OPERATING EXPERIENCE OF A SODIUM RIG FOLLOWING THE INGRESS OF OIL

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Summary

The experience of operating the Small Water Leak Rig at Dounreay in the two years following the ingress into the sodium of silicone oil from the pump is reported. The carbon penetration into the rig pipework has been monitored and has been found to agree with a diffusion model. The predictions based on this model has enabled an operating strategy to be determined to allow continued operation of the rig.

1. INTRODUCTION

The Small Water Leak Rig (SWLR) at DNE is a sodium loop for investigation of water into sodium leaks up to 50 g/s. It is manufactured from 321 type stainless steel and consists essentially of a Reaction Test Vessel (RTV) 20 cm diameter, 220 cm long, an expansion tank, a centrifugal sodium pump and a dump tank (Fig 1)). Total capacity is 5 tonnes of sodium. Sodium is circulated between the RTV and the expansion tank resulting in a velocity of 0.23 m/s in the RTV and 0.82 m/s in the 4" interconnecting pipework. The loop operates isothermally, the maximum operating temperature being 580°C.

The rig was commissioned in 1974 and had been operating at a high load factor.

2. INGRESS OF OIL

On 1 July 1977 14 litres of oil entered the Rig sodium during an experiment with a sodium temperature of 500°C due to a failure of the centrifugal pump shaft mechanical seal. The design arrangement allowed oil which may pass the mechanical seal to be spun by a guard (flinger) attached to the shaft and hence to drain via a gutter and pipe to a collecting tank. The gutter was of small capacity and did not hold the contents of the oil system before overflowing. The oil leakage was noted due to a rise in temperature of the circulating oil. A check was carried out to see if the oil had leaked from the upper seal onto the surrounding floor area, however, no oil was found and it was deduced that the oil had leaked past the lower mechanical seal into the rig. The pump was shutdown. Since the experimental programme required a further 12 hours for its completion it was decided to continue the experiment until the following day. The sodium temperature was then reduced to 350°C and the sodium was dumped to the dump tank at 06.00 on 3 July 1977. The test section was removed and examined in a glove box. There was no sign of oil contamination or carbonaceous deposits. A perspex cover was fitted to the reaction test vessel and a visual examination of the test vessel carried out. This showed no signs of oil contamination or carbanaceous deposits either above or below the sodium, the vessel looked generally clean but with a dark surface. The discharge pipe from the vessel was in a similar clean condition.

On stripping down the drain from the gutter to the catch pot the line was found to be blocked with sodium and therefore the oil leakage could not drain into the catch pot, overflowing the gutter and hence into the sodium. Subsequent strip down showed the gutter and part of the gap between the shaft and the housing to be full of sodium.

The pump had been running for about 65% of the time during the previous 3 years and had given little trouble.

3. SUBSEQUENT OPERATION

The test section which had just been removed (2¼ Cr steel) was examined for evidence of carburisation but none was found. However to estimate the level of carbon activity, it was decided that stainless steel foils should be inserted into the rig and the rig run for a two day period at 500°C. On removal of the foil samples it was found that there was considerable evidence of carburisation extending to a depth of 20 um of heavy carburisation, with a further 20 um of lighter carburisation and signs of carburisation throughout the foil thickness. In subsequent discussion it was felt that these foil results could be pessimistic and since a requirement existed to remove a section of 4" main loop pipework to incorporate stubs for proposed instrument modules, it was decided to subject this pipework to metallurgical examination. Results of this examination showed heavy carburisation to an extent of 18-20 um from the sodium surface followed by a further layer 20 um thick of decreasing density with a total of 150 um showing some signs of carburisation.

In the light of the results it was obvious that two main courses of action existed.

(1) Discontinue operation of the SWLR, remove the carburisation sources and devise a clean up method for the loop steel work.

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(2) Continue to run the SWLR with the present sodium charge accepting some degree of carburisation until such times as the loop could be shutdown.

It was concluded that the effect of the carburised layer would be similar to corrosion, the brittle layer not contributing to steel strength. On this basis and using a simple mass transfer model it was calculated that further operation of the loop at 500°C for 4 to 6 months with an availability of 65% would result in a carburised layer 0.3 mm in depth. In view of the pressing need to obtain further sodium water test data from the rig it was decided to run the rig as outlined above, for a period of 4 to 6 months, whilst pursuing efforts to obtain an alternative facility or to clean up the rig sodium.

Since some doubt existed about the carburisation rate it was decided to carry out a further test to obtain data on carburisation. The opportunity was taken at this time to carry out an experiment on the thermal sleeve test section. This test lasted for 140 hours at temperatures greater than 460°C. On this occasion the section of 4" pipe previously removed for examination and which had seen previous carburisation was used as a teller. Examination of this showed that the depth of significant carburisation had increased to around 54 um.

As these results were found to be in general agreement with a carbon transport model based on diffusion theory, it was decided to continue operation of the rig using the section of the original 4" pipe to provide an indication of the extent of carburisation which would then enable a prediction to be made of the number of days operation which would be allowed. The effect of carburisation of the rig would only be significant in the sodium pipework which had a thickness of 3.25 mm (4" NB) or 2.2 mm (1" and 2" NB). The RTV and expansion tank, being 25 mm and 12.5 mm thick respectively would take considerably longer to carburise to a significant proportion of their thickness. It was decided that providing the penetration of the rig pipework of carbon did not exceed 20% of thickness, operation could continue. This gave a large margin of safety from fracture mechanics considerations and was well within the corrosion tolerance allowed in the design of the rig. (80%).

The rig has continued to operate in the two years following this incident but since the temperatures have in general been lower than 500°C, the carburisation rate as expected has been considerably reduced.

4.   THE MONITORING PROGRAM

The section of the original main rig pipework was removed under an inert atmosphere and the residual sodium removed using methanol. Part of this pipe section (monitor sample) was then bolted onto an extension of each experimental test block such that during rig operation, the pipe section lay well beneath the experimental zone in the lower regions of the reaction test vessel.

Following each test, the experimental test block is bagged out of the reaction test vessel with the monitor sample and is placed in a glove box. The monitor sample was then unbolted from the extension piece, removed from the glove box and the residual sodium removed by immersion in methanol and air dried. A small coupon is removed, some 20mm by 10mm in size, using a hacksaw under grease free conditions, for metallurgical examination. The monitor sample is then resecured onto the new experimental test block using grease free tools and gloved hands to avoid any possibility of anomalous carburisation due to grease deposits.

The coupon is divided into three sections using a metallurgical cutting saw to avoid localised overheating and hence modification of the carbon penetration. One section is mounted and polished and the microhardness profile measured from both edges inwards until the background level is attained. This section is then etched using 5% sulphuric acid at 3 volts for 10 to 15 seconds in order to display the typical "white etch" layer, see Figure 2.   A second section is initially heat treated at 750°C under vacuum for 30 minutes to precipitate the carbon.   The section is then mounted, polished and electrolytically etched using the weaker ammonium persulphate electrolyte at 3 volts for 10 seconds in order to display the precipitated carbides, see Figure 3. The third section is sent to AERE Harwell for carbon profile analysis using the nuclear microprobe technique (1).

The resultant profiles and microphotographs are then examined to assess the depth of carbon penetration. That for the "as received" section is based on a subjective assessment of the width of the "white etch" layer. Similarly, the "heat treated" section is based upon a subjective assessment of the depth of penetration as shown by the extremities of the carbide precipitates which decorate the grain boundaries. The depth of penetration for the microhardness profile and also the carbon concentration profile is arbitrarily defined by the depth at which the measured profile reaches 105% of the mean measured backgroun level. The choice of this 5% difference is related to the sensitivity of the two methods, though this is not an accurate reflection of their sensitivities.

Early experience showed that the two subjective assessment techniques did not give reproducible results (as might be expected) and as a consequence Table 2 presents the penetrations as determined by the carbon concentration profile and microhardness methods only, for a range of coupons removed from the pipe section. Since the pipe section was reimmersed

in sodium within the reaction test vessel, both the interior and exterior surfaces are exposed to the carburising sodium and hence suffer carbon penetration. In addition, as the pipe section was removed some time after the ingress of oil into the circuit, the interior surface has an increased exposure time over the exterior surface.

A least mean squares analysis of the penetration data gives the equation

$$P_c = 54 + 0.62 \ P_m \tag{A}$$

between the penetration depth measured by carbon profile, P_c and that measured by microhardness, P_m. Equation A has a correlation coefficient of 0.83, indicative of a moderate fit.

This relationship has been used to give confidence in the relatively simple method of predicting the depth of carbon penetration by microhardness measurements. However carbon profile analysis are carried out from time to time to confirm the microhardness predictions.

As microhardness measurements can be made quickly on site, thus provide a rapid means of verifying the predictions of carburisation after each test. These can then be backed up by carbon profile measurements.

5. PREDICTIONS OF FURTHER PENETRATION

In addition to knowing what has happened to the rig, there is an obvious need to predict the carbon penetration which would occur during a proposed test program, to ensure that the safety criterion is maintained.

The calculation of carbon diffusion behaviour is based upon the diffusion system where one surface of a two parallel surface plane body is kept at a constant concentration C_s and the other surface is impermeable to carbon transport. The system may be described by the following equation (2).

$$C = C_s + \frac{2}{L} \sum_{n=0}^{\infty} exp \left(-D(2n+1)^2 . \pi^2 . t/4 . L^2 \right)$$

$$\times \ cos \left((2n+1) \pi . x/2L \right)$$

$$\times \left\{ \frac{2L(-1)^{n+1}}{(2n+1)\pi} . C_s + \int_0^L f(x') \ cos \left((2n+1).\pi.x'/2L . dx \right) \right\} \quad \dots (B)$$

where

$f(x')$ is the function of concentration with depth x'
l the distance between the two surfaces such that at $x = 1$,
$C = C_s$. The other parameters have their usual meaning.

The initial concentration profile may be taken as a constant C_0 and hence the above equation may be re-evaluated to give

$$\frac{C}{C_s} = 1 + \frac{4}{\pi} \sum_{n=0}^{\infty} exp \left(-D(2n+1)^2 . \pi . \frac{t}{4} . L^2 \right)$$

$$\times \ cos \left((2n+1) \pi . \frac{x}{2} . L \right)$$

$$\times (-1)^n \ (C_0/C_s - 1) / (2n+1) \quad \dots\dots\dots\dots (C)$$

Equation C approximates the two diffusion systems of carbon in steel through grains and grain boundaries, to a single system. This approximation has been made in other studies of the system (3), where it has been found that the quantity of carbon associated with the grain boundaries is very small compared to that in the grains. Thus the techniques of measurement are following the dominant grain diffusion system and hence a single system description is a reasonable approximation.

The application of equation C is made more difficult by the fact that the rig operates over a range of temperatures and not at a single temperature. The diffusion coefficient may be expressed by the Arrhenius equation

$$D_T = D_0 \ exp \ (-Q/RT) \tag{D}$$

Hence the ratio of the diffusion coefficient at any temperature T to that at some set temperature T' is given by

$$\frac{D_T}{D_{T'}} = \frac{D_0 \ exp \ (-Q/RT)}{D_0 \ exp \ (-Q/RT')} \quad \dots \dots \dots \dots (E)$$

which may be simplified to

$$D_T = D_{T'} \ exp \left(\frac{Q}{R} \left(\frac{T-T'}{TT'} \right) \right) \quad \dots \dots \dots \dots (F)$$

Since it was required to predict a time scale for carbon penetration, a standard temperature of 773°K was chosen, representing the nominal working temperature of the rig. A value for Q, of 40.9 kcal/gmole K was used, based on an average value obtained by Agarwala et al, (3) to produce the resultant equation of

$$\mathcal{D}_T = \mathcal{D}_{T'} \, exp \, (26.5 \, (T-773)/T) \quad \dotsc\dotsc\dotsc\dotsc\dotsc\dotsc (G)$$

Since equation C contains the product term Dt within the exponential, it is possible to transform the variation in the diffusion coefficient to an apparent variation in time. Thus equation G may be re-expressed as

$$t_{773} = t \, exp \, (26.5 \, (T-773)/T) \quad \dotsc\dotsc\dotsc\dotsc\dotsc (H)$$

where t_{773} is the equivalent time to produce the same carbon penetration at 773K as occurs in time t at temperature T, being called the "500°C equivalent time".

Thus the rig operating history is given in Table 1. Using the expression (H), this was summed into 500°C equivalent days and Table 2 indicates the relevant times. Hence using equation C, the value of the 500°C equivalent diffusion coefficient was calculated by an iterative technique and the results shown in Table 2 obtained. The mean value of $5 \pm 3 \times 10^{-16}$ m^2 s^{-1} compares favourably with that quoted by Agarwala et al of 5×10^{-16} m^2 s^{-1} for AISI Type 316 stainless steel. This computed value of the diffusion coefficient is thus used to make predictions on depths of penetration.

6. ANALYSIS OF RESULTS

The carbon and microhardness profiles as found on a typical sample are shown in Figures 4 and 5. In addition, the diffusion predicted profiles are also shown based upon the mean diffusion coefficient of $5.0 \pm 2.5 \times 10^{-16}$ m^2 s^{-1}. It is evident that the simple diffusion system used as a means of predicting carbon penetration, will not also predict carbon profiles or total carbon up take with any accuracy. The microhardness profile shows little change over the first ten to twenty microns, indicative of a saturation of the hardening effect caused by the presence of carbon. It is also evident that the microhardness profile is not a good indication of the carbon profile.

The anomalous trough observed in the interior surface carbon profile, in every sample, has been correlated with a high nitrogen concentration in the surface region (Figure 6). This correlation is also demonstrated in the near surface concentrations (at a depth of 3 um) of carbon and nitrogen, measured on the samples for both the interior and exterior surfaces (Table 3). Electron probe microanalysis of the interior surface samples have not shown any major variation in the composition of the steel near the surface. It is thus considered that the trough is due to the preferential formulation of nitrides, thus effectively lowering the concentration of available carbide forming elements. Hence although the chemical activity of the carbon remains near

constant over this region, the carbon concentration varies in this dramatic manner. It is interesting to note that the interior surface profile beyond the trough is similar to the exterior surface profile in the same region; this feature being common to most of the samples.

Tables 3 and 4 also demonstrate that the carburising "force" varies from run to run. The variation of the near surface carbon concentration shows that the carburising potential of the sodium does vary from run to run, though curiously the variation does not always correspond with both surfaces. The averaged carbon uptake indicates that the steel was effectively carburising up to sample C or D but subsequently has decarburised. The tentative conclusion from these observations is that batch cold trapping has been effective in reducing the carbon level. It should be noted however that the rig sodium contains considerable quantities of oxygen and hydrogen, resulting from repeated water injections and that these injections may play a considerable role in removing the carbon.

This conclusion would also explain why the predicted carbon profiles are such a poor fit with the measured profiles. However despite loss of carbon via the surface, there still remains sufficient carbon to provide an effective constant inward driving force. Thus the penetration criterion can be described by the simple diffusion model. It is noted that if the carbon loss to the sodium is maintained, then eventually the penetration will slow down and stop. Estimates of this can be made using equation B, with an appropriate function describing the carbon profile at the time of change from carburising to decarburising conditions. The near surface nitrogen concentration has also shown a diminution over the first 5 samples (see Table 3) but has remained relatively constant thereafter. However this effect is confined to the near surface; at beyond 10 um there appears to be no change in the nitrogen profile. It is postulated that this drop may be due to the removal of the nitrogen by cyanide formation; the effect being limited to the near surface due to the much lower diffusion constant for nitrogen in steels. This effect is surprising and contrary to that expected of enhanced transport of nitrogen from the cover gas into the steel. However, much longer times are required before any conclusive evidence of nitrogen transport will be gained.

7. PRESENT POSITION

The latest measurements from the monitor sample, taken after a total of 64 500°C equivalent days operation show that the rate of penetration has decreased significantly (Sample H). This is to be expected from the flattening of the carbon profile and consequent difficulty in the determination of the point at which the microhardness increases significantly above the

background level. However it is likely that the rate of penetration has also decreased as a result of the continuation of the trend shown in table A where the total carbon uptake in the steel is decreasing. This trend has probably been accelerated by the type of tests carried out recently where significant quantities of water were injected. It is expected that microprobe analysis will confirm the pattern of carbon uptake.

The last rig shutdown has also given the opportunity of checking the effectiveness of the monitoring technique. A section of pipe was removed to allow replacement of one of the sodium valves. This pipe section had been subject to the carburising conduction of the rig during its operation since the oil ingress incident. The depth of penetration of its inner surface by carbon as indicated by microhardness, is similar to that of the monitor samples thus indicating that the monitoring technique is representative.

The rig is scheduled for a major overhaul during the next year. Immediately prior to this, it is planned to replace the sodium charge. The main purpose of this is to remove oxide impurities resulting from water injections but it is likely to remove the source of carbon.

In subsequent operation, the carbon profile in the rig pipework will tend to flatten even further, as the steel is decarburised by the sodium and further penetration of carbon will be undetectable.

It is now evident that continued operation of the rig at temperatures below 500°C will be possible for several hundred days before the arbitrary limit of 20% penetration is reached.

8. CONCLUSIONS

8.1 It has been demonstrated that providing a monitoring programme can be devised, continued operation of a sodium loop following ingress of a carbonaceous substance is possible.

8.2 Microhardness can be used to provide a rapid check on the carburisation depth.

8.3 The ratio of carbon penetration during the early stages of carburisation can be predicted using a simple diffusion model.

8.4 Microhardness measurements, and the diffusion model cannot be used to give an accurate indication of the carbon profile.

REFERENCES

1. PIERCE T B et al. Nuclear Instrum. Methods 118(1) 115-24. 1974.

2. CARSLAW and JAEGER. "Conduction of heat in solids". Ch 34. OUP.

3. AGARWALA et al. J Nuclear Materials 36 1970 pp41-47.

TABLE 1

SWLR TESTS SINCE OIL INFLUX
DURING JULY 1977

2 days @ 470°C
2 days @ 500°C
8 days @ 500°C
6 days @ 450°C
2 days @ 470°C
28 days @ 450°C
25 days @ 430°C
3 days @ 430°C
16 days @ 500°C
1 day @ 470°C
29 days @ 470°C
48 days @ 470°C
2 days @ 470°C

Table 2

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by   A C Bell, R D Mehew and C M Robertson

Corrections to Table II

Sample	Penetration μM		Equiv. Time (500%) Days	Diff.Coefft. $\times 10^{16}$ M^2S^1	
	c^1	M^2		C	M
A/I[3]					
B/I					
B/E[4]					
C/I					
C/E					
D/I					
D/E					
E/I			33.0	4.2	3.9
E/E			30.8	3.5	4.1
F/I			33.1	4.1	3.7
F/E			30.9	3.4	3.8
G/I			37.0	5.4	5.7
G/E			34.8	3.1	6.2
H/I			63.0	–	4.1
H/E			60.8	–	4.2

(AS GIVEN PREVIOUSLY — handwritten diagonal note across empty cells)

Table 3

Near Surface Concentrations
of Carbon and Nitrogen (3 m)

Sample	Carbon Level Wt %		Nitrogen Level Wt %	
	Interior	Exterior	Interior	Exterior
A	0.74	0.05	1.10	–
B	0.55	1.09	1.00	0.016
C	1.48	2.03	0.83	0.009
D	1.62	2.27	0.86	0.061
E	1.75	1.74	0.68	0.003
F	1.33	1.74	0.70	0.005
G	1.22	2.16	0.69	0.002

Table 4

Averaged Carbon Uptake
Over Penetration Depth

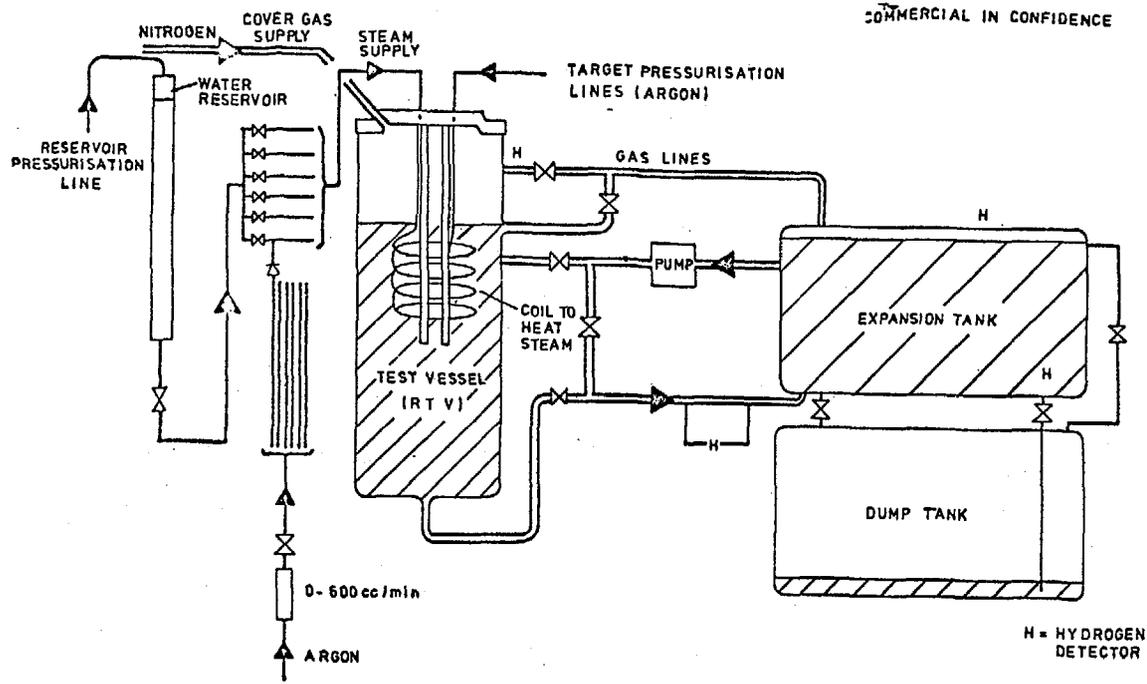| Sample	Averaged Carbon Uptake Wt %	
	Interior	Exterior
A	0.55	–
B	0.52	0.52
C	0.91	1.18
D	0.98	1.01
E	0.87	0.87
F	0.83	0.90
G	0.68	0.73

FIG 1 THE SMALL WATER LEAK RIG
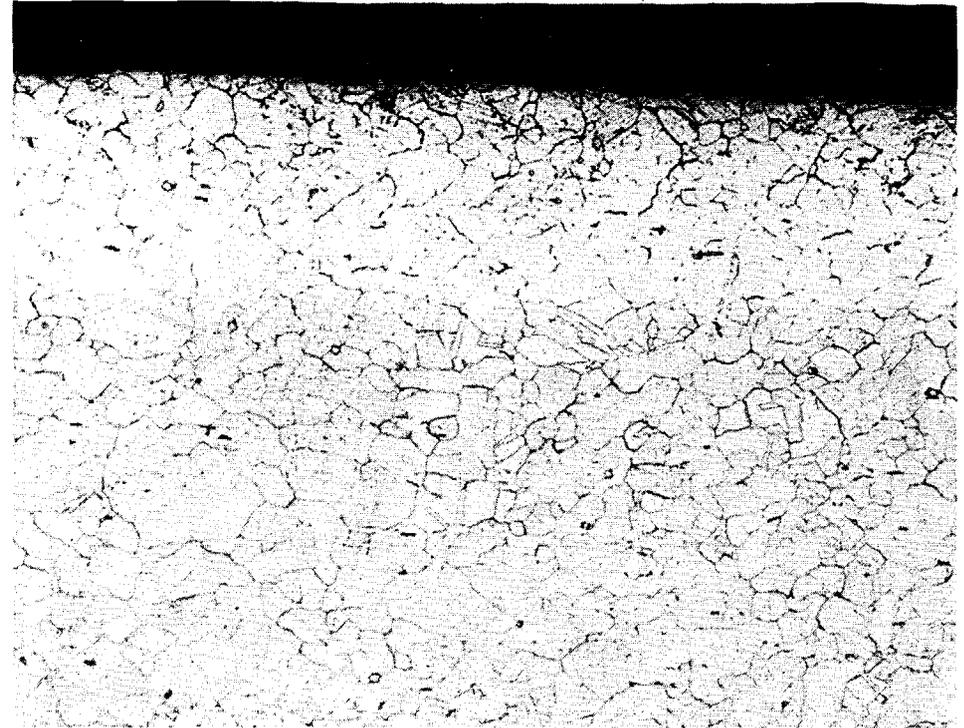(SCALE OF R T V MAGNIFIED)

Fig 2
Carburised sample after 5% sulphuric acid electrolytic
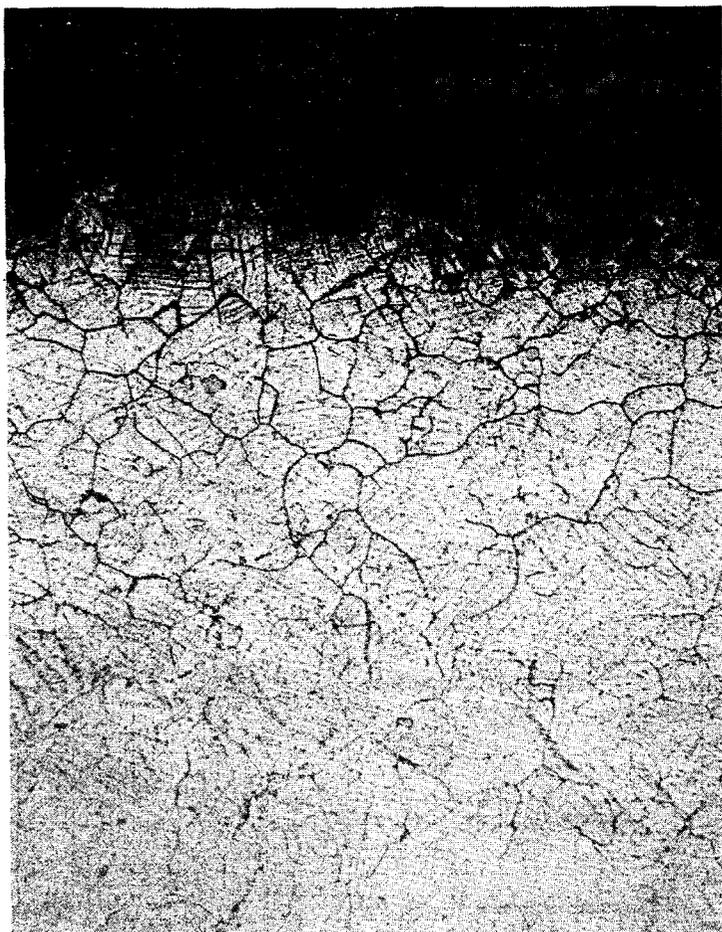etch showing 'white etch' layer

Fig 3

Carburised sample after 750°C heat treatment
and ammonium persulphate electrolytic etch
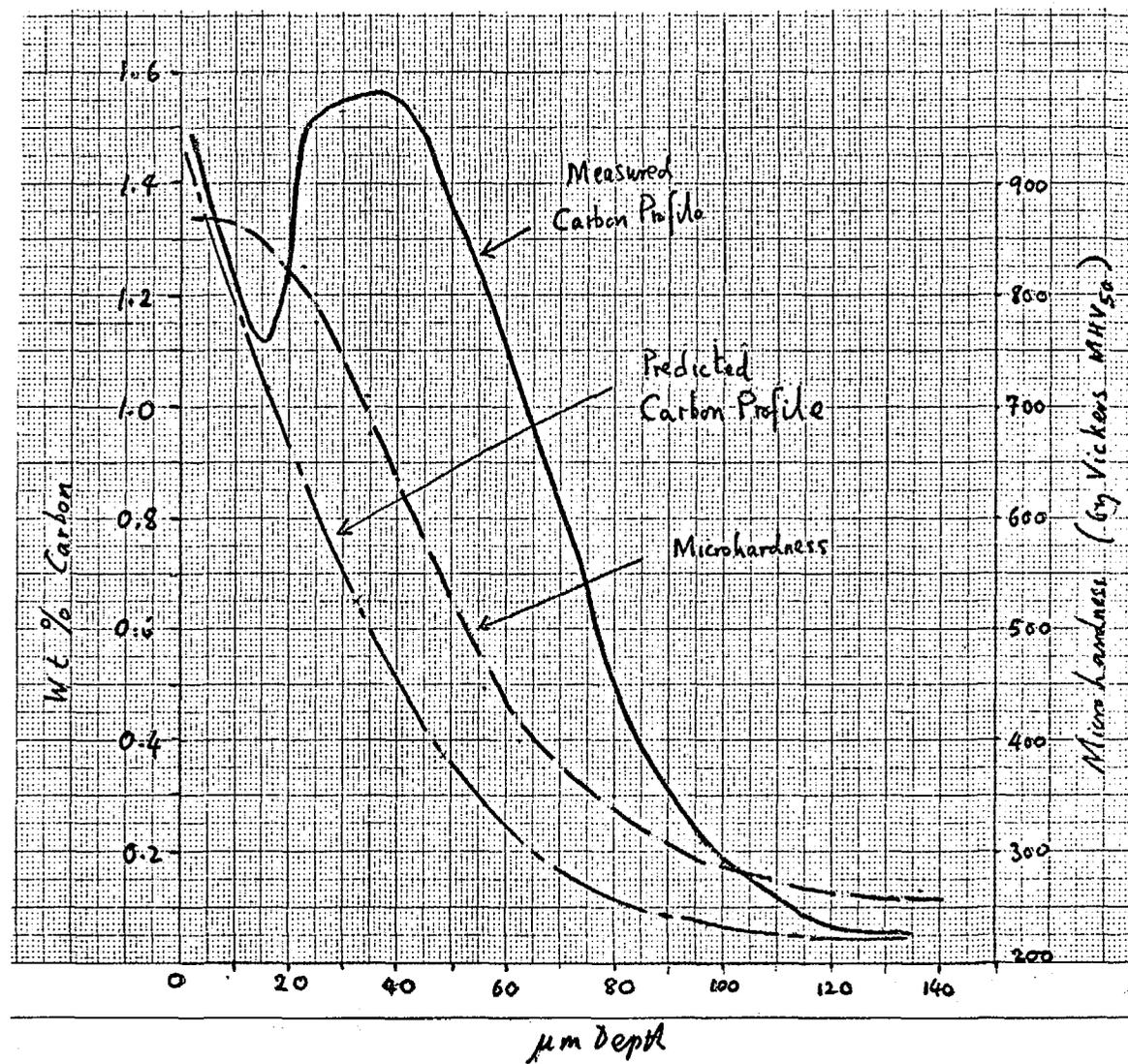showing precipitated carbides

Fig 4

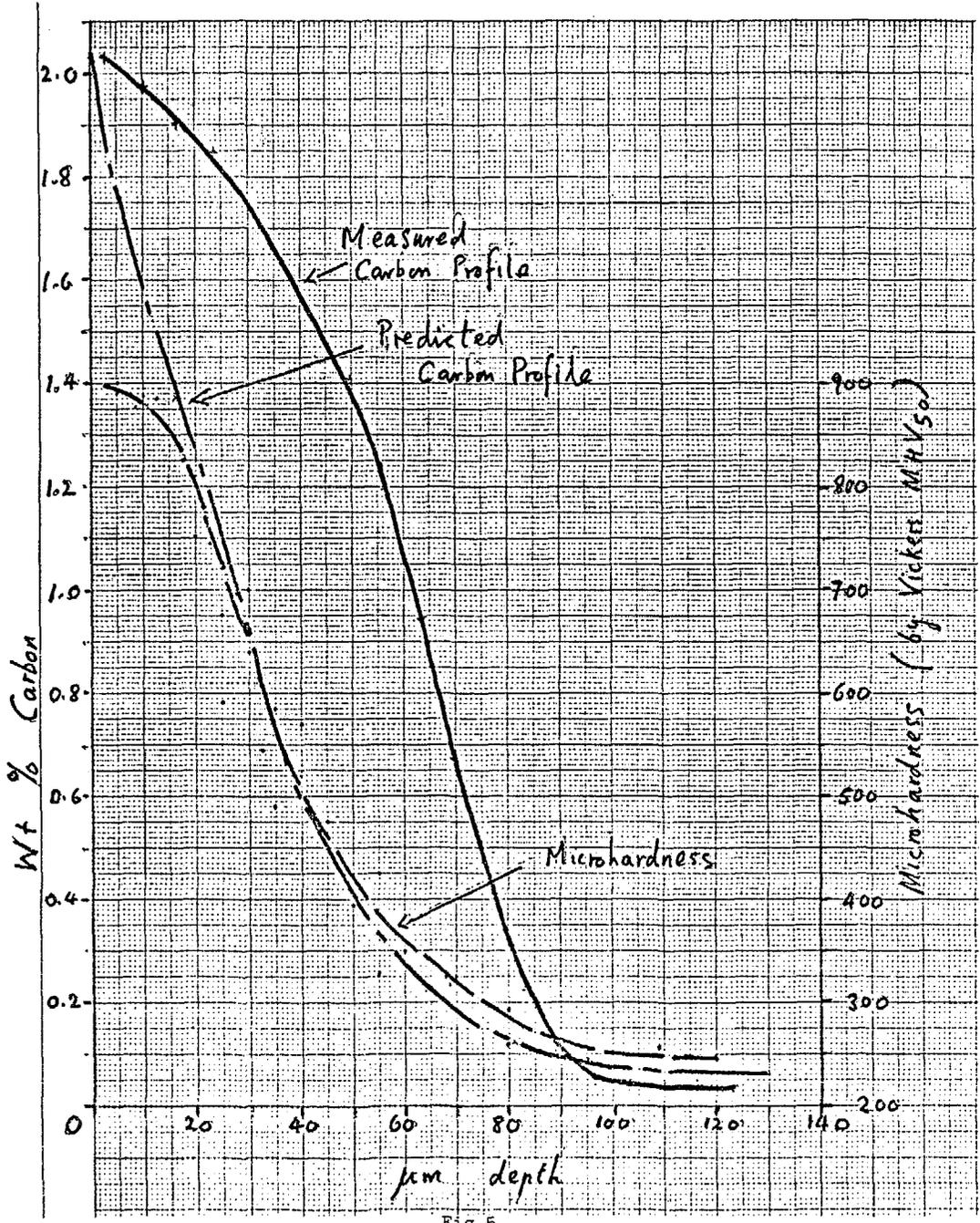Carbon and Microhardness Profile of Interior Surface Sample C/I

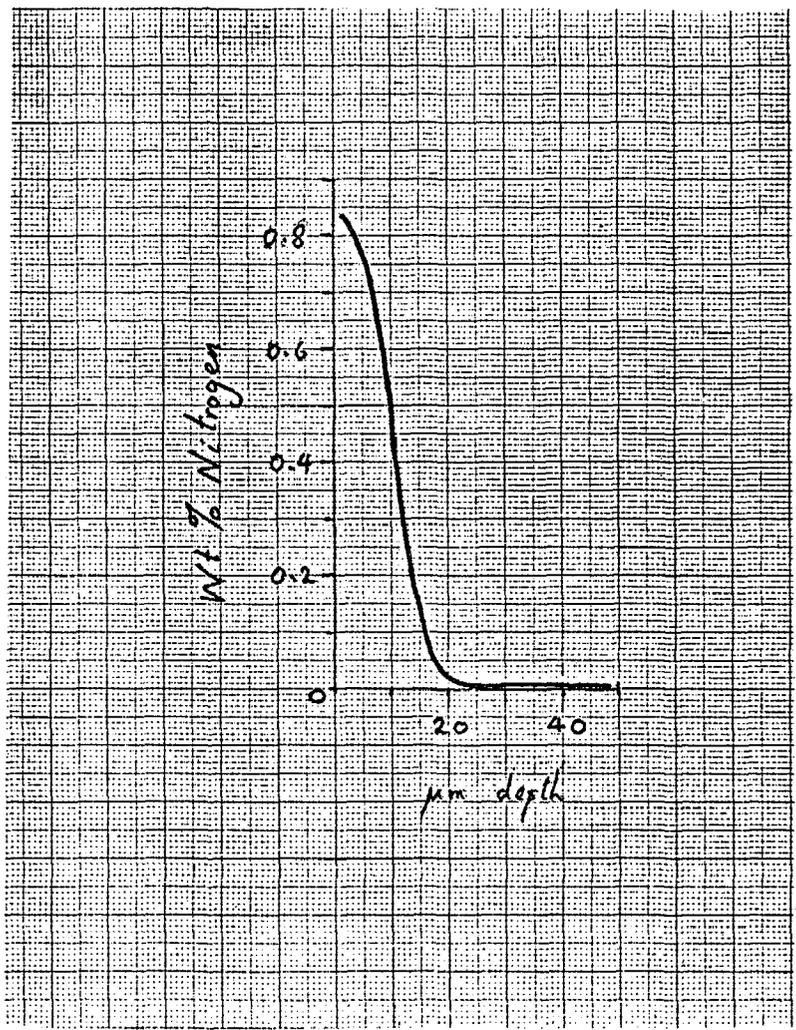Fig 5

Carbon and Microhardness Profile of Exterior Surface Sample C/E

Fig 6

Nitrogen Profile of Interior Surface Sample C/I