Plasma Nitriding

2.1. Nitriding: microstructure and properties

Nitriding is a thermochemical process which modifies the surface microstructure of the steels by introducing nitrogen, when steel is in ferritic phase (495- 570°C). The nitrogen diffuses as interstitial atom in solid solution from the surface, until the solubility limit (0.4% N) (fig. 2.1). A very fine precipitation occurs depending on alloying elements, temperature, time and concentration of nitrogen [11, 14, 21].

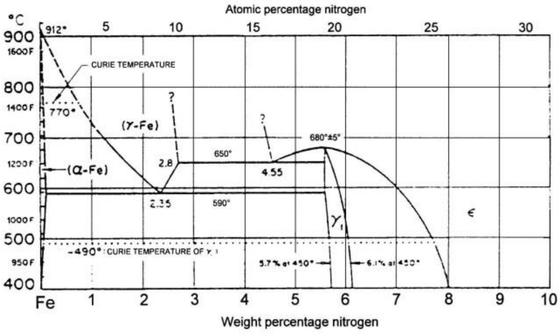

Figure 2.1: iron- nitrogen diagram [11]

On the base of nitrogen content two zones can be distinguished in the microstructure of nitrided steels:

- **Compound layer** (or white layer) presents a high nitrogen concentration. It is in principle a ceramic layer made of two iron nitrides: $Fe_{2-3}N$ (ε) and Fe_4N (γ'), in carbon steels.

- **Diffusion layer** is characterized by low nitrogen concentration. It can be described as the base microstructure hardened by solid solution and by the precipitation of nitrides; the type and size of these precipitates depend on the chemical composition of the steel. The dissolved nitrogen and the volume expansion of nitrides precipitation causes a compressive residual stress field in the diffusion layer, whilst the compound layer results in a tensile residual stress.

In order to obtain an appreciable hardening and depth of the diffusion layer, materials containing alloying elements with a high affinity for nitrogen, like chromium, aluminum and, molybdenum, have to be selected (fig. 2.2). Copper, nickel and manganese have a negligible interaction with nitrogen.

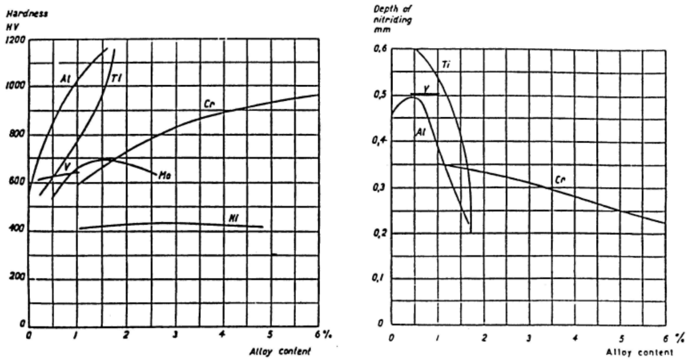

Figure 2.2: alloying elements effect on hardness and case depth [21]

Aluminum is the strongest nitride former, however, more than 1% causes the formation of surface cracks in working condition because the ductile core cannot support the hard case layer. Chromium is a very desirable element because it increases the mechanical properties of steels on increasing both hardenability and nitrability [21, 22]. Chromium forms stable nitrides, but, with high concentration, makes difficult the nitriding treatment because of the high affinity for oxygen that induces surface oxidation. Molybdenum forms stable nitrides at nitriding temperature and reduces the risk of embrittlement. The presence of nickel in the 18 steel is ineffective to the hardness of the nitride layers due to the low affinity for nitrogen [23].

Looking at the mechanical properties of nitrided steels, the increase in the fatigue resistance is due to the hardened surface and mainly to the compressive residual stresses in the diffusion layer. The fatigue crack nucleate below the surface, where the maximum tensile stress results from the superimposition of residual stress and applied stress, and stop growing inside the diffusion layer [24, 25].

Nitriding can be considered like a finishing operation because it permits minimum distortions and high dimensional control due to the absence of phase transformation.

2.2. Plasma nitriding

2.2.1. Introduction

Plasma nitriding (or ion nitriding) is an extension of conventional nitriding processes using plasma- discharge physics. An electric current is applied in vacuum, in order to reach a differential potential of about 500-1000V, and consequently nitrogen particles are dissociated, ionized and accelerated on the surface components. N^+ ions impact on the steel surface, acquiring an electron and emitting a photon. This emission, which represents the return of nitrogen ions to their atomic state, creates the visible glow discharge that is typical of plasma techniques. The impact between ions and components takes place at high kinetic energy and maintains the component at the nitriding temperature . This results in a very fast saturation of α-iron so only a few minutes later a coherent layers of iron nitrides exist in equilibrium with the saturated iron.

The two essential factors of the fast diffusion of nitrogen in plasma nitriding are: the high surface concentration of nitrogen, which is of particular relevance at the beginning of the process, and the increased rate of nitrogen penetration due to the different diffusion mechanism.

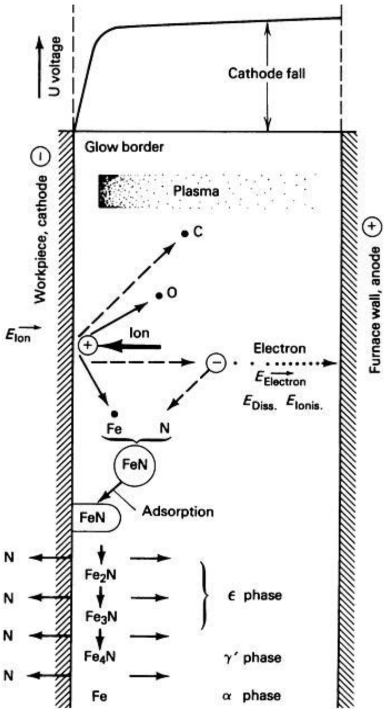

Figure 2.3: interaction between nitrogen ions and surfacepiece [11]

In the early stage of the plasma nitriding process a nitrogen rich phase (FeN) is condense on the nitrided surface as the result of sputtered Fe atoms combining with the incoming nitrogen atoms. Because FeN is not a thermally stable compound it immediately dissociates into lower nitrides. At each dissociation stage, one atom of nitrogen is released, which becomes ready to diffuse into the iron matrix. The nitrogen atoms undergo a volume diffusion, allowing a plane diffusion front (fig. 2.3).

Ion nitriding, like other nitriding processes, produces several distinct structural zones on the base of nitrogen content which include a layer of iron-nitride compounds at the surface (ε and γ’) and the diffusion layer made of a saturated solid solution with a fine dispersion of sub micrometric nitride particles. During the process, different alloy and iron atoms combine with the nitrogen as it diffuses into the material, forming a hardened surface and case [6, 7].

The facility in control of the plasma nitriding variables (temperature, pressure, gas mixture, gas flux, current and voltage) allows a better control of the surface layer with thickness, microstructure and properties well defined. The limitation of plasma nitriding is the equipment cost in comparison with the traditional nitriding process and therefore it is not suitable for the treatment of small components.

2.2.2. The process

A plasma nitriding system is shown in figure 2.4.The component to be nitrided are cleaned and charged in a vacuum furnace. The process of plasma nitriding can be resumed in four steps [11, 14]:

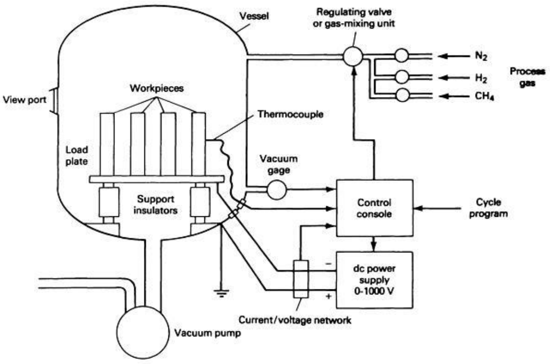

Figure 2.4: typical ion-nitriding system [11]

Vacuum. Vacuum is carried out by mechanical pump until about 7-13Pa. This operation is necessary to remove the air and some contaminates presented in the furnace atmosphere.

Heat. Heating is assured by resistors, connected to the cathode (work surface piece). During the heating the pressure is increased to lead over the electrical discharge concentration.

Plasma. After load is heated to desired temperature, process gas is admitted at a flow rate determined by the load surface are, on increasing pressure up to 10^2-10^3Pa. An electric current is applied and consequently nitrogen particles are dissociated, ionized and accelerated to the surface. The thickness of the glow discharge can be modified by pressure, temperature, composition, potential, electrical current and gas mixture. Usually the thick is about 6mm. **Cooling.** The load is cooled by inert-gas circulation.