Metallographic analysis of compound layers on ferritic nitrocarburized plain low carbon steel

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A simple method for the structural analysis of the compound layers on nitrocarburized steel is presented. The method involves light microscopical metallographic observation, and is supported by X-ray diffractometry data. The method has been used to examine the structure of compound layers on nitrocarburized plain low carbon steel.

1. Introduction

Ferritic nitrocarburizing [1, 2] is the term used to describe a class of heat treatment processes which involve the diffusional addition of principally nitrogen and carbon into the surface of a ferrous material, usually in the temperature range 550 to 580° C. The aim of these heat treatments generally is to bring about improvements in the tribological, fatigue endurance, and often also the corrosion resistance properties of a range of ferrous engineering components. Examples of the type of components to which ferritic nitrocarburizing has successfully been applied are rocker-arm spacers, textile machinery gears, pump cylinder blocks, jet nozzles, crankshafts and drive shafts. Although ferritic nitrocarburizing may be applied to most ferrous materials, the most marked improvements in properties, relative to untreated material, are generally found with plain low carbon steels.

When a steel is nitrocarburized, there are two main features which develop. Firstly, a "compound layer" forms on the surface of the material which is composed predominantly of iron carbonitrides. This compound layer, which is typically 10 to 20 μm thick (depending upon material and processing parameters) is responsible for improvements in wear, seizure and corrosion resistance. Secondly, there is a subsurface "diffusion zone" into which nitrogen has diffused to form either an interstitial solid solution or iron and alloy nitrides (depending upon material, and whether or not the work was quenched from the treatment tempera-ture). Improvements in fatigue endurance may be attributed to the characteristics of the diffusion zone.

It would appear [2] that, from the point of view of tribological performance, the optimum compound layer composition is one which consists essentially of the epsilon iron carbonitride phase (ϵ-Fe$_{2-3}$(C,N)). A number of other phases may also be present in the compound layer, most notably gamma prime iron nitride (γ'-Fe$_4$N). However, only a few detailed structural characterizations of compound layers have been undertaken [3–7], and in particular the relationship between layer structure and mechanical performance has not received much attention. One of the problems in this respect is a difficulty in evaluating the structure of the compound layer in a simple and effective manner, in particular using optical microscopy techniques. When a section of nitrocarburized steel is metallographically prepared and etched with a Nital etchant, the compound layer remains virtually unetched with practically no features being discernable. This is illustrated in Fig. 1. Clearly, very little information about the structure of the layer can be obtained in this way.

A recent attempt has been made by Colijn *et al.* [4] to optically resolve the structure of the layer using Murakami's reagent, and by vapour depositing a ZnTe interference filter onto the metallographic specimen. However, Murakami's reagent does not reveal much general detail of the matrix structure, and the vapour deposition of an
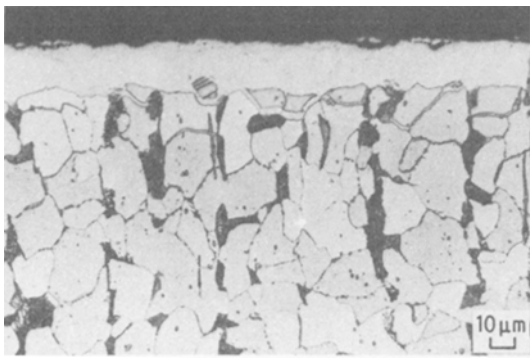
Figure 1 Nitrocarburized low carbon steel, etched with 2% Nital. No features can be discerned in the compound layer.

interference filter is not a technique which readily lends itself to the "shop-floor" environment. Wells and Bell [6] resolved the structure of compound layers on iron, nitrocarburized in methanol and ammonia atmospheres, by etching with an alcoholic solution of ferric chloride, hydrochloric acid, and iodine. Matauschek and Trenkler [7] examined iron, nitrocarburized by the salt bath method, using Marble's reagent as an etchant. However, both Marble's reagent and the etchant used by Wells and Bell have the disadvantage that little detail is generated in the subsurface diffusion zone.

From the practical point of view, a simple method of evaluating compound layer structure would not only offer a useful quality control tool, but would also lead indirectly to a greater understanding of the performance of nitrocarburized components in service. This paper describes a simple method of analysis of compound layer structure using optical microscopy, which overcomes the problems discussed above.

2. Specimen preparation
Specimen edge retention and the prevention of edge bevelling are important from a practical standpoint. The problem may be overcome in a number of ways, the most common being:

(a) specimens may be coated with nickel deposited from an electroless deposition bath and subsequently sectioned, and mounted using one of the commercially available hard mounting compounds,

(b) a specimen having a flat surface may be mounted together with a flat block of material of similar hardness which is clamped adjacent to the surface to be observed,

(c) lower hardness ferrous materials (e.g. pure iron, mild steel) may be mounted without any additional edge protection in a suitable hard mounting compound.

3. Etchant composition
A suitable general purpose etchant for the compound layer and matrix microstructure is Nital to which a small addition of hydrochloric acid has been made. 5% Nital containing 0.1% concentrated hydrochloric acid (i.e. 1 ml concentrated hydrochloric acid added to 10 ml ethanol and 1 ml of this solution added to 100 ml 5% Nital) is recommended, particularly for plain low carbon steel materials. The etchant is used at room temperature. An exposure time of the order of 15 sec is suitable for plain low carbon steels.

4. X-ray diffractometry
Further information, to supplement the evaluation made by optical metallographic investigation, may be gained by X-ray diffractometry. The surface of the sample is first scanned in the as-nitrocarburized condition. A few micrometres of the surface layer are then carefully ground off and the sample is analysed again. This procedure is repeated until the compound layer is completely removed, thus producing a series of X-ray "tomographs" of the layer which may then be evaluated in conjunction with the metallographic data.

In the present work a Philips PW 1050 vertical diffractometer was used in conjunction with a Philips PW 1010/80 X-ray generator employing CuKα radiation ($\lambda = 0.154\,178$ nm). Generator voltage and current settings were 40 V and 20 mA respectively. Fluorescence was minimized by use of an exit beam monochromator.

5. Ferritic nitrocarburizing conditions
A series of samples of 0.2% carbon steel (EN3) were gas nitrocarburized under controlled laboratory conditions. The heat treatments were carried out using a gas-tight vertical tube furnace. The treatment time used was 5 h throughout and the samples were quenched from the treatment temperature. The nitrocarburizing atmospheres were mixed from bottles via a volume flow control system prior to entering the reaction tube. The linear flow of treatment gas through the furnace was maintained in the region of 30 cm min^{-1}. The atmosphere compositions and treatment temperatures employed are given in Table I.

TABLE I Nitrocarburizing temperatures and nominal atmosphere compositions

Sample	Nitrocarburizing temperature (°C)	Atmosphere composition (%)			
		NH_3	CO	N_2	O_2
A	570	25	20	55	<1
B	580	3	13	84	<1
C	580	3	31	65	<1

No analyses of the actual furnace atmosphere compositions were made during the preparation of the samples discussed in this paper. Control of the nitrocarburizing atmospheres was made via control of the composition of the inlet gas mixtures alone. In the absence of more detailed information on the gas composition in the furnace, the compositions listed in Table I must be regarded as nominal values only.

6. Results

Micrographs of prepared sections of Samples A, B and C (see Table I) are reproduced in Figs. 2, 3 and 4. It can be seen from these micrographs that detail of the compound layer structure has been revealed, in addition to the structure of the matrix, in all three examples (cf. Fig. 1). The structure of the layer on Sample A (Fig. 2) is apparently two-phase with one phase constituting the bulk of the layer, and a secondary phase occurring predominantly towards the compound layer/matrix interface rather than near the layer surface. Sample B (Fig. 3) has a layer which again is two-phase, but the secondary phase is dispersed more evenly throughout the layer. The layer on Sample C (Fig. 4) would appear to be composed essentially of one phase. In all three layers, a region of poros-

Figure 3 Sample B, etched with Nital plus hydrochloric acid. The compound layer is composed of two phases. The bulk of the layer is composed of ϵ-Fe_{2-3}(C,N). The darker etched phase is γ'-Fe_4N. A region of porosity is visible at the surface of the layer. The specimen was coated with nickel prior to mounting.

ity adjacent to the surface of the layer may be discerned.

Selected X-ray diffractometer traces from parts of Sample A are shown in Figs. 5 and 6, and from Samples B and C in Figs. 7 and 8 respectively. The interplanar lattice spacings, d, corresponding to the peaks on the diffractographs were determined from the Bragg relationship, $n\lambda = 2d\sin\Theta$. From the d spacings the components of the compound layers under investigation were determined by reference to the ASTM index [8]. These data demonstrate that two phases are present in the compound layer on Sample A, namely epsilon iron carbonitride and gamma prime iron nitride; the latter of which is found predominantly in the deeper regions of the layer. The alpha iron (α-Fe) reflection shown in Fig. 6 most probably arises from the
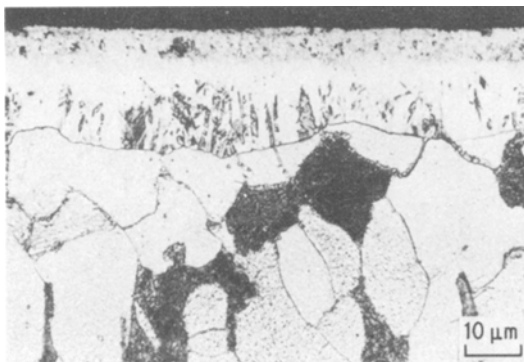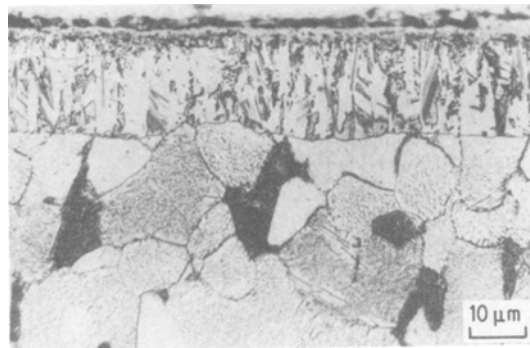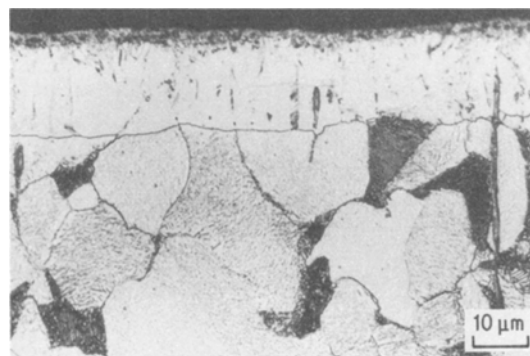

Figure 2 Sample A, etched with Nital plus hydrochloric acid. A region of porosity is visible at the surface of the compound layer, and a secondary phase in the deeper regions of the layer. The bulk of the compound layer is composed of ϵ-Fe_{2-3} (C,N). The darker etching secondary phase is γ'-Fe_4N.

Figure 4 Sample C, etched with Nital plus hydrochloric acid. The compound layer is essentially monophased and composed of ϵ-Fe_{2-3} (C,N). A region of porosity is visible at the surface of the layer. A number of inclusions may be seen extending from the matrix into the surface layer.
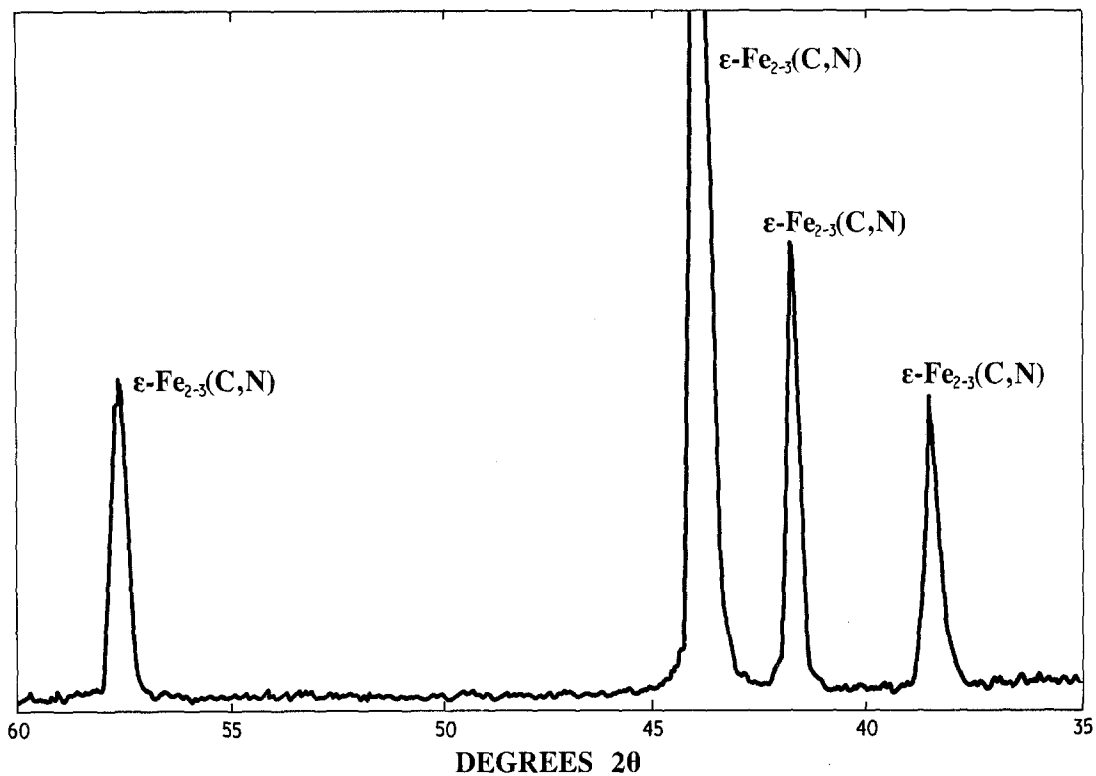
Figure 5 X-ray diffractometer trace from as-nitrocarburized surface of sample A. Cu*K*α radiation.

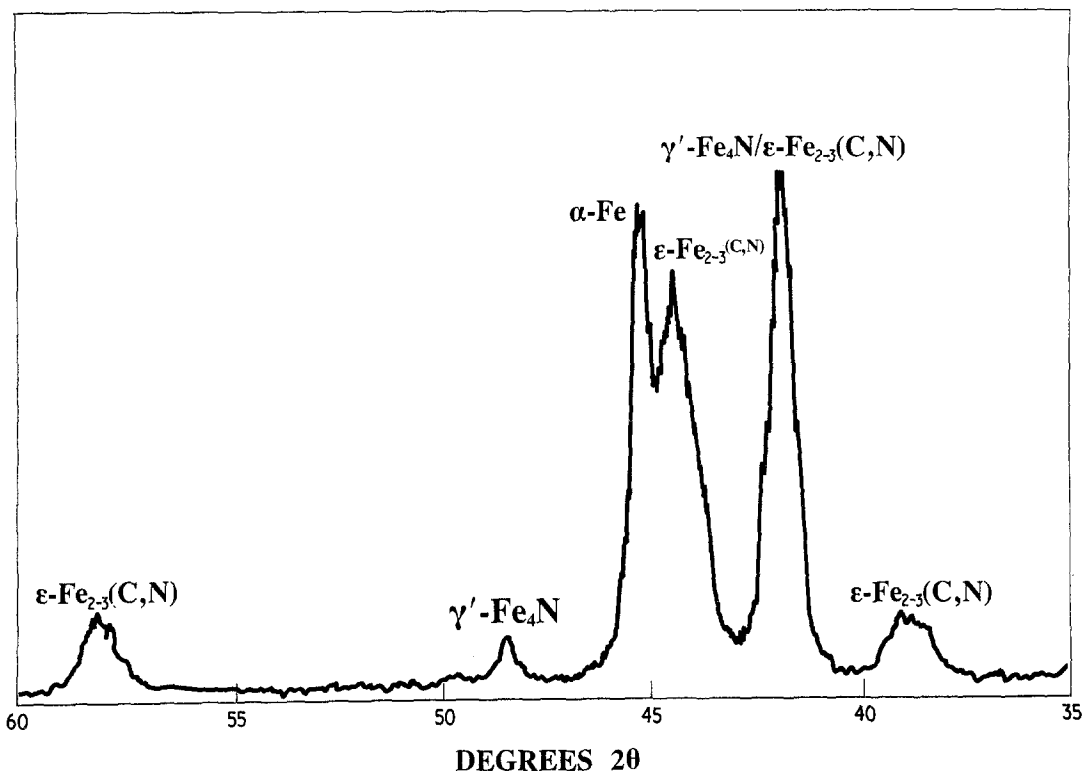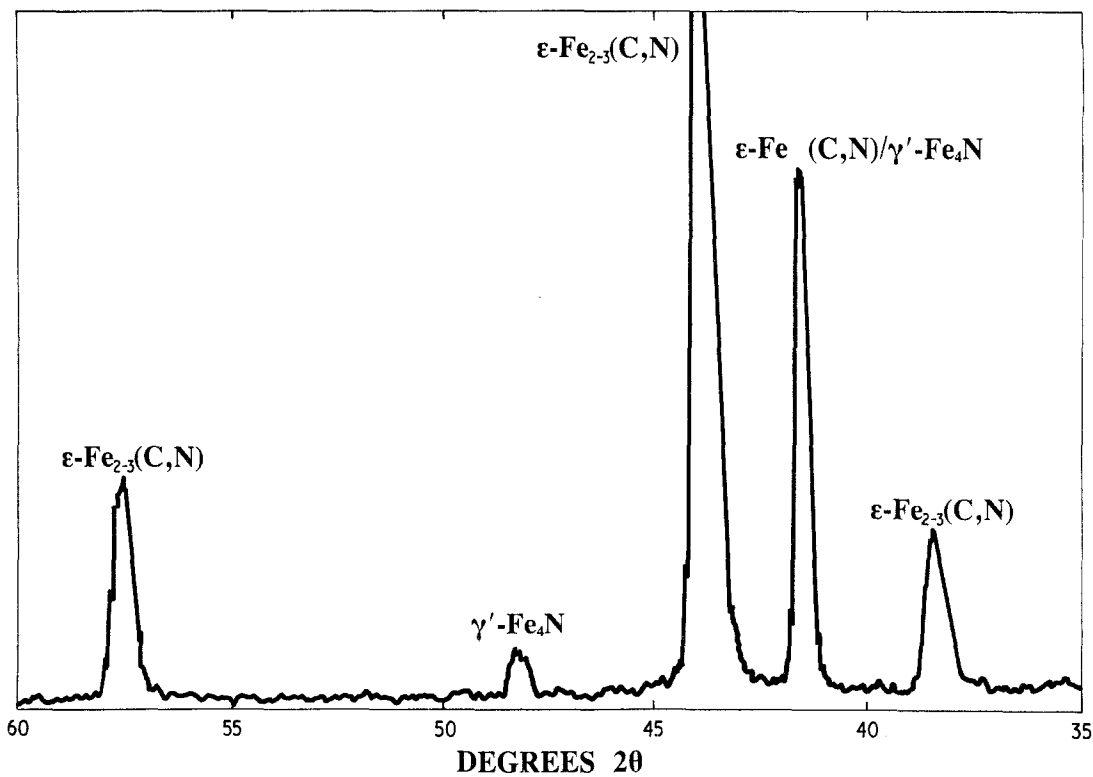*Figure 6* X-ray diffractometer trace from sample A. Approximately 15 μm of surface ground away. Cu*K*α radiation.

Figure 7 X-ray diffractometer trace from as-nitrocarburized surface of sample B. Cu$K\alpha$ radiation.
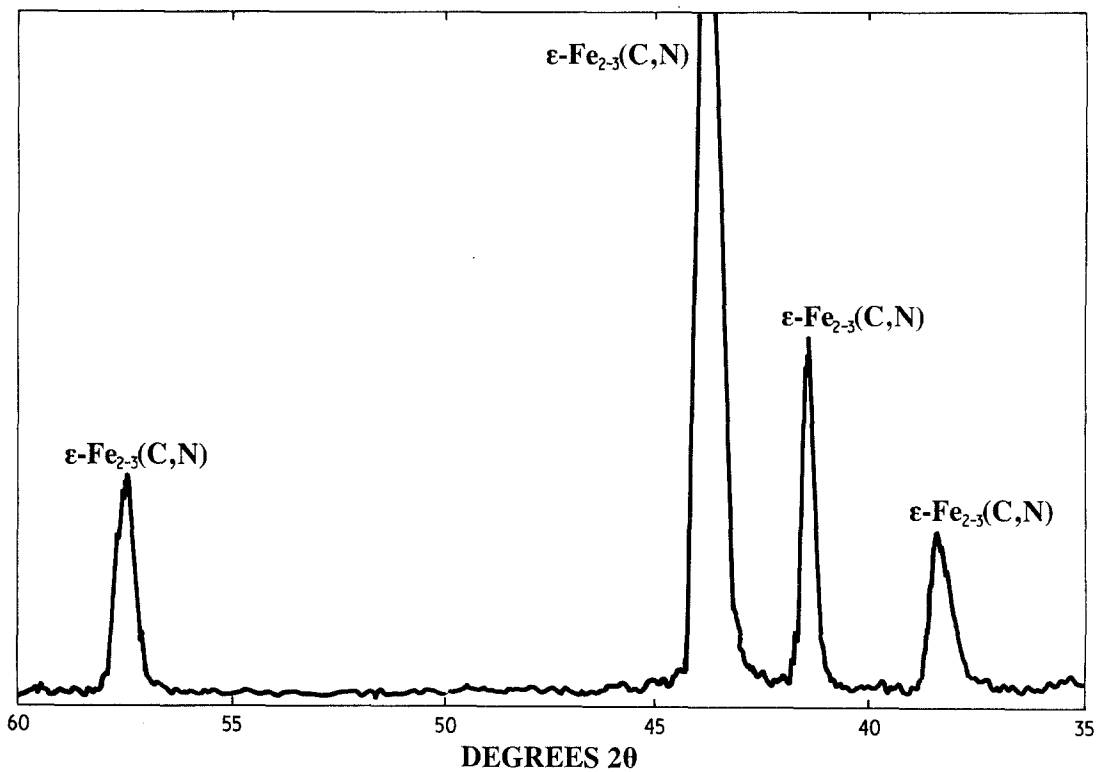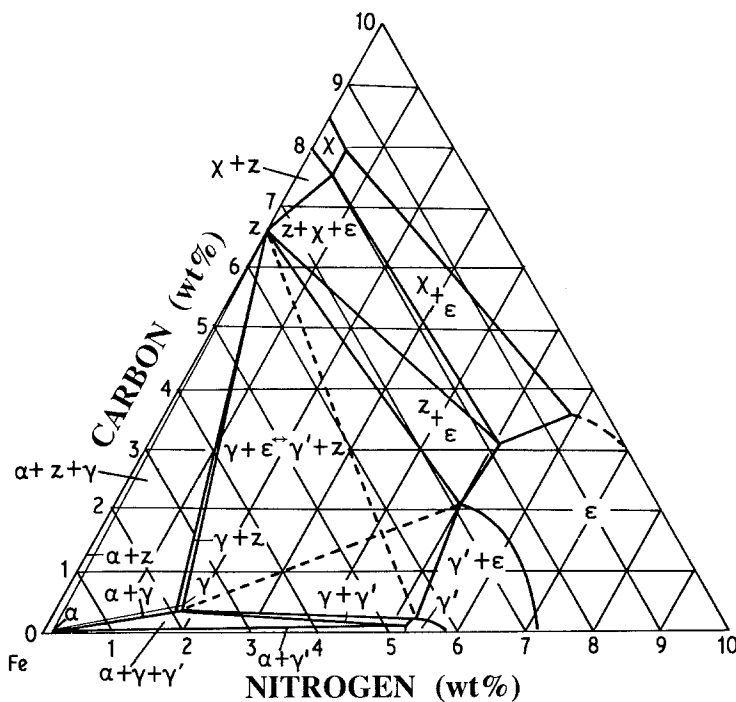

Figure 8 X-ray diffractometer trace from as-nitrocarburized surface of sample C. Cu$K\alpha$ radiation.

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Figure 9 Isothermal section of iron–carbon–nitrogen system at 575° C, according to Naumann and Langenscheid [9].

matrix rather than from within the layer itself. Sample B is predominantly composed of the epsilon iron carbonitride phase in which there is some gamma prime iron nitride phase, and sample C has a layer which is essentially monophased epsilon iron carbonitride in composition.

7. Discussion

The metallographic evaluation of and X-ray diffractometry data from Sample A demonstrate that the bulk of the compound layer is composed of the epsilon iron carbonitride phase, and that the secondary phase which occurs in the layer is gamma prime iron nitride. Similarly, data demonstrate that the layer on Sample B is one which is composed predominantly of epsilon iron carbonitride phase in which gamma prime iron carbonitride is dispersed (darker etching component of the layer in Fig. 3). Sample C has a monophased epsilon iron carbonitride surface layer.

Of particular note in the present study is the observation of the interface between the predominantly epsilon iron carbonitride phase compound layers produced here, and the matrix (which is ferrite with some pearlite). The observation of what appears to be a stable interface between the inward growing h c p epsilon carbonitride layer (inward growth is indicated by the inclusions visible in the layer in Fig. 4 for example) and the

b c c alpha iron matrix would not be expected from the iron–carbon–nitrogen ternary phase diagram [9]. The currently accepted version of the iron–carbon–nitrogen system, which is illustrated in Fig. 9, does not show a phase field containing both the alpha and epsilon phases. This particular point reinforces a recent view [6] that the iron–carbon–nitrogen system diagram has some significant shortcomings when applied in the context of the ferritic nitrocarburizing operation. However any further information regarding the nature of the compound layer/matrix interface or any relationship between the epsilon iron carbonitride phase and alpha iron cannot be advanced at this stage.

It is mentioned in the results section that some porosity is evident at the surface of the compound layers. Such porosity is a well-known result of the nitrocarburizing operation [7, 10, 11], and indeed in other thermochemical processes involving the diffusional addition of nitrogen to ferrous materials [12, 13]. Porosity in compound layers formed by ferritic nitrocarburizing has been suggested to be beneficial in some circumstances [1]. The porosity arises from a tendency for interstitial nitrogen atoms in the nitrogen-rich phase to combine to form nitrogen molecules, which then evolve to form pores [12]. This tendency is particularly marked at grain boundaries.

8. Conclusions

1. A simple method has been described which adequately resolves the structure of the compound layers on nitrocarburized plain low carbon steel.

2. It has been demonstrated that information regarding the structure of the compound layer may be readily obtained using the method.

3. Nital, modified by the addition of a small quantity of hydrochloric acid is recommended as an etchant for the compound layer.

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