CHEMICOTHERMAL TREATMENT

THE MECHANISM OF ACCELERATED NITROGEN DIFFUSION IN IRON

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Ion nitriding shortens the processing time, eliminates the necessity of preliminary depassivation in treating stainless steels, and reduces the brittleness of the case. However, the mechanism of accelerated nitrogen diffusion has not yet been studied.

Some authors have explained the observed acceleration by the sharp increase in the rate of processes occurring at the surface [1-2]. The purpose of this study was to clarify this mechanism.

To determine the preeminence of the rate at which the limit nitrogen concentration in the surface is created during ion nitriding as compared with gas nitriding, a spectral analysis* was made of the nitrogen concentration [3] on the surface of commercial iron samples during ion and conventional nitriding. The samples were nitrieded at 550°C for 1 min to 6 h. It can be seen in Fig. 1 that the nitrogen concentration in the surface is identical in both methods. This concentration is attained after 1 min in ion nitriding and after 10 min in gas nitriding.

In ion nitriding the maximum case depth in commercial steels is reached after 6-20 h [4-7]. Consequently, the process of creating a thin surface layer a few microns thick with the limit concentration of nitrogen, which is of major importance in the formation of the diffusion layer at the beginning of saturation, has an effect on the acceleration of diffusion that is visible in 10-20 h but does not control it.

Obviously, the role of ion bombardment of the cathode surface is not limited only to cleaning of the surface and applying a film of nitrides. The energy of the ions occurring in the plasma of the glow discharge and bombarding the surface of the sample — the cathode — at a potential difference of 800 V is more than 3000 times the energy of the dissociated nitrogen atom at the surface of the iron during gas nitriding at 520°C [5]. The ion is embedded in the surface of the metal and interacts with the crystal lattice. Under the influence of ion bombardment (ion energy 3.8·10^-17 J) [5] the density of defects in a thin surface layer of the metal can become high, which should induce an increase of the diffusion rate. This has been confirmed experimentally. †

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Fig. 1. Blackening intensity of nitrogen line in the spectrum from the surface as a function of saturating time in ion (1) and gas (2) nitriding.

Fig. 2. Autoradiographs of the surface of nickel samples after electropolishing (a) and after cathode sputtering of the surface (b).

The autoradiographic method was used to determine the self-diffusion coefficient of nickel (Fig. 2). The annealed nickel samples were electropolished to remove a layer 60 μ thick. Some of the samples were subjected to cathode sputtering in a medium of spectrally pure argon. After electropolishing, the self-diffusion coefficient of nickel at 700°C was $3.56 \times 10^{-14}$ cm$^2$/sec; after ion bombardment of the surface it was $2.06 \times 10^{-13}$ cm$^2$/sec. Evidently the increased rate of self-diffusion is due to the increased density of defects in the surface layer. The existence of defects of the dislocation type was confirmed in a study of commercial iron foil by transmission electron microscopy.* The previously annealed foil 0.1 mm thick was subjected to cathode sputtering in ammonia at a potential of 1100 V and pressure of 0.14–0.17 mm Hg. After electrothinning from both sides the foil was examined in the IEM-6A microscope with an accelerating potential of 100 kV. The character of the dislocation arrays observed in the foil after annealing and after ion bombardment is shown in Fig. 3. As the result of cathode sputtering the dislocation density increases. Electron diffraction studies were made to determine the slip planes (from the direction of the long and straight dislocations). In Fig. 3b the dislocations are located in slip planes (112) and (121), which intersect the plane of the foil (111) from directions [110] and [101] respectively. Both planes, (112) and (121), are perpendicular to the plane of the foil (111). With (113) orientation of the foil (Fig. 3c and d) the dislocations are located in slip plane (110), which intersects (113) from direction [332]. The (110) plane is perpendicular to the plane of the foil (113). Consequently, the dislocations occurring during cathode sputtering move on slip planes perpendicular to the outer surface of the foil, i.e., the directions of dislocation movements and diffusion of nitrogen atoms coincide. Dislocation dipoles can be seen in some sections of the foil, which indicates dislocation movement from both outer surfaces of the foil subjected to cathode sputtering. Straight dislocations are characteristic of deformation at low temperatures or high deformation rates. During sputtering, the surface of the foil reaches 300–400°C, and therefore it is probable that the rate of the effect on the surface during ion bombardment is very high. The foil was thinned from both sides, and therefore it can be considered that the dislocations observed are located in the middle of the foil, i.e., at a depth of 0.05 mm, since it is generally considered [4, 5] that the depth of the action of ions on the crystal lattice during ion bombardment does not exceed a few atomic layers. Nitride precipitates can be seen on the dislocations.

From comparison of the diffusion coefficients of nitrogen in ε-, γ'- and α-phases, determined in [6], it can be seen that at 550°C the diffusion rate of nitrogen in α-phase is 60 times higher than in ε-phase and 25.5 times higher than in γ'-phase. Evidently, after creation of a surface layer of ε- and γ'-phases (completed in 10 min in the case of gas nitriding at 550°C) the further increase of the depth of the diffusion layer is controlled by the diffusion rate of nitrogen through the ε- and γ'-phases. During nitriding for 6 h at 550°C the total depth of these two phases amounted to about 0.04 mm [6]. The creation of an elevated density of dislocations, the direction of which coincides with the direction of diffusion, in a layer 0.05 mm deep should substantially increase the diffusion rate of nitrogen during prolonged saturation commensurable with the chemicothermal treatment.

**CONCLUSIONS**

1. Accelerated diffusion during ion nitriding is due to the more rapid creation of a surface layer with the limit nitrogen concentration and elevated dislocation density.

2. A preeminence in the rate of formation of a layer with the limit nitrogen concentration in the surface of iron samples during ion and gas nitriding at 550°C was observed only in the first 10 min.

3. Under the influence of ion bombardment the self-diffusion coefficient of nickel at 700°C increases 5.8 times.

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