8.4 CYANIDING AND CARBONITRIDING

In cyaniding and carbonitriding processes, the surface layer of steel (with 0.3–0.4% C) is hardened by addition of both carbon and nitrogen.

Cyaniding is carried out in a liquid bath of NaCN. If the process is carried out in a gaseous atmosphere, it is called carbonitriding.

8.4.1 Cyaniding

In this process, the parts to be heat treated are immersed in a liquid bath (at 800–960°C) of NaCN with the concentration varying between 25% and 90%. The measured amount of air is passed through the molten bath. NaCN reacts with the oxygen in the air and is oxidized. The basic reactions in the bath are

$$\begin{gathered} 2NaCN + O_2 \rightarrow 2NaCNO \\ 2NaCNO + O_2 \rightarrow Na_2CO_3 + CO + 2N \\ 2CO \rightarrow CO_2 + C \end{gathered}$$

Carbon and nitrogen so formed in atomic form diffuse into the steel and give thin wear resistant layer of the carbonitride ε-phase. Usually, this process requires 30–90 minutes for completion.

For obtaining case depth from 0.5 mm to 2 mm, the process is carried out at higher temperature (950°C) in a bath containing 8% NaCN, 82% $BaCl_2$ and 10% NaCl. This process takes 1.5–6 hours for completion. For case depth from 0.13 mm to 0.35 mm, the bath is maintained at 850°C with the following concentration:

$$\begin{aligned} NaCN &= 30\% \\ NaCl &= 35\% \\ Na_2CO_3 &= 35\% \\ \text{(Soda ash)} & \end{aligned}$$

The higher the temperature at a given cyanide level, the higher is the percentage of carbon diffusion (up to 0.8–1.2% C) into the surface of steel as compared to nitrogen (0.2–0.3%). After cyaniding, the pieces are taken out and are quenched in water or oil. For thick sections, mineral oil is preferred for quenching. The final operation is low temperature tempering. After heat treatment, the case has a hardness of 850 VHN. This process is less time consuming. Because of the high heat transfer coefficient in liquid bath and uniform bath temperature, distortion of pieces is less. This process is not suitable for hardening those parts which are subjected to shock, fatigue and impact because nitrogen addition has adverse effects on such properties of steels.

8.4.2 Carbonitriding

This process is specifically used for improving wear resistance of mild, plain carbon or very low alloy steels.

Carbonitriding is carried out at lower temperatures (in the range 800–870°C) in a gas mixture consisting of a carburizing gas and ammonia. A typical gas mixture contains about 15% NH_3, 5% CH_4 and 80% neutral carrier gas. Carbon and nitrogen are diffused at the same time into the surface of the steel in the austenitic-ferritic condition and gives case thickness of the order of 0.05–0.75 mm. Nitrogen is more effective in increasing hardenability of the case as compared to carbon. Nitrogen content of the steel depends on ammonia content and temperature.

After carbonitriding, quenching is done in oil to avoid cracking. This is followed by tempering at 150–180°C. Heat treatment produces a case having a hardness of 850 VHN.

In this process, surface hardenability, wear resistance and corrosion resistance are better than in the carburizing process. But the time required for heat treatment is longer than that for carburizing.

8.5 NITRIDING

Nitriding is most effective for those alloy steels which contain stable nitride forming elements such as aluminium, chromium, molybdenum, vanadium and tungsten. Examples of popular medium-carbon alloy steels which are used for nitriding are: 708A37 and 817A40 to B5970: Part 2. The typical composition of such steel is 0.1–0.5% C, 0.75–1.25% Al, 1–1.5% Cr, and 0.2% Mo.

Nitriding is carried out in a ferritic region below 590°C. So there is no phase change after nitriding. Before nitriding, proper heat treatment should be given to steel components (hardening by heating to 930°C and quenching in oil, then tempering at 650°C) to develop bainitic structure, which increases the strength and toughness of the core. All machining and grinding operations are finished before nitriding. The portions which are not to be nitrided are covered by thin coating of tin deposited by electrolysis. The coating checks diffusion of nitrogen due to its surface tension. Anhydrous ammonia gas is passed into the furnace at about 550°C, where it dissociates into nascent nitrogen and hydrogen. Thus,

$$2NH_3 \rightarrow 2[N]_{Fe} + 3H_2$$

The treatment time varies from 21 hours to 100 hours. Actually, it depends an the desired case depth and size of the steel parts. After nitriding, the steel part is allowed to cool in furnace itself in the presence of ammonia. The furnace container is made of heat resisting alloy steel. The time required for a case depth of 0.5 mm is about 100 hours.

The hardness achieved at the surface of steel varies from 900 VHN to 1100 VHN. The hard layer so formed imparts good wear resistance, hot hardness and corrosion resistance.

During nitriding process, a white layer of Fe_4N (γ' nitride) and Fe_2N (ε nitride) form on the outer layer of surface. This layer is problematic as it is very brittle and tends to crack. Formation of this layer is caused by high nitrogen potential. So this can be avoided by keeping nitrogen potential at the desired level. White layer should be removed from component by mechanical polishing or by boost diffusion techniques.

There are two ways by which white layer can be totally suppressed.

(a) *Floe process* or double-stage nitriding, where a white layer is first produced and then decomposed.

The first stage is carried out between 495 and 525°C for 15–20 hours with around 20% dissociated ammonia to achieve faster growth of nitrided case. The second stage is done between 550 and 565°C with 75–80% dissociated ammonia (atmosphere of low nitrogen potential). The iron nitrides formed in first stage dissociate, so that white layer reduces from

0.05 mm to 0.01 mm, or even gets eliminated. Elimination of white layer means case depth is increased by that thickness. Higher nitriding temperatures in the second stage lower case hardness, increase case depth.

The decomposition of the white layer takes place by means of three fundamental processes:

(i) Diffusion of nitrogen out of the white layer into the vacuum of the ion nitriding vessel.
(ii) Diffusion of nitrogen from the white layer into the diffusion layer.
(iii) Sputtering of the white layer by bombardment with *inert* ions.

The first two processes cause a decomposition of the white layer by a phase transformation of the nitrogen depleted iron nitride γ back to the α(N)-ferrite. The third process results in a reduction of the white layer by a removal of material from the surface. All three processes at the same time contribute to the reduction of the white layer during the second stage. However, the part each process plays varies according to the size of the voltage or the temperature of the work piece.

(b) Ion Nitriding Process or Plasma Nitriding which is described in the following section.

8.6 PLASMA NITRIDING (ION NITRIDING)

Plasma nitriding is also known as ion nitriding process. In this process the steel component to be nitrided acts as cathode (Figure 8.5), the component is heated by electrical heaters to 370 to 650°C. This heating operation is followed by switching on supply of a gas mixture of hydrogen and nitrogen at 1–10 torr. Sufficiently high DC voltage (500–1000 V) is applied between the cathode (component) and anode to form plasma. Current flows between two electrodes and the mixture of hydrogen and nitrogen gas gets ionized. When the part to be treated is subjected to this ionized discharge, the nitrogen ions that are formed bombard the surfaces of the component (cathode) with considerable energy. Part of this energy heats the cathode and allows diffusion of nascent nitrogen inwards from nitrides. The remaining part of energy is used for displacing the secondary electrons from the cathode surface. These secondary electrons gain energy from the applied voltage (potential). Bombarded ions clean the surface, heat the component and gives nascent nitrogen. A glow envelops the component and nitriding starts. Nitrided case depth depends on current temperature and time of nitriding. After ion-nitriding, the

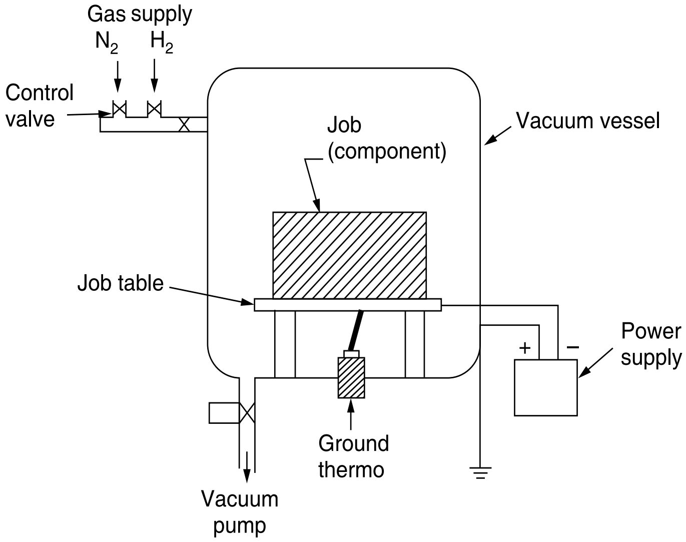

Figure 8.5 Plasma nitriding process.