

THE MECHANISM AND KINETICS OF CARBON

TRANSPORT INTO IRON AND STEEL DURING PLASMA CARBURIZING

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ABSTRACT

Plasma carburizing is being developed as a cost effective and metallurgically superior method of case hardening engineering steel components. Aims of this work were (a) to establish enhanced transport rates of carbon into samples via high resolution measurements with a unique X-ray microanalyser, and (b) to elucidate the mechanisms underlying the enhanced kinetics.

1. INTRODUCTION

Vacuum processing, particularly methods of enhancing the surface properties of materials, is a rapidly expanding technology of major importance to engineering industries. Plasma nitriding and ion plating (e.g. with titanium nitride) are already attracting considerable commercial interest. Plasma carburizing is being developed as a superior process for introduction into the vast market which utilises case hardened components. Currently the commonest process being operated is gas carburizing, which uses an endothermic gas at atmospheric pressure. Plasma carburizing operates on very different principles¹ - low pressure (1 to 20 torr) and with a glow discharge struck within a hydrocarbon and hydrogen gas mixture - and it offers the heat treater the following very important advantages:

- much shorter processing times (at least a 50% reduction)
- carburized components with superior metallurgical structures (better uniformity, no internal oxidation, no surface decarburization in finished components)
- better mechanical properties (e.g. improved fatigue life and enhanced wear resistance)
- accurate automatic control
- lower gas and energy consumptions
- less pollution

This paper concentrates on the metallurgical kinetics of plasma carburizing and reports accurate measurements (via high resolution electron probe microanalysis) of carbon transport into iron and steel samples. It also outlines a mechanistic model for the process, supported by experimental observations, and exposes its merits compared with vacuum and gas carburizing.

2. EXPERIMENTAL

Plasma carburizer The experimental plasma carburizer used in this work was built by TI Abar and installed in TI Research Laboratories for extensive metallurgical evaluation and development. Figure 1 is a block diagram of the complete assembly. Gas requirements are in the range 1 to 20 torr total pressure, with methane levels a few percent (actual composition depends upon the carbon case required). The processing sequence involves three steps:

- heat to temperature range 850°C to 1050°C in presence of a hydrogen glow discharge which sputter-cleans the workload
- plasma carburize - this employs methane and other carrier gases such as hydrogen and argon in a glow discharge of about 500 V potential and a total current density of a few mA/cm².
- slow cool in nitrogen or oil quench

During plasma carburizing the system is operated in the abnormal glow discharge region². Samples placed on the cathode plate are enveloped in the cathode glow; this accurately follows the surface contours and is displaced by about 1 mm from the surface by the well-known cathode dark space. The cathode glow is the source of medium-energy ions and neutrals which bombard the hot surfaces of the steel samples.

Measurement of carbon profiles A unique electron probe microanalyser, designed and built at TI Research Laboratories³, was used to measure accurately carbon profiles normal to surfaces of polished sample sections. The instrument was routinely operated under "clean" vacuum conditions, which negated the common problem with carbon contamination of specimens under the electron beam. Other design features employed, crucial to high resolution and reliable measurement of carbon in steels, were a high brightness (lanthanum hexaboride) electron gun and a high sensitivity crystal spectrometer with optics specially designed for soft X-ray (e.g. carbon K) detection. Great care was exercised to preserve the true edges of specimens. X-ray microanalysis to an accuracy of +0.05 wt.% with a spatial resolution of 1 μm, and to within 1 μm of the surface was routinely performed. The instrument can also generate quantitative colour maps for carbon and other elements⁴ - Figure 2 shows a grey-level reproduction of such a map with its corresponding line profile.

3. RESULTS

Clean-up The plasma clean-up operation, which takes place simultaneously during heating of samples, is essential. Sputter cleaning certainly occurs; hydrogen ion bombardment probably also reduces surface oxides. Figure 3 compares sections of two steel samples which were plasma carburized identically except that one was plasma-cleaned whereas the other was heated under vacuum with no glow discharge (note the much shallower and irregular case in the latter sample).

Carburizing Figure 4 compares carbon profiles in pure iron after 15 minutes treatment at 950°C. Gas carburizing was carried out with a 0.9%C potential; vacuum carburizing⁵ employed 300 torr of methane; two profiles are included for plasma carburizing - one where the methane level was held constant at 2%, the other where the processing parameters were varied and computer controlled to optimise the kinetics. Note that both the surface concentration and the penetration depth are appreciably larger with plasma carburizing. Figure 5 plots the increase in surface carbon

levels of gas, vacuum and plasma carburizing during the early stages for treatment. The ability of the microanalyser to measure close to the surface proves the rapid rate of increase in the case of plasma carburizing. The rise is so rapid that a simple Fick's law diffusion calculation (which assumes the high level is attained instantaneously) is conformed with very closely, see Figure 6.

Figure 7 shows that steels with significantly different compositions respond very similarly to plasma carburizing, a result of considerable importance to the heat treater. Also of engineering importance is the fact that plasma carburizing conditions may be adjusted to generate independently the desired surface carbon level and penetration depth (which, after hardening, translate into the desired surface hardness and case depth). Figure 8 demonstrates that such control is readily accomplished. Likewise, correct control of operating conditions allows complex shapes, such as gears, to be uniformly carburized, Figure 9.

4. DISCUSSION

This work confirms the faster transport rate of carbon into components found by other workers^{1, 6-8}. The new and most important results reported here involved, for the first time, accurate and high resolution measurement of carbon levels very close to the surface and then inwards into samples. The dramatic feature of plasma carburizing that this highlighted was the very rapid mass transfer of carbon across the plasma/metal interface, particularly during the early stages of the process. Other revealing experimental observations were (a) the crucial importance of the clean-up operation, and (b) that conventional diffusion theory applies within the steel, indeed measurements indicated a conventional diffusion coefficient of approximately $2 \times 10^{11} \text{ m}^2/\text{s}$ applied at 950°C . The basis for a model can be constructed from these observations, as follows:

- the 'clean-up' cycle removes surface contamination which, if present, acts as a barrier to carbon (adatom) transfer into the surface.
- the fact that carbon ions and neutrals bombard the surface with energies significantly higher than the thermal energies operating in vacuum and gas carburizing leads to a high "effective" carbon potential.
- ion bombardment of the surface gives rise to enhanced adatom surface mobilities⁹; ion implantation is only a few monolayers⁹, although adatom mobilities are probably very high in this surface layer due to a high defect concentration^{9,10}; it is therefore postulated that these processes allow carbon to be readily absorbed into the surface; a high surface carbon concentration gradient maximises the driving force for conventional mass transport, J , of carbon into the steel interior (Fick's first law);

$$J = -D\rho \frac{\partial C}{\partial x} = K(A_p - A_s)$$

where D is the diffusion coefficient, ρ is density, the concentration gradient is that at the surface, K is a surface reaction coefficient, A_p and A_s are the carbon activities outside and inside the steel surface respectively¹¹ - it will be seen that the mass transport flux can be enhanced by increasing the concentration gradient at the surface and the surface reaction coefficient.

5. CONCLUSIONS

The rapid kinetics of plasma carburizing are due to enhanced surface reactions; conventional laws of metallurgical diffusion apply inside the steel components.

6. ACKNOWLEDGEMENT

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7. REFERENCES

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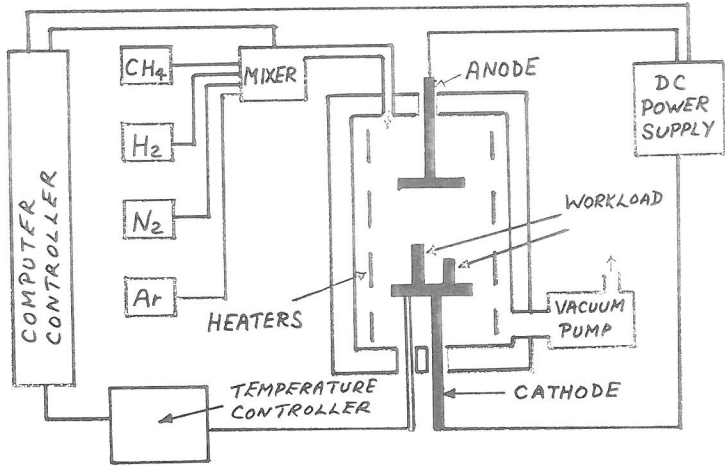


Figure 1. Block diagram of plasma carburizing equipment

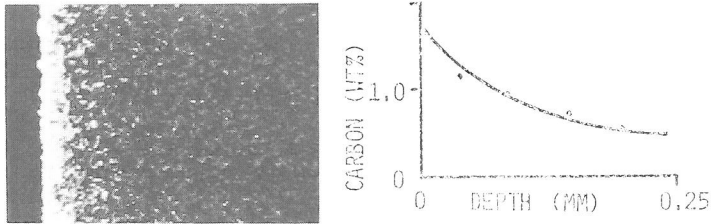


Figure 2. Grey-level carbon map and its corresponding profile

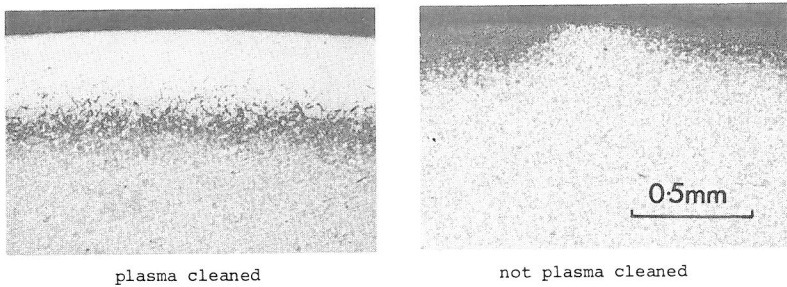


Figure 3. Benefit of plasma cleaning prior to a 10 min. carburize

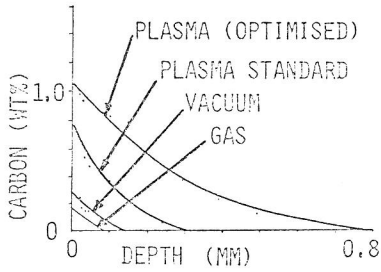


Figure 4. Carbon profile in pure iron after carburizing for 15 minutes

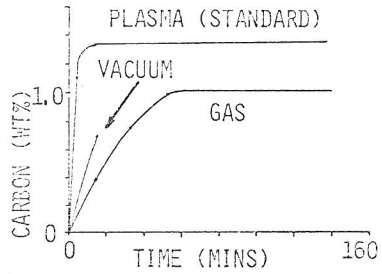


Figure 5. Increases in surface carbon levels measured by electron probe microanalysis

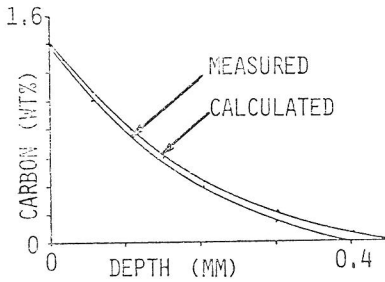


Figure 6. Comparison of measured and calculated (via simple Fick's Law) carbon profiles in iron

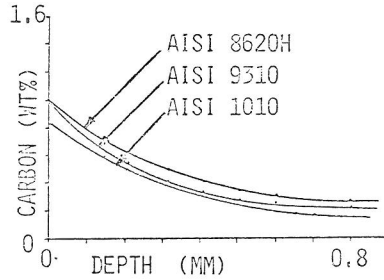


Figure 7. Steels of different compositions respond similarly to plasma carburizing

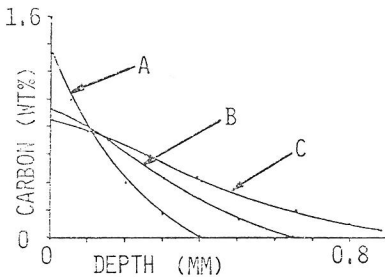


Figure 8. Sequence A, B and C of carbon profiles showing control of surface levels and case depths

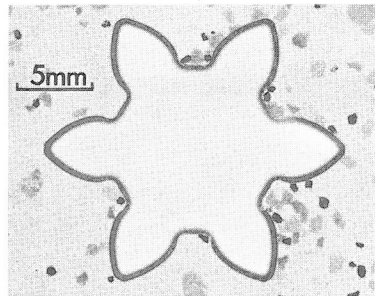


Figure 9. Plasma carburized gear (note uniform case depth)