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Influence of Carburisation on the Room Temperature Tensile Properties of High Temperature Alloys
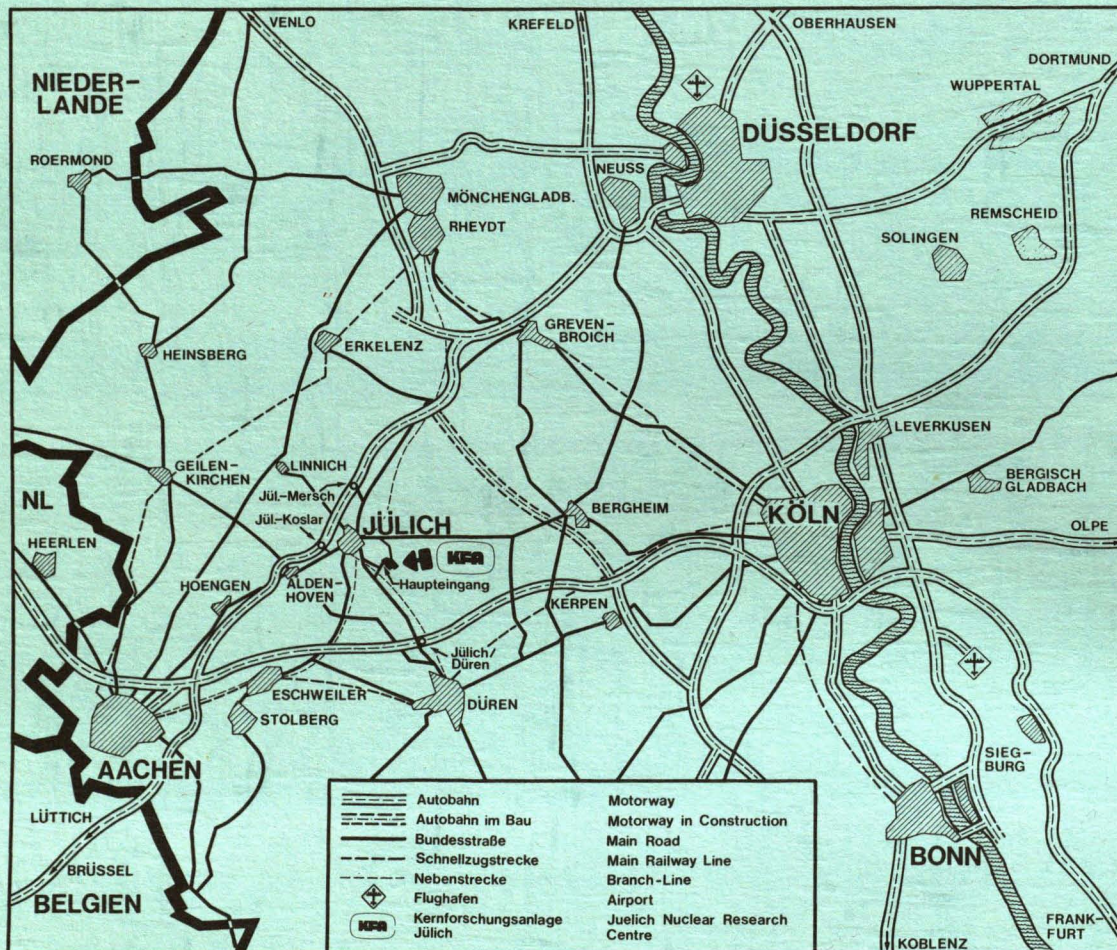
by

P. J. Ennis, D. F. Lupton, H. Nickel a. H. Schuster

	Autobahn	Motorway
	Autobahn im Bau	Motorway in Construction
	Bundesstraße	Main Road
	Schnellzugstrecke	Main Railway Line
	Nebenstrecke	Branch-Line
	Flughafen	Airport
KFA	Kernforschungsanlage Jülich	Juelich Nuclear Research Centre

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INFLUENCE OF CARBURISATION ON THE ROOM TEMPERATURE

TENSILE PROPERTIES OF HIGH TEMPERATURE ALLOYS

by

P. J. Ennis, D. F. Lupton, H. Nickel and H. Schuster

Abstract

A series of doctoral and diploma investigations which have been carried out at the Institute of Reactor Materials of the KFA are reported.

The influence of both thermal exposure and carburisation at 800 ^{O}C and above on the room temperature tensile properties of INCOLOY 800 H, INCONEL 617, HASTELLOY X and NIMONIC 86 has been studied and the results have been compared with literature data.

It is shown that the room temperature ductility of INCOLOY 800 H is much less sensitive to carburisation than that of the nickel-base alloys. This is attributed to the greater volume fraction of carbide formed in the nickel-base alloys for a particular bulk carbon content. In the nickel-base alloys carbide volume fractions are higher than in iron-base alloys due to the lower solubility of carbon and to the formation of M_6C carbides.

The ductility of reformer and intermediate heat exchanger (IHX) tubes after long service times in a process heat high temperature reactor has been estimated using carburisation rates found in corrosion experiments. The data indicate that a reformer tube of INCOLOY 800 H should retain a room temperature ductility equivalent to 5 % tensile elongation - a normal minimum requirement in conventional engineering design - over the anticipated service life of 140 000 h. For the IHX tubes, the impurity concentrations in the primary coolant must be carefully controlled in order to avoid embrittlement by carburisation. Alternatively, a design concept to allow the use of low ductility tubes will be required.

Suggestions are given for future work, in particular for alloy development to produce alloys which are less severely embrittled by carburisation.

Contents

1. INTRODUCTION

Carburisation is one of the most commonly met processes of degradation for alloys used in high temperature applications. It is found, for example, in the petrochemical industry, in heat-treatment equipment and in both liquid metal and gas cooled nuclear reactors. The main problem arising from the carburisation of high temperature alloys is a loss of toughness at temperatures below about 600 °C.

Until recently, most studies of carburisation had been largely empirical and aimed principally at the development of new alloy compositions with improved carburisation resistance. In such studies, a series of alloys would be exposed to a carburising environment and the carbon uptake of the alloys then compared. Although studies of this type have yielded major improvements in carburisation resistant materials since the 1930s, the very large step from this test procedure to final industrial application constitutes a substantial "activation barrier" to the introduction of new materials in established applications or, even more significantly, to the introduction of established materials in new applications such as nuclear reactors.

In the last 10 years, however, considerable effort has been devoted to developing a better understanding of the process of carburisation (gas/metal reactions, carbon activities in alloys, carbide types and their stabilities, diffusion) and of the influence of carburisation on mechanical properties. Most of this effort has been concentrated on austenitic stainless steels, which are widely used in steam generators and other components of nuclear reactors. A good example of an investigation of this type is the work of Thorley and Tyzak[1] which dealt with the thermodynamics of carbide precipitation during the carburisation of austenitic steels, the kinetics of carburisation in sodium and the influence of carbon content on the tensile properties of AISI 316 L stainless steel (Fe - 17 % Cr - 13 % Ni - 2.5 % Mo) at room temperature, 500, 600 and 650 °C.

For even more demanding high temperature applications, for example, in the heat exchanging components (He/He heat exchanger or helium-heated reformer tubes) of nuclear process heat systems, alloys are required which have higher strengths and/or better oxidation resistance than the austenitic

steels. These alloys normally contain higher levels of nickel and of carbide-forming elements such as chromium and molybdenum. INCOLOY 800 H (Fe - 20 % Cr 32 % Ni. - 0.3 % Ti - 0.3 % Al) is by far the most widely used of these higher strength alloys and has been the subject of investigations concerning the kinetics of carburisation and carbide precipitation[2, 3], the interaction between carbon diffusion and carbide precipitation[4], and the influence of carburisation on the mechanical[3, 5] and physical[3] properties of the alloy. Relatively little work has been done on the carburisation of nickel-base alloys, although Schnaas and Grabke[2, 3] studied the carburisation kinetics of NiCrSi 60 16 (Ni - 16 % Cr - 18 % Fe - 3 % Si), and INCONEL 617 (Ni - 22 % Cr - 12 % Co - 9 % Mo - 1 % Al). The work described in the present report was aimed at providing a better quantitative understanding of the influence of various carburisation parameters (carbon uptake, carburisation depth, exposure time) on the room temperature tensile properties of INCOLOY 800 H and the nickel-base alloys INCONEL 617, HASTELLOY X and NIMONIC 86. These alloys are important candidate materials for the fabrication of components from sheet or tube for advanced high temperature reactor (HTR) systems.

The data presented in this report formed the basis of an earlier, shorter publication[6].

2. TEST PROGRAMMES AND RESULTS

The experimental work described in this report was carried out as a series of student projects. The various programmes are summarised in Table 1, and details of test materials are given in Table 2.

2.1 Programme A

- Thermal stability of alloys at 800 and 850 $^{\circ}$C

In this programme[7] the thermal stability of INCOLOY 800 H, INCONEL 617, and NIMONIC 86 at 800 and 850 $^{\circ}$C was investigated by means of room temperature hardness and tensile tests. Details of the heats examined are given in Table 2. The aim was to produce reference data on the effect of thermal exposure, for comparison with the results obtained after carburisation treatments.

Hardness measurements were carried out on specimens which were exposed for up to 3000 h and metallographically polished. The results are shown in Figure 1.

Tensile specimens according to DIN 50 125 were machined from bars annealed for up to 3000 h. The specimens of INCONEL 617 had a gauge length of 40 mm with a diameter of 8 mm, while the remaining specimens had a gauge length of 50 mm with a diameter of 10 mm.

2.2 Programme B

- Tensile properties after various carburising treatments

The aim of this programme[8, 9] was to study the influence of different carburising media and surface finishes on the carburisation response and room temperature ductility of INCOLOY 800 H (heat ABD), INCONEL 617 (ABC) and NIMONIC 86 (AAH).

The tensile specimens (gauge length 18.1 mm, diameter 4.53 mm) were exposed for 1000 h at 950 ^{O}C in impure helium of composition given in Table 3 and in solid carburising compound (60 % charcoal + 40 % $BaCO_3$) under an argon stream. Surface finishes examined were:

-    machined,
-    pre-oxidised for 50 h in air at 950 ^{O}C, and
-    nickel-plated (thickness approximately 30 μm).

The specimens were subsequently tested at room temperature. For comparative purposes, the following specimens were also tested:

-    untreated,
-    nickel-plated but not heat treated,
-    nickel-plated and heat treated 1000 h at 950 ^{O}C in air,
-    machined from heat treated bar (1000 h/950 ^{O}C).

The small specimen size was used because large numbers of specimens were available to this geometry. However, the gauge length is somewhat shorter than that specified by DIN 50 125. Additionally, the tensile test machine used did not permit the 0.2 % proof stress to be determined to DIN 10 145 on these small specimens, although all other parameters could be established according to this standard.

The broken, carburised tensile specimens were sectioned, examined metallographically (see reference 8), and subjected to microhardness tests in a region remote from the fracture face. Carbon analyses were also carried out on the broken specimens: two layers each 0.5 mm thick were removed by machining and the carbon contents of these and the remaining centre portion were determined by combustion analysis (LECO-IR 12; Inco Europe Limited, Birmingham, England).

Carbon concentration and hardness profiles determined on the carburised specimens are shown in Figure 2.

2.3 Programme C

- Room temperature ductility of alloys exposed under stress in impure helium

The programme was undertaken to establish whether the creep behaviour is affected by maintaining the stress on creep specimens in multi-specimen rigs during the cooling down required to enable removal of specimens for strain measurement[10]. Normal practice is for the load to be removed before cooling. An additional experiment was carried out on the unbroken test pieces available after creep testing; the room temperature tensile properties were measured.

The test pieces which were of 4.53 mm gauge diameter and 18.1 mm gauge length were creep tested at 850 and 950 °C for 3400 and 2200 hours respectively. The impure helium was the same as that used in the work described in Section 2.2, i.e. the helium environment of the creep rig commissioning phase (see Table 3).

Room temperature tensile tests were made on the unbroken creep specimens, followed by carbon analysis and metallography.

2.4 Programme D

- Influence of exposure time and specimen geometry on ductility after carburisation

The original aim of this programme was to determine the relative importance of the shape of the carbon concentration profile and the average bulk carbon content on the residual room temperature tensile properties of three high temperature alloys[11]. The alloys tested were INCOLOY 800 H (heat ADK), INCONEL 617 (ADL) and HASTELLOY X (AEK).

On the basis of earlier work (Programme B), all specimens were nickel-plated before exposure in the carburising medium. Preliminary tests to establish optimum carburising conditions showed that solid carburising compound, as used in Programme B, was highly effective at 850 ^{O}C. However, it was much less effective at 950 ^{O}C and thus a gaseous carburising medium (He - 5 % H$_2$ - 0.15 % CO - 0.24 % CH$_4$) was used at this temperature (This gas mixture was selected because it was available in the Institute and was known to be strongly carburising).

Three test specimens were used, all designed according to DIN 50 125:

type X: gauge length 25 mm, diameter 5.0 mm;
type XI: hollow, gauge length 25 mm, diameter 7.1 mm with 5 mm bore;
type XII: gauge length 35 mm, diameter 7.0 mm.

The three specimen types were chosen to provide a variety of volume : surface area ratios and carbon diffusion distances in order to permit the influences of bulk carbon content and carburisation profile to be separated. However, for reasons discussed below (Section 3.2), this aim of the programme was not achieved.

Specimens of each type and each alloy were subjected to carburisation/homogenisation treatments giving total exposure times of 100, 300 and 1000 h at 950 ^{O}C, i.e.:

```
  100 h   carburisation
  100 h   carburisation + 200 h homogenisation
  100 h   carburisation + 900 h homogenisation
  300 h   carburisation
  300 h   carburisation + 700 h homogenisation
1 000 h   carburisation.
```

The homogenisation treatments were carried out in an argon atmosphere. A similar set of specimens (i.e. 3 alloys x 3 specimen types) was carburised for 1000 h at 850 $^{\circ}$C. For comparative purposes, a set of unexposed specimens was prepared, and further sets were heat treated in argon for 100, 300 and 1000 h at 950 $^{\circ}$C and for 1000 h at 850 $^{\circ}$C. Four additional sets were made from bars which had been similarly treated in air.

After pickling in dilute nitric acid to remove the nickel plating, all specimens were tensile tested at room temperature according to DIN 50 145. The broken specimens were analysed for carbon and the 7 mm specimens (Type XII) were examined metallographically using the scanning electron microscope. The carbon contents of the 5 mm (Type X) and 7.1 mm hollow specimens (Type XI) were determined in the IRW by combustion analysis. The carbon concentration profiles in the 7 mm specimens (Type XII) were determined by electron probe micro-analysis (EPMA). To evaluate the EPMA analyses, carburised specimens of the three alloys examined were subjected to layer analysis (LECO-IR 12, Inco Europe Limited), and the same specimens were then used to calibrate the EPMA profiles. To obtain a carbon analysis representing the average of matrix and carbides, the electron beam was rapidly scanned normal to the radial direction of the profile determination. A similar, but qualitative, technique has been described Bøye, et al.[12]. The average bulk carbon contents of the full 7 mm (Type XII) specimens were determined from the EPMA carbon profiles.

2.5 Programme E

- The properties of niobium-modified INCOLOY 800

In this programme, experimental heats of INCOLOY 800 were prepared with niobium additions up to 1.5 %. The effects of niobium on the structural stability, carburisation resistance in impure helium and creep strength were investigated[13]. Room temperature tensile tests were carried out on test-

pieces (5 mm gauge diameter, 25 mm gauge length - specimen Type X of Programme D) machined from blanks aged for up to 3000 hours at 650, 800 and 900 ^{O}C; on test pieces (4.5 mm gauge diameter, 18.1 mm gauge length) exposed unstressed in PNP-Standard helium; and on the unbroken creep test-specimens (4.5 mm gauge diameter, 18.1 mm gauge length) which had been exposed in PNP-helium under stress for ca. 2000 hours at 900 ^{O}C. Each test-piece exposed in PNP-helium was analysed for carbon.

2.6 Metallography

In addition to the routine metallographic examination of the tested specimens using optical or scanning electron microscopy[7 - 11, 13], a number of carburised specimens were selected for more detailed examination, to identify the carbides present. These were specimens of Type XII (7 mm diameter) from Programme D, which had been carburised for 300 h and subsequently homogenised for 700 h at 950 ^{O}C. To facilitate a comparison of these specimens, the relevant tensile test data and bulk carbon analyses are summarised in Table 4.

Metallographic samples of the test pieces were polished and etched in Groesbeck's reagent (100 ml water, 1 g sodium hydroxide, 4 g potassium permanganate) which was found to be particularly effective for distinguishing the carbide types. Typical micrographs showing the structures of the alloys near the surface, at a depth of about 1 mm and near the centre of the specimen are shown in Figure 3 (INCOLOY 800 H), Figure 4 (INCONEL 617) and Figure 5 (HASTELLOY X). Scanning electron micrographs of the INCOLOY 800 H and INCONEL 617 specimens are compared in Figure 6.

Carbide volume fraction profiles were determined on micrographs of each of the three carburised specimens using the Classimat quantitative metallographic instrument. The profiles obtained are shown in Figure 7 with the corresponding carbon concentration profiles determined by electron probe microanalysis. The volume fraction measurements should be regarded as preliminary results. It is shown below (Section 3.3.3) that the measured volume fractions are higher than would be expected on the basis of the carbon contents. The discrepancy may result from the tendency for etching to exaggerate the size of small particles. Further work is in progress to improve the accuracy of the technique.

The carbides in the specimens of INCONEL 617 and HASTELLOY X were examined
by EPMA using the ARL instrument at Inco Europe Limited. Two main carbide
types were found and the measured contents of chromium, molybdenum and carbon
about 1 mm beneath the specimen surface both in the particles and in the
surrounding matrix are given in Table 5. The analyses have not been correc-
ted for possible absorption affects. The compositions of the two carbide
types in the two alloys were very similar, Type I containing 65 wt. % Cr and
14 wt. % Mo, and Type II containing 31 - 32 wt. % Mo and 9.5 wt. % Cr. A full
analysis of the carbides was not obtained, but it is probable that the balance
of the metal atoms would be largely nickel, possibly with some cobalt in
INCONEL 617 and iron in HASTELLOY X.

3. RESULTS AND DISCUSSION

3.1 Effect of thermal exposure on mechanical properties

In the development of high temperature alloys, an important consideration is
structural stability, and compositions are required which do not produce
undesirable precipitates in the envisaged temperature and time range of appli-
cation. In many cases, compositional requirements for structural stability and
for high strength are contradictory so that in practice a compromise is needed.
For example, high levels of solid solution hardening elements and interstitial
elements increase strength, but may lead to damaging precipitation during
exposure at service temperatures.

For the alloys under consideration in this report, some effects on mechanical
properties due to thermal exposure are to be expected, as the alloys have
specified carbon contents of ca. 0.1 % and contain carbide-forming elements
(Cr, Mo, Ti). The alloys are supplied in a solution treated condition so that
most of the secondary carbide precipitation formed during the hot-working pro-
cesses is re-dissolved. During service at high temperatures, secondary carbides
will form and affect the mechanical properties depending on the form and amount
of carbide.

The structural stability of each of the alloys of interest will be discussed,
using data from published literature and from the KFA/IRW experimental
programmes.

3.1.1   INCOLOY 800 H

The high structural stability of this alloy has been a major factor in its
success. Ageing effects are encountered in the intermediate temperature range
in which limited amounts of γ' can form in alloys containing a Ti + Al content
of greater than 0.6 %, with an associated increase in strength and a small
decrease in ductility in room temperature tensile tests[14]. The rupture elon-
gations however remained above 60 % for alloys with a Ti + Al content of
0.9 %, aged at 550 and 650 °C for up to 4000 hours. At higher temperatures,
carbide precipitation can produce ageing effects, principally a strengthening
in creep[15]. A deleterious effect of γ'-precipitation on creep-rupture ductility
has been reported in tests at 550 - 650 °C[16], which can be avoided by

a)   limiting Ti + Al to a maximum of 0.56 % in low carbon alloys (< 0.05 % C)
       with 34 - 35 % Ni.
b)   limiting (Ti + Al) to a maximum of 0.65 % in alloys with > 0.05 % carbon
       and 30 - 32 % Ni.

Figure 8 summarises the effects of ageing at 800, 850, 900 and 950 °C, the
temperatures which are of particular interest for nuclear process heat, on
the room temperature tensile properties of INCOLOY 800 H, as determined in
the KFA/IRW test programmes A, B, D and E. The room temperature tensile
properties were hardly affected by exposure for up to 3000 hours at these
temperatures.

3.1.2   INCONEL 617

The effect of long-time exposure (200 to more than 10 000 h) at temperatures
up to 1093 °C on the microstructure and phase stability of INCONEL 617 has
been studied[17]. The creep strength of the alloy was found to increase due
to the precipitation of $M_{23}C_6$ carbides which formed discrete particles and
remained stable at temperatures up to 1090 °C. The ductility at room temper-
ature was reduced slightly by ageing, as shown in Figure 9. It is interesting
to note that no MC or M_6C carbides were found in these tests, but small quanti-
ties of γ' were identified after ageing at temperatures up to 800 °C. The
γ'-precipitates did not cause any appreciable hardening in the alloy, however.

The results of the KFA/IRW ageing tests are shown in Figure 10. The two heats tested had similar tensile strengths at room temperature after ageing at 800, 850 and 950 $^{\circ}$C for up to 1000 hours. Heat ABC showed no significant ageing effect after 100 h at 800 and 850 $^{\circ}$C. The room temperature ductility of ADL was reduced by ageing for times above 100 hours at 800, 850 and 950 $^{\circ}$C. The difference in ductility may be due to the iron contents of the heats, ADL having considerably more iron (1.43 %) than ABC (0.15 %) - see Table 2.

3.1.3 HASTELLOY X

In this alloy, the precipitation of M_6C carbides at temperatures in the range 650 - 850 $^{\circ}$C is a major factor controlling the thermal stability. Long time exposures in this temperature range have been found to cause severe reductions in room temperature tensile elongation and impact strength[18, 19], as shown in Figures 11 and 12, respectively. It is also clear from Figure 11 that the effect was most severe at room temperature, and that with increasing temperature the ductility of aged material steadily increased.

Although the impact strength was severely reduced by ageing at 871 $^{\circ}$C as shown in Figure 12, no significant effect on the room-temperature tensile properties of exposure for up to 3000 hours at 850 and 950 $^{\circ}$C has been observed in the KFA/IRW investigations, the results of which are shown in Figure 13.

3.1.4 NIMONIC 86

There is no published data on the effect of long-time exposure on the mechanical properties of this relatively new alloy.

The data available from the KFA/IRW programmes are shown in Figure 14; the test data shows no significant effect of ageing at 800 and 850 $^{\circ}$C for up to 3000 hours on the tensile properties. The two results available for 1000 hours exposure at 950 $^{\circ}$C show somewhat higher strengths and lower ductility than obtained after ageing at 800 and 850 $^{\circ}$C, but ductilities remained high at around 40 %.

3.2 Influence of carburisation on mechanical properties

The room temperature tensile properties of the alloys carburised at 950 ^{o}C, determined in the test programmes described in Section 2, are plotted in Figures 15, 16, 17 and 18 against the average bulk carbon content of the gauge section of the test piece.

-   Strength properties. The 0.2 % proof stress ($R_{p\ 0.2}$) and the ultimate tensile strength (R_{m}) of carburised alloys are shown in Figure 15. Although the proof stress was hardly affected by carbon uptake during carburisation, a rapid decrease in the ultimate tensile strength was observed for all four alloys with increasing carbon uptake. The decrease was less steep for the iron-base INCOLOY 800 H than for the nickel-base alloys.

-   Elongation. The relationship between room temperature rupture elongation and the average bulk carbon content is shown in Figure 16. Some data determined by the General Atomic Company on specimens exposed under stress at 900 and 1000 ^{o}C in a simulated HTR-helium environment[20, 21] are also included. Details of the environment (Oslo "Phase 4" helium) are given in Section 3.4.2. The elongation values fell rapidly with increasing carbon content, and again for INCOLOY 800 H the decrease in elongation was less steep than for the nickel-base alloys.

    Figure 17 shows the room temperature rupture elongations of the niobium-modified INCOLOY 800 H. With increasing niobium content the carbide morphology changed, high niobium contents producing a fine distribution of carbide particles within the grains with no grain boundary carbide formation. During creep exposure of these alloys, the observed increases in carbon content were too small to show any beneficial effect of the carbide morphology modification on the ductility, and the test results were generally within the scatter band for the commercial heats (Figure 17). For specimens which after stressed exposure had high creep strains some low ductility values were observed, due to the accumulation of creep damage.

-   Reduction of Area. Figure 18 shows the reduction of area data plotted against carbon pick-up, and shows the same features as the elongation curves.

Comparing the mechanical properties curves for the four alloys by considering the level of the properties at a carbon pick-up of 0.3 %, it is seen that:

1. The ultimate tensile strength is decreased by around 10 % for INCOLOY 800 H, and by at least 30 % for the nickel-base alloys.

2. The mean rupture elongation is reduced by a half for INCOLOY 800 H and by a factor of 8 - 10 for the nickel-base alloys.

3. The reduction of area falls by a third for INCOLOY 800 H and by a factor of 5 - 10 for INCONEL 617 and HASTELLOY X.

The only correlation that could be found between carburisation and mechanical properties was the room temperature ductility (elongation and reduction of area) and the ultimate strength on the average bulk carbon content of the alloys. Despite the use of a wide variety of different specimen geometries and carburisation/homogenisation treatment combinations, no systematic influence of carburisation depth or the shape of the carbon concentration profile on the room temperature ductility could be found. This was probably due to the high temperature (950 $^{\circ}$C) used for most of the exposures. Even after the shortest exposure time (100 h) at this temperature, the depths of carburisation corresponded to 30 - 50 % of the cross-sectional area of the largest, 7 mm diameter solid specimen. Thus, a further increase in the carburisation depth produced by longer exposure would not be expected to affect the ductility significantly. A greater effect of carburisation depth would be expected for lower exposure temperatures and with thicker section material.

Another somewhat surprising observation was the presence of nearly continuous grain boundary networks of carbides at a fairly early stage of carburisation in all the alloys studied. It is sometimes suggested that nickel-base alloys show a greater tendency for carbide precipitation at grain boundaries than the iron-base alloys such as INCOLOY 800 H, in order to explain the greater sensitivity of the properties of nickel-base alloys to carburisation. However, no evidence for this effect was found in the present work.

The only observation which could account for the differences in ductility of the carburised alloys was that, for a given carbon content, the volume fraction of carbide in INCOLOY 800 H was considerably less than in the nickel-base alloys. This can be seen from a comparison of the scanning elec-

tron micrographs in Figure 6 and from the carbide volume fraction and carbon concentration profiles in Figure 7. The volume fraction of carbide in INCONEL 617 with 0.3 % carbon is at least as great as that in INCOLOY 800 H with 0.7 % carbon.

3.3 Relationship between carbon content and amount of carbide formed

As discussed above, the most probable cause of the difference in the ductility loss for INCOLOY 800 H and the nickel-base alloys is the difference in the volume fraction of carbide observed for a particular carbon content. There are two possible reasons for the difference in carbide volume fraction:

-    the lower solubility of carbon in the nickel-base alloys than in INCOLOY 800 H;
-    the formation of carbides with different carbon : metal atom ratios.

The composition of INCOLOY 800 H is reasonably simple in comparison with the nickel-base alloys. Thus it is possible to estimate from thermodynamic data the relationship between carbon content and carbide volume fraction for this alloy and to use this estimate as a basis for comparison with the nickel-base alloys.

3.3.1   Titanium carbide in INCOLOY 800 H

The most effective carbide-forming element in INCOLOY 800 H is, of course, titanium. However, at typical alloy service temperatures (< 1000 $^{\circ}$C), the formation of chromium carbide is kinetically favoured[15]. At the solution treatment temperature (1150 - 1175 $^{\circ}$C), little or no chromium carbide will form, but the solubility of titanium carbide or carbo-nitride will be small. Thus, the carbon content in the matrix of solution treated material will be determined by the solubility of Ti(C,N) at the solution treatment temperature.

The solubility product of TiC in AISI 321 stainless steel (Fe - 10 % Ni - 18 % Cr - 0.5 % Ti) over the temperature range 1000 to 1200 $^{\circ}$C has been determined as[22]:

$$\ln K \left(\frac{\text{moles}}{100\ \text{g}} \right)^2_{\text{alloy}} = 5.83 - \frac{2.39 \times 10^4}{T} \ , \ T \ K \qquad (1)$$

Defining a solubility parameter (the reciprocal of the solubility product) as:

$$K_{S(TiC)} = \frac{1}{N_{Ti} \cdot N_C} \quad , \qquad (2)$$

where N_{Ti} and N_C are the mole fractions of titanium and carbon in solution in the austenite, we obtain

$$K_{S(TiC)} = 1.4 \times 10^5 \text{ at } 1175\ ^O C, \qquad (3)$$

which should approximate to the reciprocal solubility product of TiC in INCOLOY 800 H. If N^O_{Ti} and N^O_C represent the total mole fractions of titanium and carbon in the bulk alloy, and N^{carb}_{Ti} and N^{carb}_C are the mole fractions tied up in stoichiometric TiC, we have:

$$N_{Ti} + N^{carb}_{Ti} = N^O_{Ti},$$

$$N_C + N^{carb}_C = N^O_C,$$

$$N^{carb}_{Ti} = N^{carb}_C \qquad (4)$$

These equations and the expression for the solubility product reduce to a quadratic equation in N_C:

$$(N_C)^2 + (N^O_{Ti} - N^O_C) \cdot N_C - K^{-1}_{S(TiC)} = 0 \qquad (5)$$

The solutions to this give

$$N_C = \frac{(N^O_C - N^O_{Ti}) \pm \sqrt{(N^O_{Ti} - N^O_C)^2 + 4 \cdot K^{-1}_{S(TiC)}}}{2} \qquad (6)$$

Considering the INCOLOY 800 H heat ADK, the titanium and carbon contents (Table 2) were 0.33 % and 0.11 % respectively, i.e. $N^O_{Ti} = 3.8 \times 10^{-3}$ and $N^O_C = 5.1 \times 10^{-3}$. The alloy also contained 0.021 % nitrogen, which must also be considered because titanium reacts to form a carbo-nitride rather than pure carbide and nitride. The nitride and carbide have similar stabilities[23]. Thus, as an approximation, we can replace N_C, N^O_C and $K_{S(TiC)}$ in equation (6) directly by $N_{(C + N)}$, $N^O_{(C + N)}$ and $K_{S(Ti(C,N))}$, and assume that the ratio of C : N in the alloy is the same as that in the carbo-nitride. $N^O_{(C + N)}$ is then

5.9×10^{-3}. After solution treatment at 1175 $^{\circ}$C, the mole fraction of [carbon + nitrogen] remaining in solution, $N_{(C + N)}$, would be 3.9×10^{-3}, in which $N_C \approx 3.4 \times 10^{-3}$ and $N_N \approx 0.5 \times 10^{-3}$ (the above quadratic equation has only one positive solution). These mole fractions correspond to 0.073 wt. % carbon and 0.014 wt. % nitrogen. The mole fraction of titanium in solution would be

$$1.8 \times 10^{-3}, \text{ i.e., } 0.15 \text{ wt. \%.}$$

After prolonged exposure at significantly lower temperatures, almost all the titanium would be removed from solution as carbo-nitride, leaving approximately 0.039 wt. % carbon and 0.007 wt. % nitrogen in solution. However, in view of the low rate of formation of titanium carbide, chromium carbide formation is likely to predominate in short term exposures at these lower temperatures. This is supported by the observations of Lucks[13] who reported no coarsening of the Ti(C,N) particles in this heat after exposure for 1000 h at 900 $^{\circ}$C, although the total amount of carbide increased significantly. Presumably the increase in carbide volume fraction was due to the precipitation of chromium carbide. Thus, at normal service temperatures (< 1000 $^{\circ}$C), the main carbides formed in INCOLOY 800 H, particularly under the influence of carburisation, will be chromium carbides.

3.3.2   Chromium carbides in INCOLOY 800 H

Two main chromium-rich carbides have been found in carburised INCOLOY 800 H, $M_{23}C_6$ and M_7C_3[3]. The latter carbide was observed only when the bulk carbon content of the alloy exceeded about 1 wt. %. At this level of carburisation, the room temperature ductility of the alloy is so low that it is no longer of interest in the context of this report. Thus, the discussion will be restricted to the carbide $M_{23}C_6$.

-    Carbide composition:

Schnaas and Grabke[3] determined the composition of $M_{23}C_6$ formed in INCOLOY 800 during carburisation at 900 $^{\circ}$C. Their results corresponded approximately to a composition $Cr_{16}(Fe,Ni)_7C_6$. Tůma, Gröbner and Löbl[24] studied the solubility and activity of carbon in a Fe - 18 % Cr - 9 % Ni steel and determined carbide compositions at 950 $^{\circ}$C ranging from $Cr_{18.4}Fe_{4.6}C_6$ at a bulk carbon content in

the alloy of about 0.04 % to $Cr_{16.4}Fe_{6.6}C_6$ at a carbon content of about 0.2 %. These results also indicate that the composition of $M_{23}C_6$ in carburised INCOLOY 800 H can be approximated to $Cr_{16}Fe_7C_6$.

- Free energy of formation:

Several different values are available for the free energy of formation of $M_{23}C_6$ and, as will be shown below, it is necessary to take some care in selecting a value which corresponds reasonably well with the experimental observations on INCOLOY 800 H.

For the carbide $Cr_{16.4} Fe_{6.6}C_6$, Tûma, et al[24] derived the free energy expression (on the basis of 1 mole of carbide):

$$\Delta G^0 = - 696\ 700 + 144.7\ T\ \text{joules}$$
$$= - 520\ \text{kJ at 950 } ^0C \tag{7}$$

They contrasted this value with those obtained by Alekseev and Svarcman[25] for $Cr_{15.2}Fe_{7.8}C_6$ and by Richardson[26] for $Cr_{23}C_6$, which are, respectively:

$$\Delta G^0 = - 591\ 900 + 153.0\ T\ \text{joules}$$
$$= - 405\ \text{kJ at 950 } ^0C \tag{8}$$
$$\Delta G^0 = - 410\ 800 - 38.62\ T\ \text{joules}$$
$$= - 458\ \text{kJ at 950 } ^0C \tag{9}$$

More recent work by Kulkarni and Worrell[27] led to the following expression for $Cr_{23}C_6$:

$$\Delta G^0 = - 321\ 900 - 76.49\ T\ \text{joules}$$
$$= - 415\ \text{kJ at 950 } ^0C \tag{10}$$

- Solubility parameter:

A solubility parameter K_S of $Cr_{23}C_6$ or $M_{23}C_6$ (approximated to $Cr_{16}Fe_7C_6$) can be defined as:

$$K_{S(Cr_{23}C_6)} = \frac{1}{N_{Cr}^{23} \cdot N_C^6} \ , \tag{11 a}$$

or

$$K_{S(M_{23}C_6)} = \frac{1}{N_{Cr}^{16} \cdot N_{Fe}^{7} \cdot N_{C}^{6}} \, , \tag{11 b}$$

where N_i is the mole fraction of element i in the austenite. These parameters are the reciprocals of the solubility products. If a_i is the activity and γ_i the Raoultian activity coefficient of i in the austenite, we have:

$$N_i = \frac{a_i}{\gamma_i} \quad . \tag{12}$$

Thus,

$$K_{S(Cr_{23}C_6)} = \frac{\gamma_{Cr}^{23} \cdot \gamma_{C}^{6}}{a_{Cr}^{23} \cdot a_{C}^{6}} = \gamma_{Cr}^{23} \cdot \gamma_{C}^{6} \cdot K_{Cr_{23}C_6} \tag{13 a}$$

$$K_{S(M_{23}C_6)} = \frac{\gamma_{Cr}^{16} \cdot \gamma_{Fe}^{7} \cdot \gamma_{C}^{6}}{a_{Cr}^{16} \cdot a_{Fe}^{7} \cdot a_{C}^{6}} = \gamma_{Cr}^{16} \cdot \gamma_{Fe}^{7} \cdot \gamma_{C}^{6} \cdot K_{M_{23}C_6} \tag{13 b}$$

where $K_{Cr_{23}C_6}$ and $K_{M_{23}C_6}$ are the equilibrium constants of the reactions for the formation of the carbides and are related to the free energy of formation:

$$\triangle G^0 = - RT \ln K. \tag{14}$$

The above expressions for the solubility parameter of the carbides then become:

$$\ln K_{S(Cr_{23}C_6)} = 23 \ln \gamma_{Cr} + 6 \ln \gamma_{C} - \frac{1}{RT} \cdot \triangle G^0_{Cr_{23}C_6} \tag{15}$$

$$\ln K_{S(M_{23}C_6)} = 16 \ln \gamma_{Cr} + 7 \ln \gamma_{Fe} + 6 \ln \gamma_{C} - \frac{1}{RT} \cdot \triangle G^0_{M_{23}C_6} \tag{16}$$

The term Υ_C can be divided up into a contribution due to the solution of carbon in pure Fe-C austenite Υ_C^C, a contribution due to the presence of nickel in the austenite γ_C^{Ni} and a contribution due to the presence of chromium in the austenite γ_C^{Cr}. Thus

$$\ln \Upsilon_C = \ln \Upsilon_C^C + \ln \gamma_C^{Ni} + \ln \Upsilon_C^{Cr} . \tag{17}$$

The relevant interaction parameters have been determined in the temperature range 725 - 1060 ^{O}C by Natesan and Kassner[28] for chromium and nickel contents from 0 to 22 % and 0 to 16 % respectively, and in the temperature range 850 - 1150 ^{O}C by Schürmann, Harre and Rimkus[29] for chromium and nickel contents from 0 to 9 % and 0 to 35 % respectively. For the basic Fe - 32 % Ni - 20 % Cr composition the data presented in these papers gives (for 950 ^{O}C):

Natesan, et al:

$$\ln \gamma_C^C = + 2.33$$

$$\ln \gamma_C^{Ni} = + 1.20$$

$$\ln \gamma_C^{Cr} = - 2.87 \tag{18}$$

Schürmann, et al.:

$$\ln \gamma_C^C = + 2.29$$

$$\ln \gamma_C^{Ni} = + 1.30$$

$$\ln \gamma_C^{Cr} = - 1.97 . \tag{19}$$

The only significant discrepancy between these values is in the data for γ_C^{Cr}. Using the value from Natesan, et al., which was determined for the appropriate chromium concentration, and averageing the remaining parameters we obtain

$$6 \ln \Upsilon_C = 4.1, \quad \Upsilon_C = 2 \tag{20}$$

A value for $\ln \Upsilon_{Cr}$ for the basic composition of INCOLOY 800 H (Fe - 32 % Ni - 20 % Cr) can be obtained from the publication of Mazandarany and Pehlke[30]. Thus at 950 ^{O}C

$$\ln \gamma_{Cr} = 0.99, \quad \gamma_{Cr} = 2,7 \tag{21}$$

It can reasonably be assumed that $\gamma_{Fe} = 1.0$, so that expressions (15) and (16) reduce to

$$\ln K_{S(Cr_{23}C_6)} = 22.8 + 4.1 - \frac{1}{RT} \cdot \Delta G^o_{Cr_{23}C_6} \tag{22 a}$$

and

$$\ln K_{S(M_{23}C_6)} = 15.8 + 4.1 - \frac{1}{RT} \cdot \Delta G^o_{M_{23}C_6} \tag{22 b}$$

Inserting in these the free energy values in equations (7) - (10) we obtain for 950 ^{o}C:

$$K_{S(M_{23}C_6)} = 6.8 \times 10^{30} \qquad \text{(Tůma, et al.)}$$

$$K_{S(M_{23}C_6)} = 8.3 \times 10^{25} \qquad \text{(Alekseev, et al.)}$$

$$K_{S(Cr_{23}C_6)} = 1.7 \times 10^{31} \qquad \text{(Richardson)}$$

$$K_{S(Cr_{23}C_6)} = 2.4 \times 10^{29} \qquad \text{(Kulkarni, et al.).}$$

- Comparison with experimental observations:

In tests at the KFA, significant quantities of chromium carbide were observed in heat ABD of INCOLOY 800 H after annealing at 950 ^{o}C. This heat with 0.08 wt. % carbon, 0.023 wt. % nitrogen and 0.46 wt. % Ti contained less carbon and more Ti than the heat previously considered in Section 3.3.1. Thus, on the basis of the considerations presented in Section 3.3.1 above, it would be expected that about 0.04 wt. % carbon would have remained in solution after solution treatment, which suggests that the amount of carbon in solution in equilibrium with chromium carbide at 950 ^{o}C would be less than about 0.04 wt. %.(This is equivalent to the "solubility" of carbon in the basic Fe - 20 % Cr - 32 % Ni austenite of INCOLOY 800 H).

Considering a typical heat of INCOLOY 800 H in which $N_{Cr} \approx 0.21$ and $N_{Fe} \approx 0.48$, the above solubility parameters would correspond to the following mole fractions of carbon in solution at 950 ^{o}C:

$$1.1 \times 10^{-3} = 0.024 \text{ wt. \%} \quad (\text{Tůma})$$
$$7.2 \times 10^{-3} = 0.16 \text{ wt. \%} \quad (\text{Alekseev})$$
$$2.5 \times 10^{-3} = 0.053 \text{ wt. \%} \quad (\text{Richardson, } Cr_{23}C_6)$$
$$0.9 \times 10^{-3} = 0.020 \text{ wt. \%} \quad (\text{Richardson, applied to } M_{23}C_6)$$
$$5.0 \times 10^{-3} = 0.11 \text{ wt. \%} \quad (\text{Kulkarni, } Cr_{23}C_6)$$
$$1.9 \times 10^{-3} = 0.042 \text{ wt. \%} \quad (\text{Kulkarni, applied to } M_{23}C_6).$$

Clearly, the value derived from the data of Alekseev and Kulkarni is too high to apply to INCOLOY 800 H at 950 ^{O}C. The other values lie reasonably close together and as the data of Tůma relate to a carbide very similar to the $M_{23}C_6$ identified in INCOLOY 800 H, they have been adopted for the present work after a minor modification described below.

- Revised value for solubility parameter:

An examination of the derivation of the data of Tůma shows that they used the chromium activity data of Jeanin, Mannerskantz and Richardson[31] for the Fe-Cr system which gave $\gamma_{Cr} = 1.79$ at 950 ^{O}C for the alloy composition investigated. More recent work[30, 32] has shown a significant influence of nickel on the activity of chromium in austenite. For the alloy composition studied by Tůma, the data of Mazandarany[30] would give $\gamma_{Cr} = 2.25$ at 950 ^{O}C. Recalculating the free energy of formation of $M_{23}C_6$ we now obtain:

$$\Delta G^O = -491 \text{ kJ/mole,}$$

which leads to

$$\underline{K_{S(M_{23}C_6)} = 3.9 \times 10^{29}}$$

This revised value, which corresponds to a carbon solubility of 0.036 wt. % in Fe - 20 % Cr - 32 % Ni at 950 ^{O}C, has been used in all calculations presented below.

- <u>Simplified solubility parameter:</u>

As the mole fraction of iron in the austenite does not change greatly during the progress of carburisation, it is possible to simplify further the above expression for the solubility of $M_{23}C_6$.

Thus, instead of

$$K_{S(M_{23}C_6)} = \frac{1}{N_{Cr}^{16} \cdot N_{Fe}^7 \cdot N_C^6} \quad ,$$

we can define a new parameter

$$K'_{S(M_{23}C_6)} = \frac{1}{N_{Cr}^{16} \cdot N_C^6} = K_{S(M_{23}C_6)} \cdot N_{Fe}^7$$

$$= 3.9 \times 10^{29} \times 0.48^7$$

$$= 2.3 \times 10^{27}.$$

By eliminating one of the high index terms in the solubility parameter, the use of the parameter $K'_{S(M_{23}C_6)}$ can lead to considerable savings in computing time particularly in complex, iterative calculations such as those presented by Bongartz, Lupton and Schuster[4] for determining carburisation profiles.

- <u>Influence of carburisation on carbide volume fraction:</u>

Figure 19 shows the relationship between the solubility of carbon in INCOLOY 800 H at 950 ^{O}C and the bulk carbon content of the alloy. Also shown is the relationship between bulk carbon content and the volume fraction of $M_{23}C_6$. It has been assumed that the composition and solubility parameter of $M_{23}C_6$ are independent of the bulk carbon content, and that the specific weights of the bulk alloy and the $M_{23}C_6$ are 7.95 and 7.0 respectively.

The influence of Ti(C,N) on the effective carbon content in solution and the observed carbide volume fraction has been neglected in Figure 19. If 0.04 wt. % carbon is tied up as Ti(C,N), the curves would be transposed by this amount to the right along the abscissa. However, 0.04 wt. % carbon would form approximately 0.24 wt. % Ti(C,N), which would correspond to an additional 0.4 vol. % carbide (assuming specific weight of Ti(C,N) = 4.9).
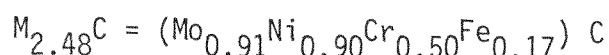
3.3.3   Carbides in nickel-base alloys

Detailed estimates of carbon solubility and carbide volume fraction are not possible for the nickel-base alloys, because of scarcity of the necessary thermodynamic data. However, it is possible to estimate upper and lower limits.
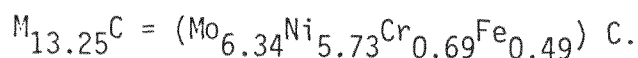
-   Carbide types:

Table 5 shows the compositions determined in the electron probe microanalyser of the carbides found in INCONEL 617 and HASTELLOY X after 300 h carburisation and 700 h homogenisation at 950 ^{O}C. It is clear that two distinct carbide types were present in each alloy, presumably Cr-rich $M_{23}C_6$ and Mo-rich M_6C, as described by Decker and Sims[33]. The observed composition for "Carbide I" (Table 5) corresponds very closely to the composition $(Cr_{17.5}Ni_{3.5})$ Mo_2C_6, which agrees well with the statement of Decker, et al.[33] that, in the presence of Mo, the composition of the carbide $M_{23}C_6$ is rigidly fixed with two atoms of Mo.

The range of stoichiometry reported for the M_6C carbide is much greater[34]. For HASTELLOY X, compositions from $M_{2.48}C$ to $M_{13.25}C$ were observed, where

$$M_{2.48}C = (Mo_{0.91}Ni_{0.90}Cr_{0.50}Fe_{0.17})\ C$$

and

$$M_{13.25}C = (Mo_{6.34}Ni_{5.73}Cr_{0.69}Fe_{0.49})\ C.$$

Assuming that the balance (approx. 55 %) of the composition of Carbide II is Ni, the composition given in Table 5 would approximate to $(Mo_{1.4}Ni_{4.0}Cr_{0.7})$ corresponding to a much higher Ni:Mo atom ratio than given above. It is not certain whether this difference is real or results only from the incomplete EPMA measurements. Furthermore, in view of the uncertainties in EPMA determinations of carbon content, it is not clear whether the difference in carbon content for Carbide II in the two alloys (1.9 % and 4.6 %) is significant; the stoichiometric composition $(Mo_{1.4}Ni_{4.0}Cr_{0.7})$ C would correspond to 2.9 % carbon. An interesting point is that Mankins, Hosier and Bassford[17] reported finding no M_6C in INCONEL 617 after creep testing at temperatures

between 649 and 1083 ^{O}C (1200 - 2000 ^{O}F). This observation is not in agreement with the results of the present study, but it is possible that the carburising treatment used in the present work led to the formation of M_6C.

3.3.4 Comparison of carbide volume fractions in the alloys

From the carbon concentration profiles shown in Figure 7, the average carbon content of the first 0.5 mm thick subsurface zone can be estimated for each of the specimens which had been carburised for 300 h and homogenised for 700 h at 950 ^{O}C. These carbon contents are:

INCOLOY 800 H:	0.7 %
INCONEL 617:	0.3 %
HASTELLOY X:	0.4 %.

For each mole of carbon, a larger amount of M_6C can be formed than $M_{23}C_6$ (assuming stoichiometry of both carbides). Thus, an upper limit to the volume fraction of carbide would be given if we assumed that only M_6C were formed. Furthermore, the solubility of carbon in the matrix of nickel-base alloys is lower than in INCOLOY 800 H[35], and the higher contents of carbide-forming elements in the nickel-base alloys would further reduce the solubility. For the nickel-base alloys with 0.3 - 0.4 % carbon, the solubility of carbon would be much less than the 0.05 % indicated for INCOLOY 800 H in Figure 19, probably close to 0.01 %. In terms of the total volume fraction of carbide formed, this quantity of dissolved carbon can be neglected.

If all 0.3 % carbon in INCONEL 617 formed stoichiometric $(Mo_{1.4}Ni_{4.0}Cr_{0.7})C_6$ with a specific weight of 9.0, the total volume fraction of carbide would be 10 %. Similarly, for HASTELLOY X with 0.4 % carbon, the carbide volume fraction would be 13 %. Higher volume fractions could only be formed if the average metal : carbon atom ratio in the carbide were greater than 6. If, on the other hand, the carbon in the alloys formed only $M_{23}C_6$ with a specific weight of 7.0, the corresponding volume fractions would be 7 and 9 %. Thus, the expected carbide volume fractions in INCOLOY 800 H (from Figure 19, allowing for the formation of Ti(C,N)) and the nickel-base alloys would be:

INCOLOY 800 H	(0.7 % C):	11 vol. %
INCONEL 617	(0.3 % C):	7 - 10 vol. %
HASTELLOY X	(0.4 % C):	9 - 13 vol. %.

Although these values can only be regarded as approximations, they demonstrate clearly that similar volume fractions of carbide can form in INCOLOY 800 H with 0.7 % C and in the nickel-base alloys with 0.3 - 0.4 % C. The values also indicate that the measured carbide volume fractions shown in Figure 7 are too high by a factor of approximately 1.5 for INCOLOY 800 H and 2 for the nickel-base alloys.

3.4 Application of results to the assessment of materials for HTR service

3.4.1 Estimation of maximum acceptable carburisation rates

Because of the severe problems and high cost involved in the replacement of components in the primary circuit of a nuclear reactor, long service times are required for the components. For the intermediate heat exchanger (IHX), which requires thin-walled tubing of around 2.5 mm wall thickness, and for the reformer furnace tubes, which have a wall thickness of 15 mm, only one replacement in the life of the plant is planned. This means that operation times of 140 000 hours are required.

Using the ductility data shown in Figure 16, curves relating room temperature elongation after service for 140 000 hours to mean linear carburisation rate (in $g.cm^{-2}.h^{-1}$) can be drawn for components of different wall thickness, as shown in Figure 20. A linear carburisation rate has been assumed although as discussed in Section 3.4.2 this may give pessimistic estimates. Although most of the ductility data shown in Figures 15 - 17 were determined for alloys carburised at 950 ^{o}C, the few data points determined after carburisation at 850 ^{o}C[6] and 900 ^{o}C lay in the same scatterbands so that at least in the temperature range 850 - 950 ^{o}C, the curves are not temperature sensitive.

In conventional engineering practice, a minimum room temperature ductility of 10 % elongation is normally required although under some circumstances ductilities as low as 5 % elongation may be allowed. For aerospace applications, it has been assumed that 2 % elongation is needed simply to allow for design tolerances, and that 15 % elongation is required before a material can be classed as sufficiently ductile for the influence of notches and stress-

raisers to be neglected[36]. For discussion purposes we will, therefore, assume that a minimum ductility requirement of 5 % RT elongation will be required.

A minimum ductility of 5 % elongation, corresponds approximately to an average ductility of 10 % elongation. Using the data shown in Figure 16, the maximum linear carburisation rates which can be accepted if a 5 % minimum elongation and a service life of 140 000 h are required have been calculated (Figure 20). For intermediate heat exchanger tubes fabricated from the nickel-base alloys, carburisation rates should not exceed $(0.20 - 0.25) \times 10^{-7}$ $g.cm^{-2} h^{-1}$; for tubes fabricated from INCOLOY 800 H, the maximum carburisation rate is 0.5×10^{-7} $g.cm^{-2} h^{-1}$.

For the reformer tubes, again assuming a minimum ductility requirement of 5 % elongation and a service life of 140 000 h, the maximum carburisation rate for INCOLOY 800 H is 3×10^{-7} $g.cm^{-2}.h^{-1}$, and for the nickel-base alloys, $(1.0 - 1.5) \times 10^{-7}$ $g.cm^{-2}.h^{-1}$.

3.4.2 Carburisation rates in HTR helium

Carburisation measurements have been carried out on corrosion specimens of high temperature alloys exposed in two helium environments with the following nominal impurity levels:

	Oslo "Phase 4"[+]	"PNP Standard helium"[++]
H_2	500 /ubar	500 /ubar
H_2O	1.5 /ubar	1.5 /ubar
CO	30 - 50 /ubar	15 /ubar
CH_4	50 /ubar	20 /ubar
CO_2z	ca. 1 /ubar	ca. 1 /ubar

These atmospheres have similar oxidation potentials. However, the carburising potential of the "Phase 4" atmosphere is significantly higher than that of the PNP standard atmosphere, due to its higher CH_4 and CO contents.

[+] Standard composition of the final DRAGON reactor programme

[++] Standard composition of the project "Prototype Plant for Nuclear Process Heat"

- Oslo "Phase 4" atmosphere

Typical carburisation results determined on the alloys considered in this report after exposure at 900 $^\circ$C in creep rigs operating with the Oslo "Phase 4" environment are presented in Figure 21 which shows the increase in the bulk carbon content of a 5 mm diameter specimen. The dashed line in Figure 21 represents a linear, surface-related carburisation rate of 2.5 x 10^{-7} g.cm^{-2}.h^{-1}. The carburisation kinetics of HASTELLOY X for exposure times up to 7000 h in "Phase 4" helium at 900 $^\circ$C have been shown to correspond closely to this rate[37] Dean[38, 39] has also shown that this rate constant describes the carburisation kinetics of a wide range of iron-base and nickel-base alloys at 900 $^\circ$C in the "Phase 4" environment.

- PNP standard helium atmosphere

More recent corrosion tests in PNP standard helium have shown that, because of the rapid reaction at the metal surfaces at 900 $^\circ$C and above, the impurity content of the gas changes significantly as the gas flows through the test retorts. Specimens located near the gas inlet are therefore exposed to an atmosphere which contains more water vapour and more methane than the atmosphere near the gas outlet which is richer in carbon monoxide and hydrogen. The results for INCONEL 617 specimens exposed in a test gas near to the specified PNP standard helium composition (i.e. exposed near the gas inlet of the test retorts) are shown in Figure 22[40]. For comparison, some test points obtained near the gas outlet, where the gas has a water content of less than 0.1 μbar, are included.

From the limited amount of data, it is not possible to derive a definitive relationship between carbon uptake and exposure time. It has been suggested[40] that the carburisation shows an initial steep increase and then reaches a maximum with no further increase in carbon uptake as the exposure time increases, a protective oxide preventing the diffusion of carbon into the alloy. Because of the wide scatter in the data, however, other time laws can be fitted equally well to the experimental points. In the following discussion we will consider a linear time dependence of the carburisation process, a perhaps pessimistic assumption which will produce a conservative evaluation of the data.

Using Figure 16 the maximum linear carburisation rates for retention of 5 %
room temperature elongation after 50 000 and 140 000 h exposure of a 5 mm
diameter specimen were calculated, and are shown as broken lines in Figure 22.
It can be seen that some of the experimental points lie below the 5 %/50 000 h
line, indicating that it may be possible to retain 5 % minimum ductility after
50 000 h service. This would, however, require strict control of the gas com-
position in a reactor, in particular to ensure that sufficient water vapour
is present to allow the formation of a protective oxide film.

The importance of the test parameters, such as gas flow rate, supply rates of
the various impurities and the metallic surface area in a test retort, has
been discussed in relation to the formation of oxide films by Lupton[41]; the
relevance of the data from test rigs for the operation of a process heat HTR
was also discussed.

3.4.3   Other considerations

In the previous discussion, the effect of carburisation on the room temper-
ature ductility has been considered. Of course, other mechanical properties
of importance in design will also be affected by carburisation; some of these
will be briefly discussed in this section.

The effect of carburisation on the tensile ductility at elevated temperatures
is also an important consideration. Thorley and Tyzak[1] showed that for stain-
less steels, the low ductility of carburised material persisted up to tempe-
ratures around 600 ^{O}C; INCOLOY 800 H can reasonably be expected to show a
similar ductility-temperature relationship. For HASTELLOY X, Matthews[17]
showed that the ductility of thermally aged material is lowest at around
room temperature and increases steadily with increasing test temperature (see
Figure 11). A more detailed study of the temperature dependence of the mecha-
nical properties of carburised alloys is required.

The creep-rupture properties of alloys exposed to carburising atmospheres
is being studied as part of the PNP materials test programme. Results to
date which are based on tests of around 20 000 hours duration indicate no
significant effect of carburisation on creep strength[42], but testing is
continuing to 30 000 hours.

Finally, the effect of carburisation on the fatigue properties requires investigation as the presence of grain-boundary carbide films may significantly influence the initiation and propagation of fatigue cracks. Initial tests[43] have however indicated that the low cycle fatigue strength is higher in HTR helium atmospheres than in air.

3.4.4   Alloy development possibilities

There are several lines of investigation which should be considered for the development of alloys having improved carburisation resistance.

In Section 3.2 we showed that the difference in the room temperature ductilities of INCOLOY 800 H and the two nickel-base alloys INCONEL 617 and HASTELLOY X after carburisation was related to the volume fraction of carbide present for a given average bulk carbon content. A promising approach to alloy development would therefore be to limit the volume fraction of carbide formed, which means increasing the solubility of carbon in the matrix and avoiding carbides having a high metal : carbon atom ratio.

The solubility of carbon can be increased in iron-base and nickel-base alloys by reducing the chromium content, and the addition of elements such as tungste and niobium which form stable mono-carbides may discourage the formation of carbides which have higher metal : carbon atom ratios. In addition, because tungsten and niobium atoms are relatively large, they diffuse only slowly in the face-centred cubic matrix and therefore promote the formation of carbide within the grains instead of at the grain boundaries. In the IRW such alloys with chromium contents of 8 - 16 % and with additions of tungsten, titanium or niobium are being investigated.

The morphology of the carbides precipitated during carburisation is also being investigated using nickel-iron alloys containing ternary additions of chromium, tungsten, molybdenum, niobium and titanium. The mechanical properties after various carburisation and homogenisation treatments are being determined, with the aim of relating the loss of ductility to the morphology and distribution of the carbides formed.

4. SUMMARY

1. Average bulk carbon content was the only carburisation parameter in this study which could be correlated with the room temperature tensile ductility.

2. The room temperature ductility of INCOLOY 800 H is less sensitive to carbon content than that of the nickel-base alloys INCONEL 617, HASTELLOY X and NIMONIC 86. This is attributed to the higher volume fraction of carbide which forms in the nickel-base alloys for a given bulk carbon content. The higher volume fraction appears to result both from the lower solubility of carbon in the nickel-base austenite than in INCOLOY 800 H and from the formation of M_6C, with a high metal : carbon atom ratio, in the former alloys.

3. On the basis of available room temperature tensile data, carburisation does not appear to lead to insurmountable ductility problems for INCOLOY 800 H reformer tubes operating at 850 - 950 $^{\circ}$C in a nuclear process heat system.

4. The carburisation of IHX tubes in service could lead to ductility problems. Possible solutions are:
    -   ensuring the formation of protective oxide films to prevent carbon diffusion into the alloy. This appears possible provided the impurities in the primary coolant helium can be carefully controlled, especially important being the maintenance of sufficient water vapour in the helium.
    -   relaxing the ductility requirement. A detailed analysis of start-up and shut-down procedures may indicate whether low ductility at temperatures below the normal service temperatures is an important factor affecting service life.

5. In the context of alloy development, it should be possible to minimise the loss of ductility resulting from carburisation by:
    -   maximising the solubility of carbon in the austenite matrix, in particular by reducing the chromium content of the alloy;
    -   optimising the composition of the alloy to reduce the tendency for the formation of carbides such as M_6C which have high metal : carbon atom ratios and thus lead to high volume fractions of carbide;
    -   increasing the levels of elements such as niobium and tungsten which diffuse slowly and thus promote the formation of fine intra-granular carbides rather than grain boundary carbides.

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Table 1: Summary of experimental programmes

Programme	Topic	Author, Date	Reference
A	Thermal stability of high temperature alloys	R. Bach Winter 1977	7
B	The effect of carburisation on room temperature tensile properties of high temperature alloys	U. Thiele Summer 1978	8, 9
C	Room temperature tensile properties of high temperature alloys after stressed exposure in impure helium	G. Hachenberg, P. J. Ennis	10
D	Relationship between extent of carburisation and room temperature ductility of high temperature alloys	G. C. Deventer September 1979	11
E	The influence of niobium additions on the mechanical properties and corrosion behaviour of INCONEL 800 H	I. Lucks Summer 1979	13

Table 2:   Details of Test Materials

Alloy	KFA/IRW Mark	Manuf.*	Heat No.	Form ‡	Chemical Composition (wt. %)**														
					Cr	Ni	Fe	C	Si	Mn	Mo	Ti	Al	Co	W	P	S	N	others
INCOLOY 800 H	ABD	1	HH7782A	bar 19 mm Ø	19.6	31.3	bal	0.078	0.35	0.84	-	0.46	0.32	-	-	-	0.003	0.0229	0.68 Cu
	ADK	2	143904	tube 80x15 mm	19.5	32.9	bal	0.11	0.56	0.68	-	0.33	0.24	-	-	0.022	0.012	0.0211	0.22 Cu
	AKC	3	ZEWS		21.1	32.8	bal	0.058	0.33	0.58	-	0.37	0.27	-	-	-	-	-	0.05 Nb
	AKD	3	ZEWT	bar	21.2	32.7	bal	0.055	0.36	0.58	-	0.38	0.27	-	-	-	-	-	0.24 Nb
	AKE	3	ZEWU	15 and	20.8	32.8	bal	0.050	0.33	0.56	-	0.38	0.28	-	-	-	-	-	0.51 Nb
	AKH	3	ZEWW	9 mm Ø	21.0	33.0	bal	0.049	0.35	0.58	-	0.37	0.29	-	-	-	-	-	1.01 Nb
	AKJ	3	ZEWX		20.8	32.9	bal	0.053	0.35	0.58	-	0.37	0.29	-	-	-	-	-	1.55 Nb
	AKK	3	ZEWY		20.8	32.9	bal	0.051	<0.05	0.49	-	<0.05	<0.05	-	-	-	-	-	1.48 Nb
INCONEL 617	ABC	2	XXAAOA4US	bar 12 mm Ø	22.3	bal	0.15	0.075	-	-	9.1	-	1.06	12.5	-	-	0.007	0.0146	-
	ADL	2	XXA2A3UK	bar 25.4 mm Ø	21.1	bal	1.43	0.08	-	-	9.3	-	0.82	12.4	-	-	0.002	-	-
HASTELLOY X	AAX	4	2600-4-4330	plate 13 mm	22.3	bal	19.0	0.064	0.40	0.65	9.0	-	-	1.46	0.34	0.028	0.005	0.0358	-
	AEK	4	2600-4-2809	bar 19 mm Ø	20.7	bal	18.7	0.11	0.41	0.50	8.7	-	-	2.10	0.55	0.021	0.005	-	-
NIMONIC 86	AAH	3	3216-14	plate 20 mm	25.5	bal	-	0.053	0.1	-	10.3	-	-	-	-	-	-	0.0023	0.05 Ce

* 1-Huntington Alloys, 2-Schoeller-Bleckmann, 3-Inco Laboratory, Birmingham, GB; 4-Cabot Corporation

‡ All alloys supplied in solution treated condition

** Manufacturer's analysis

Table 3: Average impurity levels in helium used in Programme B
(ZEMAK IV, commissioning period)

Impurity	Pressure (μbar)
H_2O	< 1
H_2	ca. 1800
CO_2	ca. 120
CH_4	ca. 100
CO	ca. 70

Table 4: Tensile test data and bulk carbon analyses
(single determinations using 7 mm gauge diameter specimens)

Alloy	Treatment	Average bulk C-content wt. %	RT tensile test results			
			0.2 % PS (N/mm^2)	UTS (N/mm^2)	Elongation (%)	Red. of Area (%)
INCOLOY 800 H (ADK)	Untreated	0.11	213	500	37	69
	Aged 1000 h at 950 $^oC^{+)}$	0.11	164	486	39	64
	300 h carburisation + 700 h homogenisation at 950 ^oC	0.50	184	417	3.2	-
INCONEL 617 (ADL)	Untreated	0.08	330	816	55	50
	Aged 1000 $h^{+)}$ at 950 ^oC	0.08	311	833	40	37
	300 h carburisation + 700 h homogenisation at 950 ^oC	0.20	339	534	1.6	-
HASTELLOY X (AEK)	Untreated	0.11	300	735	51	65
	Aged 1000 $h^{+)}$ at 950 ^oC	0.11	274	733	38	40
	300 h carburisation + 700 h homogenisation at 950 ^oC	0.21	280	523	2.6	1.4

+) Specimen machined from blank after ageing treatment

Table 5: Electron probe microanalysis of carburised INCONEL 617
and HASTELLOY X
(specimens carburised 300 h and homogenised 700 h at 950 $^\circ$C)

| Alloy | Phase | Analysed concentration (wt. %) | | |
		Cr	Mo	C
INCONEL 617	Carbide I	65	14	6.2
	Carbide II	9.5	32	1.9
	Matrix	19	5.0	-
HASTELLOY X	Carbide I	65	14	7.5
	Carbide II	9.5	31	4.6
	Matrix	18	6.2	-

Carbide I and II tentatively identified as $M_{23}C_6$ and M_6C respectively
(see text).
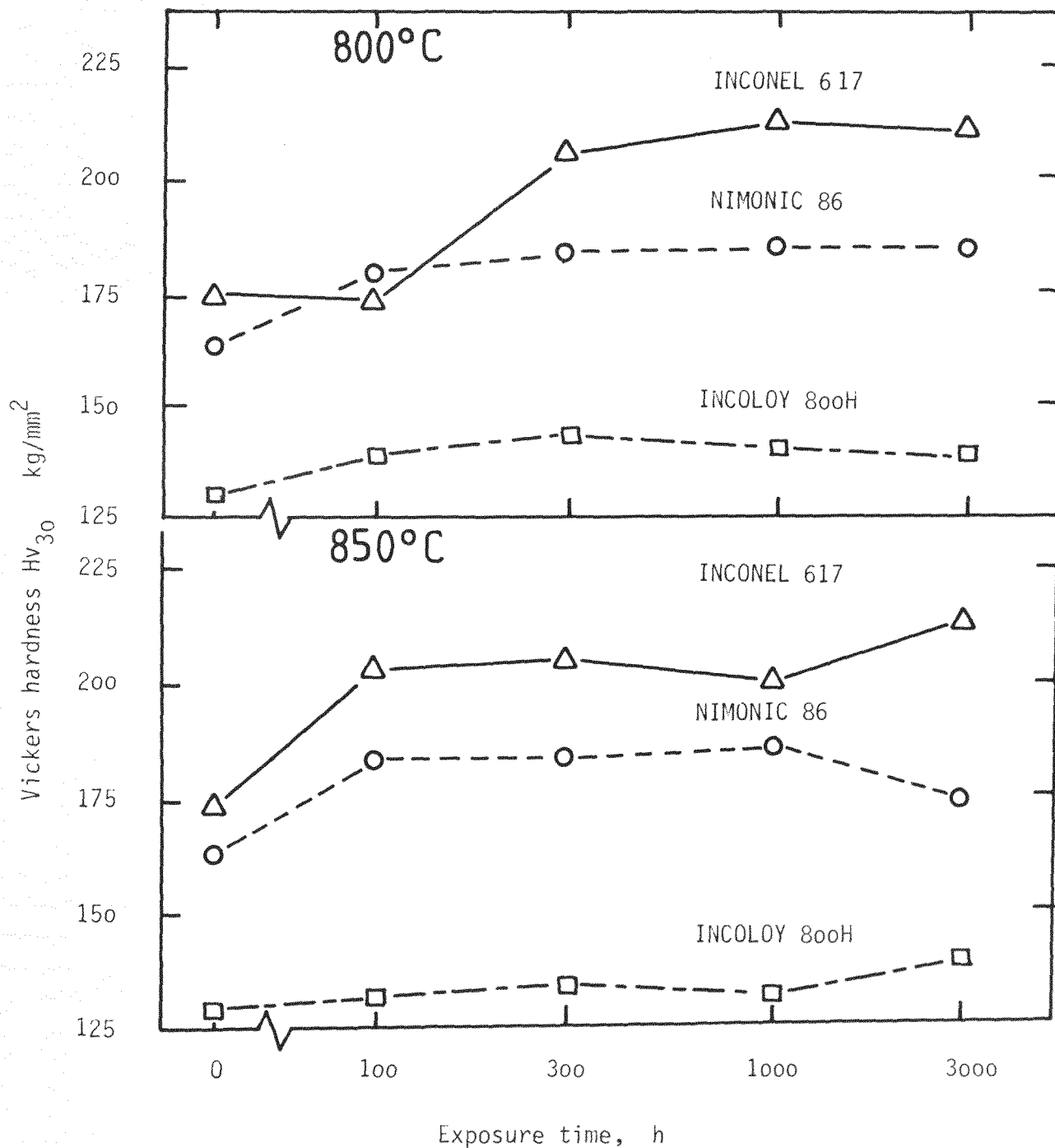
Figure 1

Influence of thermal exposure on the hardness of
INCONEL 617, NIMONIC 86 and INCOLOY 800H
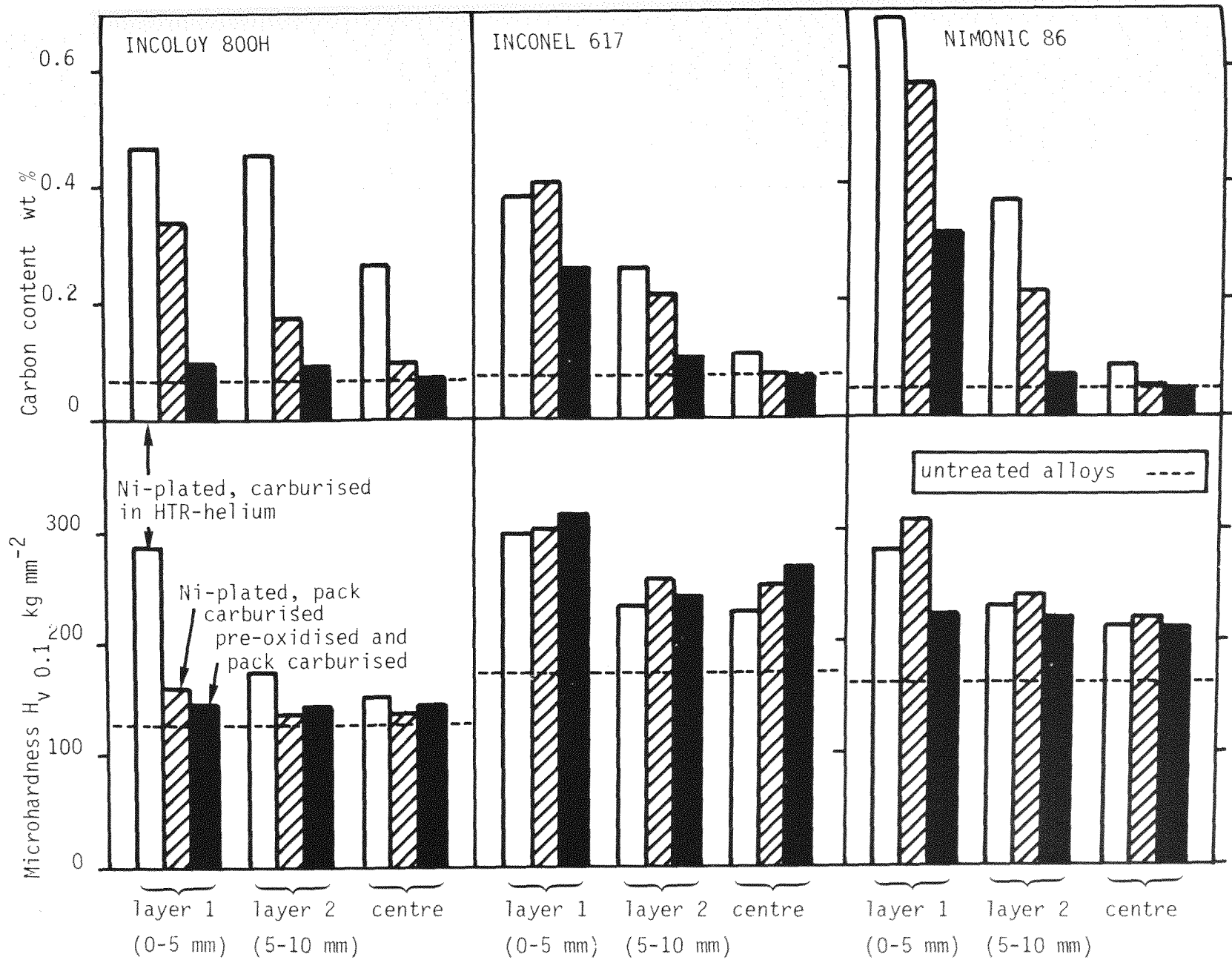
Figure 2 Carbon concentration and microhardness profiles of carburised INCOLOY 800H, INCONEL 617 and NIMONIC 86
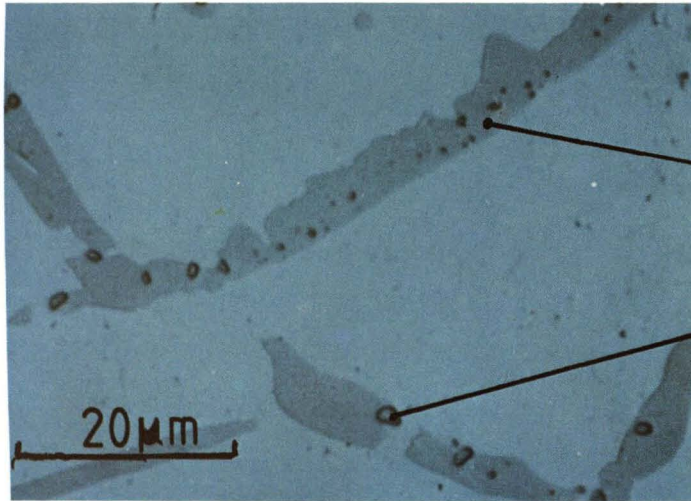
$M_{23}C_6$

$M_7C_3(?)$
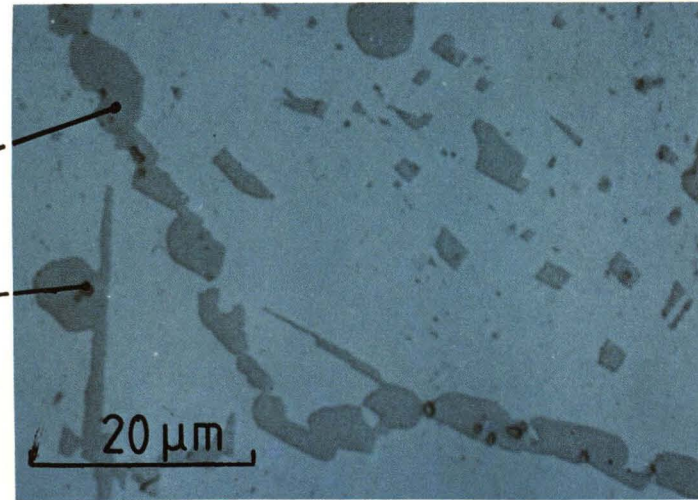
Near surface

Approx. 1 mm from surface

$M_{23}C_6$

Figure 3

Carbide structures in INCOLOY 800H
after 300 hours carburisation and
700 hours homogenisation at 950°C
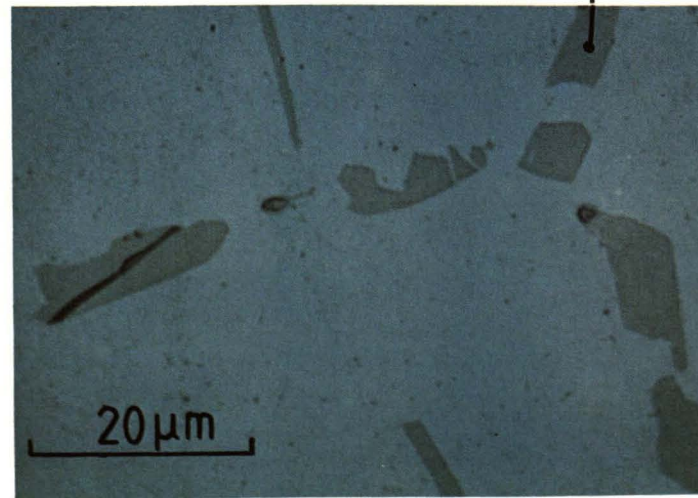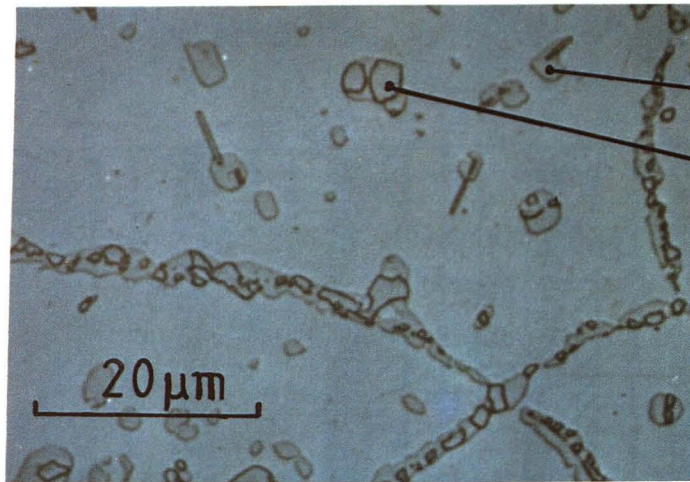
Near surface

M$_{23}$C$_6$

M$_6$C
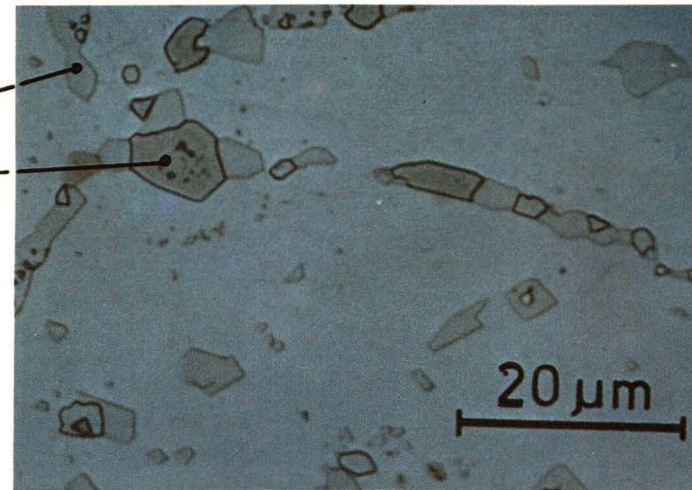
Approx. 1 mm from surface

M$_{23}$C$_6$ M$_6$C
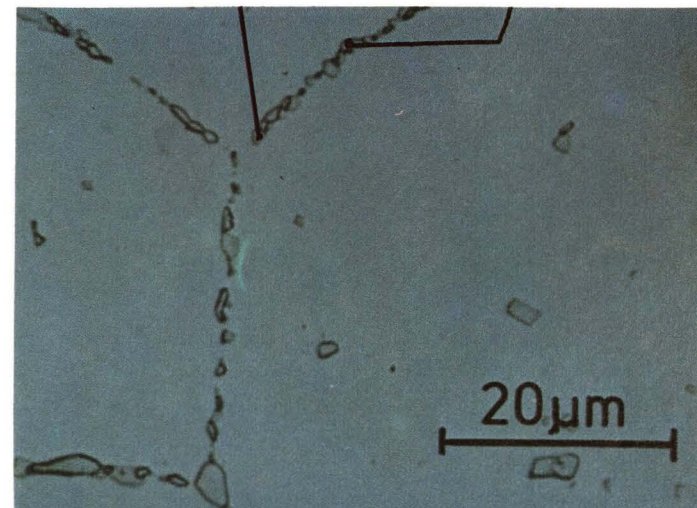
Near centre

Figure 4

Carbide structures in INCONEL 617
after 300 hours carburisation and
700 hours homogenisation at 950°C
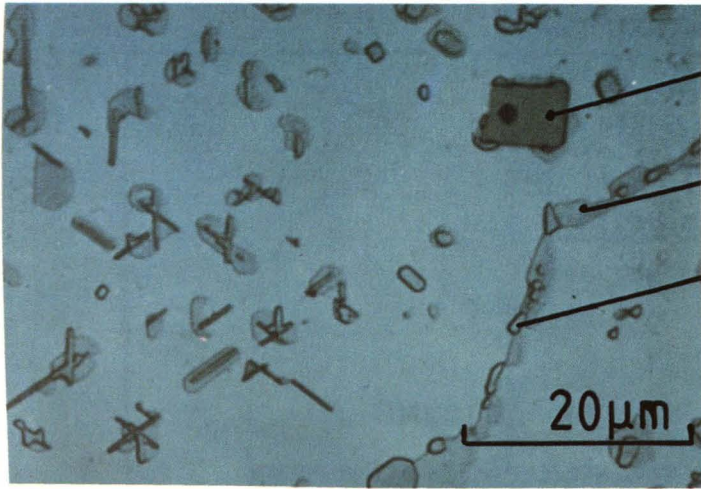
primary carbide

$M_{23}C_6$

M_6C

20μm

Near surface

20μm

Approx. 1 mm from surface

M_6C

$M_{23}C_6$

20μm
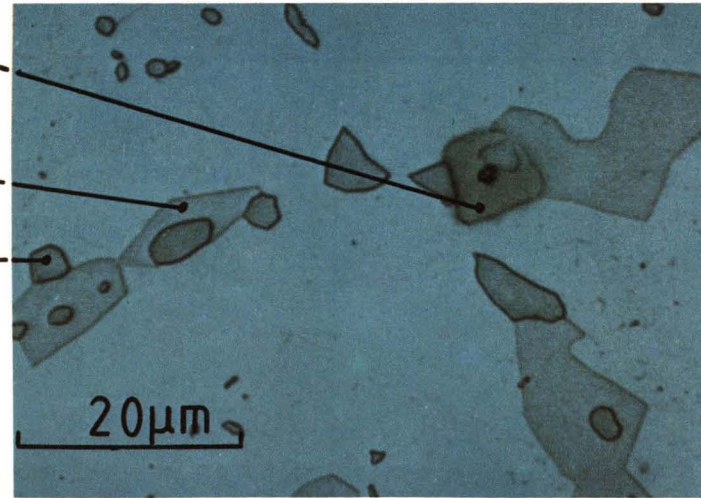
Near centre

Figure 5

Carbide structures in HASTELLOY X
after 300 hours carburisation and
700 hours homogenisation at $950^{\circ}C$

50 μm
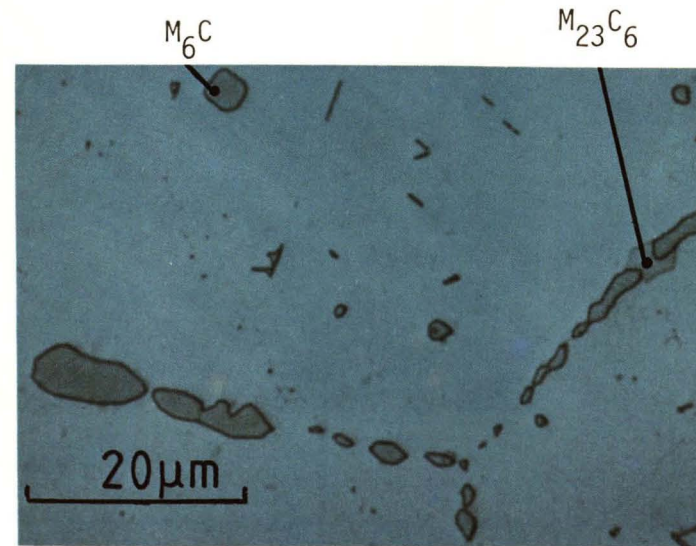
INCOLOY 800 H   INCONEL 617
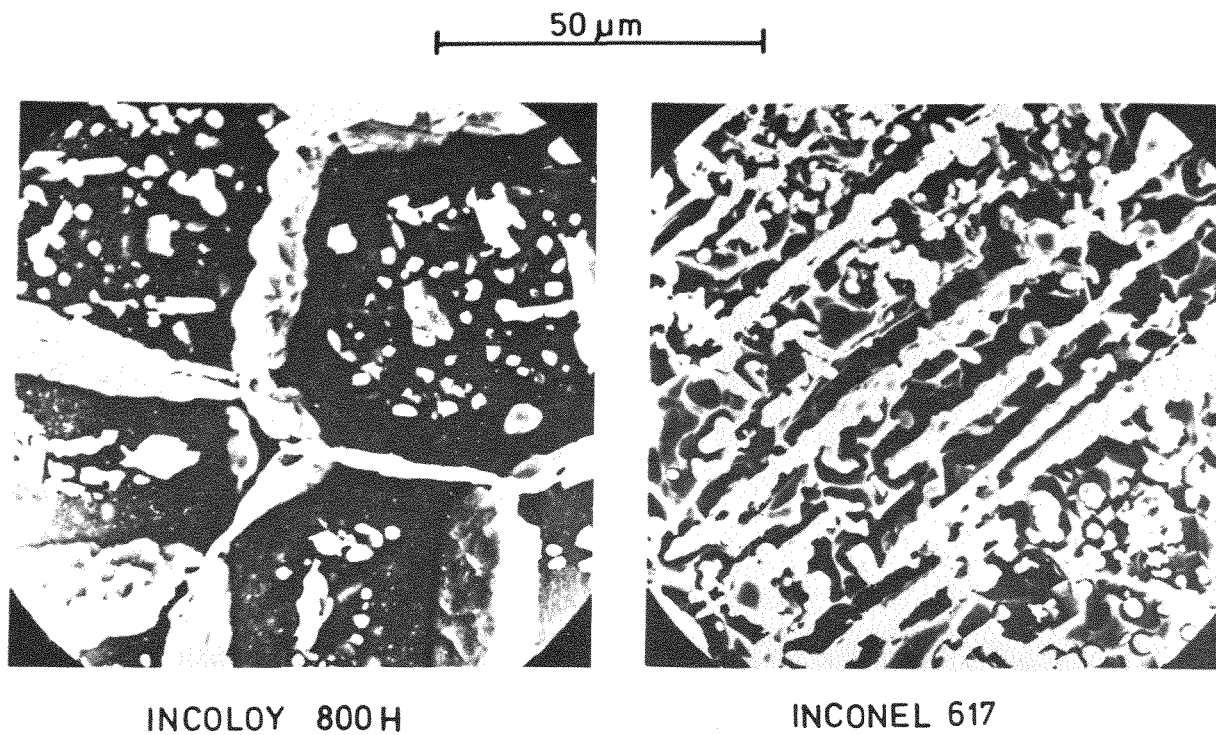
Figure 6
Scanning electron micrographs of carbide
structures in carburised INCOLOY 800H
(0,7% C) and INCONEL 617 (0,3% C) after
300 hours carburisation and 700 hours
homogenisation at 950^OC. Carbides were
revealed by deep etching
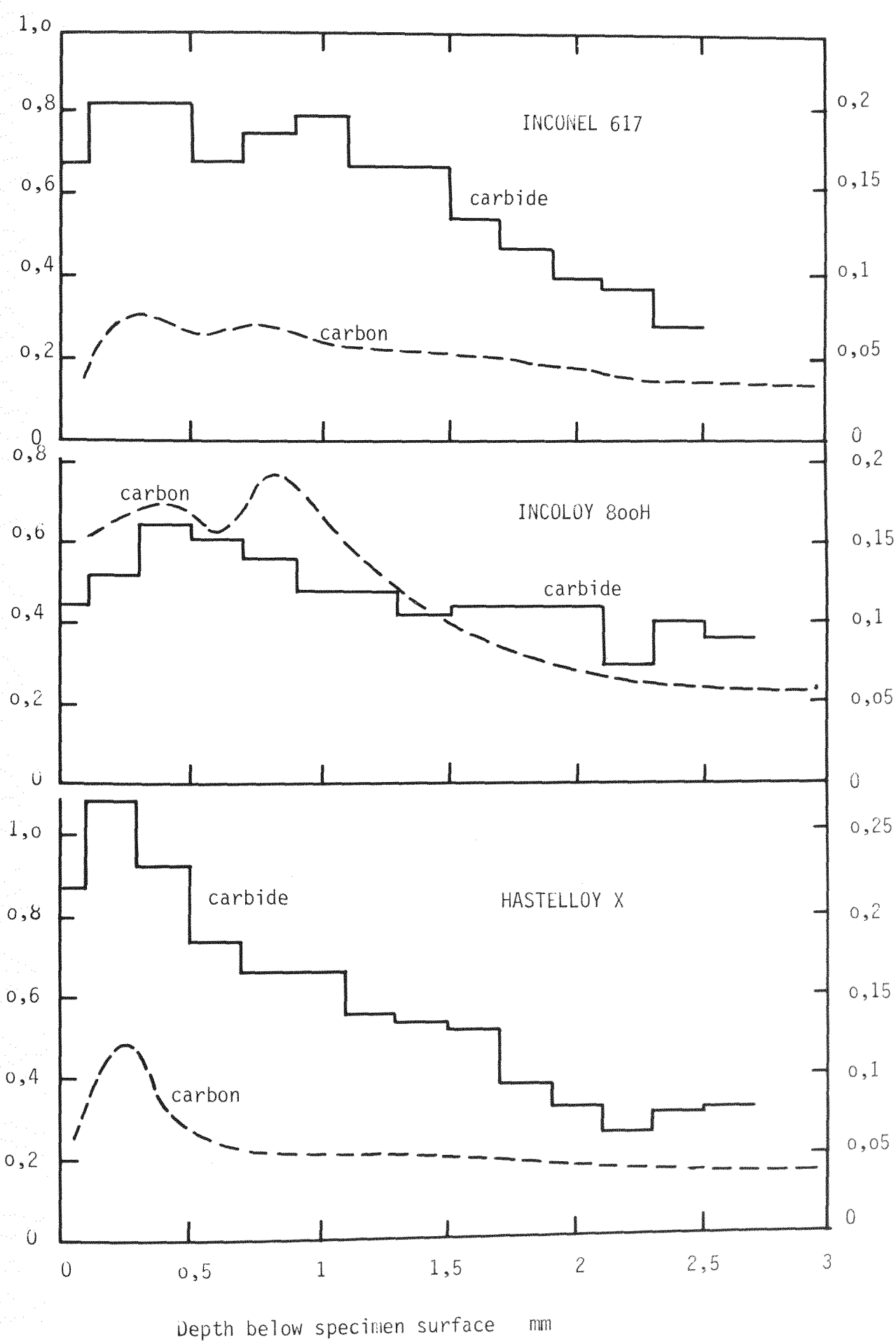
Figure 7

Carbon concentration and carbide voloume
fraction profiles for INCONEL 617, INCOLOY 800H
and HASTELLOY X after 300 h carburisation and
700 h homogenisation at 950°C
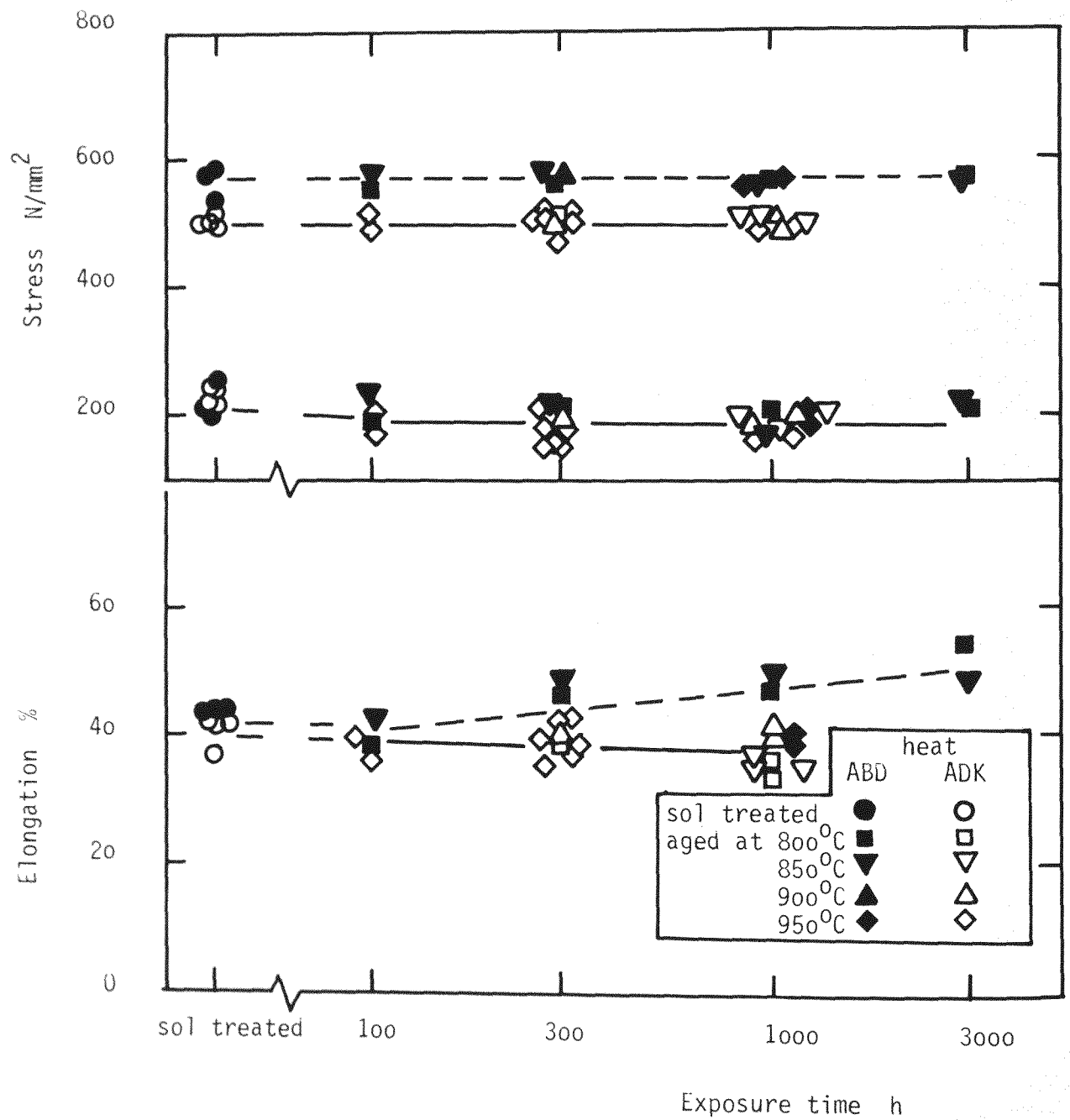
Figure 8

Effect of exposure at 800-950°C on the room temperature tensile properties of INCOLOY 800H
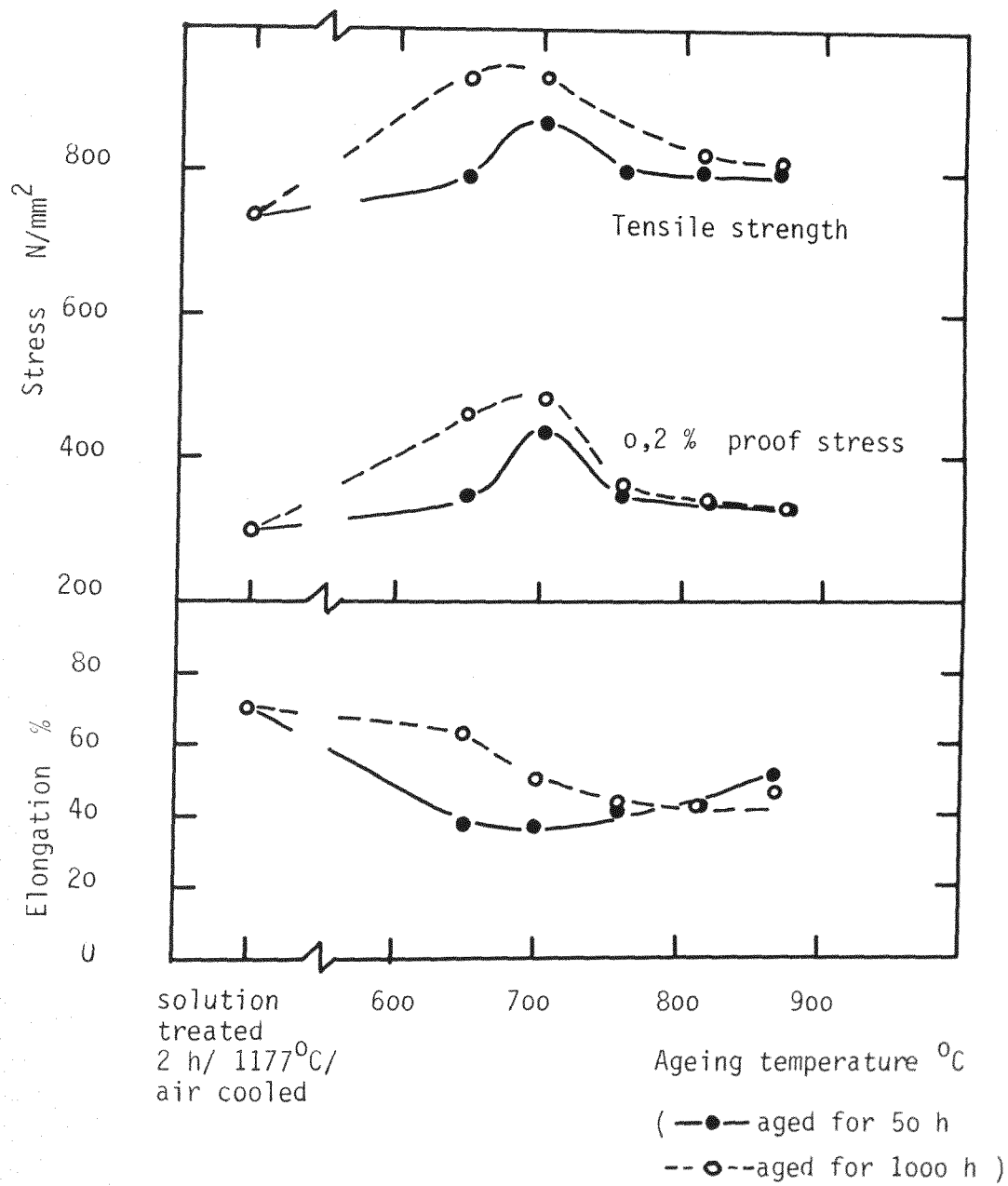
Figure 9

Effect of ageing on the room temperature tensile
properties of INCONEL 617 [17]
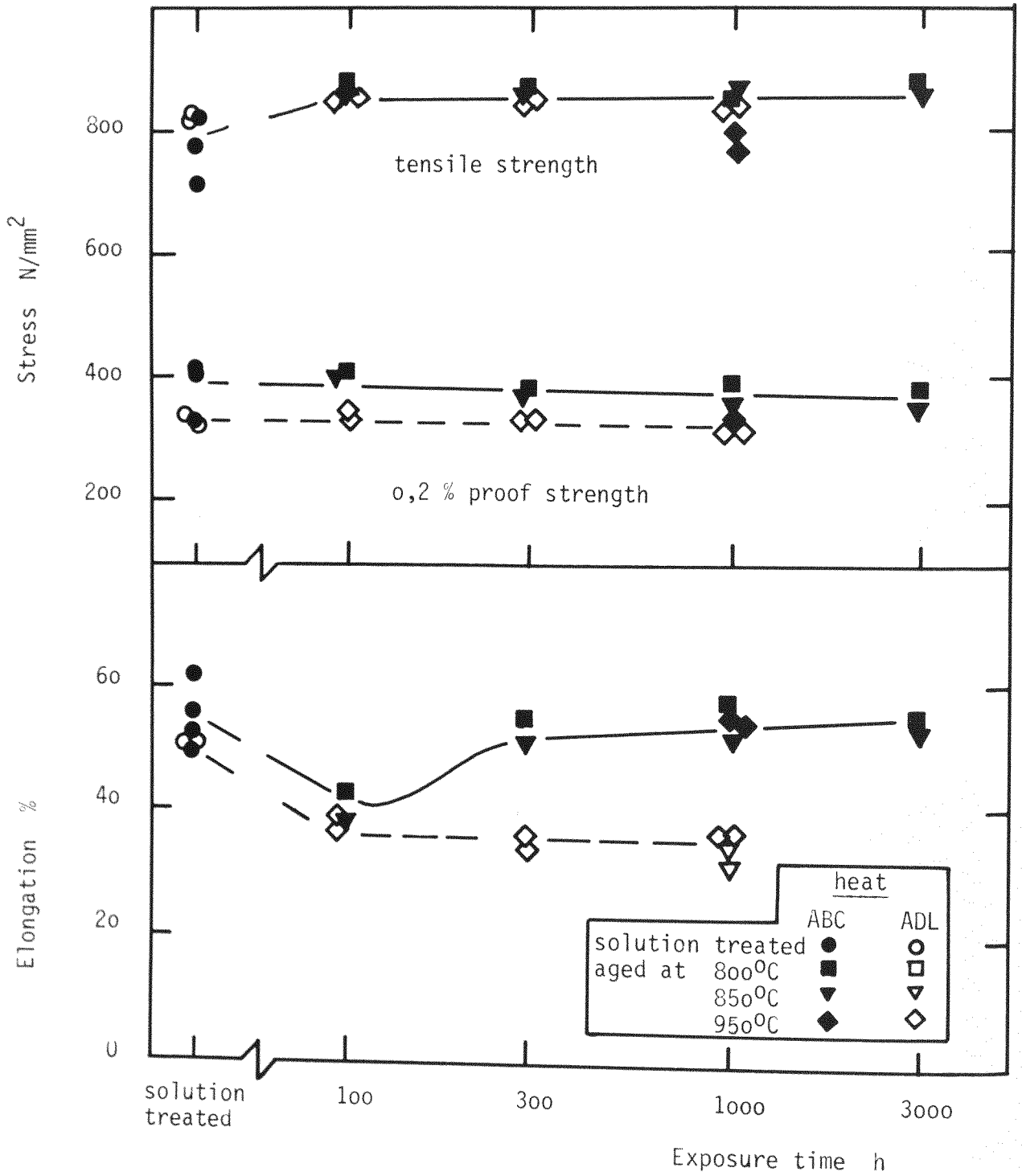
Figure 10

Effect of ageing at 800-950°C on the room
temperature tensile properties of INCONEL 617
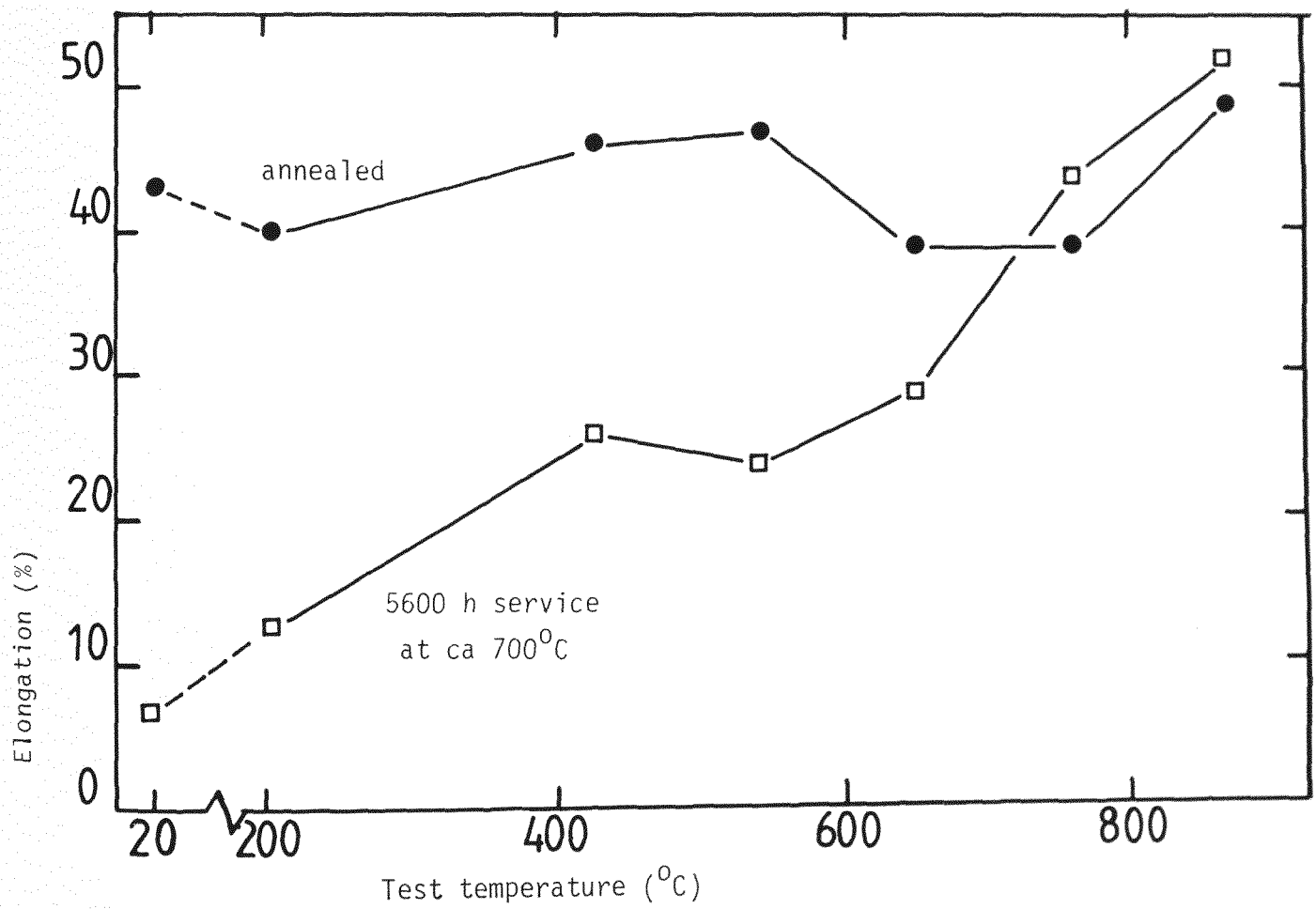
Figure 11
Tensile ductility of HASTELLOY X in
annealed condition and after 5600
hours service at around $700^{\circ}C$ [18]
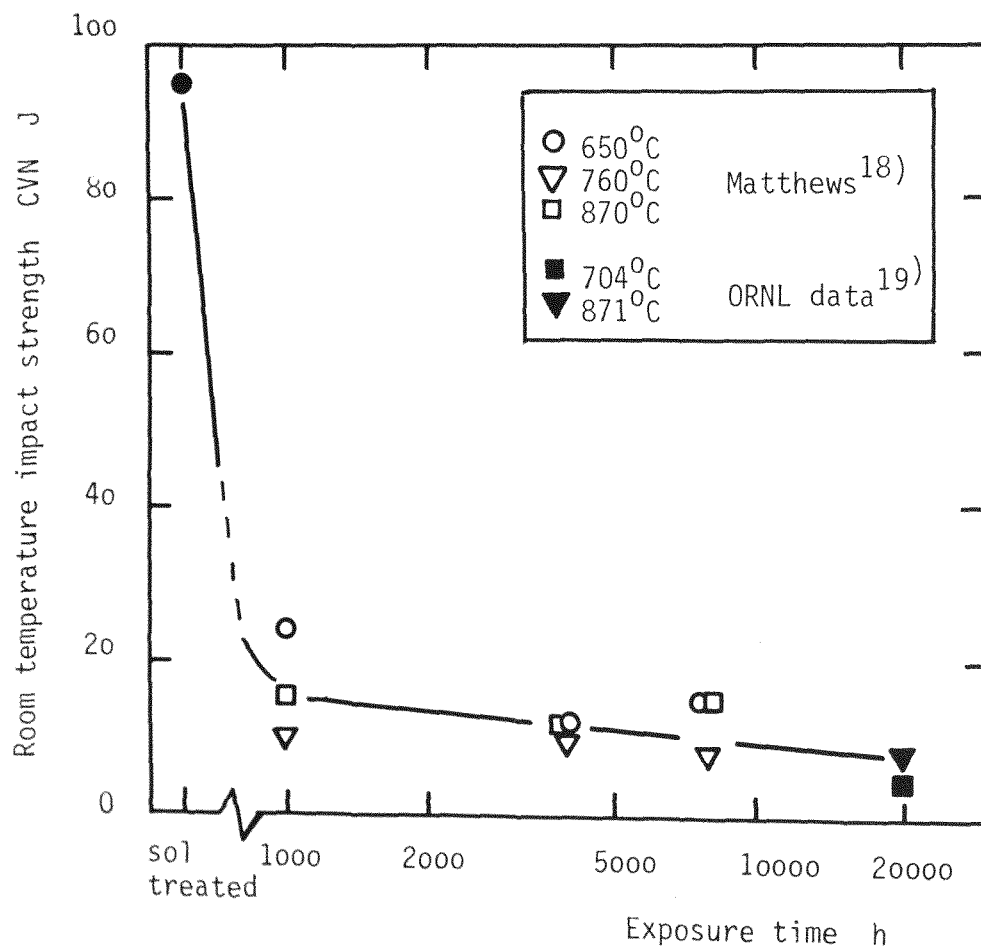
Figure 12

Effect of ageing on the room temperature impact strength of HASTELLOY X
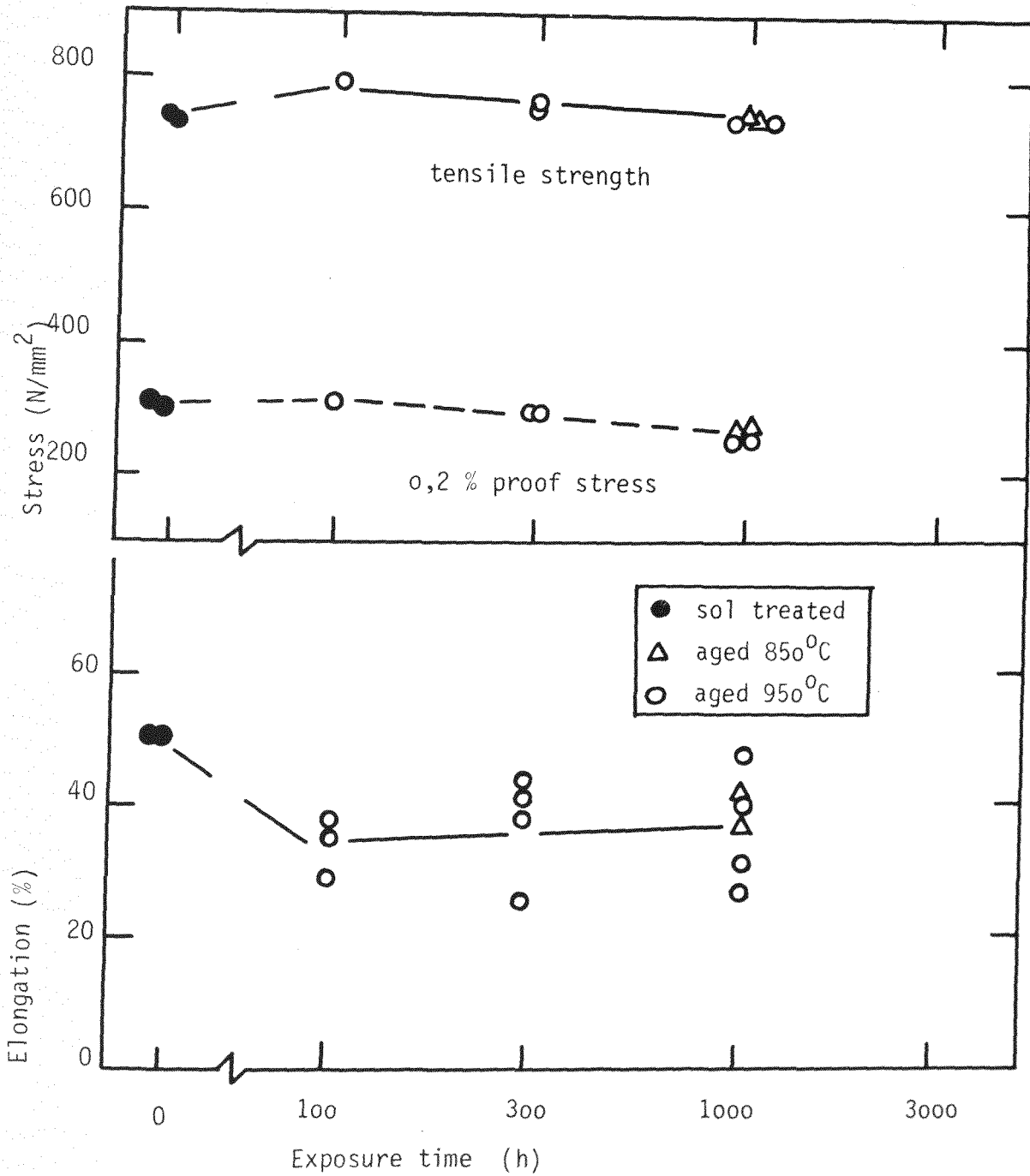
Figure 13

Effect of ageing at 800-950°C on the room
temperature tensile properties of HASTELLOY X
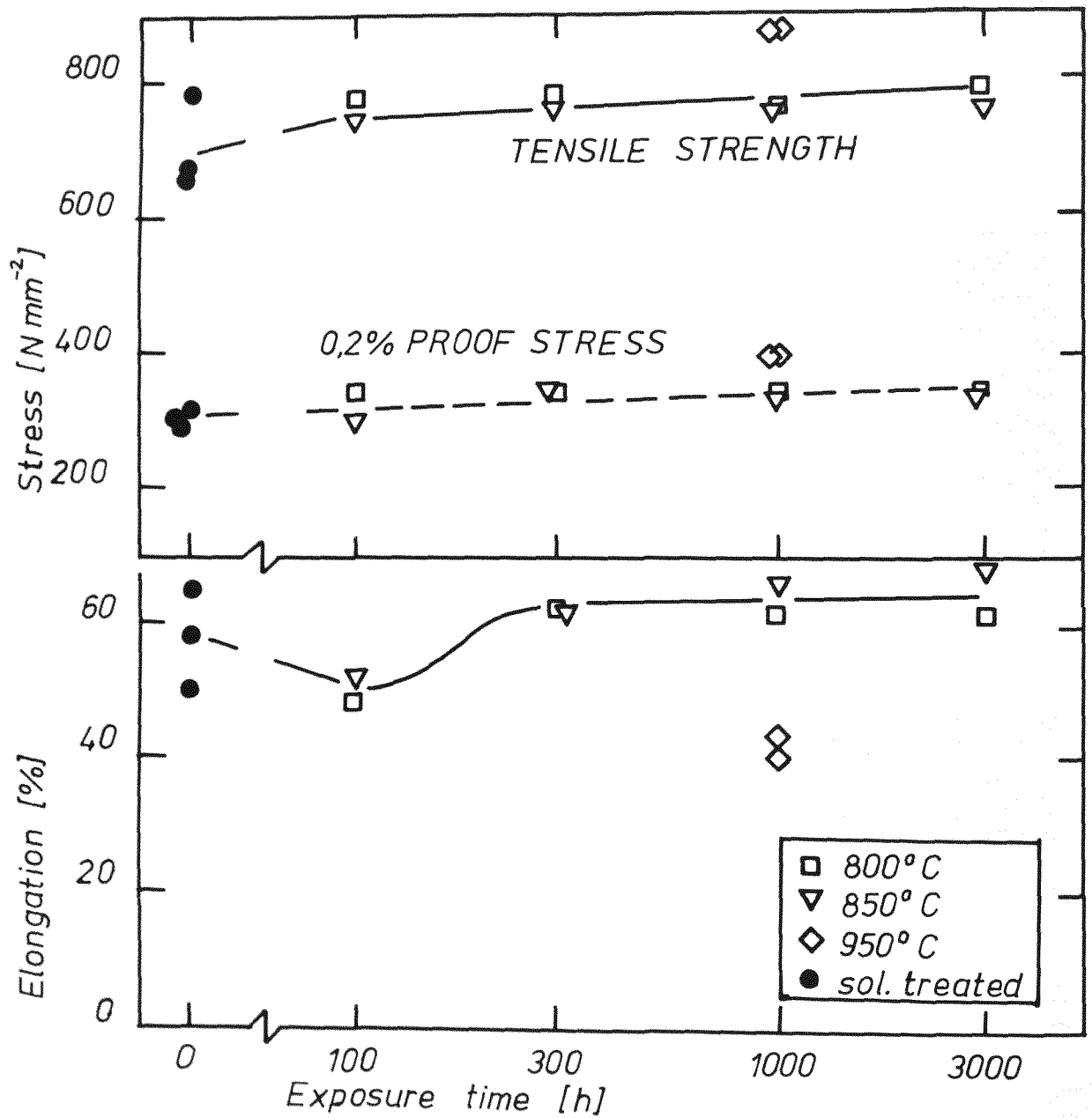
<u>Figure 14</u>

Effect of exposure at 800-950°C on the room temperature
tensile properties of NIMONIC 86
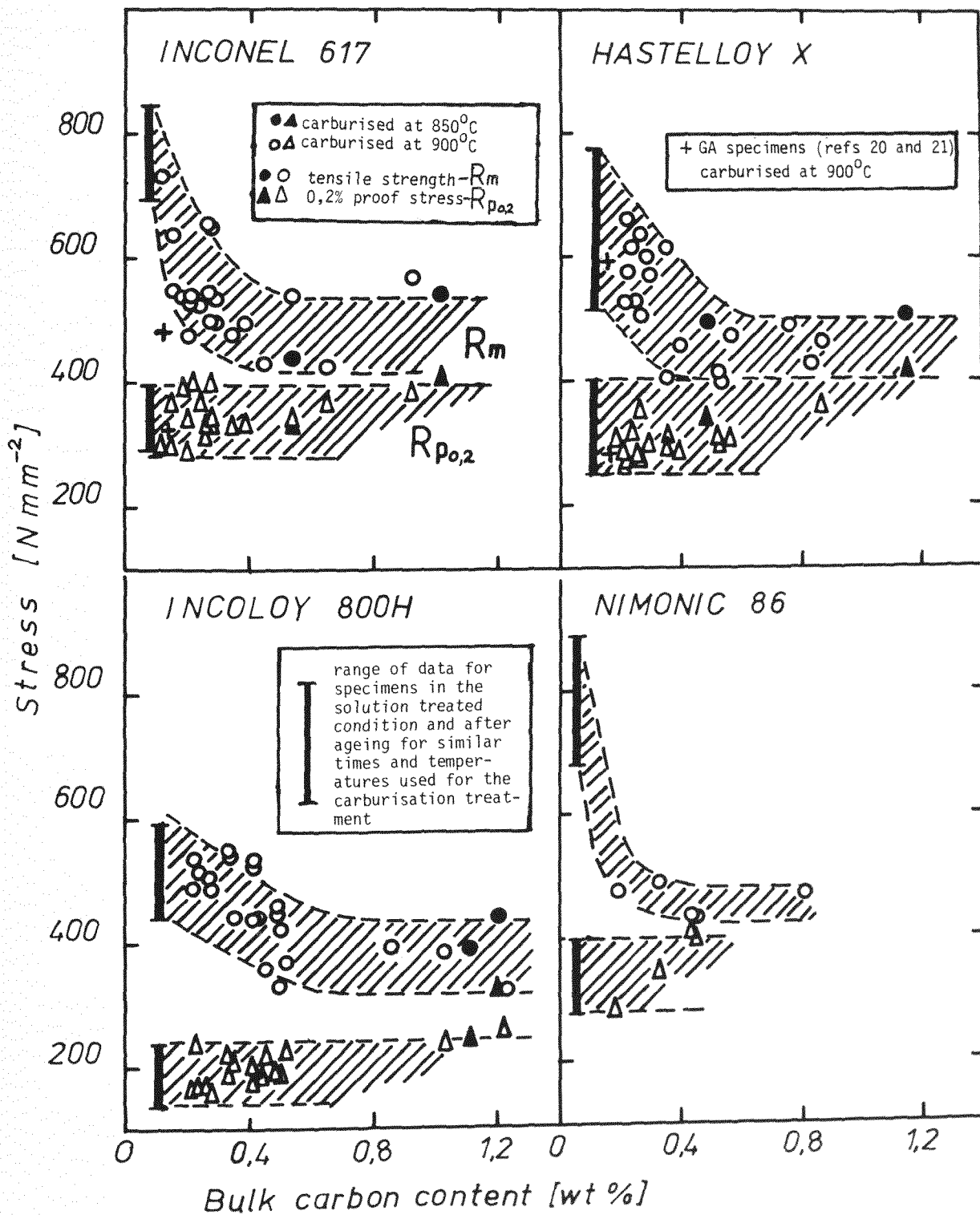
Figure 15

Relationship between room temperature strength and
carbon content for carburised INCOLOY 800H, NIMONIC 86,
INCONEL 617 and HASTELLOY X
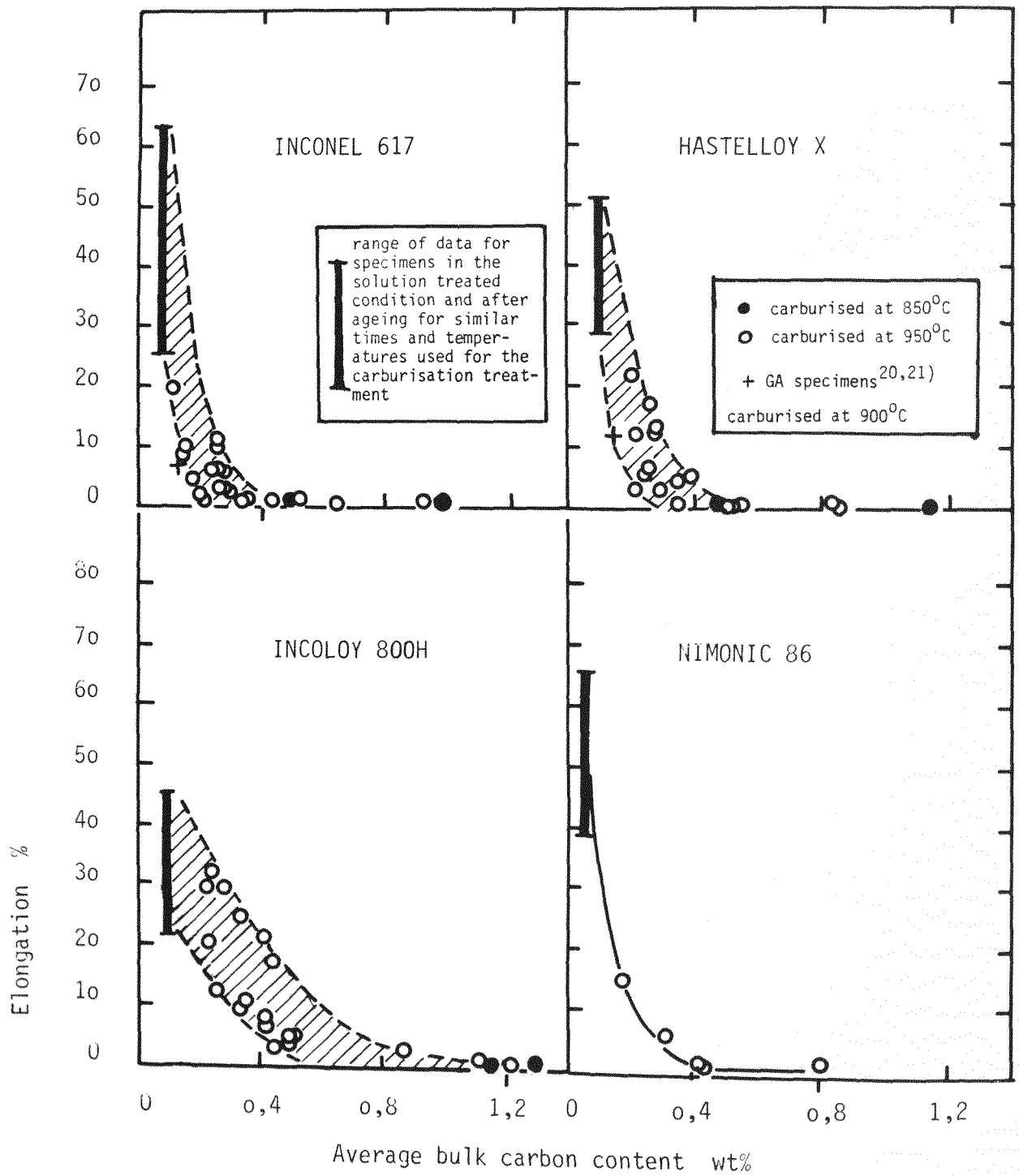
Figure 16

Relationship between room temperature elongation and
carbon content for carburised INCOLOY 800H, NIMONIC 86,
INCONEL 617 and HASTELLOY X
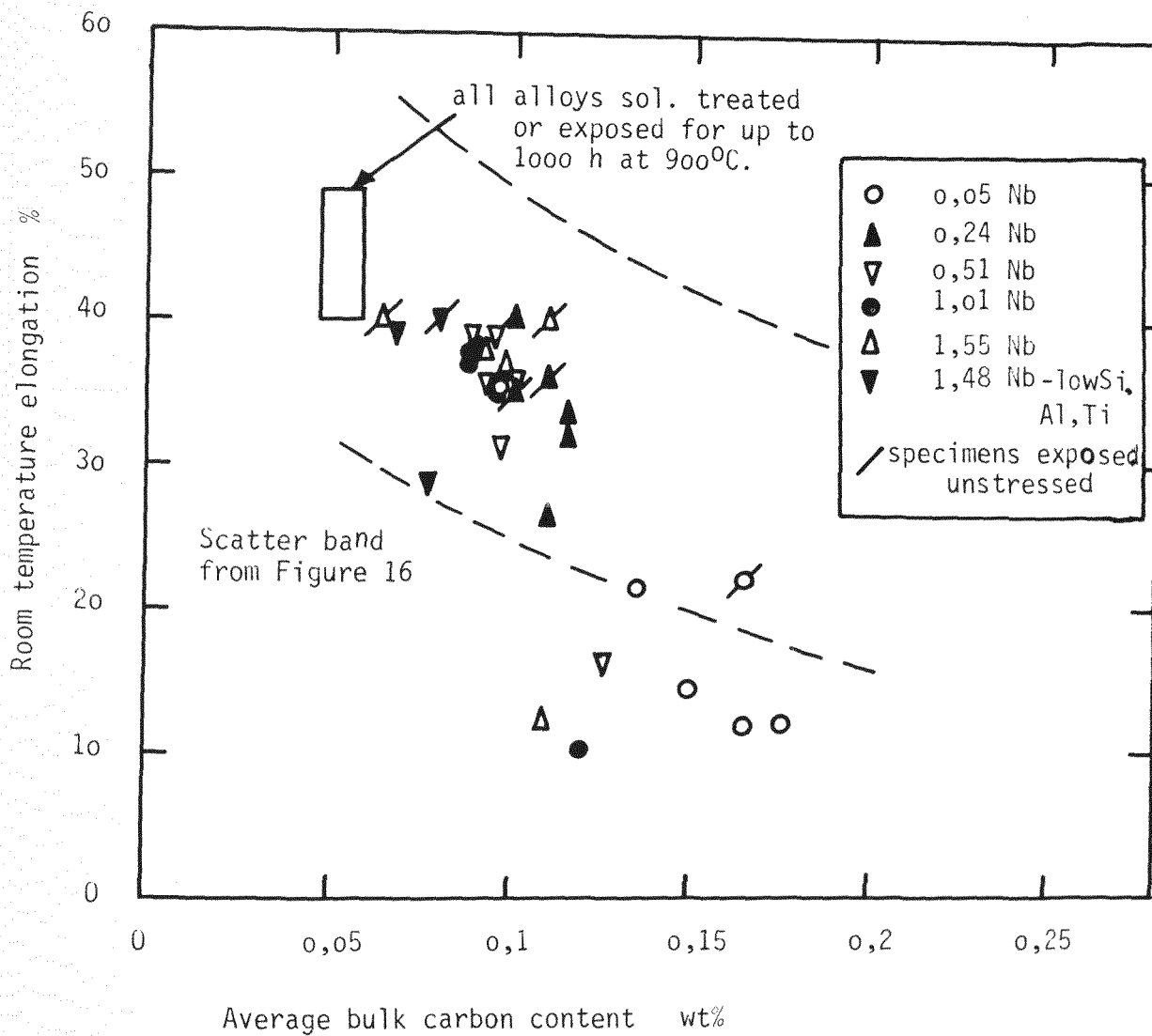
Figure 17

Relationship between room temperature elongation and
carbon content for carburised INCOLOY 800 modified
with niobium additions
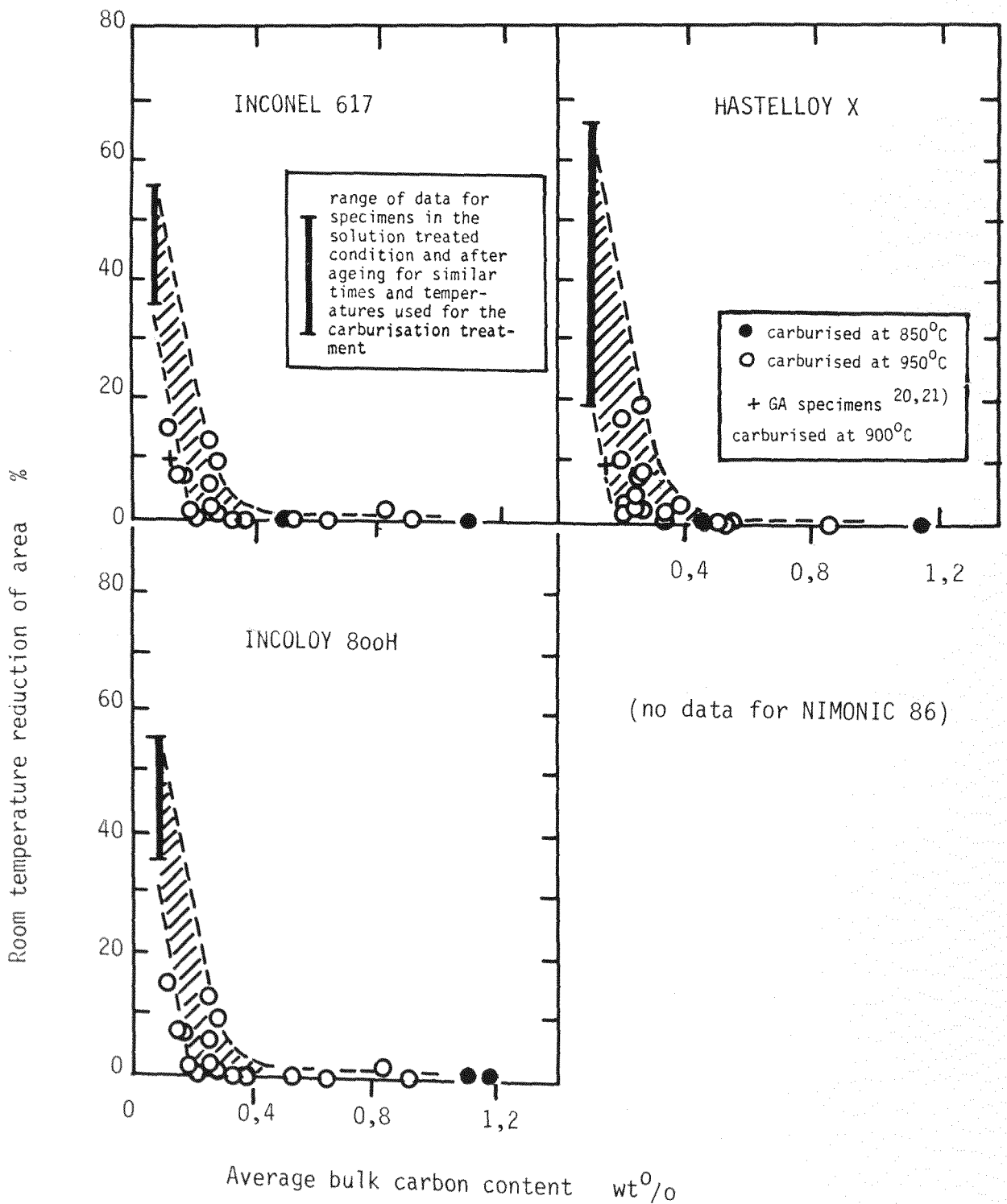
Figure 18

Relationship between room temperature reduction of
area for carburised INCOLOY 800H, INCONEL 617 and
HASTELLOY X
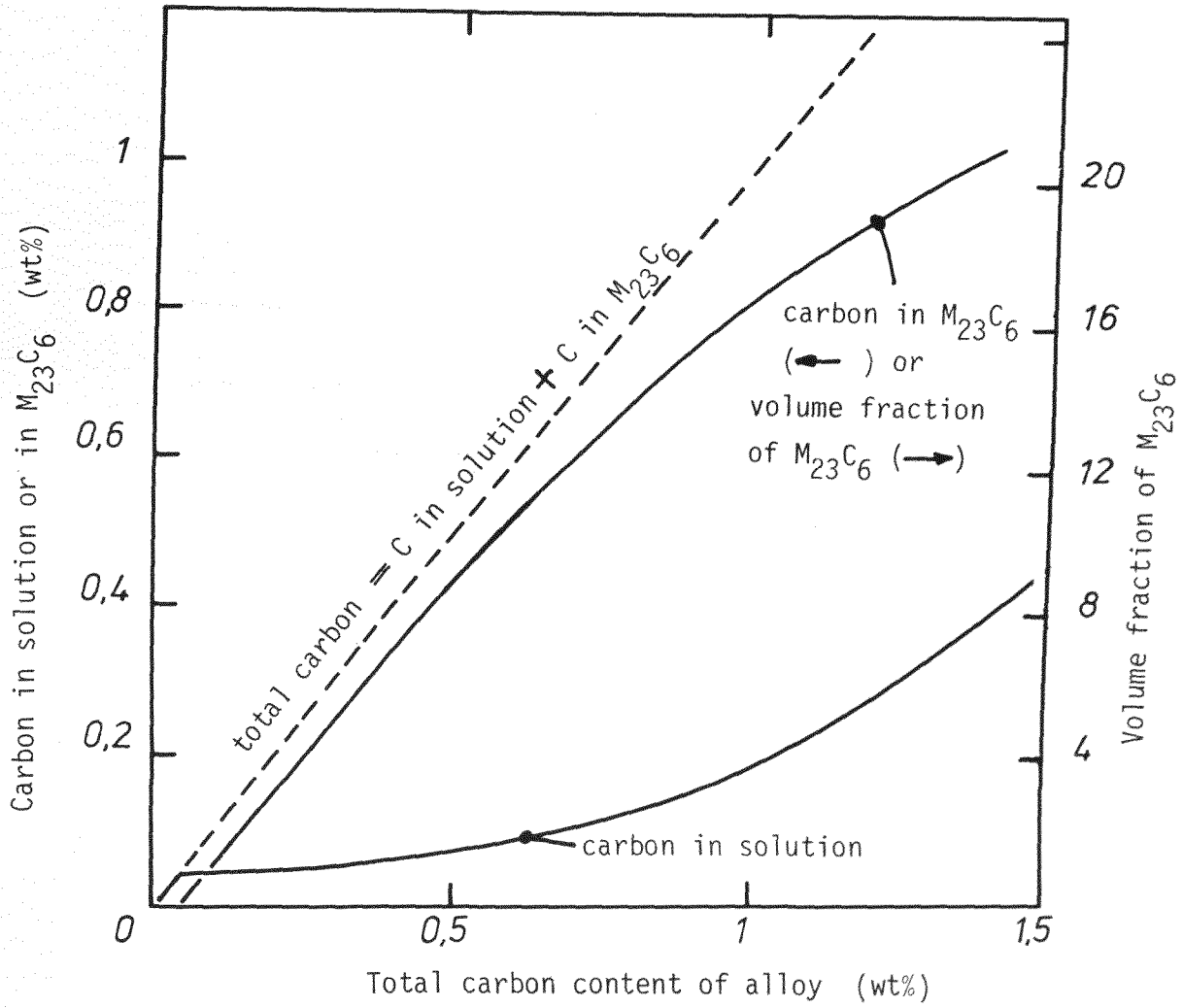
Figure 19

Relationship between carbon solubility in the matrix and carbon in the $M_{23}C_6$ carbide for an Fe-20%Cr-32%Ni alloy at 950°C. The expected volume fraction of $M_{23}C_6$ is also shown.
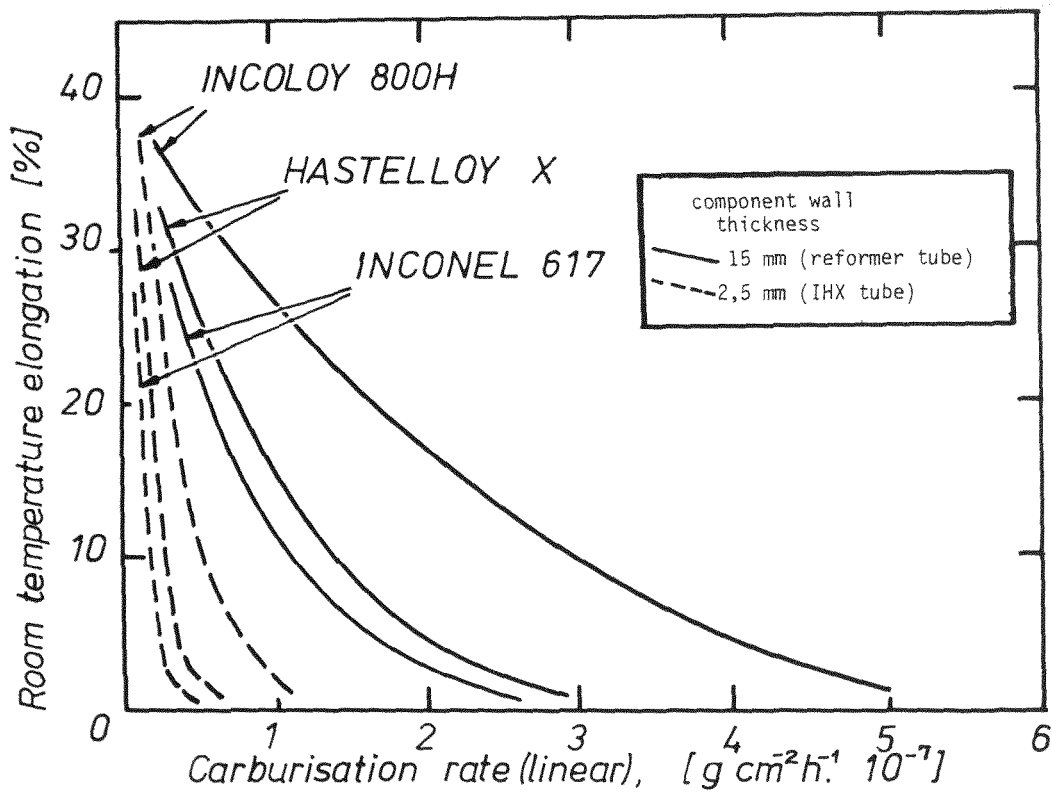
Figure 20

Predicted average room temperature elongations of
INCOLOY 800H, HASTELLOY X, and INCONEL 617 components
after 140 000 hours at 950°C as a function of linear
carburisation rate (based on the ductility vs carbon
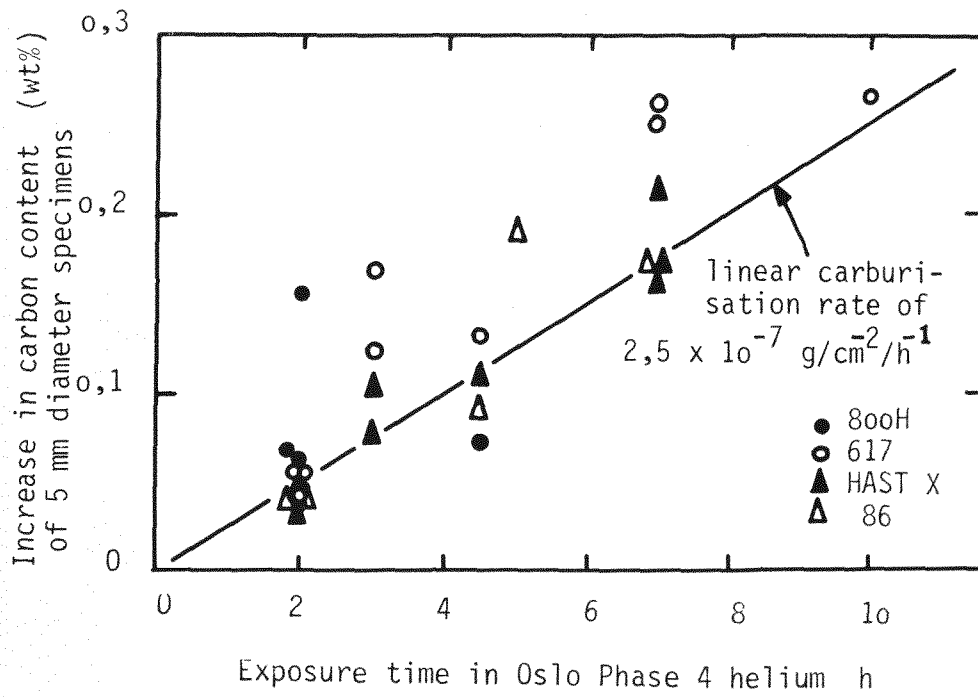content curves shown in Figure 16)

Figure 21

Carburisation of INCOLOY 800H, INCONEL 617, HASTELLOY X
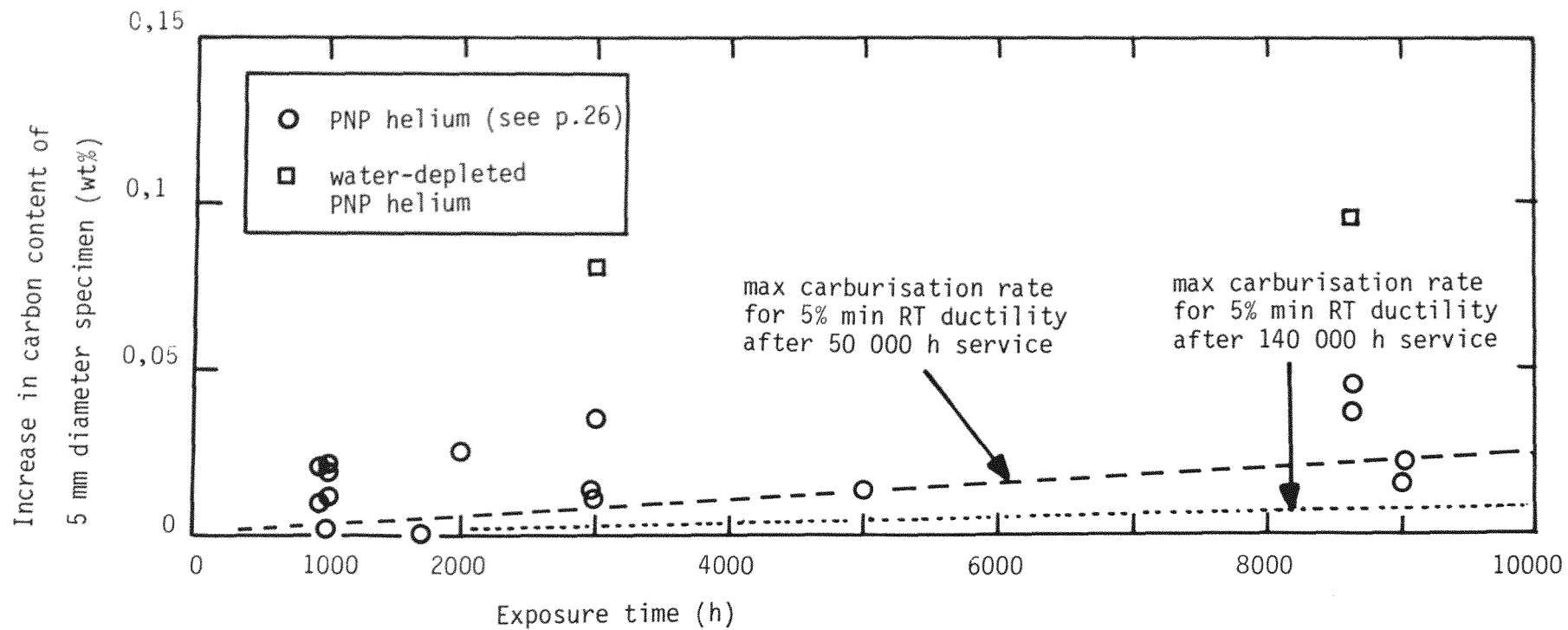and NIMONIC 86 in Oslo Phase 4 HTR helium at 900°C

Figure 22

Carburisation of INCONEL 617 in PNP standard helium and water depleted ($<$0,1 ubar) PNP standard helium at 900°C. Maximum carburisation rates for retention of 5% minimum room temperature ductility after service times of 50 000 and 140 000 hours are indicated (based on the carbon content vs ductility curves shown in Figure 16). Data from reference 40 and KFA/IRW tests.