Carbonitriding at 1050 °C in a Glow-discharge Plasma

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Carbonitriding is often preferred to carburizing because nitrogen bearing cases exhibit greater hardenability, and thus small parts made of low-carbon steels may be oil quenched. The results reported here demonstrate that the techniques developed for high-rate, high-temperature plasma carburizing may be applied to carbonitriding with comparable success. The process conditions, however, must be adjusted to ensure that neither the carbon nor the nitrogen are lost in the later stages of the carbonitriding cycle. This requires that a carbon/nitrogen plasma be maintained during both the carbonitriding and diffusion stages, and while the workpiece is cooled to <600 °C.

INTRODUCTION

As automotive components are made smaller and lighter to meet fuel economy goals, it becomes likely that the use of carbonitriding will increase because carbonitrided cases, owing to their greater hardenability and resistance to tempering, are more suitable than carburized cases for smaller, less massive parts. Earlier research on high-temperature carburizing demonstrated that exceptionally high carburizing rates could be obtained in a glow-discharge plasma. It was thus a natural extension of the research to consider plasma carbonitriding in which both carbon and nitrogen are added simultaneously. Furthermore, the plasma offers the possibility of overcoming the upper temperature barrier of ~900 °C for conventional gas carbonitriding where ammonia is employed as the source of nitrogen. Above 900 °C ammonia decomposes thermally before it reaches the steel surface and thus cannot be used for high-temperature nitriding or carbonitriding. In plasma carbonitriding, on the other hand, nitrogen (N₂) can be used at the high temperatures since it dissociates only in the plasma near the steel surface and thus becomes available to react with and enter the steel. Since the addition of nitrogen to austenite can now be made independent of the temperature, it is likely that much of the uncertainty in the iron-nitrogen equilibrium diagram above 700 °C (Figure 1) can be removed.

In plasma carburizing, described previously, carbon is not added to the steel for the entire heating cycle. Rather, all the carbon needed is added during a very short carburizing stage which is followed by a longer (by three times) diffusion stage. Although no additional carbon is introduced, the effective case depth is essentially doubled by the inward diffusion of the carbon present. This procedure is possible because, in a vacuum, no surface reaction is available which can remove carbon from the steel.

Nitrogen, on the other hand, can escape from a steel surface while it is held at a high temperature in a vacuum. The following mechanism is proposed. Dissolved nitrogen atoms at the hot metal surface recombine to form molecular nitrogen which can escape, thus reducing the near-surface concentration of dissolved nitrogen. Further outward diffusion of the subsurface nitrogen occurs and, at high temperatures, the steel becomes completely denitrogenized. Therefore, some means must be devised to retain the nitro-
gen in solution until the temperature is lowered to the critical temperature (~600 °C) at which most of the nitrogen will be chemically combined as γ' and ε nitrides (Figure 1). The objective of this work was to find a suitable treatment cycle for plasma carbonitriding which would not only introduce carbon and nitrogen simultaneously, but also retain both elements in the steel to form carbon-nitrogen martensites when the steel is subsequently hardened by quenching.

EXPERIMENTAL

The experiments were conducted in a radiantly heated, quartz-tube furnace. In this furnace a parallel-electrode geometry is employed. Both the counterelectrode (anode) and the workpiece (cathode) are circular discs of AISI C1020 steel, 25 mm in diameter. The interelectrode spacing is approximately 10 mm and the working pressure is 2.7 kPa (20 Torr). For these conditions a dc potential of approximately 500 V is required to strike the plasma. Once established, the plasma can be maintained in a steady-state condition with complete coverage of the cathode at a potential in the neighborhood of 400 V. The gases needed are introduced through suitable flow meters into a manifold where they are mixed and fed continuously into the furnace as shown schematically in Figure 2. Carbon and nitrogen profiles, as a function of depth below the surface, were determined by vacuum-fusion analysis of successive layers machined from the surface of the specimen facing the counterelectrode. Auger spectrographic analysis for nitrogen was employed for some surface analysis, but could not be used for subsurface analysis because much of the nitrogen escaped during metal removal by sputtering.

RESULTS AND DISCUSSION

To test whether nitrogen could be introduced into steel from a glow-discharge plasma, a specimen was nitrogenized at 1060 °C for 10 minutes in a nitrogen plasma at a pressure of 2.7 kPa. The glow discharge was turned off after the nitrogenizing step and the specimen allowed to cool below the critical temperature in a vacuum. The result obtained is shown in Figure 3. Although some nitrogen was apparently added, the hardness profile (also shown in Figure 3) shows that an insufficient amount was retained to give a hardened