

A COMPUTATIONAL MODEL FOR THE CARBON TRANSFER IN STAINLESS STEEL SODIUM SYSTEMS

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ABSTRACT

It is proposed a method of computing the carbon transfer in the type 316, 304 and 321 stainless steels in sodium environment as a function of temperature, exposure time and carbon concentration in the sodium.

The method is based on the criteria developed at ANL by introducing some simplifications and takes also into account the correlations obtained at WARD.

Calculated carbon profiles are compared both with experimental data and with the results available by the other computer methods.

The limits for quantitative predictions of the stainless steel carburization or decarburization exposed in a specific environment are discussed.

1) - INTRODUCTION

When exposed in high temperature liquid sodium the stainless steels can undergo carburization or decarburization¹⁻¹⁵. The driving force of the process could be in principle obtained from the thermodynamic functions of the carbon species present in all phases of the system, while the carbon transfer kinetics is characterized by its interstitial diffusion in the steel matrix accompanied by the precipitation or the dissolution of carbides^{2,3}. The dynamic conditions of the flowing sodium seem to play a minor role on the process³⁻⁸.

In pumped sodium loops the "local" carbon uptake or release by the piping materials depend on the carbon concentration in sodium (C^{Na}), assumed to be the

same in the different components of the loop) and essentially on the "local" temperature⁴. Under steady-state conditions, carbon migrates from the highest carbon activity regions where decarburization occurs to the lowest carbon activity zones (which undergo carburization).

It is of considerable interest to get a model for quantitative predictions of carbon diffusion in steels under chemically characterized sodium environment. Snyder, Natesan and Kassner (ANL)³ developed a generalized method for computing carbon concentration-distance profiles for the austenitic reactor steels type 304 and 316 exposed in sodium as function of time, temperature and C^{Na} . The calculation is based on the thermodynamic expressions relating the activity of carbon in sodium (a_{C}^{Na}) to the activity in the steel (a_{C}^{SS}) and to the concentration of carbon at the sodium/steel interface (C^*). Moreover this model takes into account the precipitation kinetics of the chromium rich carbide $(\text{Cr, Fe})_{23}\text{C}_6$ in the biphasic diffusion problem and allows to consider the effect of the thermo-mechanical history (solution annealed versus cold worked) of the steels on the carbon transfer kinetics.

By following a more direct empirical approach, Shrock, Shiels and Bagnall (WARD)⁸ developed a method based on a standard tab-equilibration technique to measure the "carbon potential" C_s (defined as the equilibrium carbon content in the steel after its exposure at 704°C in the sodium of the system under examination) by which C^* can be evaluated in the different zones (having different temperatures) of the sodium loop.

These authors performed the calculation of the shape and depth of the carbon gradients by assuming that carbon transport within the alloy is entirely bulk diffusion.

In this work a method is proposed to evaluate the carbon transfers in austenitic steels exposed in sodium of known carbon content. This method includes the ANL approach only to obtain C^* . This important boundary parameter is alternatively evaluated calculating (instead of measuring) C_s and then by using the WARD's correlations.



2) - EFFECTIVE DIFFUSION COEFFICIENTS.

By assuming the one-phase diffusion problem to be formally valid provided an effective diffusion coefficient (D_{eff}) obtained by experimentally determined carbon concentration-distance profiles is used, the carbon profiles can be produced in simplified mathematical form. For example in the semi-infinite case the carbon concentration (C) as a function of both the distance (x) from the sodium/steel interface and the exposure time (t) is given the well-known erf function (y) of equation (1):

$$y = (C^* - C)/(C^* - C^0) = \text{erf}(x/(2\sqrt{D_{\text{eff}}t})) \quad (1)$$

C^0 being the original carbon concentration in the steel.

The D_{eff} parameter is generally obtained by best-fitting procedures to match y with the experimental profiles. Our computer technique based on the least-square method was found to work satisfactory for the analysis of the decarburization of the low alloyed $2\frac{1}{4}$ Cr-1Mo ferritic steel above 550°C as shown in the example of Fig.1.

Equation (1) was also found to be roughly representative of the carbon gradients observed in sodium exposed austenitic steels^{4,7,8}. Fig.2 reports as an example our best fit analysis of the experimental points reported by Plumlee and Lauritzen (GE)⁴ referring to the carburization of the type 316 SS at 533°C placed both upstream and downstream the carbon source in an isothermal test section.

Some D_{eff} values concerning the carburization of types 316^{1,4,6}, 304¹⁴ and 321¹ stainless steels are plotted versus temperature in Fig.3 with other values reported elsewhere^{4,7}. Among the available diffusion coefficient-temperature functions the relations reported by Walker¹⁰ for the 316 SS and by Anderson and Sneesby¹¹ for the 304 SS, seem to be the best ones to describe the carburization process for the austenitic steels.

On the other hand sufficient evidence exists to indicate that the functions of Ref.8 (the lines 3 and 4 in Fig.3, close to the true carbon diffusion equations 5 and 6, Ref.3, 18) could better describe the decarburization process^{3,8,12}

3) - THE GENERATION OF CARBON-DEPTH PROFILES.

The carbon activity in sodium is assumed to follow the Henry's law (2):

$$a_{\text{C}}^{\text{Na}} = C^{\text{Na}}/S \quad (2)$$

S being the solubility of carbon in sodium. According to Longson and Thorley¹³

$$S(\text{ppm}) = 5.03 \cdot 10^7 \exp(-13740/T(^{\circ}\text{K})) \quad (3)$$

Since at the stainless steel/sodium interface the thermodynamic equilibrium is assumed to be established it follows $a_{\text{C}}^{\text{SS}} = a_{\text{C}}^{\text{Na}}$ (4). The correlation between a_{C}^{SS} and C^* is given by the self-consistent set of thermodynamic relations reported in the Appendix A of Ref.3.

On the basis of the TTP behaviour the average solute carbon concentration (\bar{C}) in the austenite can be obtained by means of an appropriate computer subroutine³ for the temperature and exposure time specified as well as for the given microstructural parameters about geometrical characteristics of the carbide phase.

The carbon gradients considered for the diffusion problem were those concerning only the dissolved carbon in the austenite, the total carbon profiles being finally obtained by adding the carbide-segregated carbon.

In such a way C_s is also calculated to get a further evaluation of C^* by using the WARD's correlations (5) and (6) for the types 304 and 316 stainless steels respectively

$$\log_{10}(C^*/C_s) = 3.76389 - 0.005315 T(^{\circ}\text{C}) \quad (5)$$

$$\log_{10}(C^*/C_s) = 2.960524 - 0.004163 T(^{\circ}\text{C}) \quad (6)$$

In this last case the carbon profiles are produced by the direct application of the equation (1). The analysis in both cases is also performed for the finite wall specimens as required when the carbon gradient depths become comparable to the thickness of the exposed alloy. This computing technique is extended to type 321 stainless steel by simply taking into account the carbon gettered by the precipitated TiC carbide during the solution annealing treatment. If the solution treatment occurs at the temperature T_s the solute carbon can be evaluated by

knowing the original carbon and titanium composition and the carbide solubility law. We adopt an average value resulting from the crossing points of the stoichiometric Ti to C ratio line starting from the original composition point with the solubility products given by the relations (7)¹⁶ and (8)¹⁷ in the Ti-C solubility diagram.

$$\log_{10}((\text{Ti}\%)(\text{C}\%)) = - 8900/T_s(^{\circ}\text{K}) + 4.46 \quad (7)$$

$$\log_{10}((\text{Ti}\%)(\text{C}\%)) = - 6880/T_s(^{\circ}\text{K}) + 2.52 \quad (8)$$

During the exposure time in the sodium environment the only precipitating carbide is then assumed to be the $(\text{Fe,Cr})_{23}\text{C}_6$ with the same procedure employed for the type 316 SS.

4) - RESULTS AND DISCUSSION

It must be recalled that the ANL model and hence also the present reduced version, cannot be applied when the carbon concentration in the steel is more than 1.0%³. This condition implies a limit for the carbon concentration in sodium which cannot exceed about 2 ppm in many practical cases. On the other side the extrapolation of the thermodynamic correlations involved in the computation to very low carbon activity levels seems to give few allowances⁸. We compare calculated profiles with experimental data concerning some carburized stainless steels under sufficiently defined environmental conditions^{1,4,6,14}.

The reproduced carbon profiles were found to roughly follow the experimental trends, and in any case the results are comparable to those obtained by the complete ANL code³ (see the examples reported in Fig.4 and 5) while a drastically reduced computer time was needed.

The calculation based on the WARD's criteria was found to give C^* values in acceptable agreement with those directly calculated by the ANL model. This result confirms how the WARD's empirical approach⁸ is supported by pure thermodynamic correlations within the reasonable uncertainty joined to the available thermodynamic functions.

In the examples reported in Fig.4 and Fig.5 the profiles obtained by the ANL code (dotted lines) are compared with those resulting by the simplified method pro-

posed here (full lines) by using the D_{eff} following Walker¹⁰. The pointed lines are the carbon profiles resulting by the WARD's correlations (but with a different choice of D_{eff}).

For the type 321 steels the assumed simple criteria seems to reasonably work on some available experimental data were the carburization of such a steel is compared to the behaviour of the type 316 steel specimens placed in the same sodium loop^{1,6} (see the example in Fig.6).

Quantitative long-term predictions (several years) of carbon diffusion under specific environmental conditions by these computer methods have to be used with many cautions especially out of the 650-550°C temperature field where the confidence level was found to be hardly sufficient.

In fact at higher temperatures the chromium and nickel depletion occurring at the austenitic alloy surface induces a carbon level decrease in such a zone^{14,15} (see the results reported by Natesan¹⁴ some of which are plotted in Fig.4). The observed inhibition of the carburization of the stainless steel with time was ascribed by Schneider, Borgstedt and Frees¹⁵ to the ferritic layer growing in the Ni-depleted zone during the exposure in sodium at 700°C.

On the other side at lower temperatures the microstructure of the steel plays a considerable role on the carbon transfer kinetics^{1,3,7,8}, while the available thermodynamic functions and diffusion coefficients have to be extrapolated out of the temperature range for which they were verified.

For most of the environmental conditions conservative predictions can be however obtained by the proposed model.

5) - CONCLUSION AND FUTURE WORK

A method for rapid computing of carbon diffusion profiles has been obtained by simplifying the sophisticated model developed in ANL³. The simplification basically consists in the assumption that the rate of the interstitial transfer is controlled by a single-phase-like diffusion and incorporating into an "effective" diffusion coefficient parameter the effects of the involved solute carbon-carbide reactions coupled to the true carbon diffusion.

Within some specified limits, the calculated profiles were found to roughly fit the experimental data under carburizing conditions.

Since the results obtained for the type 321 stainless steel, by introducing few modifications were encouraging, we are now examining the capability of such models to describe the behaviour of the alloy-800 (also a Ti-stabilized austenitic alloy) under carburizing and decarburizing sodium environments.

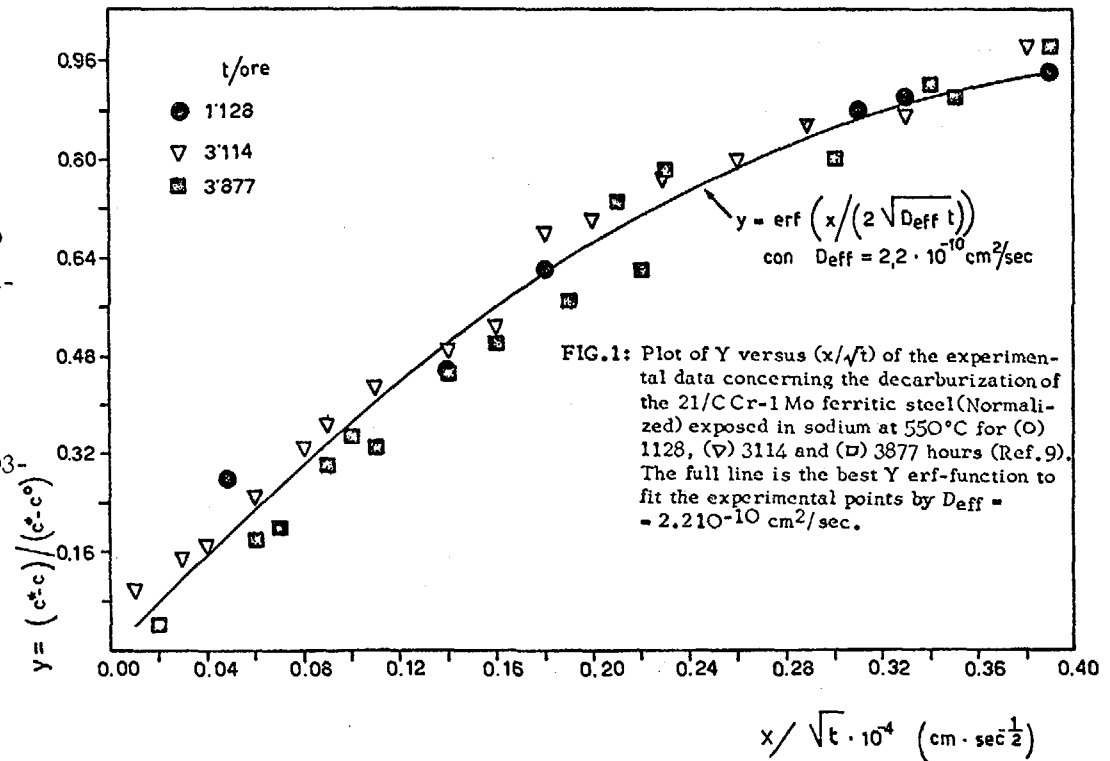
At the CNEN material lab the experiments are going on to characterize two series of six nuances of alloy-800 with different Ti/C ratio by both mechanical and microstructural tests to achieve TTP and TTS diagrams, while carbon transfer experiments are conducted at present mainly by capsule test, the type 304 SS foils being employed to detect the carbon activity in sodium or as a reference material. Since crack initiation and propagation may depend on the alterations at the surface of the alloy produced by the environment, tests under applied stress are also programmed by using a new many-pots static sodium plants recently installed at the Casaccia Nuclear Centre.

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2 1/4 Cr-1 Mo Normalizzato - Esposto in sodio a 550°C
(dai dati di Natesan, Chopra, Kassner (ANL))



AISI 316 Esposto in sodio a 533°C saturato in carbonio
(dal dati di Plumtree e Lauritzen (G.E.))

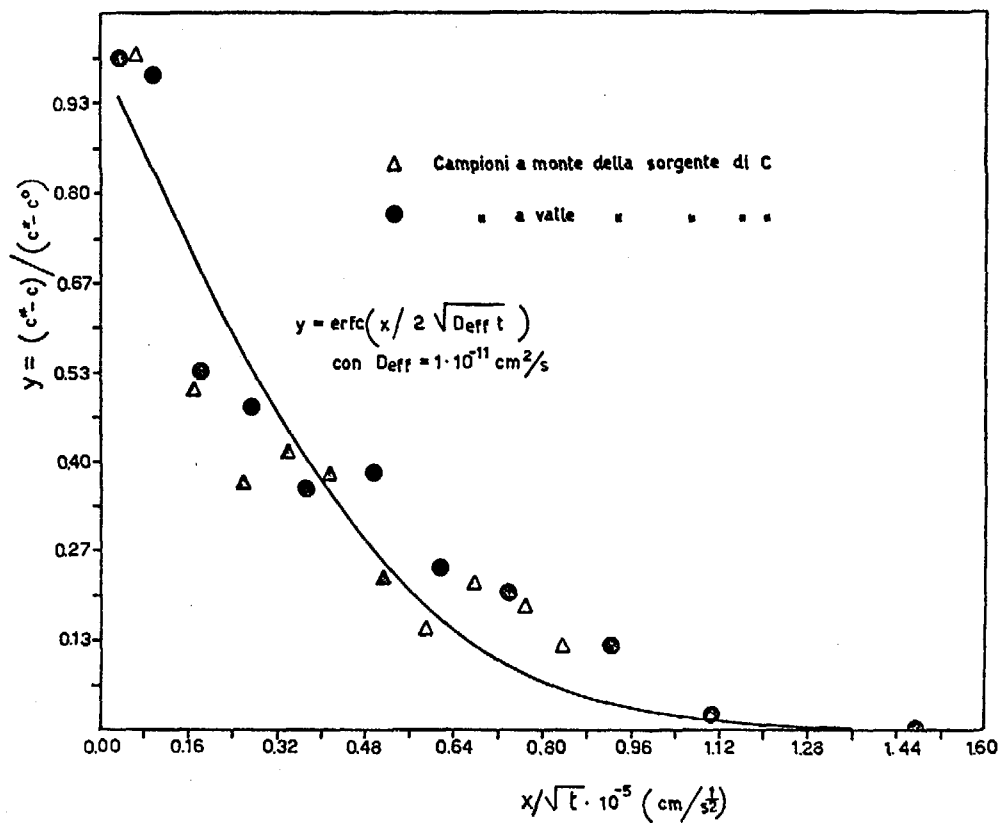


Fig.2:

Plot of Y versus (x/\sqrt{t}) of the experimental data concerning the carburization of the type 316 stainless steel exposed for 297 hours in flowing sodium at 533°C (Ref.4). The specimens were placed both up-stream (Δ) and down-stream (\circ) the carbon source in the isothermal test section. The full line is the best Y erf-function to fit the experimental points by $D_{eff} = 1.0 \cdot 10^{-11} \text{cm}^2/\text{sec}$.

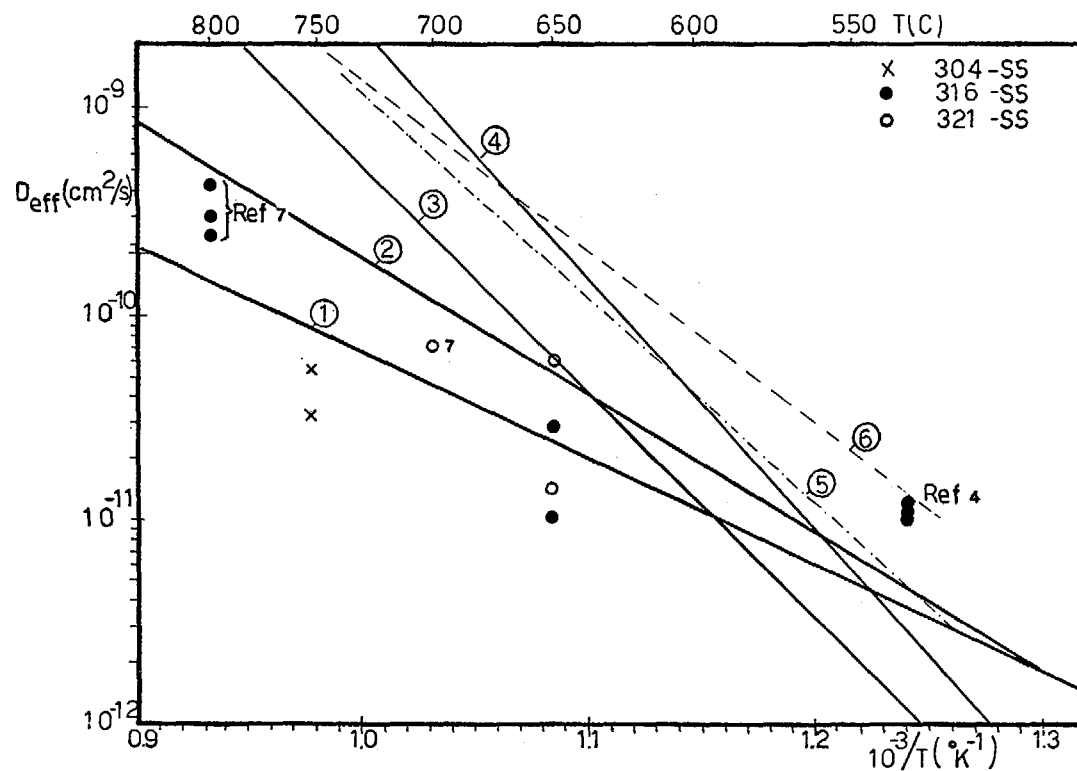


Fig.3:

Best fitting D_{eff} values of the experimental carburization data for the types (\bullet) 316^{1,4,6}, (\circ) 321¹, and (\times) 304¹⁴ stainless steels versus $(1/T(^{\circ}K))$. The full lines (1) and (2) refer to the D_{eff} functions for the carburization of the types 316¹⁰ and 304¹¹ steels respectively, compared with the correspondent functions (3) and (4) used at WARD, while the dotted lines (5) and (6) concern the true carbon diffusion in these steels^{3,18}.

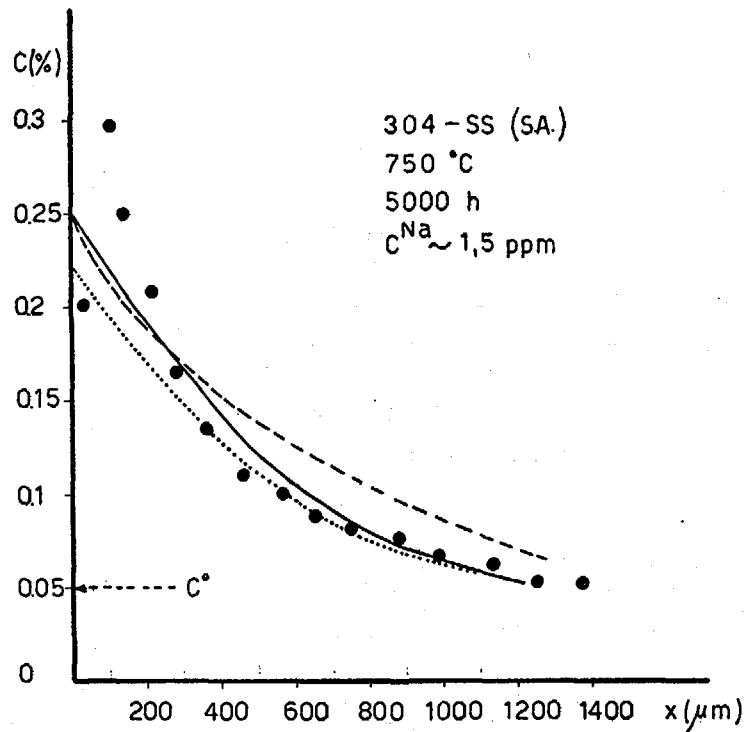


Fig.4:

Carbon concentration-distance profiles calculated by the ANL method (dotted line) and with this method (full line) for the type 304 SS (Solution Annealed) exposed in sodium containing 1.5 ppm of carbon and at 650°C for 5000 hours. The experimental points obtained by Natesan¹⁴ are also plotted here for comparison.

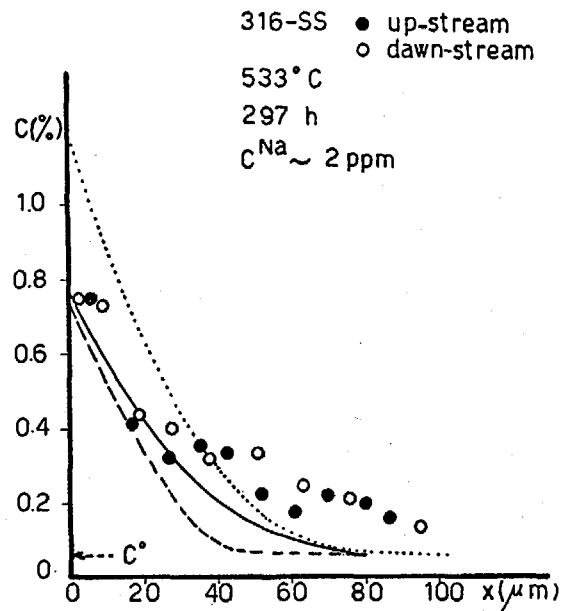


Fig.5:

- Carbon concentration-distance profiles computed by the ANL method (dotted line) and by the present model (Full line) for the type 316 SS exposed in carbon-saturated sodium at 533°C for 297 hours. The experimental points obtained under near these conditions and placed both up-stream and down-stream the carbon source are also reported here.

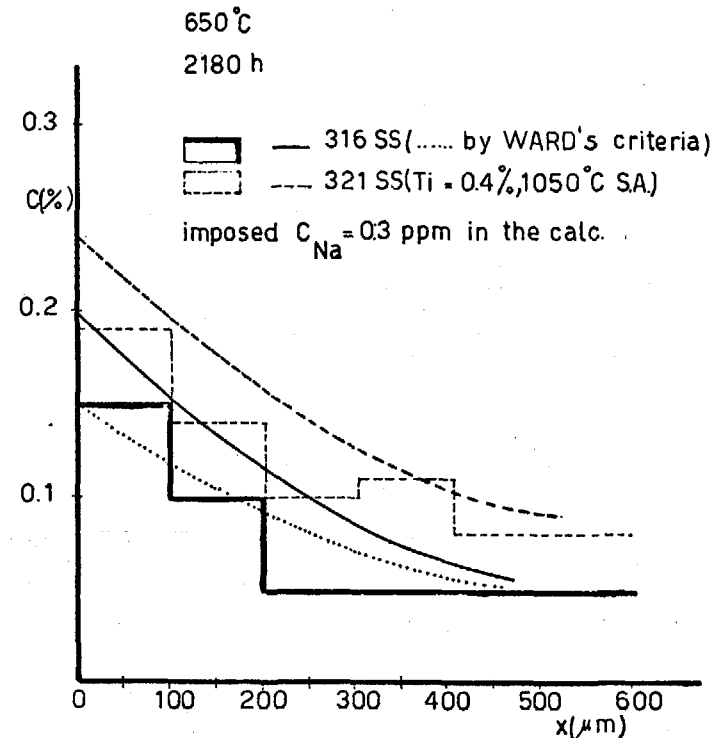


Fig.6:

The histograms of the carbon levels versus penetration depth observed by Thoreley et al. for the type 316 (full line) and 321 (dotted line) stainless steels exposed in sodium under comparable conditions at 650°C for 2180 hours. Are compared with the respective calculated profiles by assuming $C_{Na} = 0.3$ ppm. The point line refers to the computation performed by the WARD's criteria⁸.