No. 10

NITRIDING OR SURFACE-HARDENING OF STEEL BY THE NITROGEN PROCESS

The term " Case-hardening " is generally accepted as referring to the process by which a low carbon steel is given a hard surface or case by carburizing, *i.e.*, increasing the carbon content of the surface, and subsequent suitable heat-treatment.

As a result of exhaustive investigations by Dr. Fry of Krupps, it has been found that a hard surface can also be obtained by increasing the nitrogen content of the surface, and to differentiate this process from the carburizing process it has been called " Nitriding."

A comparison of the two processes is given below.

COMPARISON OF SURFACE HARDENING PROCESSES.

	Carburizing.	Nitriding.
Temperature ..	900° C. to 920° C. ..	500° C.
Time	About 3 hours for $\frac{1}{32}$ in. depth of case	90 hours for maximum hardness.
Reagent	Carburizing mixture ..	Ammonia gas.
Heat treatment of core	Refine after carburizing ..	Harden and temper before nitriding.
Heat treatment of case	Final hardening by quenching	No further treatment.
Hardness of case ..	600–780 diamond ..	950–1,100 diamond.

The main advantages of nitriding are as follows :—

(*a*) *Extreme Hardness.*—The surface hardness is greater than is obtainable by any other process.

(*b*) *Lack of Distortion.*—On account of the comparatively low temperature at which the treatment is carried out, distortion is reduced to a minimum and, except in parts of very thin section or intricate design, is practically eliminated.

(*c*) *Resistance to Corrosion.*—Although nitrided steels cannot be included in the stainless steel category, they are, nevertheless, extremely resistant to corrosive action when in contact with fresh water, sea water, steam or moist atmosphere.

(*d*) *Elimination of Quenching Cracks.*—There is no final quenching, such as is essential with ordinary case-hardening, and consequently, the great trouble due to quenching cracks does not arise.

(*e*) *Retention of Hardness at Elevated Temperatures.*—The nitrided case retains its full hardness up to 500° C., and even up to 600° C. the reduction is very small. Normal case-hardened steels begin to soften at about 200° C.

(*f*) *Mergence of Hardened Surface into Core.*—There is no rigid line of demarcation of hardness, thus eliminating the danger of spalling.

The features (*b*) and (*d*) are invaluable in cases of parts of complicated design.

The great disadvantage of the process is the time required.

In America various methods have been tried to increase the speed of the operation but, although it was found that the desired maximum hardness might be obtained, it was in all cases at the expense of the depth of penetration and the greatest depth reached in 6 hours is 0·008 in.

Development of the Nitriding Process.—It has generally been considered that nitrogen has merely a harmful effect on steel and for this reason the amount of nitrogen permissible has been kept as low as possible, the amount varying from 0·005 to 0·04 per cent. in a normal steel. On cooling such a steel, nitride of iron crystals of a needle-like form of composition Fe_4N and Fe_2N are deposited along the line DA of the iron-nitrogen equilibrium diagram. (Fig. 1.)

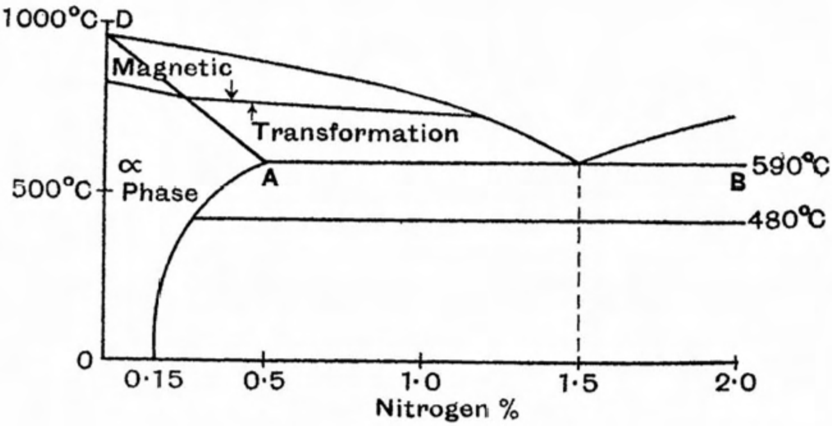

FIG. 1.

These needles can be seen clearly under the microscope.

With higher percentage of nitrogen a constituent "Braunite," a eutectoid containing 1·5 per cent. nitrogen, similar in appearance to pearlite, can be obtained. In the skin of a nitrided article no needles are found although the outside of it may contain as much as 4 per cent. Ni.

Nitriding is always done below the line AB, usually at a temperature of 500° C. ± 5° to obtain maximum hardness. Above 500° C. the depth of the hardened skin is increased and the time required to reach maximum hardness is reduced, but the maximum hardness obtainable is also reduced. A higher temperature to begin with, falling to 500° C., hastens the process, but again results in a loss of hardness. In view of the small variation in temperature and the time required, the furnace used is of the electrical type, the temperature being readily controllable by thermostat.

Preparation of Article for Nitriding.—If it is desired to nitride a part as forged, descaling by pickling or sand-blasting is not sufficient, and the decarburized zone, which always exists after forging, must be removed by grinding or machining.

Surfaces not to be hardened must be protected while in the furnace. This object is achieved by various methods :—

(*a*) Painting with an aluminium paint consisting of powdered aluminium mixed with sodium silicate.

(*b*) Painting with chromic oxide.

(*c*) Holes to be protected are filled with asbestos wool and then the surface is painted as above.

(*d*) Tinning the surface with solder (4 parts of lead to 1 of tin.) The part is dipped in the bath at 400° C. with the flux, killed spirits and sodium chloride, floating on the top of the bath.

Alternatively a soldering iron may be used.

Procedure.—The usual procedure after forging, drop-stamping or preliminary heat-treatment is on the lines given below :—

(1) Harden and temper.

(2) Machine to within $\frac{1}{32}$ in. on all surfaces to be hardened.

(3) Stabilize by heating to 550° C., generally for about four hours, cooling slowly.

(4) Finish machine or grind to finished dimensions.

(5) Wash the surfaces with petrol to ensure freedom from grease.

(6) Nitride.

(7) Polish or lap.

The articles to be nitrided are placed in a box made of a suitable nickel chrome alloy or heat-resisting steel, with welded joints and the lid machined to give a good faced joint with the top of the box.

The gas—ordinary commercial ammonia—is supplied from a cylinder at a pressure of 1 or 2 ins. of water. No air must enter the box, as it interferes with the process. The box must be full of gas circulating before the full temperature is reached, and the gas supply should be kept on till the box has cooled to about 150° C. It is essential to have a good flow of gas all over the surface of the articles, and they must be carefully packed to ensure this.

To check that the flow of gas is sufficient, samples are taken from the exit tube of the box, and the amount of dissociation which has taken place is measured. There should be at least 70 per cent. unconverted ammonia gas remaining. The sample is shaken up with water and the ammonia dissolves. The remainder is principally hydrogen. There is a tendency for the ammonia to decompose, so that some nitrogen will be present.

The depth of the core is generally 30/1000 in., and the degree of hardness reduces with depth until it merges into the core. (Fig. 2.)

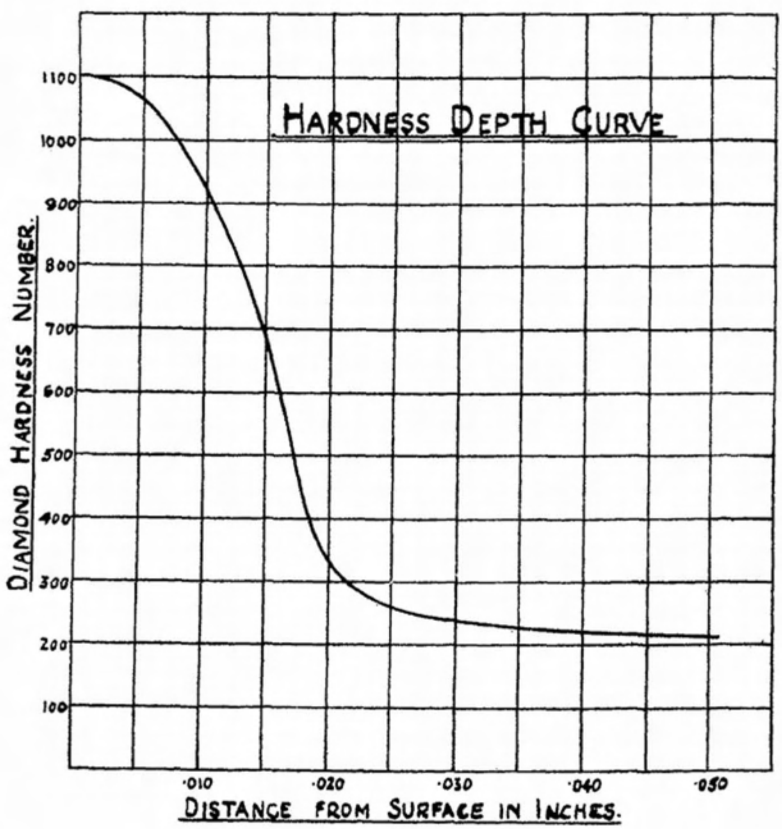

Fig. 2.

The process tends to produce a slight growth, of the order of 2½ to 4 per cent. of the depth of the case, so that with a depth of case of 30/1000 in., the growth will be about 1/1000 in. This amount will usually be removed in the final polishing after nitriding. At a corner the double growth may result in distortion of the corner, which will be brittle, and very liable to be broken off. To avoid this, it is usual to round off all corners slightly. In a strip, of which one side only is hardened, the growth will result in curvature, *e.g.*, a strip 3 ins. long, $\frac{1}{16}$ in. thick will bow about ⅛ in.

It is noteworthy that the final polishing or lapping to size would not normally penetrate to such a depth as to reduce the hardness to any serious extent.

To give an example of the small effect which the nitriding process has on an accurately finished part, a pump shaft 7 in. diameter, 11 ft. long, with keyways cut, and various collars on, was measured before and after nitriding. No variation of dimension greater than ½/1000 in. could be found. As a tolerance of 1½/1000 in. had been allowed in the grinding process, the additional inaccuracy due to nitriding was negligible.

Materials Suitable for Nitriding.—Pure iron and plain carbon steel can be hardened by nitriding, but the material is brittle and the surface obtained is not hard enough to make the process worth while. Alloy steels give greater hardness, the elements capable of producing hardness by nitriding in order of merit being :—

Aluminium, molybdenum, manganese, chromium, vanadium. titanium, tungsten.

	Max. diamond hardness after nitriding (Firth hardometer).
Air-hardening nickel-chrome steel	450
High speed steel (14 per cent. W)	700
High speed steel (18 per cent. W)	700
Chrome-vanadium (1·7 Cr, 0·6 V)	730
Chrome-molybdenum-vanadium (2·3 Cr, 0·3 Mo, 0·2 V)	820
Chrome-aluminium-molybdenum - vanadium (1 Cr, 0·5 Al, 0·3 Mo, 0·2 V)	900
Chrome - aluminium - molybdenum - tungsten (1·3 Cr, 0·5 Al, 0·3 Mo, 9·3 W)	970
Silicon - manganese - nickel - aluminium - Titanium (2·5 Si, 1·4 Mn, 2·2 Ni, 0·5 Al, 0·4 Ti)	1,000

The special feature of the last steel is a precipitation hardening effect which takes place during the nitriding operation and produces a hardening of the core.

Austenitic steels can be hardened by nitriding. The high chromium varieties give better results than the high nickel.

The process has been used for aeroplane valves made of nickel-chrome-tungsten steel. A high resistance to shock combined with a good wearing surface at high temperatures can thus be obtained (*see* Fig. 4), but it is difficult with this steel to get the gradual blend of case into core which is so desirable to prevent the case flaking off. To increase the merging the temperature of nitriding may be raised to 550° C., but the maximum hardness will not then be obtained.

Chrome-aluminium steels are most frequently used.

It is apparent from Fig. 3 that a combination of aluminium and chromium is better than either of these elements alone.

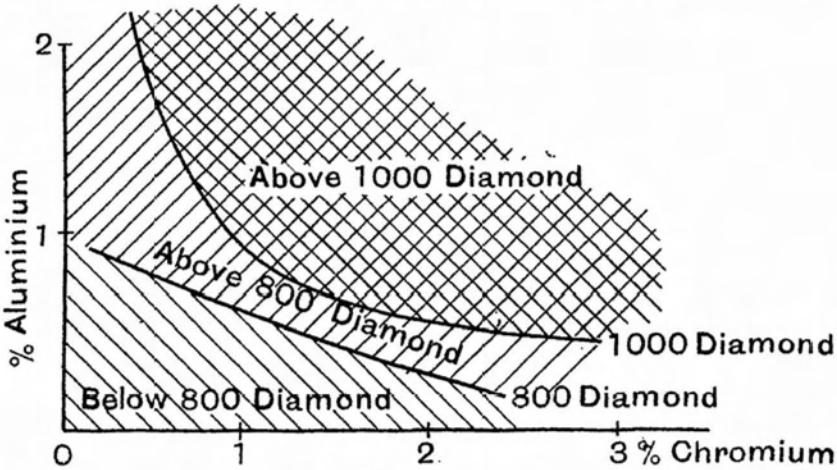

Fig. 3.

The addition of molybdenum in small quantities produces toughness in the case and controls the mass of large sections, it also gives a good machining steel.

A steel containing 1·5 per cent. Cr, 1 per cent. Al, 0·3 per cent. Mo is largely used in Sheffield and gives a hardness of over 1,000 diamond. This material, known as Nitralloy, was first marketed in seven different grades of varying carbon content, but practically the whole range can be covered by four grades.

The uses given above are merely an indication and the grade must be chosen bearing in mind both the core strength necessary and the ease of manufacture, *e.g.*, it is difficult to machine grade 1 after hardening, when its tensile strength is from 65 tons per sq. in. upwards. This grade is therefore usually supplied in the annealed condition, and the oil hardening and tempering treatment is carried out at an intermediate stage.

The hardening temperature of these steels ranges from 880° C. for grade 1 to 920° C. for grade 7.

NITRALLOY, STANDARD COMPOSITIONS.

	Grade 1.	Grade 3.	Grade 5.	Grade 7.
Uses..	Die blocks. Hot rolls.	Cylinder Liners. Pump spindles.	Gears. Gudgeon pins.	Aircraft and automobile crankshafts. Brake drums.
	Per cent.	Per cent.	Per cent.	Per cent.
Carbon	0·45–0·55	0·35–0·45	0·26–0·35	0·20–0·26
Manganese	0·5 –0·6	0·5 –0·6	0·5 –0·6	0·5 –0·6
Silicon	0·2 –0·35	0·2 –0·35	0·2 –0·35	0·2 –0·35
Chromium	1·5 –1·7	1·5 –1·7	1·5 –1·7	1·4 –1·6
Aluminium ..	1·0 –1·2	1·0 –1·2	1·0 –1·2	0·9 –1·1
U.T.S., tons/in.² ..	65–90	55–65	45–55	35–45

The tempering temperature may be varied from 550–728° C., according to the properties required of the core.

The hardness of the case is unaffected by this heat-treatment and it is of course useless to temper lower than the temperature of the nitriding process (500° C.).

Hardness at Elevated Temperatures.—Fig. 4 shows the effect of temperature on nitrided nitralloy compared with a high carbon steel water quenched.

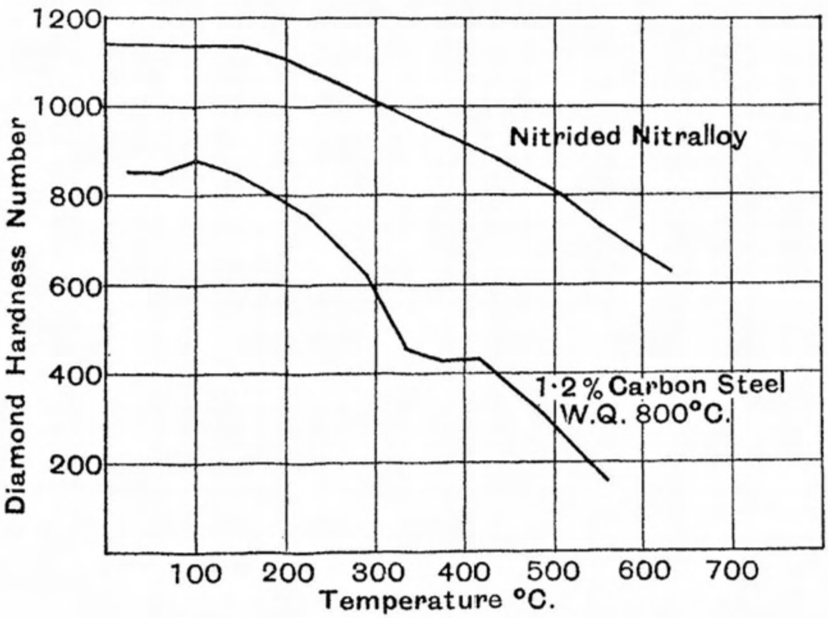

FIG. 4.

Resistance to Wear.—Wear tests on shafts of metals running in bearings of the same and different materials show that, among all combinations of the materials, nitralloy, mild steel, cast iron, phosphor bronze and gear steel, the combination of a nitralloy shaft and a phosphor bronze bearing can only be improved upon by the use of a gear steel shaft running in a nitralloy bearing.

Fatigue, Corrosion, etc.—Wohler tests showed that the nitriding process increased the fatigue limit of a certain steel from 35 to 39 tons/in.^{2}

Corrosion-fatigue limits of another specimen measured in a Wohler machine gave the following results :—

	Polished specimen.		With round notch.	With sharp notch.
	Oil-coated.	Sprinkled with water.		
Un-nitrided . .	35	8·2	21	7·6 tons/in.^{2}
Nitrided	40	40	40	35 tons/in.^{2}

The nitrided surface, slightly polished, gives good resistance to atmospheric, tap water, and sea water attack, but not to acid attack. It will resist a solution of 50 per cent. caustic soda up to a temperature of 80° C. It is nearly as good as ordinary (13 per cent. Cr) stainless steel in this respect.

Nitralloy steels can be fabricated and welded by the electric resistance butt welding or the atomic hydrogen welding processes.

If electric arc welding be used, even with nitralloy electrodes, too much aluminium and chromium will be lost at the weld for the subsequent nitriding to be satisfactory.

Oxy-acetylene welding is fairly satisfactory if nitralloy steel welding wire and a neutral flame be used.

The use of nitrided steels for centrifugal pumps, fan spindles and valve spindles would appear to offer some advantages. Used for the spindles of the stop valves of pumps fitted with the usual trip gear, the great hardness of nitrided steel might prevent the seizure of the valve on the spindle which so frequently occurs, to the detriment of valve and seating.

In internal combustion engines nitrided steel can be used with advantage wherever hardness and strength are required—for example, for cylinder liners, gudgeon pins, camshafts and crankshafts.