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**A GENERALIZED METHOD OF
COMPUTING CARBON-DIFFUSION PROFILES
IN AUSTENITIC STAINLESS STEELS
EXPOSED TO A SODIUM ENVIRONMENT**

**R. B. Snyder, K. Natesan,
and T. F. Kassner**

BASE TECHNOLOGY

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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**Prepared for the U.S. ATOMIC ENERGY COMMISSION
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Materials Science Division

June 1973

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NOMENCLATURE

English Letters			
$a_{\text{C}}^{\text{Fe-Cr-Ni-C}}$	Carbon activity in Fe-Cr-Ni-C alloys	N_{C}	Mole fraction of carbon in the austenite phase
a_{C}^{Na}	Carbon activity in sodium	N_{C}^{i}	Initial mole fraction of carbon in the austenite phase
$a_{\text{C}}^{\text{sat}}$	Carbon activity at γ/γ plus carbide-phase boundary	N_{C}^{o}	Iterative constant in Eq. 8
B_n	Constants that are a function of the eigenvalues (λ_n and δ_n) obtained from a computer solution to the boundary-value problem	N_{C}^{s}	Mole fraction of carbon in the austenite phase at the sodium-steel interface
C_o	Initial concentration of carbon in steel, ppm	N_{Cr}	Mole fraction of chromium in the austenite phase
C_{eq}	Concentration of carbon in austenite phase in equilibrium with carbide phase, ppm	N_{CrC_v}	Number of moles of precipitated carbide per mole of alloy
C_{Na}	Concentration of carbon in sodium, ppm	P	Number of carbide particles per unit volume of alloy; i.e., $P^{-1} = 4\pi R_s^3/3$
$C_{\text{Na}}^{\text{sat}}$	Solubility value for carbon in sodium, ppm	R_o	Radius of a spherical carbide particle, cm
C_s	Concentration of carbon at the sodium-steel interface, ppm	R_s	Radius of equivalent sphere surrounding a carbide particle, cm
C_{ss}^{Y}	Concentration of carbon in the austenite phase of an austenitic stainless steel, ppm	t	Time, sec
$C_{\text{ss}}^{\text{sat}}$	Solubility value for carbon in austenitic stainless steel, ppm	t_f	Exposure time in sodium, sec
C_{ss}^{T}	Total carbon concentration (carbon in austenite plus carbon in carbide) in an austenitic stainless steel, ppm	T	Temperature, °K
$\bar{C}$	Time-average carbon concentration in austenite phase, ppm	X	Distance from alloy surface, cm
$\bar{C}(t)$	Average carbon concentration in austenite phase for a given time, ppm	<u>Greek Letters</u>	
D_{C}	Diffusion coefficient for carbon in the austenite matrix, cm^2/sec	β	Ratio of particle radius R_o to radius of equivalent sphere surrounding the particle, i.e., R_o/R_s
D_{Cr}	Diffusion coefficient for chromium in the austenite matrix, cm^2/sec	γ	Austenite phase in the steel
		η	Dimensionless variable, $X/(4D_{\text{C}}t)^{1/2}$
		ν	Atom ratio of carbon to chromium in the carbide, e.g., 6/23 for the Cr_{23}C_6 carbide
		τ_n	$(\lambda_n^2 D_{\text{C}})^{-1}$

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ABSTRACT

Numerous experimental observations on the carburization-decarburization behavior of austenitic stainless steels in high-temperature flowing sodium have been reported; however, quantitative predictions of carbon diffusion in the steels under specific environmental conditions have been difficult. A mathematical analysis for the process has been developed that incorporates (1) the thermodynamic and kinetic information for carbon in the alloys, (2) the thermal-mechanical treatment of the material (solution annealed versus cold worked) that influences the microstructure, and (3) the carbon concentration in sodium and its dependence on sodium-system parameters. Carbon concentration-distance profiles in Types 304 and 316 stainless steel were generated as a function of time, temperature, and carbon concentration in sodium and compared with experimental data.

The analysis was used to evaluate the carburization-decarburization behavior of Type 316 stainless steel fuel cladding exposed to sodium and to develop carbon-diffusion profiles in Type 304 stainless steel intermediate-heat-exchanger piping upon exposure to primary- and secondary-system sodium for periods to 30 yr.

I. INTRODUCTION

The austenitic stainless steels used for the fuel cladding, in-core structural components, piping, valves, and the intermediate heat exchanger in sodium-cooled fast breeder reactors are subjected to a variety of environmental conditions that limit their performance and reliability. Most of the available mechanical-property data on Liquid Metal Fast Breeder Reactor (LMFBR) materials have been obtained in air or inert-gas environments under simple loading conditions. In comparison, limited data have been generated in either the liquid-sodium or fast-neutron environment,

and a knowledge of the integrated effect of the sodium and irradiation environments on the mechanical behavior at high temperatures is particularly lacking.¹ At present, only irradiation effects are being incorporated into the property data used in the design of core components.²⁻⁴ For out-of-core components that have a design life of 20-30 yr, large extrapolations of mechanical-property data, obtained in air and inert-gas environments, are required. Furthermore, the influence of the time- and temperature-dependent migration of carbon and nitrogen in the materials that results from exposure to flowing sodium has not been considered. Environmental effects have essentially been avoided in the ASME Boiler and Pressure Vessel Code Case 1331-6 for elevated-temperature nuclear-component design,⁵ because of insufficient mechanical-property data in sodium and the absence of adequate procedures for incorporating the mechanical-property changes that arise from compositional variations in the materials during the service life of a component.

Numerous observations on carburization and decarburization of austenitic stainless steels in high-temperature flowing sodium have been made,⁶⁻¹⁰ and the importance of the carbon concentration of the steels in relation to the microstructural stability¹¹⁻¹³ and the mechanical properties^{7,10,14-22} is well recognized. However, quantitative predictions of carbon diffusion in the materials and of the mechanical behavior under different service conditions have been difficult. In the present report, a mathematical analysis has been developed to obtain carbon concentration-distance profiles in austenitic stainless steels as a function of time, temperature, and carbon concentration in sodium. The analysis is based upon (a) thermodynamic and kinetic information for carbon in the steels, (b) the thermal-mechanical history of the material that influences the microstructure, and (c) the sodium-system parameters and operating conditions that determine the carbon concentration in sodium. This analysis, coupled with mechanical-property data being generated in ongoing programs, where the major variables are the composition, time, temperature, and metallurgical condition of the material, will provide a quantitative basis for the incorporation of sodium effects into ASME codes and Reactor Research and Development (RRD) standards and thereby reduce the uncertainty in the design of various reactor components.

II. CARBON-DIFFUSION ANALYSIS

A. Development of Diffusion Relations

Carburization and decarburization of austenitic stainless steels involve the diffusion of carbon in the austenite matrix, accompanied by the precipitation or dissolution of the $(\text{Cr,Fe})_{23}\text{C}_6$ carbide. The carburization process is somewhat analogous to the internal oxidation of a reactive metal in a noble-metal matrix, which has been the subject of experimental and

theoretical investigations.²³⁻²⁹ The major difference between the two processes is that all reactive metal in a noble-metal matrix is converted to oxide, whereas only a fraction of the chromium present in the steel reacts to form carbide during carburization, and this amount increases with an increase in carbon potential of the sodium. A direct application of the internal-oxidation-rate equations to the carburization process without incorporating these modifications would grossly underestimate the thickness and overestimate the carbide volume fraction and total carbon content of the precipitate zone for any reaction time. The mathematical formalism for internal oxidation must therefore be modified to represent the process more closely; however, the diffusion equations become more complex and a closed-form analytical solution cannot be obtained, even for simple boundary and initial conditions. Therefore, a computer is required to obtain a numerical solution to the problem. In view of the relatively low diffusivity of carbon in austenitic stainless steels between 400 and 800°C and the turbulent flow conditions in the sodium, the transfer of carbon across the liquid-boundary layer is not considered important in the overall carburization-decarburization process.

For one-dimensional diffusion of carbon accompanied by carbide precipitation, Fick's second law for the diffusion of carbon and chromium can be written as

$$\frac{\partial(N_C + vN_{Cr}C_v)}{\partial t} = D_C \frac{\partial^2 N_C}{\partial X^2} \quad (1)$$

and

$$\frac{\partial(N_{Cr} + N_{Cr}C_v)}{\partial t} = D_{Cr} \frac{\partial^2 N_{Cr}}{\partial X^2} \quad (2)$$

When chromium and carbon in austenite form the $(Cr,Fe)_{23}C_6$ mixed carbide by the reaction

the relationship between the chromium and carbon concentrations in austenite in equilibrium with the carbide can be expressed as

$$N_{Cr} = A - B \ln N_C, \quad (3)$$

where A and B are constants that are evaluated from carbon activity-concentration data for Fe-Cr-8 wt % Ni alloys at various temperatures.

With the use of Eq. 3 and the substitution of the variable $\eta = X/(4D_{Cr})^{1/2}$, the partial differential equations (Eqs. 1 and 2) can be converted into the ordinary differential equation

$$-\frac{B}{N_C} \frac{dN_C}{d\eta} - \frac{1}{v} \frac{dN_C}{d\eta} = \frac{B}{2\eta} \frac{D_{Cr}}{D_C} \frac{d^2(\ln N_C)}{d\eta^2} + \frac{1}{2v\eta} \frac{d^2N_C}{d\eta^2}. \quad (4)$$

This equation was solved numerically by Hamming's modified predictor-corrector method³⁰ for N_C in terms of η using semi-infinite boundary conditions

$$N_C = N_C^S \text{ for } \eta = 0 \quad (5)$$

and

$$N_C = N_C^i \text{ for } \eta = \infty \quad (6)$$

for uniform initial carbon concentrations in the steel N_C^i and for various surface carbon concentrations N_C^S . It was found that Eq. 4 could be simplified to

$$\frac{d^2N_C}{d\eta^2} + \frac{2Bv\eta}{N_C} \frac{dN_C}{d\eta} = 0 \quad (7)$$

without affecting the results because of the negligible contribution from the second and third terms in Eq. 4. The total carbon concentration in the steel [carbon in the austenite N_C plus the carbon in the $(Cr,Fe)_{23}C_6$ carbide] was obtained as a function of position, for any diffusion time, from solutions to Eq. 7 and the relationships between N_C and the total carbon content of the alloy given in Appendix A.

The above analysis is applicable to carburization and decarburization of an austenitic stainless steel in which the initial and surface carbon concentrations exceed the solubility limit in the material. Under decarburizing conditions in a sodium environment, in which the surface carbon concentration in the alloy can fall below the solubility value, carbon diffusion through the single-phase austenite can be described by an established solution to Fick's second law

$$N_C = N_C^S + (N_C^O - N_C^S) \operatorname{erf} \eta, \quad (8)$$

where N_C^O is an iterative constant.* The incorporation of Eqs. 7 and 8 into the computer program, described in Appendix C, along with the coupling

*In a single-phase material, N_C^O in Eq. 8 is the initial concentration of the solute element diffusing out of the alloy. During decarburization of an austenitic stainless steel, the composition of the austenite (e.g., carbon and chromium concentrations) changes in the two-phase (austenite plus carbide) region in the vicinity of γ/γ plus carbide interface. For this situation, a nonphysical value for N_C^O allows the carbon concentration N_C and the flux $D_C \partial N_C / \partial X$ at the γ/γ plus carbide interface obtained from Eq. 8, for the single-phase region, and that from Eq. 7, for the two-phase region, to attain the same respective values so that the requirement for a singular carbon activity at the interface is fulfilled.

condition at the γ/γ plus carbide interface, made it possible to generate carbon concentration-distance profiles for both carburizing and decarburizing situations.

B. Thermodynamic and Kinetic Input Parameters

The diffusion relations in Sec. A above express the driving force for carbon migration in the material in terms of carbon-concentration differences and the self-diffusion coefficient in the austenite phase, rather than changes in the total carbon concentration and the effective diffusion coefficient.* Both types of information can be used to generate carbon-diffusion profiles in austenitic stainless steels. However, the former approach is applicable to a wide range of temperatures and carbon levels in the material, whereas the latter is restricted to specific conditions because of limited data for the functional dependence of the effective diffusion coefficient on both temperature and carbon level in the steel.

Appendix A presents the relevant carbon-diffusion data for Types 304 and 316 stainless steel and the necessary information on carbon solubility, carbon activity-concentration relationships, and austenite-carbide phase equilibria used in the analysis. Appendix B discusses data for the solubility of carbon in sodium and factors that influence the carbon concentration in sodium contained in austenitic stainless steel systems.

III. RESULTS AND DISCUSSION

A. Comparison of Calculated and Experimental Carbon-diffusion Profiles in Austenitic Stainless Steels

To determine the validity of the solutions to the diffusion relations using the thermodynamic and kinetic input data given in Appendix A, carbon concentration-distance profiles were calculated for different times, temperatures, and initial and surface carbon concentrations in the materials for comparison with available experimental data. Figures 1-3 compare carbon-diffusion profiles in Type 316 stainless steel reported by Thorley *et al.*³¹ after 3864-, 4368-, and 8760-hr exposures to sodium at 650°C with calculated curves.

Andrews *et al.*²² reported carbon-diffusion profiles in Types 304 and 316 stainless steel after exposure of the materials to a high-carbon sodium environment at 650°C for up to ~5400 hr. The surface carbon concentration in steels ranged between 3.08 and 3.8 wt %, in which the predominant carbide was the $(\text{Cr,Fe})_7\text{C}_3$ type. Similarly, surface carbon

*The effective diffusion coefficient for carbon in stainless steel is obtained from experimentally determined carbon concentration-distance profiles using the solution to Fick's second law that is applicable only to diffusion in a single-phase material in the absence of second-phase formation.

Fig. 1

Comparison of Experimental³¹ and Calculated Carbon-diffusion Profiles for Type 316 Stainless Steel after Exposure to Flowing Sodium for 3864 hr at 650°C. Neg. No. MSD-58556.

Fig. 2

Comparison of Experimental³¹ and Calculated Carbon-diffusion Profiles for Type 316 Stainless Steel after Exposure to Flowing Sodium for 4368 hr at 650°C. Neg. No. MSD-58557.

Fig. 3

Comparison of Experimental³¹ and Calculated Carbon-diffusion Profiles for Type 316 Stainless Steel after Exposure to Flowing Sodium for 8760 hr at 650°C. Neg. No. MSD-58558.

concentrations in Type 304 stainless steel varied from 2.7 wt % at 538°C to 4.4 wt % at 871°C in the capsule-diffusion experiments in carbon-saturated sodium reported by Anderson and Sneesby.³² The diffusion profiles obtained in these studies cannot be compared with calculated curves, since our analysis is only applicable to carbon concentrations in the steel below 1.0 wt %, in which the predominant carbide is the $(\text{Cr,Fe})_{23}\text{C}_6$ type. Nishio and Shimokawa³³ determined carbon concentration profiles in Type 304 stainless steel at temperatures between 650 and 830°C by using a ^{14}C tracer and sectioning technique. The maximum diffusion times in this study ranged from 330 hr at 650°C to ~15 hr at 830°C, and carbon diffusion occurred predominantly along high-diffusivity paths (e.g., grain boundaries). A comparison of the results from this work with our analysis is not meaningful, since the latter is based upon volume diffusion of carbon in the materials and longer diffusion times.

B. Influence of Time, Temperature, and Carbon Concentration in Sodium on Calculated Carbon-diffusion Profiles in Austenitic Stainless Steels

Figures 4 and 5 show carbon concentration-distance profiles in 20% cold-worked Type 316 stainless steel after 1000- and 4000-hr exposures, respectively, to sodium containing 0.017 ppm carbon for temperatures between 550 and 700°C. The extent of decarburization increases with

Fig. 4

Effect of Temperature on Carbon Concentration-Distance Profiles in 20% Cold-worked Type 316 Stainless Steel after 1000-hr Exposure to Sodium Containing 0.017 ppm Carbon. Neg. No. MSD-58560.

Fig. 5

Effect of Temperature on Carbon Concentration-Distance Profiles in 20% Cold-worked Type 316 Stainless Steel after 4000-hr Exposure to Sodium Containing 0.017 ppm Carbon. Neg. No. MSD-58561.

an increase in exposure time and temperature, whereas the degree of carburization at 550°C is minimal. Profiles obtained for solution-annealed Type 316 stainless steel were essentially the same under these conditions. Figure 6 shows the influence of the carbon concentration of the sodium in the range from 0.01 to 0.1 ppm on the surface carbon concentration and the carbon profiles in solution-annealed Type 304 stainless steel after 10,000 hr at 650°C. Depending upon the carbon concentration in sodium, carburization or decarburization of the material can occur. Figures 7 and 8 show the effect of the initial carbon content of the steel in the 0.02-0.08 wt % range on the diffusion profiles after 10,000-hr exposure to sodium containing 0.13 ppm carbon at 550 and 700°C, respectively. The carbon penetration depth is relatively insensitive to the initial carbon concentration over the range representative of commercial-grade Types 304L and 304 stainless steel.

To obtain a general understanding of the influence of time, temperature, carbon concentration in sodium, and the thermal-mechanical treatment on the carburization-decarburization behavior of Types 304 and 316 stainless steel, carbon concentration-distance profiles were computed for a number of temperatures between 400 and 800°C. The results were used to construct the carbon concentration-penetration-temperature diagrams shown in Figs. 9-14. The influence of increasing the exposure time for solution-annealed Type 304 stainless steel in sodium containing 0.017 and 0.13 ppm carbon can be seen from a comparison of Figs. 9 and 10 and Figs. 11 and 12, respectively. Figures 10 and 12 illustrate the effect of the carbon concentration in sodium on the carburization-decarburization behavior for an exposure time of 10,000 hr. Types 304 and 316 stainless steel can be compared from the results in Figs. 12 and 13, whereas the influence of the thermal-mechanical treatment (solution-annealed versus cold-worked) in Type 316 stainless steel can be seen from Figs. 13 and 14. In these figures, the crossover temperature between carburization and decarburization for a steel with an initial carbon content of 0.05 wt % increases from 550 to 680°C as the carbon concentration in sodium increases from 0.017 to 0.13 ppm. The variation of the carbon concentration at the surface of the steel with temperature is shown in the plane corresponding to zero penetration in the material. For a given carbon concentration in sodium, which implies a time-invariant carbon activity at the surface of the steel, the increase in the carbon concentration at the steel surface with exposure time at temperatures below 600°C is due to a metastable equilibrium between the austenite and carbide phases. The underlying factors that lead to this condition in the material are discussed in Appendix A. In Figs. 9-14, line A indicates the variation of the region of maximum carburization, and line B represents the penetration depth for the transition between the single-phase austenite and the two-phase austenite plus carbide mixture.

A carbon concentration in sodium of 0.017 ppm was used in the analysis because this value results in decarburization of the steels from

Fig. 6

Carburization and Decarburization Profiles in Solution-annealed Type 304 Stainless Steel after 10,000 hr at 650°C for Various Carbon Levels in Sodium. Neg. No. MSD-58559.

Fig. 7

Effect of Initial Carbon Content of Solution-annealed Type 304 Stainless Steel on the Carbon-diffusion Profiles after 10,000-hr Exposure to Sodium Containing 0.13 ppm Carbon at 550°C. Neg. No. MSD-58562.

Fig. 8

Effect of Initial Carbon Content of Solution-annealed Type 304 Stainless Steel on the Carbon-diffusion Profiles after 10,000-hr Exposure to Sodium Containing 0.13 ppm Carbon at 700°C. Neg. No. MSD-58563.

Fig. 9

Effect of Temperature between 400 and 800°C on the Carburization-Decarburization Behavior of Solution-annealed Type 304 Stainless Steel after 4000-hr Exposure to Sodium Containing 0.017 ppm Carbon. Neg. No. MSD-58239.

Fig. 10

Effect of Temperature between 400 and 800°C on the Carburization-Decarburization Behavior of Solution-annealed Type 304 Stainless Steel after 10,000-hr Exposure to Sodium Containing 0.017 ppm Carbon. Neg. No. MSD-58240.

Fig. 11

Effect of Temperature between 400 and 800°C on the Carburization-Decarburization Behavior of Solution-annealed Type 304 Stainless Steel after 1000-hr Exposure to Sodium Containing 0.13 ppm Carbon. Neg. No. MSD-58237.

Fig. 12

Effect of Temperature between 400 and 800°C on the Carburization-Decarburization Behavior of Solution-annealed Type 304 Stainless Steel after 10,000-hr Exposure to Sodium Containing 0.13 ppm Carbon. Neg. No. MSD-58238.

Fig. 13

Effect of Temperature between 400 and 800°C on the Carburization-Decarburization Behavior of Solution-annealed Type 316 Stainless Steel after 10,000-hr Exposure to Sodium Containing 0.13 ppm Carbon. Neg. No. MSD-58564.

Fig. 14

Effect of Temperature between 400 and 800°C on the Carburization-Decarburization Behavior of 20% Cold-worked Type 316 Stainless Steel after 10,000-hr Exposure to Sodium Containing 0.13 ppm Carbon. Neg. No. MSD-58565.

an initial value of 0.05 wt % to the 30-50-ppm range at temperatures above 700°C. Surface and equilibrium carbon concentrations of this magnitude have been reported⁸ for austenitic stainless steel specimens that were exposed to sodium at temperatures between 705 and 760°C in a loop system. Figures 9-14 show that decarburization at high temperatures requires a comparatively short time interval; however, carburization at the lower temperatures becomes significant only at times greater than ~4000 hr. The slowness of the carbide precipitation reaction has an even greater effect on the amount of carburization observed during shorter exposure periods in the low-carbon (0.017-ppm) sodium environment; i.e., after 1000 hr, calculated curves indicated virtually no carburization of the material at lower temperatures. The carbon concentration of 0.13 ppm was chosen to set the temperature for the transition between carburization and decarburization of the steels at ~680°C in these calculations.

IV. APPLICATIONS OF THE ANALYSIS TO REACTOR COMPONENTS

A. Carburization-Decarburization Behavior of Type 316 Stainless Steel Fuel Cladding

Type 316 stainless steel fuel cladding will be exposed to flowing sodium at temperatures above 600°C in FFTF, U.S. Demonstration Reactor, and bypass flow subassemblies in EBR-II. The axial temperature profile for the fuel cladding in these systems will depend upon the sodium inlet temperature (370-440°C) as well as the maximum temperature for the cladding that occurs at the top of the fuel column. The extent of carburization or decarburization of the fuel cladding can be calculated at any axial position along the fuel pin for specified carbon levels in sodium using the mathematical formalism developed for the process in Secs. I-III.

Figure 15 shows two axial temperature profiles along a fuel pin and the corresponding average carbon content of the 15-mil-wall cladding after 1000- and 5000-hr exposures to sodium containing 0.017 and 0.05 ppm carbon. As the maximum temperature of the cladding increases from 600 to 700°C, the extent of decarburization increases significantly for a carbon concentration in sodium of 0.017 ppm. Since the crossover temperature between carburization and decarburization occurs at 615°C for 0.05 ppm carbon in sodium, only carburization is indicated by the dashed curves that correspond to the lower temperature profile. After a 5000-hr exposure, the steel, with an initial carbon content of 0.05 wt %, will have an average carbon content of 0.065 and 0.025 wt % at 500 and 700°C, respectively. The corresponding values for sodium containing 0.017 ppm carbon are 0.054 and 0.004 wt % carbon in the material at the respective temperatures. These carbon concentrations in the steel represent the maximum amount of carburization or decarburization of the 15-mil-wall cladding for the two carbon levels in sodium. The curves in Fig. 15 indicate that the region of maximum carburization occurs near the midplane of the core.

Figure 16 shows carbon concentration-distance profiles across the cladding wall at 500, 600, and 700°C after a 5000-hr exposure to sodium containing 0.05 ppm carbon. As the temperature increases from 500 to 700°C, the surface carbon concentration in the steel decreases from 0.33 to 0.015 wt % and the depth of penetration increases from 3 mils to the entire cross section.

Fig. 15

Relationship between the Axial Temperature Profile for a Fuel Pin and the Average Carbon Content of the 15-mil-wall 20% Cold-worked Type 316 Stainless Steel Cladding after 1000- and 5000-hr Exposure to Sodium Containing 0.017 and 0.05 ppm Carbon. Neg. No. MSD-58629.

The information in Table I summarizes the mass of carbon that is either gained or lost by a segment of fuel cladding 1 cm long (~0.5 g of steel) at temperatures between 400 and 700°C for two carbon levels in sodium and exposure times of 1000 and 5000 hr. In many instances, the changes in the carbon concentration for an ~0.5-g sample of the fuel cladding are within the accuracy limits of the combustion method using a low-carbon analyzer (i.e., $\pm 20 \mu\text{g}$ of carbon for a small number of samples). For the purpose of comparing measured carbon concentrations in the fuel cladding from various subassemblies with the results of this type of analysis, the actual carbon content of the primary sodium should be determined by exposing iron-base alloy foils to the coolant in an out-of-core loop, such as the equilibration

module located on the Radioactive Sodium Chemistry Loop (RSCL)³⁴ at EBR-II, and correlating the carbon concentrations in the materials with the carbon activity.³⁵ From a knowledge of the carbon concentration in sodium and the axial temperature profile along the fuel pin, curves similar to those in Fig. 15 can be calculated for specific exposure times to identify regions that have undergone a significant change in carbon content for chemical analysis. This approach will minimize the number of samples required to obtain an accurate carbon profile along the fuel pin. Although the relationship between the carbon content of austenitic stainless steels and the

mechanical behavior in a fast-neutron environment has not been established, it may have an important bearing on the performance of fuel cladding and other core components.

Fig. 16

Carbon Concentration-Distance Profiles across the 20% Cold-worked Type 316 Stainless Steel Cladding Wall at 500, 600, and 700°C after 5000-hr Exposure to Sodium Containing 0.05 ppm Carbon. Neg. No. MSD-58633.

TABLE I. Mass of Carbon Gained or Lost from a 1-cm Length of 20% Cold-worked Type 316 Stainless Steel Fuel Cladding^a as a Function of Temperature and Carbon Concentration in Sodium after an Exposure of 1000 and 5000 hr

Temperature, °C	0.017 ppm Carbon in Sodium ^b		0.05 ppm Carbon in Sodium ^b	
	1000 hr	5000 hr	1000 hr	5000 hr
700	-108	-241	-80	-128
650	-51	-113	-25	-50
600	-18	-39	+8	+18
550	0	+1	+25	+63
500	+5	+21	+23	+81
450	+1	+16	+6	+46
400	0	+2	0	+7

^aAn initial carbon concentration of 0.050 wt % was used for the 0.23-in.-OD by 15-mil-wall fuel cladding.

^bμg of Carbon gained (+) or lost (-) by the fuel cladding.

B. Carburization of Type 304 Stainless Steel Intermediate Heat-exchanger Piping by Primary- and Secondary-system Sodium

An intermediate heat exchanger (IHX), located within the reactor containment structure, is used to transfer heat from the radioactive sodium that flows through the core of the reactor to a secondary nonradioactive-sodium system that includes the steam generator. The IHX, constructed of Type 304 stainless steel, has a maximum operating temperature slightly below the mixed-mean outlet temperature of the primary sodium. The

mixed-mean outlet temperatures for experimental test facilities such as EBR-II, Dounreay, Rapsodie, and FFTF and demonstration reactors such as the U.S. Demonstration Plant, BN-350, Fermi, MONJU, PFR, PHENIX, and SNR range between 454 and 566°C.³⁶⁻⁴¹ The commercial LMFBR's are expected to have an outlet temperature as high as 620°C.⁴¹

The carbon concentration of the sodium in the primary system in these reactors will depend upon the system operating temperatures and operating conditions that introduce carbon-bearing materials into the primary system, as discussed in Appendix B. The carbon concentration of the sodium in the secondary system will depend on the operating temperature and the material used to construct the steam generator (e.g., Fe-2.25 wt % Cr-1 wt % Mo alloy versus Incoloy 800). The carburization behavior of the IHX must therefore be examined in terms of the carbon concentrations of the sodium in both the primary and secondary heat-transport systems.

The present analysis can be used to evaluate the carburization behavior of Type 304 stainless steel IHX piping at temperatures between 443 and 600°C for up to 30 yr. Carbon concentrations in sodium of 0.05 and 0.13 ppm, which may be representative of the primary and secondary systems, were used in generating the carbon concentration-distance profiles at various temperatures shown in Figs. 17-21. The calculated average

Fig. 17

Carbon Concentration-Distance Profiles across Type 304 Stainless Steel IHX Piping after Exposure to Primary- and Secondary-system Sodium Containing 0.05 and 0.13 ppm Carbon, Respectively, for up to 30 yr at 600°C. Neg. No. MSD-58568.

Fig. 18

Carbon Concentration-Distance Profiles across Type 304 Stainless Steel IHX Piping after Exposure to Primary- and Secondary-system Sodium Containing 0.05 and 0.13 ppm Carbon, Respectively, for up to 30 yr at 550°C. Neg. No. MSD-58569.

Fig. 19

Carbon Concentration-Distance Profiles across Type 304 Stainless Steel IHX Piping after Exposure to Primary- and Secondary-system Sodium Containing 0.05 and 0.13 ppm Carbon, Respectively, for up to 30 yr at 500°C. Neg. No. MSD-58582.

Fig. 20

Carbon Concentration-Distance Profiles across Type 304 Stainless Steel IHX Piping after Exposure to Primary- and Secondary-system Sodium Containing 0.05 and 0.13 ppm Carbon, Respectively, for up to 30 yr at 467°C. Neg. No. MSD-58583.

Fig. 21

Carbon Concentration-Distance Profiles across Type 304 Stainless Steel IHX Piping after Exposure to Primary- and Secondary-system Sodium Containing 0.05 and 0.13 ppm Carbon, Respectively, for up to 30 yr at 443°C. Neg. No. MSD-58570.

carbon concentrations in sections of the piping in the region of the sodium-steel interface are given in Table II. As shown in Figs. 17-21, the carbon concentration at the surface of the steel increases and the depth of penetration decreases as the operating temperature is lowered, for any time. Below $\sim 500^{\circ}\text{C}$, the carbon concentration at the surface of the material increases with an increase in exposure time, as discussed in Appendix A. The temperatures in Figs. 20 and 21 correspond to the maximum temperature of the IHX and a secondary-sodium-system vent-line pipe, respectively, in EBR-II. Piping from the vent line was removed, sectioned, and analyzed for carbon after 6 yr of reactor operation, during which the material was at 443°C for $\sim 30\%$ of the time and at $\sim 300^{\circ}\text{C}$ for the remainder. The carbon concentrations in a section 3 mils from the surface and at the center of the pipe wall were 0.13 and 0.06 wt %, respectively.⁴² Calculated carbon concentrations for the first 3 mils of the material after exposure to sodium for periods of 3 and 5 yr at 443°C (Table II) are similar in magnitude (e.g., ~ 0.1 wt %) for a carbon concentration in sodium of 0.13 ppm. Although a comparison of this type cannot be used to establish quantitatively the validity of the mathematical analysis, it indicates that reasonable values are obtained from the calculations.

TABLE II. Calculated Average Carbon Concentrations^a for Sections of Type 304 Stainless Steel Piping^b after Exposure to Sodium Containing 0.05 and 0.13 ppm Carbon at Temperatures between 443 and 600°C for up to 30 yr

Time, yr	Distance from Na/Steel Interface, mils	0.05 ppm Carbon in Sodium					0.13 ppm Carbon in Sodium				
		Temperature, $^{\circ}\text{C}$					Temperature, $^{\circ}\text{C}$				
		443	467	500	550	600	443	467	500	550	600
1	0-3	0.052	0.059	0.081	0.094	0.061	0.058	0.076	0.133	0.200	0.137
	3-6	0.050	0.050	0.050	0.053	0.055	0.050	0.050	0.050	0.063	0.091
	6-10	0.050	0.050	0.050	0.050	0.051	0.050	0.050	0.050	0.050	0.062
3	0-3	0.065	0.090	0.130	0.117	0.062	0.075	0.155	0.270	0.267	0.151
	3-6	0.050	0.050	0.051	0.067	0.060	0.050	0.050	0.056	0.122	0.123
	6-10	0.050	0.050	0.050	0.053	0.053	0.050	0.050	0.050	0.062	0.081
5	0-3	0.081	0.123	0.171	0.125	0.063	0.122	0.231	0.393	0.297	0.155
	3-6	0.050	0.050	0.054	0.082	0.061	0.050	0.050	0.063	0.168	0.133
	6-10	0.050	0.050	0.050	0.058	0.056	0.050	0.050	0.050	0.079	0.099
15	0-3	0.164	0.250	0.255	0.137	0.063	0.320	0.572	0.647	0.346	0.155
	3-6	0.050	0.052	0.096	0.107	0.062	0.050	0.062	0.193	0.228	0.148
	6-10	0.050	0.050	0.052	0.082	0.060	0.050	0.050	0.057	0.177	0.129
30	0-3	0.280	0.370	0.302	0.143	0.063	0.617	0.923	0.757	0.365	0.156
	3-6	0.051	0.052	0.147	0.135	0.063	0.052	0.125	0.365	0.290	0.155
	6-10	0.050	0.050	0.067	0.086	0.061	0.050	0.050	0.124	0.219	0.138

^aCarbon concentration in wt %.

^bAn initial carbon concentration of 0.05 wt % in the steel was used.

Although the calculated profiles do not result in carburization of the piping in its entire cross section under these conditions, the high carbon concentration and carbon gradient at the surface of the material can have important implications with regard to the fatigue and creep-fatigue properties. Limited data on the low-cycle fatigue behavior of Type 304

stainless steel in "high-carbon" sodium indicated a significant reduction in the number of cycles to failure compared with tests in air and helium environments for cyclic strain levels up to 2%.²² The reduction of the fatigue life under carburizing conditions in a sodium environment can be rationalized in the following manner. Since it is generally known that the surface of the specimen deforms much earlier than the bulk material, the dislocation density near the surface is much higher than in the bulk of the specimen.^{43,44} When the amount of carbide in this region is small, the egress of dislocations is facilitated and leads to a condition in which slip is more favorable than crack initiation and propagation in the material. For high carbon concentrations in the material at the sodium-steel interface, the reverse situation occurs. Simultaneous carburization of the crack tip may also promote crack propagation. It is likely that a threshold value exists for the carbon concentration in the surface region of the steel, above which the fatigue and creep-fatigue properties deteriorate considerably. Therefore, a correlation of these properties with sodium-exposure conditions (e.g., time, temperature, and carbon concentration in sodium) should be possible.

V. CONCLUSIONS AND FUTURE WORK

A generalized method has been developed for computing carbon-diffusion profiles in austenitic stainless steels exposed to a sodium environment. The results of the analysis showed that carbon migration in the steels is inevitable at temperatures between 400 and 800°C. The amount of carburization or decarburization is strongly dependent upon the temperature and carbon concentration in sodium, whereas the initial carbon concentration of the material and the thermal-mechanical treatment have a lesser influence on the carbon-diffusion profiles.

A comparison of calculated and experimental carbon concentration-penetration profiles at 650°C under carburizing conditions indicated reasonable agreement; however, additional experimental data are required at temperatures below ~600°C to establish the reliability of the calculations over a wider temperature range. The analysis was used to examine the carburization-decarburization behavior of Type 316 stainless steel fuel cladding exposed to sodium and the carburization of Type 304 IHX piping for carbon concentrations in sodium that may be representative of the primary and secondary systems. A more quantitative prediction of carbon diffusion in the materials will be possible when the carbon activity of the sodium in reactor and experimental loop systems is established by the foil-equilibration method.

Decarburization at high temperatures has a profound effect on the creep-rupture properties of the steel. Also, the amount of carburization at lower temperatures can influence the creep-fatigue properties, since crack initiation and propagation can be strongly dependent on the composition and microstructure of the material in the vicinity of the sodium-steel interface. The compositional variations due to the sodium environment will be correlated with mechanical-property changes, developed in an ongoing program, and incorporated into the present analysis to provide a quantitative basis for establishing the design and performance limits of various components that operate in a sodium environment.

APPENDIX A

Thermodynamic, Kinetic, and Microstructural
Information for Austenitic Stainless Steels

The relevant materials data used in the analysis of the carburization-decarburization process are (1) the diffusion coefficient for carbon in the steel, (2) the activity and solubility of carbon in, and austenite-carbide phase-equilibria relations for, Fe-Cr-8 wt % Ni alloys, and (3) the influence of thermal-mechanical history on the microstructure and carbide-precipitation kinetics in austenitic stainless steels.

1. Carbon-diffusion Data

The diffusion of carbon in austenitic stainless steels has been determined by several investigators. Agarwala *et al.*⁴⁵ used a residual-activity technique to measure the diffusivity of ¹⁴C in Types 304, 316, and 347 stainless steel in the temperature range of 450-1200°C. The carbon concentration in these materials was 0.08 wt % and remained essentially constant during the experiment. The contribution of grain-boundary diffusion was insignificant, as evidenced by the linear dependence of $\ln D_C$ with reciprocal temperature over the entire range. The results for the three materials are summarized by the equations

Fig. A.1

Temperature Dependence of Diffusion Coefficient for Carbon in Types 304 and 316 Stainless Steel.^{45,46} Neg. No. MSD-58571.

$$D_C^{304SS} = 6.18 \exp(-22,450/T), \quad (A.1)$$

$$D_C^{316SS} = 0.19 \exp(-18,820/T), \quad (A.2)$$

and

$$D_C^{347SS} = 0.35 \exp(-20,200/T). \quad (A.3)$$

Equations A.1 and A.2, for Types 304 and 316 stainless steel, are plotted in Fig. A.1.

Bagnall⁴⁶ measured the diffusivity of carbon in Types 304L and 316L stainless steel by exposing 3-mil-thick foils to flowing sodium at temperatures between 565 and 760°C for varying lengths of time under decarburizing conditions and determining the average carbon concentration in the materials by a combustion technique. A classical solution to Fick's second law was used to compute the diffusivity values. The results are summarized by the relations

$$D_C^{304SS} = 1.75 \exp(-21,760/T) \quad (A.4)$$

and

$$D_C^{316SS} = 40.9 \exp(-25,090/T), \quad (A.5)$$

which are also shown in Fig. A.1. The diffusivity values for Type 304 stainless steel are in good agreement with the data reported by Agarwala *et al.*; however, the values for Type 316 stainless steel are a factor of ~15 smaller at temperatures below 500°C.

Anderson and Sneesby³² exposed foil samples of Type 304 stainless steel to carbon-saturated sodium in capsule experiments. The surface carbon concentration in the material ranged from 2.7 to 4.4 wt % at temperatures between 538 and 871°C. The diffusion coefficients computed from the average carbon concentrations in the steel were considerably lower than the results of the other investigations. These data, which represent "effective diffusion coefficients" because of the precipitation of a large amount of carbide, are only applicable to conditions that result in high carbon concentrations in the material.

In view of the wide temperature range and the comparatively large numbers of determinations, the results of Agarwala *et al.* were used in our analysis of carbon diffusion in the materials exposed to a sodium environment. Additional information on the carbon diffusivity in Type 316 stainless steel will resolve the uncertainty in the results shown in Fig. A.1 and can be easily incorporated into the analysis.

2. Carbon Activity, Solubility, and Phase-equilibria Data for Temperatures between 600 and 800°C

When an austenitic stainless steel undergoes carburization, the concentration of chromium in the austenite decreases while that of carbon increases as the carbide is precipitated. To obtain a quantitative description of these compositional changes for use in the computer program, mathematical expressions were developed for the activity and solubility of carbon in Fe-Cr-8 wt % Ni alloys as a function of temperature. An expression that relates the carbon concentration in the austenite phase to the total carbon content of the Fe-18 wt % Cr-8 wt % Ni alloy over a range of temperatures was also derived from austenite-carbide phase-equilibrium data.

Carbon activity-concentration relationships for Fe-Cr-Ni alloys in the composition range 0-16 wt % Ni, 0-22 wt % Cr, and 0.01-1.0 wt % C were experimentally determined over the temperature range of 725-1060°C. The results of this work are summarized by the expression⁴⁷

$$\begin{aligned}
\ln a_C^{\text{Fe-Cr-Ni-C}} = & \ln (0.048 \% \text{ C}) + \left(0.525 - \frac{300}{T}\right) \% \text{ C} - 1.845 + \frac{5100}{T} \\
& - \left(0.021 - \frac{72.4}{T}\right) \% \text{ Ni} + \left(0.248 - \frac{404}{T}\right) \% \text{ Cr} \\
& - \left(0.0102 - \frac{9.422}{T}\right) \% \text{ Cr}^2.
\end{aligned} \tag{A.6}$$

The carbon activity-concentration relationship for an Fe-18 wt % Cr-8 wt % Ni alloy was generated from the above equation and can be written as

$$\ln C_{ss}^T (\text{ppm}) = A + B \ln a_C, \tag{A.7}$$

where

$$A = A_0 + A_1/T + A_2T, \tag{A.8}$$

$$B = B_0 + B_1/T + B_2T, \tag{A.9}$$

and

$$A_0 = 14.5, \quad B_0 = 2.0,$$

$$A_1 = -1.74 \times 10^3, \quad B_1 = -4.52 \times 10^2, \text{ and}$$

$$A_2 = -9.84 \times 10^{-4}, \quad B_2 = -5.87 \times 10^{-4}.$$

The solubility of carbon in stainless steel with 18 wt % chromium and 8-10 wt % nickel has been investigated at temperatures between 750 and 1200°C,⁴⁸⁻⁵² and the results were summarized in a previous paper.⁵³ These data and more recent results for the solubility of carbon in the Fe-8 wt % Ni alloy⁴⁷ were used to compute carbon-solubility values for Fe-Cr-8 wt % Ni alloys as a function of temperature by the method described in Ref. 53. The relationship between the carbon and chromium concentrations in the austenite phase at the γ -carbide phase boundary for any temperature is given by

$$\text{Cr}(\text{wt } \%) = A' \ln C_{ss}^Y (\text{ppm}) + B', \tag{A.10}$$

where

$$A' = A_3 + A_4/T + A_5T, \tag{A.11}$$

$$B' = B_3 + B_4/T + B_5T, \tag{A.12}$$

and

$$\begin{aligned} A_3 &= 31.86, & B_3 &= -343.5, \\ A_4 &= -1.42 \times 10^4, & B_4 &= 1.47 \times 10^5, \text{ and} \\ A_5 &= -2.186 \times 10^{-2}, & B_5 &= 0.232. \end{aligned}$$

The temperature dependence of the solubility of carbon in an Fe-18 wt % Cr-8 wt % Ni alloy, consistent with Eq. A.10, becomes

$$C_{ss}^{\text{sat}}(\text{ppm}) = 1.088 \times 10^7 \exp(-11,940/T). \quad (\text{A.13})$$

Upon substitution of $C_{\text{ppm}}^{\text{sat}}$ from Eq. A.13 for C_{ppm}^T in Eq. A.7, the activity of carbon in the austenite at the γ -carbide phase boundary can be calculated. This value is used in the computer program to establish the transition between the single-phase austenite and the two-phase austenite plus carbide mixture during decarburization of the material, since different diffusion equations are applicable in the two regions (Eqs. 7 and 8). The carbon activity in the single-phase austenite for a given carbon concentration can be obtained from a knowledge of the carbon activity at the γ -carbide phase boundary and the solubility of carbon in the steel using the relation

$$a_C = \frac{C_{ss}^Y}{C_{ss}^{\text{sat}}} a_C^{\text{sat}}. \quad (\text{A.14})$$

Since the carbon-concentration gradient in the austenite phase provides the driving force for the carburization or decarburization process, it is necessary to obtain a mathematical relationship between the carbon concentration in the austenite and the total carbon content of the Fe-18 wt % Cr-8 wt % Ni alloy as a function of temperature. For this purpose, Eq. A.6 was used to generate a series of curves that relate the chromium and carbon concentrations in Fe-Cr-8 wt % Ni alloys for a number of carbon activities. A plot of this type is shown in Fig. A.2 for 700°C. Similar plots were

Fig. A.2

Carbon Isoactivity Lines and Solubility of Carbon in Fe-Cr-8 wt % Ni Alloys at 700°C. Neg. No. MSD-58572.

constructed for other temperatures between 600 and 1000°C. The γ/γ plus carbide phase-boundary line obtained from Eq. A.10 is also plotted in

Fig. A.3

Relationship between Carbon Concentration in the Austenite Phase and Total Carbon Content of an Fe-18 wt % Cr-8 wt % Ni Alloy at Temperatures between 600 and 1000°C. Neg. No. MSD-58573.

Fig. A.2. From this figure and similar plots at other temperatures, the relationship between the carbon concentration in the austenite and the total carbon content of an Fe-18 wt % Cr-8 wt % Ni alloy, shown in Fig. A.3, was constructed. For any total carbon concentration in the above alloy, the corresponding carbon concentration in the austenite phase was established from the intersection of the isoactivity line with the phase-boundary line; i.e., at a carbon activity of 0.01, a total carbon concentration of 1100 ppm corresponds to a carbon content in the austenite of 300 ppm at 700°C. The curves in Fig. A.3 were used to generate the following expression that relates the carbon concentration in the austenite phase to the total carbon content of the steel at any temperature in the two-phase region:

$$\ln C_{\text{ppm}}^{\gamma} = A'' \ln C_{\text{ppm}}^T + B'', \quad (\text{A.15})$$

where

$$A'' = A_6 + A_7/T + A_8T, \quad (\text{A.16})$$

$$B'' = B_6 + B_7/T + B_8T, \quad (\text{A.17})$$

and

$$\begin{aligned} A_6 &= 1.752, & B_6 &= -7.673, \\ A_7 &= -468, & B_7 &= 1553, \text{ and} \\ A_8 &= -7.12 \times 10^{-4}, & B_8 &= 7.93 \times 10^{-3}. \end{aligned}$$

In the single-phase region, the carbon concentration in the austenite and the total carbon content of the alloy are identical. This is indicated by the dashed line in Fig. A.3.

The equations in this section represent a self-consistent set of thermodynamic relations for the Fe-18 wt % Cr-8 wt % Ni austenitic steel. A change in either the carbon activity-concentration relation (Eq. A.6 or A.7) or the carbon solubility information for Fe-Cr-8 wt % Ni alloys

(Eq. A.10) would require a recalculation of the information of the type given in Fig. A.2 for several temperatures to obtain a revised plot analogous to Fig. A.3. The coefficients for Eqs. A.7-A.12 and A.15-A.17 would also have to be redetermined from the revised data and incorporated into the computer program.

3. Data for the Metastable Equilibrium between the Austenite and Carbide Phases at Temperatures between 400 and 600°C

Since the rate of carbide precipitation decreases markedly with a decrease in temperature, a metastable equilibrium between supersaturated austenite and the carbide phase can exist at the lower temperatures. The thermal-mechanical history of the material (solution-annealed versus cold-worked condition) influences the carbide-precipitation kinetics by altering the grain size of the material and the size and distribution of the carbide particles. The time and temperature dependence of precipitation of the various phases (e.g., carbides, sigma, chi, and eta) in austenitic stainless steels with different thermal-mechanical treatment is commonly reported in the form of time-temperature-precipitation (TTP) diagrams.¹¹⁻¹³ This type of information indicates that carbide precipitation in these materials is essentially complete within several hundred hours at temperatures above ~650°C, whereas at lower temperatures the time scale for the process extends over thousands of hours. As a result, the carbon concentration in the austenite phase is much higher than the equilibrium value; this condition leads to a decrease in the thermodynamic driving force for carburization of the steel for a given carbon concentration at the steel surface, which is established by the carbon activity in sodium. The time- and temperature-dependent carbon concentration of the austenite phase can be incorporated into our kinetic analysis of the carburization-decarburization process for steels in a sodium environment.

Nolfi et al.⁵⁴ developed the following mathematical expression for the average carbon concentration in the austenite phase as a function of time $\bar{C}(t)$ during the growth or dissolution of spherical carbide particles:

$$\bar{C}(t) = C_0 + \frac{(C_{eq} - C_0)P}{1 - \beta^3} \sum_{n=0}^{\infty} B_n^2 \left[1 - \exp\left(-\frac{t}{\tau_n}\right) \right], \quad (A.18)$$

where the symbols are as defined in the nomenclature. The following assumptions were made in deriving Eq. A.18: (a) A thermodynamic equilibrium exists between the carbide and the austenite phases at the particle surface; (b) the particle boundary movements are small, in comparison with the size of the particles; (c) the only driving force for the movement of both solute and solvent elements is that due to concentration gradients; i.e., precipitation-induced stresses are assumed to be negligible; and (d) the carbon-diffusion coefficient is independent of composition.

The input parameters required for computing the average carbon concentration in the austenite from Eq. A.18 were obtained from experimental data for solution-annealed and cold-worked austenitic stainless steels. The particle radius R_0 and interparticle distance $2R_s$ were obtained from photomicrographs of aged Types 304 and 316 stainless steel. Typical values for R_s of 7.5×10^{-4} and 5.0×10^{-4} cm for the solution-annealed and 20%-cold-worked materials, respectively, and 5×10^{-5} cm for R_0 were used. The equilibrium carbon concentration in the austenite C_{eq} for a steel with various initial carbon contents C_0 was obtained as a function of temperature from Eq. A.15, since $C_{ppm}^Y \equiv C_{eq}$. Values of $\bar{C}(t)$, computed for a number of times up to the desired exposure time (t_f) at each temperature, were used in Eq. A.19 to obtain a time-average carbon concentration $\bar{C}$ for the austenite,

$$\bar{C} = \frac{1}{t_f} \int_0^{t_f} \bar{C}(t) dt. \quad (A.19)$$

Figures A.4 and A.5 show the temperature dependence of the equilibrium and time-average carbon concentrations in the austenite phase of

Fig. A.4. Effect of Temperature on Concentration of Carbon in the Austenite Phase at the Sodium-Steel Interface C_s and That within the Material $\bar{C}$ for Annealing Times of 1000, 4000, and 10,000 hr for Solution-annealed Type 316 Stainless Steel with an Initial Carbon Concentration of 0.05 wt %. (A carbon concentration of 0.13 ppm in the sodium was used to obtain the variation of C_s with temperature.) Neg. No. MSD-58574.

Fig. A.5. Effect of Temperature on Concentration of Carbon in the Austenite Phase at the Sodium-Steel Interface C_s and That within the Material $\bar{C}$ for Annealing Times of 1000, 4000, and 10,000 hr for 20% Cold-worked Type 316 Stainless Steel with an Initial Carbon Concentration of 0.05 wt %. (A carbon concentration of 0.13 ppm in the sodium was used to obtain the variation of C_s with temperature.) Neg. No. MSD-58575.

Type 316 stainless steel in the solution-annealed and cold-worked conditions, respectively, for exposure times of 1000, 4000, and 10,000 hr. The initial carbon content of the materials is 0.05 wt %. At higher temperatures, the carbon concentrations in austenite closely approximate the equilibrium values, whereas at lower temperatures, the $\bar{C}$ values are substantially higher than the equilibrium carbon concentrations. As the exposure time increases, the deviation of $\bar{C}$ from C_{eq} decreases at any temperature. For any exposure time, the cold-worked condition results in a smaller deviation of $\bar{C}$ from C_{eq} , compared with the solution-annealed material at the lower temperatures. Similar plots for solution-annealed Type 304 stainless steel with initial carbon contents of 0.02, 0.05, and 0.08 wt % are shown in Figs. A.6-A.8. A comparison of Figs. A.4 and A.7 illustrates the effect of the lower diffusion coefficient for carbon in Type 304 stainless steel on the carbide-precipitation kinetics.

The carbon concentrations in austenite at the surface of the steel (C_s) for a carbon concentration in sodium of 0.13 ppm* are indicated by the dashed lines in Figs. A.4-A.8. The carbon-concentration difference $C_s - \bar{C}$

Fig. A.6. Effect of Temperature on Concentration of Carbon in the Austenite Phase at the Sodium-Steel Interface C_s and That within the Material $\bar{C}$ for Annealing Times of 1000, 4000, and 10,000 hr for Solution-annealed Type 304 Stainless Steel with an Initial Carbon Concentration of 0.02 wt %. (A carbon concentration of 0.13 ppm in the sodium was used to obtain the variation of C_s with temperature.) Neg. No. MSD-58576.

Fig. A.7. Effect of Temperature on Concentration of Carbon in the Austenite Phase at the Sodium-Steel Interface C_s and That within the Material $\bar{C}$ for Annealing Times of 1000, 4000, and 10,000 hr for Solution-annealed Type 304 Stainless Steel with an Initial Carbon Concentration of 0.05 wt %. (A carbon concentration of 0.13 ppm in the sodium was used to obtain the variation of C_s with temperature.) Neg. No. MSD-58235.

*The carbon concentration in sodium in equilibrium with the steel of a given carbon activity is based upon data for the solubility of carbon in sodium discussed in Appendix B.

Fig. A.8

Effect of Temperature on Concentration of Carbon in the Austenite Phase at the Sodium-Steel Interface C_s and That within the Material $\bar{C}$ for Annealing Times of 1000, 4000, and 10,000 hr for Solution-annealed Type 304 Stainless Steel with an Initial Carbon Concentration of 0.08 wt %. (A carbon concentration of 0.13 ppm in the sodium was used to obtain the variation of C_s with temperature.) Neg. No. MSD-58577.

establishes the driving force for decarburization and carburization at high and low temperatures, respectively, for each exposure time. It is evident that this approach does not influence the driving force at higher temperatures; however, at lower temperatures, $C_s - \bar{C}$ is considerably less than $C_s - C_{eq}$. Driving forces for carbon diffusion in the austenite, computed on this basis, were incorporated into the computer program to obtain carbon-concentration-versus-distance profiles in the austenite phase for various exposure times and temperatures. A relationship between the carbon concentration in the austenite phase and the total carbon content in the material (similar to Fig. A.3) under metastable equilibrium conditions was also developed. The solution treatment of a stainless steel at $\sim 1050^\circ\text{C}$ results in the dissolution of the carbides, and, upon fast cooling, the initial amount of carbon in the material is retained in the austenite phase. The amount of carbon that precipitates upon thermal aging depends upon the exposure time and temperature, as is evident from Figs. A.4-A.8. The relationship between the carbon concentration in austenite and total carbon content of the material was obtained from Eqs. A.18 and A.19 in a computer subroutine for the temperature and exposure time specified in the main program. Figure A.9 shows this type of relationship for solution-annealed Type 304 stainless steel after a 4000-hr exposure at temperatures between 400 and 550°C . The 400°C line indicates that almost all the carbon in the steel is retained in the austenite phase because of the slowness of the carbide-precipitation reaction. As the temperature increases, the curves tend toward the values predicted from the γ -carbide phase equilibrium shown in Fig. A.3.

Fig. A.9

Relationship between Carbon Concentration in the Austenite Phase and Total Carbon Content of Solution-annealed Type 304 Stainless Steel after 4000 hr at Temperatures between 400 and 550°C under Metastable Austenite-Carbide Equilibrium Conditions. Neg. No. MSD-58578.

APPENDIX B

Solubility of Carbon in Sodium

The solubility of carbon in sodium has been measured by a number of investigators⁵⁵⁻⁵⁹ using different equilibration techniques and analytical methods. Gratton⁵⁵ reported values between 40 and 80 ppm for the temperature range of 150-700°C in sodium containing 40 ppm oxygen. Problems encountered in the separation of particulate carbon with a 5- μ m stainless steel filter from the carbon-saturated sodium could account for the relatively high values and the small variation with temperature. Luner *et al.*⁵⁶ equilibrated ¹⁴C-labeled graphite with sodium and concluded that the solubility was less than 0.005 ppm at temperatures below 450°C.

Longson and Thorley⁵⁷ diffused carbon through a thin-walled nickel capsule containing sodium; the external environment was either a CO/CO₂ gas mixture or sodium containing a carbon source at an activity of unity. Carbon analyses of the sodium in the capsule, along with a knowledge of the carbon activity from the gas composition and the nickel capsule material, were used to obtain solubility values at temperatures in the range of 600-950°C. Gehri⁵⁸ also used a capsule technique at temperatures between 700 and 1000°C, in which (1) the sodium was equilibrated in a carbon-saturated nickel crucible, (2) the capsule was inverted to collect the sodium in a copper crucible, and (3) the sodium was analyzed for carbon by a combustion method. Salzano and Newman⁵⁹ obtained carbon solubility values between 575 and 700°C by relating the change in the electromotive force of an electrochemical carbon cell to quantitative additions of carbon to sodium contained in a nickel vessel. The

Fig. B.1. Temperature Dependence of Carbon Solubility in Sodium.⁵⁷⁻⁵⁹
Neg. No. MSD-55721.

carbon-solubility results from the three latter investigations are shown in Fig. B.1. The temperature dependence of the carbon solubility from two of the investigations is in good agreement; however, the actual values differ by a factor of approximately five at any temperature. The data of Salzano and Newman, obtained over a relatively small temperature interval, fall within the results of the other two investigations.

During the development of a foil-equilibration method of determining the activity of carbon in liquid sodium,³⁵ no correlation could be established between measured carbon activities in the range of interest in reactor sodium systems and carbon analyses of the sodium by the oxyacidic-flux method,⁶⁰ which has a

sensitivity of $\sim 1 \mu\text{g}$ of carbon for a 1-g sample. Since the temperature dependence of the solubility of carbon in sodium is of major importance in establishing the driving force for carbon migration in athermal loop systems, the carbon-solubility results of either Longson and Thorley or Gehri could be used with measured carbon activities by the foil-equilibration method to obtain carbon concentrations in sodium. In the present report, the carbon concentrations in sodium were obtained by applying Henry's law to the carbon-solubility results of Longson and Thorley; i.e., $C_{\text{Na}} = a_{\text{C}}^{\text{Na}} C_{\text{Na}}^{\text{sat}}$, where

$$C_{\text{Na}}^{\text{sat}} (\text{ppm}) = 5.03 \times 10^7 \exp(-13,740/T). \quad (\text{B.1})$$

The actual carbon concentration in the sodium is determined by the rate at which carbon is introduced into and removed from the sodium by the loop materials and by other sources or sinks that may be present in the system. For example, operating procedures such as the periodic insertion or removal of test specimens or hardware through a cover gas can dislodge "frost" containing sodium carbonate and other carbon-bearing species into the sodium. This material, upon dissolution, can increase both the oxygen and carbon concentrations of the sodium. Other circumstances and changes in operating conditions can also alter the carbon concentration in the sodium, since no provision exists for carbon control that is analogous to the cold trap, which is used to maintain the oxygen and hydrogen concentrations of the sodium within a narrow range of values. To a large extent, these circumstances account for the wide range of carbon levels that have been observed in reactor materials upon exposure to high-temperature flowing sodium. Since reactor operations (e.g., fuel handling and maintenance) and operating conditions influence the carbon concentration in sodium, it is difficult to predict probable values with the degree of certainty required to relate this information to microstructural changes and the mechanical behavior of materials in the absence of a direct knowledge of the sodium purity (i.e., carbon concentration determined by a foil-equilibration method rather than by sodium sampling and analyses). The reported carbon concentration of $1.2 \pm 0.8 \text{ ppm}^{61}$ for the sodium in the EBR-II primary system is at the sensitivity limit of the oxyacidic-flux method. Foil equilibrations will be conducted in a specimen-exposure module on the Radioactive Sodium Chemistry Loop (RSCL) at EBR-II to obtain an accurate measure of the carbon activity in sodium. Measurements of this type are routinely performed in out-of-reactor loop systems to correlate microstructural and compositional changes in materials and the mechanical-property behavior with the sodium purity.

APPENDIX C

Computer Program for Generating Solutions to the Diffusion Equations

A computer program, based upon the diffusion equations and the mathematical expressions for the thermodynamic and kinetic information described in the present report, was developed to generate carbon concentration-distance profiles in austenitic stainless steels. The simplified flow diagram, shown in Fig. C.1, indicates the operating conditions and the material parameters that must be specified as well as the sequence for performing the computations. The program was written in FORTRAN language for use on the ANL IBM-360 computer. Table C.1 is a listing of the program with a description of the various symbols, pertinent comment statements, and an example of the computer output.

Fig. C.1. Simplified Flow Diagram for Generating Carbon-diffusion Profiles. Neg. No. MSD-58579.

TABLE C.1. Program Listing and an Example of Computer Output

THIS PROGRAM NUMERICALLY CALCULATES CARBURIZATION
-DECARBURIZATION PROFILES IN TYPES 304 AND 316
STAINLESS STEEL AS A FUNCTION OF TIME, TEMPERATURE
AND CARBON CONCENTRATION IN SODIUM. OTHER
VARIABLES INCLUDE THE INITIAL CARBON AND CHROMIUM
CONCENTRATION OF THE STEELS AND THE CARBIDE
PARTICLE RADIUS AND INTERPARTICLE DISTANCE WHICH
ARE DEPENDENT UPON THE THERMAL-MECHANICAL
CONDITION OF THE MATERIAL. THE ANALYSIS TAKES
INTO ACCOUNT THE SLOWNESS OF THE CARBIDE
PRECIPITATION PROCESS AT TEMPERATURES BELOW 600
DEGREES CENTIGRADE.

DEFINITION OF SYMBOLS

ACNA	- ACTIVITY OF CARBON IN SODIUM
ACSAT	- ACTIVITY OF CARBON AT THE AUSTENITE-CARBIDE PHASE BOUNDARY IN THE STEEL
ADY	- ABSOLUTE VALUE OF YD FINAL, I.E., YD(K)
AP, ADP	
ATP, BP	- TEMPERATURE DEPENDENT CONSTANTS IN EQS. (A-7), BDP (A-10), AND (A-15)
BTP	
AO-A8	- COEFFICIENTS IN EQS. (A-8), (A-9), (A-11), BO-B8 - (A-12), (A-16), AND (A-17)
C1-C6	- COEFFICIENTS ANALOGOUS TO A3 TO A5 AND B3 TO B5 IN EQS. (A-11) AND (A-12) IN MOLE FRACTION UNITS
BADD	- VALUE TO READJUST THE ITERATIVE CONSTANT IN EQ. (8)
BOTOM	- DENOMINATOR OF EXPRESSION TO CHANGE THE CARBON AND CHROMIUM CONCENTRATIONS FROM PPM AND WT% UNITS TO MOLE FRACTION UNITS
CAVG	- TIME AVERAGE CARBON CONCENTRATION IN THE AUSTENITE PHASE FROM EQ. (A-19)
CBG	- INITIAL CARBON CONCENTRATION IN THE AUSTENITE PHASE FROM EQ. (A-15) FOR ANY GIVEN INITIAL CARBON CONTENT OF THE STEEL
CBM	- CBG IN MOLE FRACTION UNITS
CBT	- INITIAL CARBON CONCENTRATION IN THE STEEL, PPM
CBTGCC	- CBT IN UNITS OF G/CC
CBULK	- VALUE OF THE ITERATIVE CONSTANT IN EQ. (8)
CGBRY	- CARBON CONCENTRATION IN THE AUSTENITE PHASE AT THE AUSTENITE / AUSTENITE + CARBIDE PHASE BOUNDARY, NC IN EQ. (8)
CGSAT	- SOLUBILITY OF CARBON IN THE FE - 18%CR - 8%NI ALLOY FROM EQ. (A-13), PPM
CG(I)	- CARBON CONCENTRATION IN THE AUSTENITE PHASE AT ANY POSITION, I, IN THE STEEL FROM THE SOLUTION TO THE DIFFUSION EQUATION, PPM

TABLE C.1 (Contd.)

CMSAT	- CGSAT IN MOLE FRACTION UNITS
CNA	- CARBON CONCENTRATION IN SODIUM, PPM.
CR	- CHROMIUM CONCENTRATION, WT%
CRBG	- INITIAL CHROMIUM CONCENTRATION IN THE AUSTENITE PHASE, WT%
CRBM	- CRBG IN MOLE FRACTION UNITS
CRBT	- INITIAL CHROMIUM CONTENT IN THE STEEL, WT%
CRBTM	- CRBT IN MOLE FRACTION UNITS
CRM(I)	- CHROMIUM CONCENTRATION IN THE AUSTENITE PHASE AT ANY POSITION, I, IN THE STEEL FROM THE SOLUTION TO THE DIFFUSION EQUATIONS, MOLE FRACTION UNITS
CRSG	- CHROMIUM CONCENTRATION IN THE AUSTENITE PHASE AT THE SURFACE OF THE STEEL, WT%
CRSM	- CRSG IN MOLE FRACTION UNITS
CSG	- CARBON CONCENTRATION IN THE AUSTENITE PHASE AT THE SURFACE OF THE STEEL, PPM
CSM	- CSG IN MOLE FRACTION UNITS
CSNA	- CARBON SOLUBILITY IN SODIUM FROM EQ. (B-1), PPM
CST	- CARBON CONCENTRATION AT THE SURFACE OF THE STEEL AFTER EXPOSURE TO SODIUM, PPM
CT	- CARBON CONCENTRATION AT ANY POSITION IN THE STEEL FROM THE SOLUTION TO THE DIFFUSION EQUATIONS, PPM
CTF	- CARBON CONCENTRATION IN THE STEEL FOR A GIVEN CARBON CONCENTRATION IN THE AUSTENITE, CAVG, UNDER METASTABLE EQUILIBRIUM CONDITIONS, PPM, (E.G., FIG A-9)
DC	- CARBON DIFFUSION COEFFICIENT IN STAINLESS STEEL, EQS. (A-1) AND (A-2)
DELX	- INCREMENT OF DISTANCE, X, CM
DERY(1)	- INPUT VECTORS OF ERROR WEIGHTS FOR USE IN HPCG
DERY(2)	- SUBROUTINE
ETA	- DIMENSIONLESS VARIABLE, $X/(4*DC*TIME)**0.5$
FRAC	- FRACTIONAL VALUE TO RE-ESTIMATE THE INITIAL SLOPE OF THE CARBON CONCENTRATION VS ETA PROFILE IN AUSTENITE AT THE STEEL SURFACE
GDELX	- GRAMS OF CARBON IN THE STEEL AT ANY POSITION, X, WITHIN THE STEEL, GRAMS/CC
GRAMS	- AMOUNT OF CARBON THAT DIFFUSED IN THE STEEL AT ANY TIME, GRAMS
IC	- COUNTER FOR PRINTING CYCLE
IHLF	- AN OUTPUT VALUE ALLOWING A TERMINATION OF THE PROGRAM IF THE NUMBER OF BISECTIONS OF THE INITIAL INCREMENT SIZE REACHES THE VALUE SPECIFIED -- REQUIRED FOR HPCG
IPETA	- CONSTANT THAT DETERMINES NUMBER OF INCREMENTS WITHIN ONE PRINTING CYCLE OF THE CARBON IN AUSTENITE VS ETA PROFILE
IPX	- CONSTANT THAT DETERMINES NUMBER OF INCREMENTS WITHIN ONE PRINTING CYCLE OF THE CARBON IN AUSTENITE VS DISTANCE PROFILE
ITIME	- THE NUMBER OF TIMES THE PROGRAM WILL BE RUN FOR VARIOUS TIMES
J	- COUNTER FOR INCREMENTS IN CARBON IN AUSTENITE VS DISTANCE PROFILE

TABLE C.1 (Contd.)

JJ	- COUNTER FOR PRINTING CYCLE IN CARBON IN AUSTENITE VS DISTANCE PROFILE
J1	- VALUE OF J AT A PRINTING CYCLE
J2	- VALUE OF J AT THE NEXT PRINTING CYCLE
K	- TOTAL NUMBER OF INCREMENTS
L	- COUNTER FOR INCREMENTS IN CARBON IN AUSTENITE VS ETA PROFILE
LSAT	- NUMBER OF INCREMENTS INTO WHICH THE SINGLE-PHASE REGION OF THE STEEL IS DIVIDED
LSTART	- INITIAL INCREMENT VALUE FOR THE TWO-PHASE REGION OF THE STEEL
M	- COUNTER FOR NUMBER OF ADJUSTMENTS TO INITIAL SLOPE OR ITERATIVE CONSTANT
MSS	- TYPE OF STEEL, 304 OR 316
NDIM	- NUMBER OF EQUATIONS THAT ARE USED IN HPCG SUBROUTINE
PPM	- PARTS PER MILLION BY WEIGHT
PRMT(1)	- INITIAL VALUE OF ETA -- REQUIRED BY HPCG
PRMT(2)	- FINAL VALUE OF ETA -- REQUIRED BY HPCG
PRMT(3)	- INCREMENT SIZE OF ETA -- REQUIRED BY HPCG
PRMT(4)	- UPPER ERROR BOUND -- REQUIRED BY HPCG
PRMT(5)	- CONSTANT INITIALIZED AT ZERO -- REQUIRED FOR HPCG
R	- GAS CONSTANT, 1.987 CAL/G-MOLE-DEGREE K
RO	- RADIUS OF THE CARBIDE PARTICLE, CM
RS	- THE RADIUS OF THE EQUIVALENT SPHERE SURROUNDING A CARBIDE PARTICLE, CM
S	- TEMPERATURE DEPENDENT CONSTANT
SLOPE	- VALUES OF Y(1) STORED IN THE COMPUTER
T	- TEMPERATURE, DEGREES K
TC	- TEMPERATURE, DEGREES C
THRS	- TIME, HRS
TIME	- TIME, SEC
TLAST	- TIME -- REQUIRED FOR SUBROUTINES CTCG AND CGCT, SEC
TRCEPT	- TEMPERATURE DEPENDENT CONSTANT ANALOGOUS TO BP IN EQS. (A-13) AND (A-12), IN MOLE FRACTION UNITS
TYEAR	- TIME, YEARS
X	- PENETRATION DISTANCE, CM
YADD	- VALUE USED IN RE-ESTIMATING THE CARBON CONCENTRATION GRADIENT AT THE SURFACE OF THE STEEL
YFIN	- CARBON CONCENTRATION IN THE AUSTENITE PHASE FOR THE LAST INCREMENT IN THE STEEL AT LARGE X, IN MOLE FRACTION UNITS
Y1	- INITIAL VALUE FOR THE CARBON CONCENTRATION GRADIENT IN THE AUSTENITE PHASE IN THE TWO-PHASE AUSTENITE + CARBIDE REGION
Y(1)	- Y1 -- REQUIRED BY THE PHCG SUBROUTINE
Y(2)	- CARBON CONCENTRATION IN THE AUSTENITE PHASE AT THE SURFACE OF THE STEEL FOR USE IN HPCG SUBROUTINE, MOLE FRACTION UNITS
ZEROSL	- MAXIMUM VALUE OF THE CARBON CONCENTRATION GRADIENT IN THE AUSTENITE PHASE IN THE LAST INCREMENT INTO THE STEEL AT LARGE ETA

TABLE C.1 (Contd.)

THIS IS THE MAIN PROGRAM

```

INTEGER W
DIMENSION PRMT(5), Y(2), DERY(2), AUX(16,2)
DIMENSION YMOLE(4000), ETA(4000), YD(4000), YDD(4000)
DIMENSION SLOPE(25), DIFY(25), YFIN(25), ADIFY(25)
DIMENSION CG(4000), CRM(4000), CRG(4000), CBULK(25)
DIMENSION TIME(20)
COMMON /A/ ZEROSL
COMMON /B/ L, YMOLE, ETA, YD, YDD
COMMON /C/ S
COMMON /D/ CTF, DC, CAVG, RO, RS
EXTERNAL FCT, OUTP

```

SYSTEM INPUT PARAMETERS

```

CNA = 0.5
T = 873.
ITIME = 1
MSS = 304
CBT = 500.
CRBT = 18.0
RO = 0.5E-4
RS = 0.000747
IPETA = 50
IPX = 50
DO 1 I = 1, ITIME
1  READ 2, TIME(I)
2  FORMAT(E11.5)

```

REQUIRED CONSTANTS

```

R = 1.987
A0 = 14.15
A1 = -1.74E+03
A2 = -9.84E-4
A3 = 31.86
A4 = -1.42E+04
A5 = -2.186E-2
A6 = 1.752
A7 = -468.0
A8 = -7.12E-04
B0 = 2.0
B1 = -4.52E+02
B2 = -5.87E-4
B3 = -343.5

```

TABLE C.1 (Contd.)

B4 = 1.47E+05
B5 = 0.232
B6 = -7.673
B7 = 1553.0
B8 = 7.93E-3
C1 = 0.339881
C2 = -1.51352E+02
C3 = -2.32864E-04
C4 = 0.539688
C5 = -3.03159E+02
C6 = -4.05861E-04
PPM = 1.0E+6
ZEROSL = 1.0E-5

CALCULATION OF THE ACTIVITY AND SOLUBILITY OF
CARBON IN SODIUM AND THE SOLUBILITY OF CARBON IN
THE STEEL

AP = A0 + A1/T + A2*T
BP = B0 + B1/T + B2*T
ADP = A3 + A4/T + A5*T
BDP = B3 + B4/T + B5*T
ATP = A6 + A7/T + A8*T
BTP = B6 + B7/T + B8*T
S = C1 + C2/T + C3*T
TRCEPT = C4 + C5/T + C6*T
CSNA = 5.0E+07 * EXP(-13740.0/T)
ACNA = CNA / CSNA
CGSAT = 1.088E+07 * EXP(-11940.0/T)
ACSAT = EXP((ALOG(CGSAT) - AP) / BP)
BOTOM = CRBT/52.00 + CGSAT/1.0E+04/12.01 + (100.0 - CRBT 1- (CGSAT/1.0E+04))/55.85
CMSAT = CGSAT/1.0E+04/12.01/BOTOM
CRBTM = CRBT/52.00/BOTOM
TC = T - 273.0
PRINT 11, T, TC, CNA, MSS, CBT, CRBT, RO, RS
11 FORMAT(1H1,15X,'SYSTEM INPUT PARAMETERS'///15X, 1'TEMPERATURE = ',F7.2,' K ',F7.2,' C'/15X, 1'CARBON IN SODIUM = ',E12.4/15X,'TYPE OF STEEL = ', 1I4/15X,'INITIAL CARBON CONC.',F7.2/15X, 1'INITIAL CHROMIUM CONC.',F7.2/15X, 1'RO -- PARTICLE RADIUS ',E12.4/15X, 1'RS -- 1/2 INTERPARTICLE DISTANCE ',E12.4////) PRINT 12, CNA, CSNA, ACNA
12 FORMAT(15X,'CARBON CONCENTRATION, ACTIVITY OF CARBON,', 1'AND SOLUBILITY OF'/15X,'CARBON IN SODIUM'///15X,'CNA = ', 1E10.3,' CSNA = ',E10.3,' ACNA = ',E10.3//) PRINT 13, CGSAT, CMSAT, ACSAT, CRBT, CRBTM
13 FORMAT(15X,'VALUES FOR THE CARBON AND CHROMIUM ', 1'CONCENTRATIONS AND THE'/15X,'CARBON ACTIVITY IN ', 1'AUSTENITE AT THE AUSTENITE / AUSTENITE'/15X,'+ CARBIDE ', 1'PHASE BOUNDARY'///15X,'CGSAT = ',F7.2,' CMSAT = ',E12.3, 1' ACSAT = ',E10.3//15X,'CRBT = ',F7.2,' CRBTM = ', 1E10.3//)

TABLE C.1 (Contd.)

CALCULATION OF THE DIFFUSION COEFFICIENT OF CARBON
IN THE STEEL

```

      IF(MSS .EQ. 304) GO TO 20
      DC = 0.19 * EXP(-37400.0/(R*T))
      PRINT 21, T, DC
21  FORMAT(//15X,'DC FOR 316 S.S. AT TEMP =',F7.2,2X,'IS',
1E12.3//)
      GO TO 22
20  DC = 6.18 * EXP(-44610.0/(R*T))
      PRINT 23, T, DC
23  FORMAT(//15X,'DC FOR 304 S.S. AT TEMP =',F7.2,2X,'IS',
1E12.3//)

```

CALCULATION OF THE TOTAL CARBON AND CARBON
CONCENTRATION IN AUSTENITE PHASE AT THE SODIUM-
STEEL INTERFACE

```

22  DO 30 W = 1,ITIME
      TLAST = TIME(W)
      IF(ACNA .GE. ACSAT) GO TO 31
      CST = ACNA * CGSAT / ACSAT
      CSG = CST
      CRSG = CRBT
      CR = CRBT
      GO TO 32
31  CSG = EXP(ATP * (AP + BP * ALOG(ACNA)) + BTP)
      CAVG = CSG
      CALL CGCT(TLAST,T)
      CST = CTF
      IF(CST .GE. CSG) GO TO 33
      PRINT 34, CST, CSG
34  FORMAT(////20X,'CSG IS LARGER THAN CST'//5X,'CST =',
1F11.5,' CSG = ',F11.5//) SET CSG = TO CST'////)
      CSG = CST
33  CRSG= ADP * ALOG(CSG) + BDP
      CR = CRSG
32  BOTOM = (CSG *1.0E-4/12.01 + CR /52.0 + (100.0-CR -
1CSG * 1.0E-04)/55.85)
      CSM = CSG /12.01*1.0E-4/BOTOM
      CRSM = CRSG / 52.0 / BOTOM
      PRINT 35, CST, CSG, CSM, CRSG, CRSM
35  FORMAT(//15X,'CARBON AND CHROMIUM CONCENTRATIONS IN THE ',
1'STEEL AT THE'//15X,'SODIUM-STEEL INTERFACE'//15X,
1'CST =',F9.2,' CSG = ',F9.2,' CSM = ',E12.4//15X,
1'CRSG = ',F9.3,' CRSM = ',E12.3////)

```

TABLE C.1 (Contd.)

CALCULATION OF CARBON CONCENTRATION IN THE
AUSTENITE PHASE FOR A SPECIFIED INITIAL CARBON
CONTENT IN THE STEEL

```

IF(CBT .LT. CGSAT) GO TO 40
CT = CBT
CALL CICG(TLAST,CT,T)
CBG = CAVG
CRBG= ADP * ALOG(CBG) + BDP
CR = CRBG
GO TO 41
40  CBG = CBT
    CRBG = CRBT
    CR = CRBG
41  BOTOM = (CBG * 1.0E-4/12.01 + CR / 52.0 + (100.0-CR -
    ICBG * 1.0E-04)/55.85)
    CBM = CBG / 12.01 * 1.0E-4 / BOTOM
    CRBM = CBG / 52.0 / BOTOM
    CBTGCC = CBT * 8.04 / PPM
    PRINT 42, CBT, CBG, CBM, CBTGCC, CRBG, CRBM
42  FORMAT(///15X,'INITIAL CARBON AND CHROMIUM ',
    1'CONCENTRATIONS IN THE STEEL'///15X,'CBT =',F9.3,' ',
    1'CBG =',F9.3,' CBM =',E10.3///15X,'CBTGCC =',E10.3,' ',
    1'CRBG =',F9.3,' CRBM =',E10.3///)

```

THIS SECTION DETERMINES THE CARBON CONCENTRATION
VS ETA PROFILE

```

YADD = 0.2E-2
BADD = 1.0E-3
M = 1
IF(ACNA .GE. ACSAT) GO TO 50
CBULK(M) = CBM
121 L = 1
    ETA(L) = 0.0000
52  CFRAC = ERFC(ETA(L))
    YMOLE(L) = (CSM - CBULK(M)) * CFRAC + CBULK(M)
    IF(YMOLE(L) .GE. CMSAT) GO TO 51
    L = L + 1
    ETA(L) = ETA(L-1) + 1.0E-03
    GO TO 52
51  BOTOM= YMOLE(L) * 12.01 + CRBTM*52.00 + (1.0 - YMOLE(L) -
    1CRBTM)*55.85
    CGBRY = YMOLE(L) * 12.01 * 1.0E+06 / BOTOM
    CSATDF = ABS(CGSAT - CGBRY)
    IF(CSATDF .LT. 1.0) GO TO 53
    PRINT 54, CGSAT, CGBRY
54  FORMAT(/10X,'CARBON MATCH UP AT PHASE BOUNDARY IS NOT',
    1' WITHIN 0.1 PPM PROGRAM CONTINUES'//,
    1' CGSAT =',F11.5,' CGBRY =',F11.5)
53  LSAT = L
    Y(1) = -(CSM - CBULK(M))*2.0/ ((3.1416)**0.5) *
    1EXP(-(ETA(L)**2))

```

TABLE C.1 (Contd.)

```

SLOPE(M) = Y(1)
Y1 = Y(1)
Y(2) = YMOLE(L)
PRMT(1) = ETA(L)
PRMT(2) = ETA(L) + 4.0
L = L + 1
GO TO 55

```

ESTIMATE INITIAL CARBON GRADIENT IN THE TWO-PHASE REGION

```

50 IF(CST .GT. 20000.) GO TO 56
   Y(1) = -5.20E-9 * (CST - CBT)
   GO TO 57
56 Y(1) = -5.20E-11 * (CST - CBT)
57 Y1=Y(1)
132 SLOPE(M) = Y1
    Y(2) = CSM
    Y(1) = Y1
    L = 1
    PRMT(1) = 0.0
    PRMT(2) = 4.0
55 PRMT(3) = 1.0E-3
    PRMT(4) = 2.0E-6
    PRMT(5) = 0.0
    DERY(1) = 0.5
    DERY(2) = 0.5
    NDIM = 2
    IHLF = 1
    CALL HPCG(PRMT,Y,DERY,NDIM,IHLF,FCT,OUTP,AUX)

```

THIS SECTION CHECKS FINAL VALUE FOR CARBON CONCENTRATION IN AUSTENITE PHASE OBTAINED NUMERICALLY WITH CBM. IF NOT WITHIN SPECIFIED LIMIT THEN PROGRAM GOES TO SECTION WHICH DETERMINES NEW INITIAL CARBON GRADIENT, OTHERWISE GO TO SECTION WHICH PRINTS OUT RESULTS

```

K = L - 1
ADY = ABS(YD(K))
IF(ADY .GT. ZERO5L) GO TO 63
DIFY(M) = YMOLE(K) - CBM
ADIFY(M) = ABS(YMOLE(K) - CBM)
YFIN(M) = YMOLE(K)
IF(ADIFY(M) .LE. 1.0E-07) GO TO 60
PRINT 62, M, SLOPE(M), YMOLE(K), DIFY(M)
62 FORMAT(/20X,'FINAL VALUE DOES NOT EQUAL CBM.',
1'E13.5, 'SLOPE = ',E13.5, 'YMOLE(K) = ',E12.4, 'DIFY(M) = ',E12.4)
GO TO 61
63 PRINT 64
64 FORMAT(/20X,'THE FINAL SLOPE IS NOT ZERO THEREFORE DO',
1' NOT CONTINUE'/20X,'PRINT OUT THE PROFILE AS IS'/)

```

TABLE C.1 (Contd.)

THIS SECTION PRINTS OUT CARBON CONCENTRATION
VS ETA PROFILE

```

60 PRINT 71, M, SLOPE(M), YMOLE(K), DIFY(M)
71 FORMAT(/20X,'THIS IS THE DESIRED SLOPE, DC/DX, THAT',
1' GIVES CBM'/' M = ',I3,' SLOPE = ',E13.5,
1' YMOLE(K) = ',E12.4,' DIFY(M) = ',E12.4////////4X,
1'THIS IS THE CARBON IN AUSTENITE VS ETA PROFILE'//)
JJ = IPETA - 1
IF(ACNA .GE. ACSAT) GO TO 72
PRINT 73
73 FORMAT(/4X,'I',5X,'ETA(I)', 7X,'YMOLE(I)',5X,'YD(I)',
1 6X,'CG(I)', 4X,'CRG(I)')//)
DO 74 I = 1,LSAT
BOTOM = YMOLE(I) * 12.01 + CRBTM*52.00 + (1.0 - YMOLE(I)
1- CRBTM)*55.85
CG(I) = 1.0E+06 * YMOLE(I) * 12.01/ BOTOM
CRG(I) = CRBT
YD(I) = -(CSM - CBULK(M))*2.0/ ((3.1416)**0.5) *
1EXP(-(ETA(I)**2))
JJ = JJ + 1
IF(JJ .EQ. IPETA) GO TO 75
GO TO 74
75 JJ = JJ - IPETA
PRINT 77, I, ETA(I), YMOLE(I), YD(I), CG(I), CRG(I)
77 FORMAT(3X,I4,2X,E10.3,2X,E10.3,2X,E10.3,2X,F7.2,2X,F7.2)
74 CONTINUE
I = LSAT
PRINT 78, I, ETA(I), YMOLE(I), YD(I), CG(I), CRG(I)
78 FORMAT(/ 4X,'VALUES AT THE AUSTENITE / AUSTENITE + ',
1'CARBIDE PHASE BOUNDARY'/3X,I4,2X,E10.3,2X,E10.3,2X,
1E10.3,2X,F7.2,2X,F7.2//)
LSTART = LSAT + 1
GO TO 79
72 LSTART = 1
79 PRINT 80
80 FORMAT(5X,'I', 6X,'ETA', 7X,'YMOLE', 8X,'YD', 8X,'YDD',
17X,'CG', 4X,'CRG')
DO 81 I = LSTART,K
CRM(I) = S * ALOG(YMOLE(I)) + TRCEPT
BOTOM = YMOLE(I)*12.01 + CRM(I) *52.00 + (1.0-YMOLE(I)-
1CRM(I))*55.85
CG(I) = 1.0E+6 * YMOLE(I)*12.01 / BOTOM
CRG(I) = ADP * ALOG(CG(I)) + BDP
JJ = JJ + 1
IF(JJ .EQ. IPETA) GO TO 82
GO TO 81
82 JJ = JJ - IPETA
PRINT 83, I, ETA(I), YMOLE(I), YD(I), YDD(I), CG(I),
1CRG(I)
83 FORMAT(3X,I4,4(1X,E10.3),1X,F7.2,1X,F5.2)
81 CONTINUE

```


TABLE C.1 (Contd.)

THE TOTAL CARBON PROFILE IS DETERMINED FROM THE
CARBON IN AUSTENITE PROFILE. ALSO THE MASS OF
CARBON GAINED OR LOST PER SQUARE CENTIMETER OF
THE STEEL IS CALCULATED.

```

K1 = K - 1
THRS = TIME(W) / 3600.0
TYEAR = THRS / 24.00 / 365.0
PRINT 90, TIME(W), THRS, TYEAR
90  FORMAT(/ /3X,14HTIME IN SEC. =,E11.5/3X,14HTIME IN HRS. =,
1F11.5/3X,'TIME IN YEARS =',F10.5/3X,'THIS IS THE ',
1'CARBON IN AUSTENITE AND TOTAL CARBON'/3X,
1'VS X PROFILE AND THE MASS OF CARBON GAINED OR LOST'/3X,
1'PER SQUARE CENTIMETER OF THE STEEL')

PRINT 91
91  FORMAT(/ /4X,'J',4X,'X(CM)', 6X,'CG', 8X,'CT',6X,'CT2',
1 6X,'GRAMS', 6X,'GDELX')
GDELX = 0.0
GRAMS = 0.0000
X = 0.0000
J = 1
IC = 0
IF(ACNA .GE. ACSAT) GO TO 92
CT = CG(1)
GO TO 93
92  CAVG = CG(1)
CALL CGCT(TLAST,T)
CT = CTF
IF(CT .LT. 50000.0) GO TO 93
CT = 50000.0
93  CT1 = (CT*8.04/PPM) - CBTGCC
CT2 = CT1
PRINT 100, J, X, CG(J), CT, CT2, GRAMS, GDELX
100 FORMAT(2X,I4,1X,E10.3,1X,F6.1,1X,F7.1,1X,E10.3,1X,
1E10.3,1X,E10.3)
J1 = J
97  J = J + 1
IC = IC + 1
IF(ACNA .GE. ACSAT) GO TO 94
IF(J .EQ. LSAT) GO TO 95
94  IF(J .EQ. K) GO TO 96
IF(IC .EQ. IPX) GO TO 96
GO TO 97
96  IC = IC - IPX
IF(CG(J) .GE. CGSAT) GO TO 98
CT = CG(J)
GO TO 99
98  CAVG = CG(J)
CALL CGCT(TLAST,T)
CT = CTF

```

TABLE C.1 (Contd.)

```

IF(CT .LT. 50000.0) GO TO 99
CT = 50000.0
99  CT2 = (CT*8.04/PPM) - CBTGCC
    J2 = J
    DELX = (ETA(J2) - ETA(J1)) * ((4.0*DC *TIME(W))**0.5)
    GDELX = DELX * CT2 + 0.5 * DELX * (CT1-CT2)
    X = X + DELX
    GRAMS = GRAMS + GDELX
    PRINT 100, J, X, CG(J), CT, CT2, GRAMS, GDELX
    IF(J .EQ. K) GO TO 30
    GO TO 101
95  CT = CG(J)
    XS = (ETA(J) - ETA(J1)) * ((4.*DC*TIME(W))**0.5) + X
    PRINT 102, J, XS, CG(J), CT
102  FORMAT(/5X,'VALUE AT THE AUSTENITE / AUSTENITE + ',
1'CARBIDE PHASE BOUNDARY'/2X,I4,I4,1X,F10.3,1X,F6.1,1X,
1F7.1//)
    GO TO 94
101  CT1 = CT2
    J1 = J2
    GO TO 97
30  CONTINUE
    GO TO 103

```

THIS SECTION REESTIMATES THE CARBON CONCENTRATION
GRADIENT

```

61  IF(ACNA .GE. ACSAT) GO TO 110
    IF(M-1) 111,111,112
111  IF(YMOLE(K) - CBM) 113,60,114
113  CBULK(M+1) = CBULK(M) + BADD
    GO TO 115
114  CBULK(M+1) = CBULK(M) - BADD
    GO TO 115
112  IF(DIFY(M) .LT. 0.0) GO TO 116
    IF(DIFY(M-1) .GT. 0.0) GO TO 114
    GO TO 117
116  IF(DIFY(M-1) .LT. 0.0) GO TO 113
    FRAC = (CBM - YFIN(M)) / (YFIN(M-1) - YFIN(M))
    CBULK(M+1) = CBULK(M) + FRAC * (CBULK(M-1) - CBULK(M))
    GO TO 118
117  FRAC = (YFIN(M) - CBM) / (YFIN(M) - YFIN(M-1))
    CBULK(M+1) = CBULK(M) - FRAC*(CBULK(M) - CBULK(M-1))
118  BADD = BADD/10.0
115  IF(M .GT. 20) GO TO 119
    M = M + 1
    GO TO 121
110  IF(M - 1)122,122,123
122  IF(YMOLE(K) - CBM) 124,60,125
124  Y1=Y1+YADD
    GO TO 126
125  Y1 = Y1-YADD
    GO TO 126

```

TABLE C.1 (Contd.)

```

123 IF(DIFY(M) .LT. 0.0) GO TO 127
    GO TO 128
127 IF(DIFY(M-1) .LT. 0.0) GO TO 124
    GO TO 129
128 IF(DIFY(M-1) .GT. 0.0) GO TO 125
    GO TO 130
129 FRAC = (CBM - YFIN(M)) / (YFIN(M-1) - YFIN(M))
    Y1 = SLOPE(M) + FRAC * (SLOPE(M-1) - SLOPE(M))
    GO TO 131
130 FRAC = (YFIN(M) - CBM) / (YFIN(M) - YFIN(M-1))
    Y1 = SLOPE(M) - FRAC * (SLOPE(M) - SLOPE(M-1))
    GO TO 131
131 YADD = YADD / 10.0
126 IF(M .GT. 20) GO TO 119
    M = M + 1
    GO TO 132
119 PRINT 133
133 FORMAT('//2X,'M IS LARGER THAN 20'//)
    GO TO 60
103 CONTINUE
    STOP
    END

```

THIS SUBROUTINE NUMERICALLY DETERMINES THE CARBON
IN AUSTENITE VS ETA PROFILE

```

SUBROUTINE HPCG(PRMT,Y,DERY,NDIM,IHLF,FCT,OUTP,AUX)
DIMENSION PRMT(1),Y(1),DERY(1),AUX(16,1)
DIMENSION YMOLE(4000),ETA(4000),YD(4000),YDD(4000)
COMMON /A/ ZEROSL
COMMON /B/ L, YMOLE,ETA,YD,YDD
COMMON /C/ S
N=1
IHLF=0
X=PRMT(1)
H=PRMT(3)
PRMT(5)=0.
DO 1 I=1,NDIM
    AUX(16,I)=0.
    AUX(15,I)=DERY(I)
1  AUX(1,I)=Y(I)
    IF(H*(PRMT(2)-X))3,2,4

ERROR RETURNS
2 IHLF=12
GOTO 4
3 IHLF=13

COMPUTATION OF DERY FOR STARTING VALUES
4 CALL FCT(X,Y,DERY)

```

TABLE C.1 (Contd.)

```

RECORDING OF STARTING VALUES
CALL OUTP(X,Y,DERY,IHLF,NDIM,PRMT)
AYD = ABS(Y(1))
IF(AYD .LT. ZEROSL) RETURN
IF(PRMT(5))6,5,6
5 IF(IHLF)7,7,6
6 RETURN
7 DO 8 I=1,NDIM
8 AUX(8,I)=DERY(I)

COMPUTATION OF AUX(2,I)
ISW=1
GOTO 100

9 X=X+H
DO 10 I=1,NDIM
10 AUX(2,I)=Y(I)

INCREMENT H IS TESTED BY MEANS OF BISECTION
11 IHLF=IHLF+1
X=X-H
DO 12 I=1,NDIM
12 AUX(4,I)=AUX(2,I)
H=.5*H
N=1
ISW=2
GOTO 100

13 X=X+H
CALL FCT(X,Y,DERY)
N=2
DO 14 I=1,NDIM
AUX(2,I)=Y(I)
14 AUX(9,I)=DERY(I)
ISW=3
GOTO 100

COMPUTATION OF TEST VALUE DELT
15 DELT=0.
DO 16 I=1,NDIM
16 DELT=DELT+AUX(15,I)*ABS(Y(I)-AUX(4,I))
DELT=.06666667*DELT
IF(DELT-PRMT(4))19,19,17
17 IF(IHLF-10)11,18,18

NO SATISFACTORY ACCURACY AFTER 10 BISECTIONS. ERROR
MESSAGE
18 IHLF=11
X=X+H
GOTO 4

```

2

TABLE C.1 (Contd.)

```

THERE IS SATISFACTORY ACCURACY AFTER LESS THAN 11
BI SECTIONS.
19 X=X+H
   CALL FCT(X,Y,DERY)
   DO 20 I=1,NDIM
     AUX(3,I)=Y(I)
20  AUX(10,I)=DERY(I)
   N=3
   ISW=4
   GOTO 100

21 N=N+1
   X=X+H
   CALL FCT(X,Y,DERY)
   X=PRMT(1)
   DO 22 I=1,NDIM
     AUX(11,I)=DERY(I)
22  OY(I)=AUX(1,I)+H*(.375*AUX(8,I)+.7916667*AUX(9,I)
     1-.2083333*AUX(10,I)+.0416667*DERY(I))
23  X=X+H
     N=N+1
     CALL FCT(X,Y,DERY)
     CALL OUTP(X,Y,DERY,IHLF,NDIM,PRMT)
     AYD = ABS(Y(1))
     IF(AYD .LT. ZEROSL) RETURN
     IF(PRMT(5))6,24,6
24  IF(N-4)25,200,200
25  DO 26 I=1,NDIM
     AUX(N,I)=Y(I)
26  AUX(N+7,I)=DERY(I)
     IF(N-3)27,29,200

27  DO 28 I=1,NDIM
     DELT=AUX(9,I)+AUX(9,I)
     DELT=DELT+DELT
28  Y(I)=AUX(1,I)+.3333333*H*(AUX(8,I)+DELT+AUX(10,I))
     GOTO 23

29  DO 30 I=1,NDIM
     DELT=AUX(9,I)+AUX(10,I)
     DELT=DELT+DELT+DELT
30  Y(I)=AUX(1,I)+.375*H*(AUX(8,I)+DELT+AUX(11,I))
     GOTO 23

THE FOLLOWING PART OF SUBROUTINE HPCG COMPUTES BY MEANS
OF RUNGE-KUTTA METHOD STARTING VALUES FOR THE NOT
SELF-STARTING PREDICTOR-CORRECTOR METHOD.
100 DO 101 I=1,NDIM
    Z=H*AUX(N+7,I)
    AUX(5,I)=Z
101 Y(I)=AUX(N,I)+.4*Z
    Z IS AN AUXILIARY STORAGE LOCATION

```

TABLE C.1 (Contd.)

```

Z=X+.4*H
CALL FCT(Z,Y,DERY)
DO 102 I=1,NDIM
Z=H*DERY(I)
AUX(6,I)=Z
102 Y(I)=AUX(N,I)+.2969776*AUX(5,I)+.1587596*Z

```

```

Z=X+.4557372*H
CALL FCT(Z,Y,DERY)
DO 103 I=1,NDIM
Z=H*DERY(I)
AUX(7,I)=Z
103 Y(I)=AUX(N,I)+.2181004*AUX(5,I)-3.050965*AUX(6,I)+
13.832865*Z

```

```

Z=X+H
CALL FCT(Z,Y,DERY)
DO 104 I=1,NDIM
104 OY(I)=AUX(N,I)+.1747603*AUX(5,I)-.5514807*AUX(6,I)
+1.205536*AUX(7,I)+.1711848*H*DERY(I)
GOTO(9,13,15,21),ISW

```

POSSIBLE BREAK-POINT FOR LINKAGE

STARTING VALUES ARE COMPUTED.

NOW START HAMMINGS MODIFIED PREDICTOR-CORRECTOR METHOD.

```

200 ISTEP=3
201 IF(N-8)204,202,204
N=8 CAUSES THE ROWS OF AUX TO CHANGE THEIR STORAGE
LOCATIONS
202 DO 203 N=2,7
DO 203 I=1,NDIM
AUX(N-1,I)=AUX(N,I)
203 AUX(N+6,I)=AUX(N+7,I)
N=7

```

N LESS THAN 8 CAUSES N+1 TO GET N

```

204 N=N+1

```

COMPUTATION OF NEXT VECTOR Y

```

DO 205 I=1,NDIM
AUX(N-1,I)=Y(I)
205 AUX(N+6,I)=DERY(I)
X=X+H
206 ISTEP=ISTEP+1
DO 207 I=1,NDIM
ODELT=AUX(N-4,I)+1.333333*H*(AUX(N+6,I)+AUX(N+6,I)-
1AUX(N+5,I)+AUX(N+4,I)+AUX(N+4,I))
Y(I)=DELT-.9256198*AUX(16,I)
207 AUX(16,I)=DELT

```

PREDICTOR IS NOW GENERATED IN ROW 16 OF AUX, MODIFIED
PREDICTOR IS GENERATED IN Y. DELT MEANS AN AUXILIARY
STORAGE.

TABLE C.1 (Contd.)

```

CALL FCT(X,Y,DERY)
DERIVATIVE OF MODIFIED PREDICTOR IS GENERATED IN DERY

DO 208 I=1,NDIM
ODELT=.125*(9.*AUX(N-1,I)-AUX(N-3,I)+3.*H*(DERY(I)+
1AUX(N+6,I)+AUX(N+6,I)-AUX(N+5,I)))
AUX(16,I)=AUX(16,I)-DELT
208 Y(I)=DELT+.07438017*AUX(16,I)

TEST WHETHER H MUST BE HALVED OR DOUBLED
DELT=0.
DO 209 I=1,NDIM
209 DELT=DELT+AUX(15,I)*ABS(AUX(16,I))
IF(DELT-PRMT(4))210,222,222

H MUST NOT BE HALVED. THAT MEANS Y(I) ARE GOOD.
210 CALL FCT(X,Y,DERY)
CALL OUTP(X,Y,DERY,IHLF,NDIM,PRMT)
AYD = ABS(Y(1))
IF(AYD .LT. ZEROSL) RETURN
IF(PRMT(5))212,211,212
211 IF(IHLF-1)213,212,212
212 RETURN
213 IF(H*(X-PRMT(2)))214,212,212
214 IF(ABS(X-PRMT(2))-1*ABS(H))212,215,215
215 IF(DELT-.02*PRMT(4))216,216,201

H COULD BE DOUBLED IF ALL NECESSARY PRECEEDING VALUES ARE
AVAILABLE
216 IF(IHLF)201,201,217
217 IF(N-7)201,218,218
218 IF(ISTEP-4)201,219,219
219 IMOD=ISTEP/2
IF(ISTEP-IMOD-IMOD)201,220,201
220 H=H+H
IHLF=IHLF-1
ISTEP=0
DO 221 I=1,NDIM
AUX(N-1,I)=AUX(N-2,I)
AUX(N-2,I)=AUX(N-4,I)
AUX(N-3,I)=AUX(N-6,I)
AUX(N+6,I)=AUX(N+5,I)
AUX(N+5,I)=AUX(N+3,I)
AUX(N+4,I)=AUX(N+1,I)
DELT=AUX(N+6,I)+AUX(N+5,I)
DELT=DELT+DELT+DELT
2210AUX(16,I)=8.962963*(Y(I)-AUX(N-3,I))-3.361111*H*(DERY(I)+
1DELT+AUX(N+4,I))
GOTO 201

```

TABLE C.1 (Contd.)

```

      H MUST BE HALVED
222 IHLF=IHLF+1
      IF(IHLF-10)223,223,210
223 H=.5*H
      ISTEP=0
      DO 224 I=1,NDIM
        OY(I)=.00390625*(80.*AUX(N-1,I)+135.*AUX(N-2,I)+40.*
        1AUX(N-3,I)+AUX(N-4,I))-.1171875*(AUX(N+6,I)-6.*
        1AUX(N+5,I)-AUX(N+4,I))*H
        OAUX(N-4,I)=.00390625*(12.*AUX(N-1,I)+135.*AUX(N-2,I)+
        1108.*AUX(N-3,I)+AUX(N-4,I))-.0234375*(AUX(N+6,I)+18.*
        1AUX(N+5,I)-9.*AUX(N+4,I))*H
        AUX(N-3,I)=AUX(N-2,I)
224 AUX(N+4,I)=AUX(N+5,I)
      X=X-H
      DELT=X-(H+H)
      CALL FCT(DELT,Y,DERY)
      DO 225 I=1,NDIM
        AUX(N-2,I)=Y(I)
        AUX(N+5,I)=DERY(I)
225 Y(I)=AUX(N-4,I)
      DELT=DELT-(H+H)
      CALL FCT(DELT,Y,DERY)
      DO 226 I=1,NDIM
        DELT=AUX(N+5,I)+AUX(N+4,I)
        DELT=DELT+DELT+DELT
        OAUX(16,I)=8.962963*(AUX(N-1,I)-Y(I))-3.361111*H*
        1(AUX(N+6,I)+DELT+DERY(I))
226 AUX(N+3,I)=DERY(I)
      GOTO 206
      END

```

```

      THIS SUBROUTINE COMPUTES THE FIRST AND SECOND
      DERIVATIVES OF CARBON CONCENTRATION WITH ETA FOR
      USE IN HPCG SUBROUTINE

```

```

      SUBROUTINE FCT(X,Y,DERY)
      DIMENSION Y(2), DERY(2)
      COMMON /C/ S
      ANEW = 6.0/23.0
      DERY(1) = 2.0 * S * ANEW * X * Y(1) / Y(2)
      DERY(2) = Y(1)
      RETURN
      END

```

TABLE C.1 (Contd.)

THIS SUBROUTINE STORES VALUES OF ETA, CARBON
CONCENTRATION AT VARIOUS ETAS AND FIRST AND SECOND
DERIVATIVES OF CARBON CONCENTRATION FOR FUTURE USE

```

SUBROUTINE CUIP(X,Y,DERY,IHLF,NDIM,PRMT)
  DIMENSION Y(2), DERY(2), PRMT(5)
  DIMENSION YMOLE(4000), ETA(4000), YD(4000), YDD(4000)
  COMMON /B/ L, YMOLE,ETA,YD,YDD
  YMOLE(L) = Y(2)
  ETA(L) = X
  YD(L) = Y(1)
  YDD(L) = DERY(1)
  L = L + 1
  RETURN
END

```

THIS SUBROUTINE CALCULATES CARBON CONCENTRATION
IN AUSTENITE PHASE FOR A GIVEN INITIAL CARBON
CONTENT OF THE STEEL

```

SUBROUTINE CTCGITLAST,CT,I)
  COMMON /D/ CTF, DC, CAVG, RO, RS
  DIMENSION CRATIO(30), SUMT(30), CAV(2000)
  PI=3.14159
  A0=1.752
  A1=-468.0
  A2=-7.12E-4
  B0=-7.673
  B1=1553.0
  B2=7.93E-3
  SIGMA=0.00
  BETA = RO/RS
  VOL = BETA**3
  RS=RO/BETA
  N = 100
  IF(TLAST .GT. 3.16E+07) N=200
  IF(TLAST .GT. 1.58E+08) N=400
  A=A0+A1/T+A2*T
  B=B0+B1/T+B2*T
  CAV(1) = CT
  CEQ=EXP(A*ALOG(CAV(1))+B)
  N2 = N * 2
  DTIME = TLAST / N
  DO 1 J = 1,N2
  IFRAC = CTIME * J / 2
  SUM = 0.0
  DO 2 M=1,10
  XQ=(M-1)*PI/(1.0-BETA)

```

TABLE C.1 (Contd.)

```

      X1=M*PI/(1.0-BETA)
5     X=(X0+X1)/2.0
      FX=ATAN((X*(1.0-SIGMA*BETA))/(1.0+SIGMA*BETA*X*X))-(1.0
1-BETA)*X + (M-1)*PI
      FX1=ATAN((X1*(1.0-SIGMA*BETA))/(1.0+SIGMA*BETA*X1*X1))-
1(1.0-BETA)*X1+(M-1)*PI
      IF (ABS(FX) .LT. 0.0001) GO TO 3
      IF((FX .GT. 0.00 .AND. FX1 .GT. 0.00) .OR. (FX .LT.
10.00 .AND. FX1 .LT. 0.00)) GO TO 4
      X0=X
      GO TO 5
4     X1=X
      GO TO 5
3     ALPHA = X
      DELTA = X - ATAN(X)
      CN = 1.0 / (((2.0*PI*RO) * ((1.0-BETA) * (ALPHA**2) -
1BETA) / (BETA * (1.0 + ALPHA**2))) + (SIGMA/(1.0+(SIGMA*
1BETA*X)**(2.0))))*(0.5))
      BN = (4.0 * PI * RO*RO*CN*COS((BETA*ALPHA) - DELTA)) /
1(BETA*ALPHA)*(1.0 - SIGMA)
      TAU = RO * RO / (DC * (BETA*ALPHA)**2)
      TOTAU = IFRAC / TAU
      CRATIO(M) = (3.0 / ((4.0*PI*RS**3) * (1-BETA**3))) *
1(BN**2) * (1.0 - EXP(-TOTAU))
      SUM = CRATIO(M) + SUM
      SUMT(M) = SUM
2     CONTINUE
      CAV(J+1)=CI+(CEQ-CI)*SUMT(10)
1     CONTINUE
      K = 1
      TAREA = 0.0
10    ACT = DTIME / 6.0 * (CAV(K) + 4.0*CAV(K+1) + CAV(K+2))
      TAREA = TAREA + ACT
      IF((K+2) .EQ. (N2+1)) GO TO 6
      IF((K+2) .LE. (N2+1)) GO TO 7
      PRINT 8
8     FORMAT(/5X,'WARNING IN SUBROUTINE CTCG  K+2 IS LARGER',
1'THAN N+1'/)
      GO TO 9
7     CONTINUE
      K = K + 2
      GO TO 10
9     CONTINUE
6     CAVG = TAREA / TLAST
      RETURN
      END

```

TABLE C.1 (Contd.)

THIS SUBROUTINE CALCULATES THE TOTAL CARBON
CONTENT FOR A GIVEN CARBON IN AUSTENITE

```

SUBROUTINE CGCT(TLAST,T)
COMMON /D/ CTF, DC, CAVG, RO, RS
DIMENSION SUMI(2000)
DIMENSION CRATIO(30), SUMT(30)
PI=3.14159
A0=1.752
A1=-468.0
A2=-7.12E-4
B0=-7.673
B1=1553.0
B2=7.93E-3
SIGMA=0.00
BETA = RO/RS
VOL = BETA**3
RS=RO/BETA
N = 100
IF(TLAST .GT. 3.16E+07) N=200
IF(TLAST .GT. 1.58E+08) N=400
A=A0+A1/T+A2*T
B=B0+B1/T+B2*T
N2 = N * 2
DTIME = TLAST / N
DO 1 J = 1,N2
TFRAC = DTIME * J / 2
SUM = 0.0
DO 2 M=1,10
X0=(M-1)*PI/(1.0-BETA)
X1=M*PI/(1.0-BETA)
5 X=(X0+X1)/2.0
FX =ATAN((X*(1.0-SIGMA*BETA))/(1.0+SIGMA*BETA*X*X))-(1.0
1-BETA)*X + (M-1)*PI
FX1=ATAN((X1*(1.0-SIGMA*BETA))/(1.0+SIGMA*BETA*X1*X1))-
1(1.0-BETA)*X1+(M-1)*PI
IF (ABS(FX) .LT. 0.0001) GO TO 3
IF((FX .GT. 0.00 .AND. FX1 .GT. 0.00) .OR. (FX .LT.
10.00 .AND. FX1 .LT. 0.00)) GO TO 4
X0=X
GO TO 5
4 X1=X
GO TO 5
3 ALPHA = X
DELTA = X - ATAN(X)
CN = 1.0 / (((2.0*PI*RO) * (((1.0-BETA) * (ALPHA**2) -
1BETA) / (BETA * (1.0 + ALPHA**2)))) + (SIGMA/(1.0+(SIGMA*
1BETA*X)**(2.0))))**(0.5))
BN = (4.0 * PI * RO*RO*CN*CCS((BETA*ALPHA) - DELTA)) /
1(BETA*ALPHA)*(1.0 - SIGMA)

```

TABLE C.1 (Contd.)

```

      TAU = RO * RO / (DC * (BETA*ALPHA)**2)
      TOTAU = TFRAC / TAU
      CRATIO(M) = (3.0 / ((4.0*PI*RS**3) * (1-BETA**3))) *
1 (BN**2) * (1.0 - EXP(-TOTAU))
      SUM = CRATIO(M) + SUM
      SUMT(M) = SUM
2  CONTINUE
      SUMI(J+1) = SUMT(10)
1  CONTINUE
      K = 1
      SUMI(1) = 0.0
      TAREA = 0.0
10  ACT = DTIME / 6.0 * (SUMI(K) + 4.0*SUMI(K+1) +SUMI(K+2))
      TAREA = TAREA + ACT
      IF((K+2) .EQ. (N2+1)) GO TO 6
      IF((K+2) .LE. (N2+1)) GO TO 7
      PRINT 8
8  FORMAT(/5X,'WARNING IN SUBROUTINE CGCT   K+2 IS LARGER',
1 'THAN N+1'/)
      GO TO 9
7  K = K + 2
      GO TO 10
9  CONTINUE
6  SUMAVG = TAREA / TLAST
      MM = 0
      CT1 = 50.0
      Y = SUMAVG
13  FX=(Y *EXP(A*ALOG(CT1)+B)-CAVG)/(Y -1.0)-CT1
      DFX=Y / (Y -1.0)*EXP(A*ALOG(CT1)+B)*A/CT1-1.0
      CT2=CT1-FX/DFX
      MM = MM + 1
      IF(MM .EQ. 50) GO TO 11
      IF(ABS(CT1 - CT2) .LT. 0.005*CT1) GO TO 12
      CT1 = CT2
      GO TO 13
11  PRINT 14
14  FORMAT(/5X,'WARNING IN CGCT   CTF IS NOT THE DESIRED',
1 'VALUE   M IS LARGER THAN 50'/)
12  CTF = CT1
      RETURN
      END

```

TABLE C.1 (Contd.)

SYSTEM INPUT PARAMETERS

TEMPERATURE = 873.00 K 600.00 C
 CARBON IN SODIUM = 0.5000E-00
 TYPE OF STEEL = 304

INITIAL CARBON CONC. 500.00
 INITIAL CHROMIUM CONC. 18.00
 RO -- PARTICLE RADIUS 0.5000E-04
 RS -- 1/2 INTERPARTICLE DISTANCE 0.7470E-03

CARBON CONCENTRATION, ACTIVITY OF CARBON, AND SOLUBILITY OF
 CARBON IN SODIUM

CNA = 0.500E-00 CSNA = 0.731E-01 ACNA = 0.684E-01

VALUES FOR THE CARBON AND CHROMIUM CONCENTRATIONS AND THE
 CARBON ACTIVITY IN AUSTENITE AT THE AUSTENITE / AUSTENITE
 + CARBIDE PHASE BOUNDARY

CGSAT = 12.50 CMSAT = 0.573E-04 ACSAT = 0.118E-03
 CRBT = 18.00 CRBTM = 0.191E-00

DC FOR 304 S.S. AT TEMP = 873.00 IS 0.419E-10

CARBON AND CHROMIUM CONCENTRATIONS IN THE STEEL AT THE
 SODIUM-STEEL INTERFACE

CST = 6024.89 CSG = 491.66 CSM = 0.2273E-02
 CRSG = 5.793 CRSM = 0.618E-01

INITIAL CARBON AND CHROMIUM CONCENTRATIONS IN THE STEEL

CBT = 500.000 CBG = 112.299 CBM = 0.518E-03
 CBTGCC = 0.402E-02 CRBG = 10.946 CRBM = 0.120E-01

TABLE C.1 (Contd.)

THIS IS THE CARBON IN AUSTENITE VS ETA PROFILE

I	ETA	YMOLE	YD	YDD	CG	CRG
1	0.0	0.227E-02	-0.612E-02	0.0	491.67	5.79
51	0.470E-01	0.199E-02	-0.606E-02	0.275E-02	429.65	6.26
101	0.970E-01	0.169E-02	-0.583E-02	0.644E-02	365.19	6.83
151	0.147E 00	0.141E-02	-0.541E-02	0.108E-01	304.25	7.47
201	0.197E 00	0.115E-02	-0.474E-02	0.156E-01	249.18	8.16
251	0.247E 00	0.935E-03	-0.386E-02	0.196E-01	202.50	8.89
301	0.297E 00	0.767E-03	-0.283E-02	0.210E-01	166.27	9.58
351	0.347E 00	0.651E-03	-0.182E-02	0.186E-01	141.21	10.15
401	0.397E 00	0.582E-03	-0.102E-02	0.133E-01	126.09	10.54
451	0.447E 00	0.545E-03	-0.494E-03	0.777E-02	118.16	10.77
501	0.497E 00	0.528E-03	-0.212E-03	0.383E-02	114.52	10.88
551	0.547E 00	0.521E-03	-0.814E-04	0.164E-02	113.02	10.92
601	0.597E 00	0.519E-03	-0.283E-04	0.626E-03	112.46	10.94

TIME IN SEC. = 0.31450E 08

TIME IN HRS. = 8736.00000

TIME IN YEARS = 0.99726

THIS IS THE CARBON IN AUSTENITE AND TOTAL CARBON
VS X PROFILE AND THE MASS OF CARBON GAINED OR LOST
PER SQUARE CENTIMETER OF THE STEEL

J	X (CM)	CG	CT	CT2	GRAMS	GDELX
1	0.0	491.7	6025.0	0.444E-01	0.0	0.0
51	0.341E-02	429.7	4799.1	0.346E-01	0.135E-03	0.135E-03
101	0.704E-02	365.2	3648.3	0.253E-01	0.243E-03	0.109E-03
151	0.107E-01	304.3	2681.5	0.175E-01	0.321E-03	0.778E-04
201	0.143E-01	249.2	1907.8	0.113E-01	0.374E-03	0.524E-04
251	0.179E-01	202.5	1346.8	0.681E-02	0.406E-03	0.329E-04
301	0.216E-01	166.3	967.0	0.375E-02	0.426E-03	0.192E-04
351	0.252E-01	141.2	734.8	0.189E-02	0.436E-03	0.102E-04
401	0.288E-01	126.1	607.3	0.863E-03	0.441E-03	0.499E-05
451	0.325E-01	118.2	544.5	0.358E-03	0.443E-03	0.222E-05
501	0.361E-01	114.5	516.5	0.133E-03	0.444E-03	0.890E-06
551	0.397E-01	113.0	505.2	0.418E-04	0.444E-03	0.317E-06
601	0.433E-01	112.5	501.0	0.817E-05	0.444E-03	0.906E-07
647	0.467E-01	112.3	499.6	-0.283E-05	0.444E-03	0.891E-08

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