THERMO-CHEMICAL SURFACE HARDENING TREATMENT OF STEELS

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CASE CARBURISING

Case Carburising is a process in which austenised ferrous metal is brought into contact with an environment of sufficient carbon potential to cause absorption of carbon at the surface, and by diffusion, to create a carbon concentration gradient between the surface and interior of the metal. The addition of carbon preferentially to the surface layers of the steels followed by proper heat treatment develops the hard abrasive, wear resistant surface and as the core remains comparatively soft and tough the component as a whole shows high impact strength. Due to the residual stress pattern developed during the process the fatigue strength also improves.

Carburising can be done in a gaseous atmosphere (gas carburising), a salt bath (liquid carburising), or an environment where in all surfaces are covered by a solid compound (pack carburising). The transport of carbon form the carburising medium always takes place via a gaseous phase, usually carbon monoxide (CO).

Mechanism of Carburising

In the carburising process, free carbon is absorbed in the surface layer of a piece of steel that has a usually low carbon content. The free carbon is derived from a gaseous or liquid substance in intimate contact with the metal surface by means of chemical reactions that do not directly involve the metal but that may be catalysed by the presence of the metal. Absorption of carbon into the surface layer sets up a concentration gradient and carbon atoms move by diffusion away from the surface.

Successful operation of the gas carburising process depends on the control of three principal variables: temperature, time and atmosphere composition. The maximum rate of carburising at which carbon could be added to steel is limited by the rate of diffusion of carbon in austenite. This diffusion rate increases greatly with temperature. The temperature most commonly used for carburising is 925° C. This temperature permits a reasonably rapid carburising rate without excessive deterioration of furnace equipments.

The term depth of carburisation means either the distance below the surface to a definite carbon concentration or to the total depth of carbon penetration. In addition to time and temperature the depth of carburisation depends on the carbon potential of the carburising medium and on the composition of the steel. The higher the carbon potential the higher the carbon concentration at the surface of the steel, when equilibrium has been established and the deeper the carburising depth.

The carbon potential may be defined as the carbon content which a specimen of carbon steel foil acquires when equilibrium conditions have been established between the carbon content of carburising medium and the carbon content of the foil.

Gas Carburising

Gas carburising is the most commonly used carburising process especially in the automotive field. The fact that the carbon content of the case can be controlled by adjustments of the gas composition makes it far superior to old method of pack carburising. In gas carburising the furnace atmosphere is a mixture of carburising and decarburising agents, the gases most often present being carbon monoxide, hydrogen, carbon dioxide, water vapour, methane and nitrogen. The principal reactions involved in the transfer of carbon to steel are as follows :

$$Fe + 2CO \text{ ----- } Fe(C) + CO_2$$
$$Fe + CH_4 \text{ ----- } Fe(C) + 2H_2$$
$$Fe + CO + H_2 \text{ ---- } Fe(C) + H_2O$$

where Fe(C) represents carbon in solution in gamma iron (austenite). The rates of these reactions control the rate of carburising.

In current commercial practice, gas carburising uses carbon from hydrocarbon gases and easily vaporised liquids. The liquids usually range in composition from pure hydrocarbons such as terpens, dipentens or benzene to oxygenated hydrocarbons such as alcohols, glycols or ketones. They may also be blends of hydrocarbons and oxygenated hydrocarbons.

The liquid is usually pumped to a target plate in furnace where it volatilises rapidly to provide the required carbon, with hydrogen, methane and carbon monoxide as secondary by products. Forced fan circulation is necessary in furnaces where a liquid is used for the carbon source in order to have the flow direction such that the vapours crack on the work surfaces. This results in formation of carbon on the work surface where it can be absorbed immediately.

The gases most commonly used all around the world for gas carburising are natural gas and propane if available with high degree of purity. In India due to non-availability of natural gas and propane the liquid petroleum gas (LPG) is the most commonly used source of carburising. The large majority of gas carburising furnaces are operated with a carrier gas added to the hydrocarbon gas that is utilized as a principal source of carbon . The carrier gas provides better circulation of the carburising gas because of the large volume used.

The endothermic gas is generally the preferred type of carrier gas used in most carburising furnaces, as it offers a wide range of carbon control and a moderate amount of carbon availability for carburising. The ratio of carrier gas to enrichment gas can vary from 8:1 to 30:1 depending upon the dew point of the carrier gas and the application. Endo gas generator when operated at dew point of -5 to +5° C can run continuously without weekend desooting. The main constituents of the atmosphere are CO, N_2, H_2, CO_2, H_2O, and CH_4. Of these constituents,

N_2 is inert, acting only as a diluent. The amount of CO, CO_2, H_2O and H_2 present are nearly the proportions expected at equilibrium from the reversible reaction :

$$CO + H_2O \text{ ----- } CO_2 + H_2$$

given the particular ratio of C, O and H in the atmosphere.

Furnaces used and atmosphere control

Gas carburising may be carried out in either batch or continuous type furnaces. The two types differ largely in their method of handling of work. In a batch type furnace, the work is charged and discharged as a single unit or batch; in the continuous furnace, work pieces enter and leave the furnace as units in the continuing stream. In general, most of the carburising in the automotive field is done in continuous furnaces. Continuous carburising can be done in several types of furnaces - the most common type being the rotary hearth and pusher. The pusher type is most widely used in the automotive field. Its construction usually consists of welded gas tight shell with gas fired radiant tubes or electric elements for heating. The work is pushed through on trays or fixtures and, after completion of the carburising cycle, may be quenched or slow cooled. Most pusher type furnaces have purging vestibules at both the charge and discharge ends to prevent dilution of the furnace atmosphere with air. Before carburising, machined parts should be as near final dimensions as possible so that the outer most effective case will not be ground off after carburising.

The carbon potential of a carburising atmosphere can be determined on the basis of gas composition and determined with an Orsat analyser, a dew point indicator, an infra red analyser or a oxygen probe. The Orsat apparatus is usually not used in production shops due to long analysis time and large errors. The dew point appratus also can not be used for continuous monitoring of the furnace atmosphere. The infra red analyser and oxygen probe can be used for continuous monitoring and control of the furnace atmosphere by controlling the flow of enrichmen gases in the furnace. The oxygen probe, inserted directly in the working chamber of the furnace, is becoming common because of its instantaneous response and relatively easy setup. When the carbon dioxide content of the furnace remains relatively constant, both carbon dioxide and oxygen potential provide good measures of the carbon potential.

NITRIDING

Nitriding is a case hardening process whereby nitrogen is introduced into the surface of a ferrous alloy by holding the metal at a suitable temperature (below Ac_1, for ferritic steels) in contact with a nitrogen atmosphere usually ammonia. Nitriding is also carried out in presence of liquid nitriding salts containing cyanides and cyanates. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 and 565°C.

The addition of nitrogen to the surface of steels produces a hard, wear resistant surface, alongwith improved fatigue properties and better dimensional control. Because of the absence of a quenching requirement, with attendant volume changes, and comparatively low temperatures employed in the process, nitriding produces less distortation and deformation than either carburising or conventional hardening. Since nitriding is carried out below the austenite range, the steel is quenched and tempered to the final desired core properties prior to nitriding.

Of the alloying elements commonly used in commercial steels, aluminium, chromium, vanadium, tungsten and molybdenum are beneficial in nitriding, because they form nitrides that are stable at nitriding temperatures. Aluminium containing steels produce a nitrided case of very high hardness and excellent wear resistance.

In gas nitriding the process is carried out in mixtures of ammonia gas (NH_3) and hydrogen, such that atomic nitrogen is released at the metal surface. The nitriding process is based on the affinity of nascent nitrogen for iron and certain other metallic elements. Nascent nitrogen is produced by the dissociation of gaseous ammonia when it contacts hot steel parts.

Liquid nitriding is carried out in the fused salt bath containing both cyanides and cyanates. The liquid nitriding process has several proprietary modifications and is applied to a wide variety of carbon, low alloy and tool steels. A typical commercial bath for liquid nitriding is composed of a mixture of sodium and potassium salts. The sodium salts, which comprise 60 to 70% (by weight) of the total mixture, consist of 96.5% NaCN, 2.5% Na_2CO_3 and 0.5% NaCNO. The potassium salts 30 to 40% by weight of the mixture consist of 96% KCN, 0.6% K_2CO_3, 0.75% KCNO and 0.5% KCl. With aging the cyanide content of bath decreases and the cyanate and carbonate content increases. The cyanate content in all nitriding baths is responsible for the nitriding action, and the ratio of cyanide to cyanate is critical.

CARBONITRIDING

Carbonitriding is a case hardening process in which carbon and alloy steels are held at an elevated temperature (usually above the transformation range) in a gaseous atmosphere from which they absorb carbon and nitrogen simultaneously, and are then cooled to room temperature at a rate that will produce desired case and core properties. The carbon is derived from any carbon rich gas or vapourised liquid hydrocarbon that is suitable for carburising. Ammonia is the source of nitrogen.

Carbonitriding thus is a modified gas carburising process, rather than a form of nitriding. The modification consists of introducing ammonia into a gas carburising atmosphere in order to add nitrogen to the carburised case as it is being produced. Ammonia in the atmosphere dissociates to form nascent nitrogen at the work surface which diffuses into the steel simultaneously with carbon. Typically, carbonitriding is carried out at a lower temperature and for a shorter time than gas carburising, in order to obtain a case shallower than is usual in production carburising.

In its effects on steel, carbonitriding is similar to liquid cyaniding. Because of problems in disposing of cyanide bearing wastes, carbonitriding is often preferred over liquid cyaniding. In terms of case characteristics, carbonitriding differs from carburising and nitriding in that (a) carburised cases normally do not contain nitrogen and (b) nitrided cases contain no added carbon, where carbonitrided cases contain both.

Cabonitriding is used primarily to impart a hard, wear resistant case, generally from 0.075 to 0.75 mm deep. A carbonitrided case has better hardenability than a carburised case; consequently, by carbonitriding and quenching, a hardened case can be produced at less expenses within the case depth range indicated, using either carbon or low alloy steel. Full hardness with less distortion can be achieved with oil quenching or, in some instances, even gas quenching employing a protective atmosphere as the quenching media. The resistance of a carbonitrided surface to softening during tempering is markedly superior to that of a carburised surface.

The composition of a carbonitrided case depends on temperature, time and atmosphere composition for carbonitriding and type of steel. The higher the carbonitriding temperature, the less effective is the ammonia in the atmosphere. Lower temperature favour increased nitrogen concentration at the steel surface and steeper nitrogen gradients. When carbonitriding is carried out at about 840°C the percentage of carbon and nitrogen at surface varies between 0.6 to 0.8. Carbonitriding can be carried at such low temperatures as to produce a compound layer, so called because iron-carbon-nitrogen compounds are formed at surface. To produce this layer of compound, however, large percentage of ammonia is required. In some wear application this type of case is very suitable.

Almost any furnace suitable for gas carburising can be adapted to carbonitriding. If dense loads are to be processed, the furnace must be equipped with a fan to circulate the atmosphere through them. The atmosphere used in carbonitriding generally comprise a mixture of carrier gas, enrichment gas and ammonia. Basically, the atmospheres used in carbonitriding are produced by adding from 2 to 12% ammonia to a standard gas carburising atmosphere. The most commonly used carrier gas is endo gas which is enriched with LPG or propane. The gases are premixed just before the entry into the furnace. To control the furnace atmosphere dew point meter, infra red analyser and oxygen probes can be used effectively.