialty metals.

## Atmosphere Selection

The choice of atmosphere for a particular furnace operation can be critical to the succes of the operation. Table 2 summarizes the choices, which are discussed in more detail below.

## Annealing of Steel

Exothermic base - The most commonly used atmosphere. Annealing of non-ferrous metals.

Endothermic base - Bright hardening of steel of any carbon content. Annealing and normalizing steel of any carbon content.

Prepared Nitrogen Base - Heat treating of low-, medium- and high-carbon steels, including annealing, normalizing and hardening.

Dissociated ammonia - Bright annealing of stainless steel. Annealing of low-carbon steels.

Burned Ammonia - Bright annealing of ferrous and non-ferrous metals.

Commercial Nitrogen Base - For stainless steel, carbon steel, iron, copper, aluminum, nickel-iron.

Hydrogen - Annealing stainless and low-carbon steel, electrical steel and some non-ferrous metals.

# Fig.3 (a,b) Two types of generators of prepared nitrogen base atmosphere

## Fig.3a Nitrogen-base atmosphere generator incorporating molecular-sieve removal of carbon-dioxide and water vapor (and using negative-pressure-regeneration of the sieves) (2)
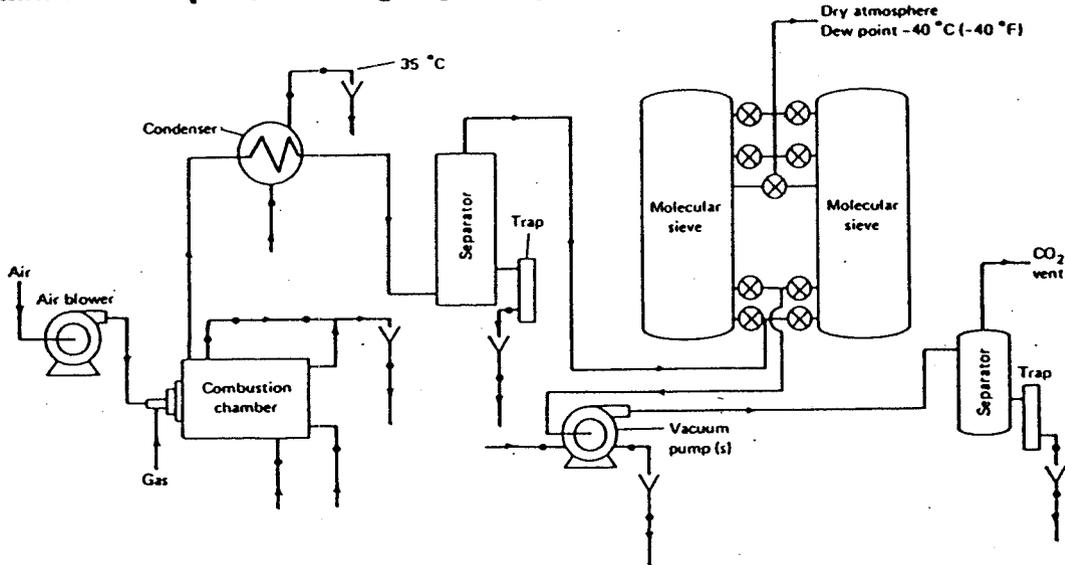


Gas lines are indicated by solid straight lines; water lines are shown as solid lines with closed circles. Auto-controlled valves are shown as the larger circles located between the molecular sieves.

## Fig.3b Nitrogen-base atmosphere generator incorporating a monoethanolamine scrubbing system (2)
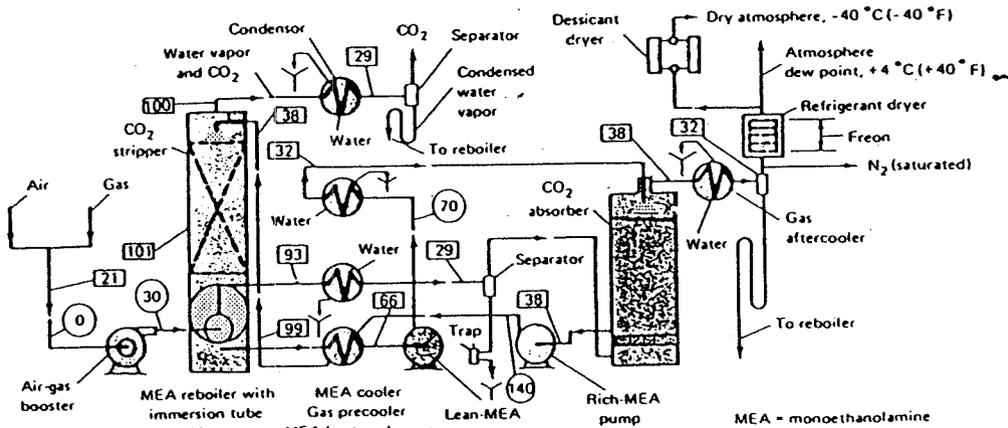


Temperature (°C) is indicated in boxes; pressure (kPa) appears in circles.

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**Fig. 4 Schematic flow diagram of an endothermic gas generator** [2]

Catalytic retort

Water jacket

Flue

Burner for heating retort

Pressure equalizer line

Gas cooler

To furnace

Air inlet

Flowmeter

Regulator

Flowmeter

Carburetor

Raw gas inlet

Filter

Mixing pump

Automatic fire check

Automatic gas pressure and flow valve
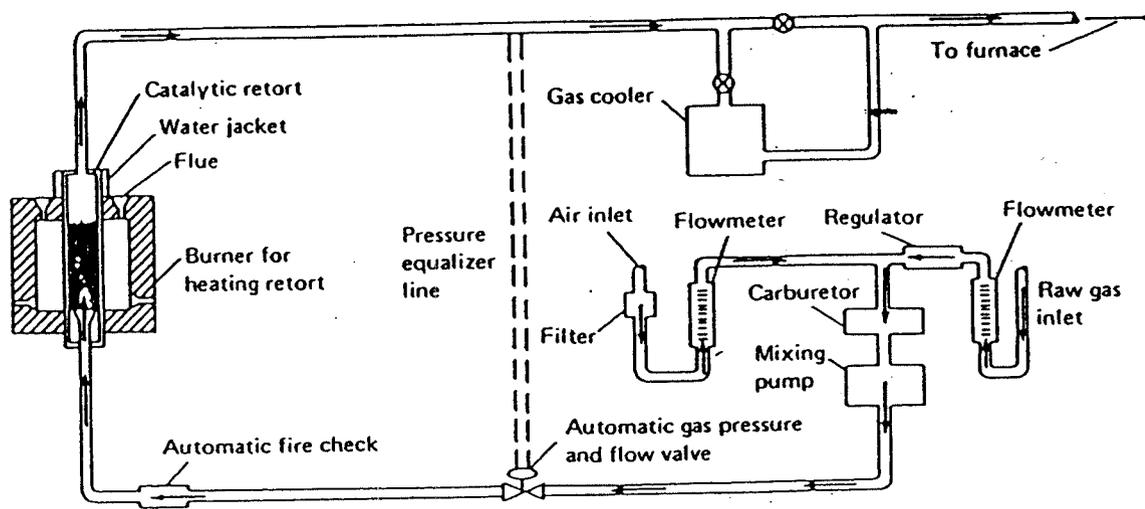
# Fig.5 Schematic of a typical commercial nitrogen base gas system[2]



H₂

Wall

N₂

(a) Protective

(b) Carbon-controlled

Methanol

Natural gas
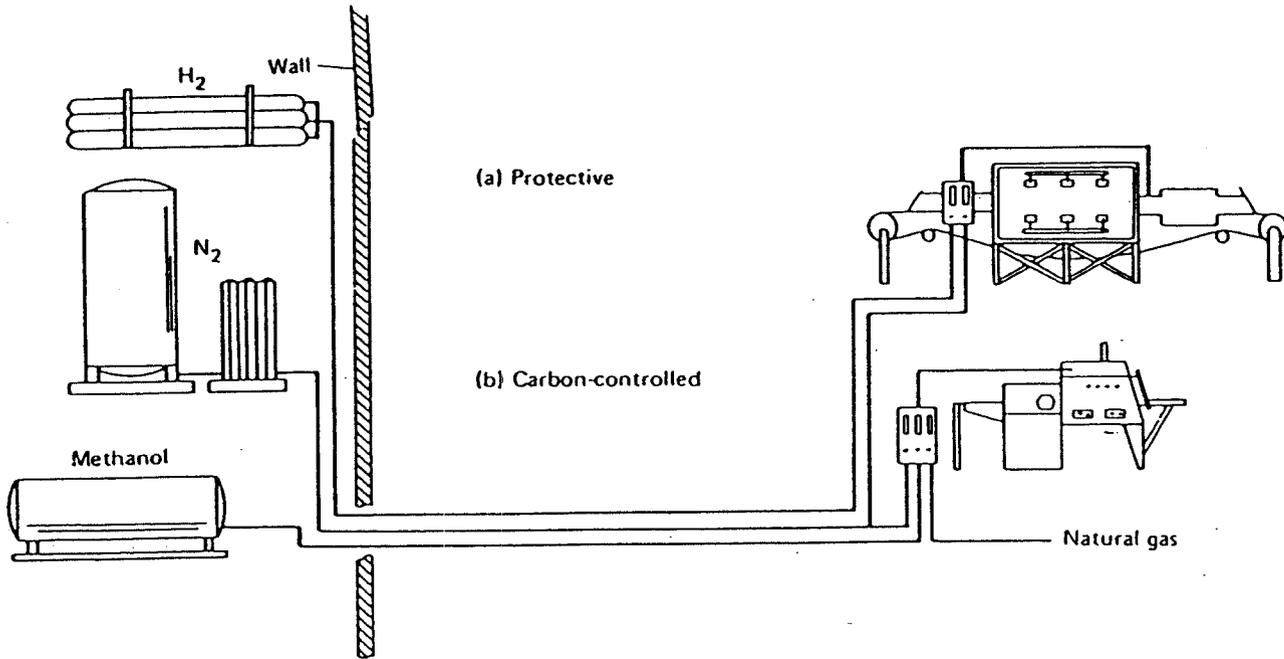
# Fig. 6 Typical liquid nitrogen storage facility [2]



Lifting lug

Vapor space: 1690 kPa (245 psig) working pressure

Inner tank, 9% nickel steel, aluminum
or stainless steel

Liquid product

Liquid tank

Outer tank, carbon steel

Perlite insulation evacuated to
a high vacuum

Instrument panel liquid level and pressure

Ambient air vaporizer
steam and electric options

Electrical panel
(440/220–60–3 phase)

Low temperature cutoff valve

Top fill valve

Houseline pressure gage

Concrete pad

Pressure control
station

Trailer fill
connection

Bottom fill valve

Gaseous product
to customer

Regulator shutoff valves

Pressure control valve

## Silver and Copper Brazing of Steel

Essentially all types of furnace atmospheres can be used for brazing.

## Heat Treating of Copper and Copper Alloys

Processes include homogenizing, annealing, stress relieving, solution treating, age hardening, quench hardening and tempering.

Exothermic Atmosphere - This is one of the least expensive atmospheres and can be used for heating both above and below 700°C.

Dissociated Ammonia - For annealing and brazing.

Hydrogen - For annealing and brazing.

Steam - Is the cheapest atmosphere for annealing; however, the annealed metal product is not as bright as when hydrogen or dissociated ammonia is used.

Commercial Nitrogen Base - For all heat treating of copper and copper alloys.

## Heat Treating of Nickel and Nickel Alloys

Treatments include annealing, stress relieving, stress equalizing and age hardening.

Exothermic Base - For all heat treating except bright annealing.

Dissociated Ammonia - For all heat treating, especially bright annealing of alloys containing chromium (stainless steel) and molybdenum which cannot be done using an exothermic base.

Burned Ammonia - For all heat treating.

Commercial Nitrogen Base - For all heat treating

Hydrogen - For all heat treating.

## Protective Atmospheres for Heat Treating of Other Metals

Beryllium copper, tungsten filaments and silicon-iron parts - use dissociated ammonia or commercial nitrogen base.

Magnesium alloys - sulfur dioxide or carbon dioxide

Titanium alloys - an oxidizing atmosphere

Uranium - requires helium, argon, carbon monoxide, carbon dioxide or a hydrocarbon gas.

Zirconium and its alloys - requires either vacuum or argon or helium.

Tantalum and Niobium - Special vacuum equipment

TABLE 2

## Atmosphere Selection for Heat Treating Processes

| | Exothermic | Prepared N Base | Endothermic | Dissociated NH₃ | Burned NH₃ | H₂ | N₂ |
|---|---|---|---|---|---|---|---|
| Annealing of Steel | | | | | | | |
|   Low-carbon | X | X | X | X | | X | X |
|   High-carbon | | X | X | | | | X |
|   Stainless Steel | | | X | X | | X | |
| Electrical Steel | | X | X | | | | |
| Bright Annealing of Steel | | | | | | X | |
| Silver & Copper Brazing of Steel | X | X | X | X | X | X | X |
| Nickel Brazing of Stainless Steel | | | | X | | X | |
| Heat Treating Copper & Copper Alloys | X | | | X | | X | X |
| Heat Treating Nickel & Nickel Alloys | X | | | X | X | X | X |
| Bright annealing | | | | X | X | X | X |
| Beryllium Copper | | | | X | | | X |
| Tungsten Filaments | | | | X | | | X |
| Silicon Iron | | | | X | | X | X |
| Sintering of Iron Powder | X | X | X | | | | |
| Sintering of Stainless Steel | X | X | X | X | | X | |
| Sintering of High Carbon Steel | | | X | | | X | |
| Sintering of Iron-Copper | | X | X | X | | X | |
| Sintering of Refractory Metals | | X | X | X | | X | |
| Carburizing | | | X | | | | |
| Carbonitriding | | | X | X | | X | |
| Nitriding | | | | X | | X | X |

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## 'Sintering

Powder metallurgy is the production of metal powders and their utilization for the manufacture of materials and shaped objects. Sintering is the process used to bond the particles in a mass of metal powder through the application of heat below the melting point of the metal. Sintering causes the strengthening of the powder mass and normally results in densification and often recrystallzation. Usually the part is first formed, pressed in a die and then heated. A protective atmosphere is used during sintering to prevent oxidation and reduce metal oxides, to control the carbon content of iron and iron alloy preforms and to flush volatilized lubricants from the furnace.

**Hydrogen** Can be the most economical for many sintering facilities. Hydrogen's high purity is suitable for stainless steel, tungsten and other refractory metals, magnetic materials and other metals where high reducing potential is required.

**Dissociated Ammonia** Is a good substitute for pure hydrogen in nearly all sintering applications, including stainless steel, iron, brass, copper and tungsten. However, this atmosphere should be avoided for molybdenum and high-carbon steel because of the danger of nitriding.

**Exothermic Gas** Rich exothermic gas can be used for sintering copper, bronze, silver, iron and iron-copper. It is strongly decarburizing. Medium rich exothermic gas can be used for nonferrous compacts.

**Purified Rich Exothermic Gas** Since this atmosphere has no carburizing or decarburizing effect it can be used for iron, iron-copper, iron-carbide and iron-copper-carbide.

**Nitrogen Base Gas** For sintering iron, iron-carbon, iron-copper and iron-copper-carbon compacts and for nonferrous compacts. It can be used for sintering stainless and refractory metals when nitriding is not critical. However, it can not be used for soft magnetic materials or highly corrosion-resistant stainless or some refractory metals.

**Endothermic Gas** Is used for sintering ferrous and most nonferrous preforms.

**Vacuum** Is increasingly used for materials that are reactive at elevated temperatures - magnetic preforms, stainless steel, tantalum, titanium, uranium, zirconium, refractory metals and superalloys that react with hydrogen, carbon or nitrogen.

## Comparison of Dissociated Ammonia with Other Furnace Gases

The most important atmosphere in competition with dissociated ammonia is commercial nitrogen used with hydrogen or other additives. Indeed, the commercial nitrogen systems were developed in response to the 1973 ammonia shortage. Exothermic gas and endothermic gas are usually used for different needs than are the nitrogen based gases. In general, the capital cost associated with dissociated ammonia is higher than for commercial nitrogen whereas the raw materials cost is higher for commercial nitrogen. As a result, large volume heat treaters are more likely to choose dissociated ammonia. Smaller companies may well choose commercial nitrogen.

Converting from dissociated ammonia to commercial nitrogen is quite simple. In telephone conversations, a representative of a company (Air Products and Chemicals) supplying commercial nitrogen felt that there have been an increased number of heat treaters converting from dissociated ammonia to purchased nitrogen. However, a representative of a company supplying dissociated ammonia (LaRoche) felt that there is much switching back and forth in the industry, depending mainly on the price of purchased nitrogen and hydrogen. In the last few years, the price of commercial nitrogen/hydrogen has been very low. This situation may be changing recently.

Vendors of commercial nitrogen use a number of arguments to try to sway users who might be considering a switch from dissociated ammonia to purchased nitrogen.

- Cost - In the recent past, the price of hydrogen has been very low. There are some signs that this period may be at an end.

- Safety - Vendors of purchased nitrogen systems claim that they are safer since a lower flow rate of gas can be used as long as pressure is maintained in the furnace. However, considering the chemistry involved, it must be argued that storing hydrogen on site is considerably more dangerous than storing ammonia. Ammonia leaks are easily detected, ammonia storage vessels are under a much lower pressure and the gas is not explosive as is hydrogen.

- Quality - Purchased nitrogen allows more precise control of furnace operations. The pressure is maintained in the furnace even if there is a loss of electrical power.

- Environment - Ammonia is on the EPA list of chemicals that must be reported under SARA Title III in the U.S.A.. Ammonia is under serious environmental pressure and there seems to be an 'emotional' reaction to its use. Most technical people who understand the properties of both materials would consider hydrogen to be by far more hazardous. One need only recall some spectacular hydrogen explosions such as the Challenger space shuttle or the Hindenburg to recognize the potential destructiveness of hydrogen explosions.

## Capital Cost

Equipment for dissociated ammonia is

- about the same as for exothermic gas
- less cost than for endothermic gas
- much less than for prepared nitrogen base
- much more than for commercial nitrogen base

## Raw Materials Cost

Dissociated ammonia is

- much more costly than exothermic gas
- much more costly than endothermic gas
- much more costly than prepared nitrogen base
- much less costly than commercial nitrogen base

## Table 3

### Comparison of the Cost of Producing 28m$^3$ of Furnace Atmosphere. [*]

| | Nat. Gas | | Power | | Water | | NH$_3$ | | Total |
|---|---|---|---|---|---|---|---|---|---|
| | m$^3$ | $ | kW | $ | l | $ | kg | $ | $ |
| **Rich Exo** | | | | | | | | | |
| Water cooled | 4.4 | 0.66 | 0.4 | 0.02 | 1135 | 0.03 | | | 0.71 |
| Refrigeration | | | 0.9 | 0.04 | | | | | 0.73 |
| Dessication | | | 1.9 | 0.08 | | | | | 0.77 |
| **Lean Exo** | | | | | | | | | |
| Water cooled | 3.3 | 0.50 | 0.4 | 0.02 | 1590 | 0.04 | | | 0.56 |
| Refrigeration | | | 0.9 | 0.04 | | | | | 0.58 |
| Dessication | | | 1.9 | 0.08 | | | | | 0.62 |
| **Prep'd N Base** | | | | | | | | | |
| molec. sieve | 3.77 | 0.57 | 7.8 | 0.30 | 2780 | 0.07 | | | 0.94 |
| MEA | 3.77 | 0.57 | 4.0 | 0.15 | 2500 | 0.07 | | | 0.79 |
| Diss'd NH$_3$ | | | 25 | 0.97 | 281 | 0.01 | 10 | 3.25 | 4.23 |
| Commercial N$_2$ (with 10% H$_2$) | | | | | | | | | 17.92 |
| Commercial H$_2$ | | | | | | | | | 28.00 |

[*] All costs in Canada and in Canadian dollars: natural gas @ $0.15/m$^3$ ; raw cooling water @ $0.0265/m$^3$ ; electrical power @ $0.03867/kWh; ammonia at $325/te

## Storage

Ammonia is stored liquified. Therefore it occupies much less space than an equivalent amount of gaseous nitrogen and hydrogen. In addition, ammonia leaks are very easy to detect - the limit of detectability by smell is about 5 ppm. Leaks of hydrogen are quite difficult to detect, so that such leaks are more dangerous.

Dissociated ammonia storage is

- somewhat more difficult than for exothermic gas
- somewhat more difficult than for endothermic gas
- somewhat more difficult than for prepared nitrogen base
- easier and requires less space than commercial nitrogen base
- easier and requires less space than commercial hydrogen base

## Safety

Many gasses are dangerous simply because they can displace breathing air. Other dangers associated with gasses are explosiveness, flammability, toxicity and carcinogenicity.

Dissociated ammonia is

- less flammable than either hydrogen or natural gas
- more toxic than either hydrogen or natural gas

## Use

Dissociated ammonia is

- less flexible than commercial nitrogen base
- uses more power than commercial nitrogen base

## Trends

- Demand for more precise metallurgical specifications implies a need for better control of furnace atmosphere
- Increased use of microcomputers and automatic controls
- Increased use of commercial nitrogen base furnace atmosphere because of its flexibility and precise controllability
- Increased use of vacuum furnaces instead of a protective atmosphere, especially for specialty products; furnace often backfilled with argon gas
- Decreased reliance on atmospheres derived from natural gas

## Competitiveness of Dissociated Ammonia

Dissociated ammonia is a relatively expensive prepared atmosphere since the atmosphere is produced entirely from purchased ammonia, unlike those atmospheres derived from natural gas where a substantial portion of the atmosphere is nitrogen from air. However, the nitrogen/hydrogen combination provides some properties essential to certain heat treating uses. Commercial nitrogen base will probably always be much more expensive than dissociated nitrogen. However, the very low capital cost and inherent flexibility of the system are strong factors in favor of purchased nitrogen gas. It is likely that dissociated ammonia will continue to be favoured by large scale users while the small heat treaters will use dissociated ammonia if they already own the equipment, but are more likely to turn to purchased nitrogen and hydrogen.

Clearly the single biggest advantage of dissociated ammonia is as a low cost replacement for hydrogen. As long as nitriding of the metal is not a concern, dissociated ammonia has all the advantages over hydrogen. The ammonia-derived atmosphere is significantly cheaper, safer and requires substantially less storage space.

## The Heat Treating Industry

The heat treating industry continues to be heathly. Its growth tends to vary with the health of the automobile industry, but typically has been about 4% per year recently. Furnace orders are down. In the United States, there has been off-shore competition for standard steels and more is anticipated in specialty steels, alloys, powder metals and stainless steel. There is essentially no off-shore competition in metals for the aerospace industry.

Powder metals are enjoying substantial growth for automobiles, appliances, garden tools and other parts formerly made by cast methods. Recent growth has been about 12-15% per year.

A growing trend is the use of vacuum furnaces as that technology has improved. Inert gas is still required to back fill the furnace after the heat treatment. However, since the technique is generally used for specialty products, argon gas is commonly used to back fill the furnace.

# CASE HARDENING OF METALS

Case hardening is a metal treatment that produces a hard surface (the case) on a metal (the core) which remains relatively soft. The result is a hard wear-resistant case backed by a strong, ductile and tough core.

## Summary of Case Hardening Processes

### Carburizing

Carburizing is the most common case hardening process. Nascent carbon is added and diffuses into a steel surface; subsequent quenching produces a hard case. Carburizing works best with low carbon steels (less than 0.3 wt% C). Low alloy steels do not harden to a significant depth. The depth of hardness increases with increasing alloy content, resulting in stronger and more uniform cores.

Gas carburizing uses natural gas or another hydrocarbon gas as the source of the nascent carbon. The carburizing material is used with a carrier gas, usually composed of nitrogen, carbon monoxide and hydrogen. Carburizing can also be done in a molten salt bath or using hardwood charcoal and coke as the source of the carbon.

### Carbonitriding

In carbonitriding, the metal absorbs both carbon and nitrogen simultaneously to produce a hard, wear-resistant case. A carbonitrided case has better hardenability than a carburized case. Therfore carbonitriding is less costly for the same case depth range. Carbonitriding can be used with both carbon and alloy steels. Carbonitriding processes use either ammonia or sodium cyanide.

### Nitriding

The addition of nascent nitrogen into the surface of the steel, forming nitrides, produces a nitrided case hardened steel. Ammonia can be used for nitriding alloy steels containing aluminum, chromium, molybdenum, vanadium or tungsten. Many stainless steels are successfully nitrided. However, plain carbon steels produce a case that is extremely brittle and that spalls readily. Liquid nitriding in molten cyanide is effective for chromium-aluminum low alloy steels. The process is very slow and requires some 15-40 hr depending on the depth of case required.

## Ionitriding

Positive nitrogen ions produced in a plasma collide with the surface to be nitrided, producing the hardened case. This technique works well with carbon steels, low alloy steels, tool steels, heat-resistant steels, stainless steels, cast iron and sintered iron.

## Other Methods

There are a variety of other methods for producing a hardened case, including siliconizing, boronizing, tufftriding, triniding, applied energy, induction hardening, and flame hardening. No details will be given about these processes.

## Economics

In general, the greatest cost of any case hardening process is the cost of bringing the furnace and the parts to be processed up to the operating temperature and maintaining that temperature. The different gases, compounds or preparations that are used as the process medium are of minor cost relative to the total. The bulk of all heat treating costs can be attributed to fuel (electricity and natural gas) and labour.

## Detailed Discussion of Ammonia-Based Case Hardening Processes

### Carbonitriding

Steel is held at an elevated temperature in a gaseous atmosphere from which it absorbs carbon and nitrogen simultaneously and is then cooled to room temperature at a rate that produces the desired case and core properties. Typically the carbon is derived from any carbon rich gas or vaporized liquid hydrocarbon; the nitrogen is derived from ammonia.

Carbonitriding is a modified gas carburizing process rather than a form of nitriding. However, it is carried out a lower temperature and for a shorter time than gas carburizing and a shallower case is formed.

The case depth is from 0.075 to 0.75 mm and has better hardenability than a carburized case. Therefore, a hardened case can be produced at less cost. However, the application of carbonitriding is more restricted than is carburizing. Carbonitriding is particularly useful with low carbon steels for which a uniform case cannot be achieved with carburization.

Case depth uniformity depends on several factors: the uniformity of the temperature within the furnace chamber; adequate circulation and replenishment of the atmosphere; distribution of the furnace charge so that it is uniformly exposed to the atmosphere.

Almost any furnace suitable for gas carburizing can be adapted to carbonitriding. Some 2 to 12% ammonia is added to the standard gas carburizing atmosphere. The ammonia must be very pure - 99.9+% ('Refrigeration', 'Premium' or 'Metallurgical' grade). 'Commercial' or 'Agricultural' grades contain too much carbon dioxide, water and oils. The amount of ammonia added must be just enough to sustain the carbonitriding reactions in the atmosphere. Excess ammonia can lead to void formation. The minimum ammonia required depends largely on the composition of the steel. Alloy steels, especially those containing nickel and manganese, require less ammonia. Usually 2.5 to 5% ammonia in the atmosphere is satisfactory. Although 10 or more percent ammonia is often used, this amount of ammonia is unnecessarily high.

After the furnace treatment, the part must be quenched. Water is used for quenching parts made of low-carbon steel, but not for brass or other copper alloys because the aqueous ammonia formed is extremely corrosive to copper based materials. Quenching in oil minimizes distortion. Gas quenching can be used for light weight parts or parts subject to sliding loads with low impact.

Tempering is not necessary for carbonitrided parts.

Carbonitriding is widely used for case hardening parts made by powder metallurgy from ferrous powders. Carbonitriding is extremely effective in case hardening high density sintered iron compacts; other case hardening techniques are not effective .

## Liquid Carburizing and Cyaniding

Liquid carburizing and cyaniding are processes for case hardening steel or iron parts in a molten salt bath containing alkali cyanide and cyanates. Cyaniding is performed in a bath containing a higher percentage of cyanide, at a lower temperature and produces a shallower case. The effects of cyaniding are similar to those produced by gas carbonitriding. The parts must be quenched in water, brine, caustic solution or oil. The parts must then be thoroughy cleaned of cyanide residues.

This type of case hardening is best suited to small and medium-size parts that do not have small holes, threads or recessed areas that are difficult to clean.

Great care is required in the handling of cyanide baths and treated parts since cyanide is extremely poisonous. The disposal of cyanide wastes poses a serious disposal problem. In general, the wastes must be chemically treated to destroy the cyanide, for example by oxidizing with chlorine gas or hypochlorite or electrochemically.

## Gas Nitriding

This is a case hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding the metal at a suitable temperature in contact with a nitrogenous gas, usually ammonia. Quenching is not required.

Alloy steels are most suitable for nitriding. Alloys containing aluminum, chromium, vanadium, tungsten or molybdenum are particularly good since stable nitrides are formed. Aluminum-containing steels yield the best results - a very high hardness and excellent wear resistance, but low ductility. Chromium-containing steels are also

very good; the nitrided parts have lower hardness than those containing aluminum, but more ductility. Nickel, copper, silicon and managanese in the alloy have little effect on the nitriding characteristics of the alloy. Unalloyed steels are not suitable for nitriding as they form an extremely brittle case that spalls readily. Nitrided stainless steel has a higher surface hardness, a lower coefficient of friction and improved abrasion resistance. However, nitriding of stainless steel is not recommended for stainless steel that must be corrosion resistant, since nitriding lowers corrosion resistance.

The nitriding process is based on the affinity of nascent nitrogen for iron and certain other metals. Nascent nitrogen is produced by the dissociation of gaseous ammonia in contact with hot steel parts (temperature of about 525°C).

The part must be hardened and tempered before nitriding. The nitriding can be accomplished in either a single-stage or a double-stage process. In either case, the process is quite slow, taking as much as 2 days for completion. A brittle, nitrogen-rich layer called the 'white nitride layer' forms at the surface of the nitrided case. In the double-stage process (the Floe process), which requires an external ammonia dissociator, the white nitride layer is somewhat thinner and less ammonia is consumed. Nitriding is not suitable for parts with sharp corners or edges which become susceptible to chipping.

Selective nitriding can be achieved by coating that portion of the part where nitriding is not desired. The most common type of coating is a plated deposit of bronze or copper.

**Pressure nitriding** uses a sealed retort which is pressurized with gaseous ammonia. This process is particularly useful for nitriding the interior of a tube or pipe which acts as its own retort.

**Bright nitriding** uses both ammonia and hydrogen gases. Little or no white layer is formed.

**Pack nitriding** employs certain nitrogenous organic compounds as the source of nitrogen, instead of ammonia.

## Ion Nitriding

Ion nitriding (also called glow-discharge nitriding or plasma nitriding) uses a high-voltage electrical discharge to form a plasma through which nitrogen ions are accelerated to impinge upon the workpiece. The process is being used increasingly as an alternative to conventional ammonia gas nitriding. It results in an excellent quality case and is suitable for all applications of conventional ammonia gas nitriding. The nitrided part retains its surface finish; control of white-layer composition and thickness enhances fatigue properties.

Ion nitriding lends itself to total process automation, ensuring reproducible metallurgical results. The process produces no pollution and consumes an insignificant quantity of gas. Energy utilization is approximately equivalent to conventional ammonia-gas nitriding operations when cold wall vessels are used. Hot-wall vessels use even less power - about 20% of the power required by cold-wall

vessels. Selective nitriding can be accomplished by simple masking techniques. The process takes significantly less time than conventional nitriding. However, the equipment does represent a high capital cost.

Process gas is ordinarily a mixture of hydrogen and nitrogen. Methane can be added to provide some metallurgical carbon.

## Table 4

## Comparison of Major Case Hardening Processes

|  | Carburizing | Carbonitriding | Liquid Cyaniding | Nitriding | Ion Nitriding |
|---|---|---|---|---|---|
| Type of Steel | carbon high alloy | carbon alloys ferrous powder metallurgy | carbon alloys | not carbon alloys | all steels |
| Medium | natural gas + carrier gas | carburizing gas + ammonia | cyanide + cyanate | ammonia | nitrogen + hydrogen |
| Economic Issues |  | less cost than carburizing | disposal of cyanide wastes | process is very slow | no pollution; low energy consumption; high capital cost |
| Safety | medium is toxic and flammable | medium is toxic and flammable | handling cyanide | medium is nonflammable; must vent exhaust properly |  |
| Other | close control of case depth wide ap- pplicability | better harden- ability, shallower case depth than carburizing | similar to carbo- nitriding; small & medium parts | difficult to control | excellent reprodu- cibility |

## Outlook for Ammonia Based Case Hardening Processes

Ammonia gas carbonitriding is a clear winner over liquid cyaniding on the grounds of safety, environment and economic issues as ammonia gas is significantly easier and safer to handle than cyanide. Carburizing will still be the case hardening treatment of choice for many case hardening requirements.

Ion nitriding is definitely growing in popularity owing to its flexibility and controllability. However, its high capital cost will somewhat limit its widespread adoption.

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## COMPANIES AND LOCATIONS

Most companies specializing in heat treatment of metals use a variety of processes depending on the requirements of their customers. Therefore it is not possible to differentiate companies who use ammonia based processes from those who do not. The Thomas Register lists many pages of companies under the heading "Heat Treating Services" and many more under "Powdered Metal Parts". All of these companies will use at least some furnace treatments and many of them also do case hardening. A listing of some of the major companies in the U.S. Northeast, by alphabetical order, follows.

### Heat Treating Services

Armco Inc. (Parsippany NJ and Baltimore MD)
Carpenter Technology Corp. (many locations)
Clarkston Metallurgical Processing Inc. (Clarkston, MI)
Fred Heinzelman & Sons Inc. (Carlstadt NJ)'
General Heat Treating Corp. (E. Syracuse, NY)
General Metal Heat Treating Inc. (Cleveland, Ohio)
Gulf & Western Manufacturing (Southfield MI)
Horsburgh & Scott Co. (Cleveland, OH)
Howmet Turbine Components Corp. (Plymouth MI and Dover NJ)
Industrial Steel Treating Co. (Jackson, MI)
Lindberg Heat Treating Co. (Westwood MA)
Metallurgical Inc. (Minneapolis MN)
Metlab (Philadelphia PA)
Nitro-VaC (Warren MI)
Owego Heat Treat Inc. (Apalachin NY)
Paulo Products Co. (several locations, including Cleveland OH)
Penna Flame Industries Inc. (Zelienople PA)
Pittsburgh metal Processing Co. (Pittsburgh PA)
Progressive Steel Treating Inc. (Rockford IL)
Solar Atmospheres Inc. (Philadelphia and Souderton PA)
Syracuse Heat Treating Corp. (Syracuse NY)
Tecmetal (Cleveland OH)
Temperature Processing Ease (North Arlington NJ)
United Technologies (Fort Wayne IN)
Weiss Industries (Mansfield, OH)

### Powdered Metal Parts

Allied Sinterings Inc. (Danbury CT)
Allread Products Co. (Terryville CT)
Alpha Sintered Metals Inc. (Ridgway PA)
Alpine Pressed Metals Inc. (Ridgway PA)
Atlantic Sintered Metals (Boston MA)
Borg-Warner Auto Powdered Metal Products (Livonia MI)
Brockway Pressed Metals Inc. (Brockway PA)
Burgess-Norton Mfg. Co. (Geneva, IL)

Cameron Diversified Products Inc. (Wilcox PA)
Chicago Powdered Metal Products Co. (Schiller Park IL)
Clearfield Powdered Metals Inc. (Clearfield, PA)
Cloyes Gear and Products Inc. (Troy MI)
Comtec Mfg. Inc. (St Marys PA)
Dubois Powdered Metals Inc. (Dubois PA)
Emporium Specialties Co. Inc. (Austin PA)
Engineered Sinterings & Plastics Inc. (Watertown CT)
Friction Products Co. (Medina OH)
Helsel Inc. (Campbellsburg IN)
Hoeganaes Corp. (Riverton NJ)
ICM Krebsoge (Livonia MI)
Keystone Carbon Co. (St Marys & Mount Jewett PA and Columbus OH)
National Sintered Alloys Inc. (Clinton CT)
Norwalk Powdered Metals (Norwalk CT)
Paramount Sintered Products (Zion IL)
Precision Pressed Powdered Metals Inc. (Dayton OH)
Reese Metal Products Inc. (Lancaster PA)
Sintered Metal Products Inc. (Coldwater MI)
Sintered Precision Components (Decatur IL)
Sinterloy (Solon Mills IL)
Sterling Sintered Technologies Inc. (Sinsted CT)
St Marys Carbon Co. (St Marys PA)
Supermet Inc. (Trotwood OH)
Symmco Inc. (Sykesville PA)

## Heat Treating of Nonferrous Metals

Ampco (many locations)
Cabot Corp. (Boyertown PA)
Colonial Metals Co. (Columbia PA)
Engelhard Corp. (Mansfield MA)
Huntington Brass Inc. (Huntington WV)
Kaiser Aluminum & Chemical Co. (many locations)
Olin Brass (Cuba MO and East Alton IL)
Viking Metallurgical Corp. (Verdi NV)