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CARBURIZATION-DECARBURIZATION BEHAVIOR OF FERRITIC STEELS IN A SODIUM ENVIRONMENT

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MATERIALS BEHAVIOR IN SODIUM AND COVER GAS

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IN A SODIUM ENVIRONMENT*

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Abstract

The kinetics of the carburization-decarburization process of Fe-Cr-Mo ferritic steels in high-temperature flowing sodium have been studied in terms of (1) the equilibrium carbon activity-carbon concentration relationship for the steels, (2) the chromium and molybdenum content in the steel, and (3) the carbon concentration in sodium. Ferritic steels with chromium and molybdenum contents in the range 0.5-12 wt % and 0.5-2.5 wt %, respectively, were exposed to sodium at temperatures between 773 and 973 K. Carbon equilibration experiments were conducted using 0.05-mm-thick foils, and cylindrical specimens (6.5 mm in diameter) were used to establish the kinetics of carbon migration in the steels. The sodium exposure time varied from 3.6 to 25 Ms.

The equilibrium carbon activity and carbon concentration data have been established at 873 and 973 K, as functions of chromium and molybdenum content in the steel. The results show that the carbon activity of the steel decreased with an increase in chromium and molybdenum concentration. The influence of molybdenum on the carbon activity of steels containing 9 and 12 wt % chromium is small compared to that of low-chromium steels.

Carbon concentration-distance profiles were obtained as a function of sodium-exposure time, and the carburization-decarburization rate constants were evaluated at various temperatures. These results were used to obtain the effective carbon-diffusion coefficient for the carburization-decarburization process. The calculated values of effective carbon diffusivity indicate that the rate of precipitation and dissolution of carbide particles play an important role in the overall process.

*Work supported by the U. S. Department of Energy.

SODIUM EFFECTS ON SECONDARY SYSTEM COMPONENT MATERIALS

OBJECTIVES

1. STUDY THE RELATIVE STABILITY OF NONMETALLIC ELEMENTS (CARBON AND NITROGEN) IN FE-CR-MO FERRITIC MATERIAL EXPOSED TO A LIQUID-SODIUM ENVIRONMENT.
2. ESTABLISH THE EQUILIBRIUM CARBON ACTIVITY-CARBON CONCENTRATION RELATIONSHIP FOR THE MATERIAL AS A FUNCTION OF
 - (A) CHROMIUM CONCENTRATION (2 TO 12 WT %)
 - (B) MOLYBDENUM CONCENTRATION (0.5 TO 2.5 WT %)
 - (C) TEMPERATURE (500 TO 700°C)
 - (D) CARBIDE MORPHOLOGY
3. DETERMINE THE KINETICS OF CARBURIZATION AND DECARBURIZATION FOR THE MATERIAL AT
 - (A) DIFFERENT CARBON CONCENTRATIONS IN SODIUM
 - (B) TEMPERATURES BETWEEN 500 AND 700°C
4. FORMULATE A MODEL FOR CARBON TRANSFER IN MEDIUM-CHROMIUM FERRITIC STEELS IN BI- AND MONOMETALLIC SODIUM HEAT-TRANSPORT SYSTEMS.

Composition of Ferritic Steels

Alloy	C	Cr	Mo	Ni	Si	Mn	Nb	V	Other
<u>Experimental Alloys</u>									
H1	0.096	0.97	0.47	0.08	0.09	0.001	0.002	-	-
H2	0.096	2.09	0.48	0.06	0.09	0.001	0.002	-	-
H3	0.094	4.48	0.46	0.06	0.13	0.005	0.005	0.002	-
H4	0.100	4.63	0.93	0.04	0.09	0.003	0.010	0.001	-
H5	0.092	4.32	1.87	0.04	0.09	0.002	0.005	0.001	-
H6	0.098	9.46	0.50	0.07	0.01	0.002	0.005	0.001	-
H7	0.091	8.63	1.41	0.04	0.13	0.007	0.005	0.005	-
H8	0.096	8.83	2.38	0.05	0.01	0.001	0.005	0.002	-
H9	0.094	11.94	0.49	0.05	0.01	0.001	0.010	-	-
H10	0.090	11.78	1.43	0.04	0.01	0.001	0.005	0.001	-
H11	0.095	11.28	2.30	0.05	0.01	0.001	0.005	0.001	-
<u>Commercial Steels</u>									
Croloy	0.11	2.40	0.97	0.05	0.58	0.51	-	-	-
Sandvik HT9	0.20	11.50	1.00	0.50	0.40	0.55	-	0.30	0.50 W
Vallourec EM12 (B)	0.09	9.46	2.13	0.07	0.33	0.88	0.39	0.18	0.026 N
C.E. ESRXA 3089 (A)	0.12	8.48	2.26	-	0.30	1.16	0.51	0.22	0.042 N
C.E. ESRXA 3177 (C)	0.087	9.58	0.80	0.08	0.17	0.44	0.11	0.15	0.46 W, 0.04 Ti 0.066 N
Japan HCM9M (J)	0.08	9.00	2.00	-	0.50	0.50	-	-	-

SPECIMENS

EQUILIBRIUM EXPERIMENTS:

SPECIMEN SIZE: 12 X 0.05 X 70 MM

EXPOSURE TIME: 1 TO 7 MS

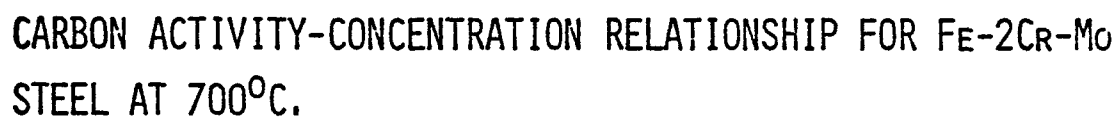
KINETIC EXPERIMENTS:

SPECIMEN SIZE: ~6.5 MM DIAMETER, 100 MM LONG

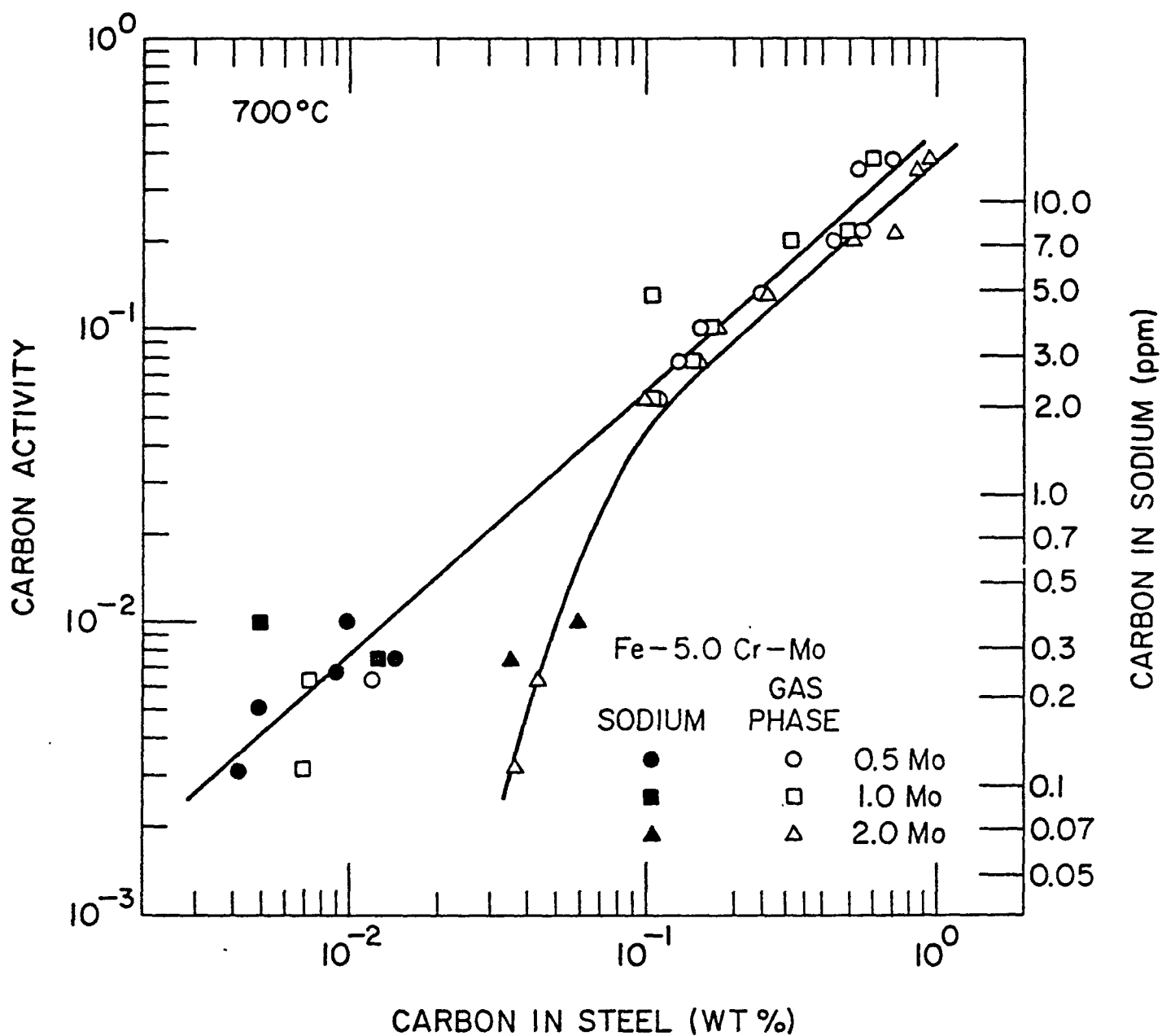
HEAT TREATMENT:

FE-0.5 TO 2.5 CR-MO: 1 H AT 930°C, AC
1 H AT 750°C, AC

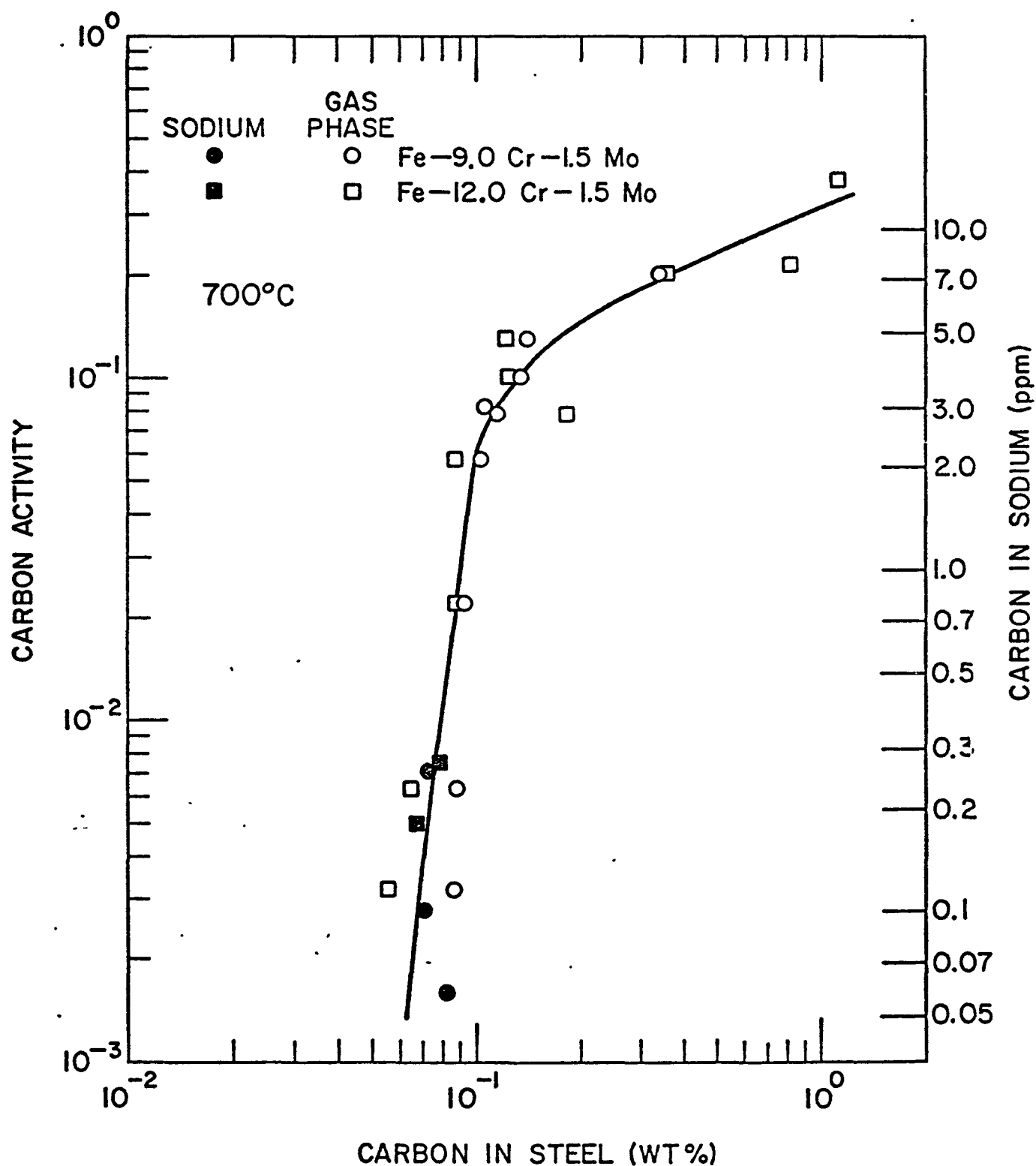
FE-5 TO 12CR-MO: 1 H AT 1050°C, AC
1 H AT 750°C, AC



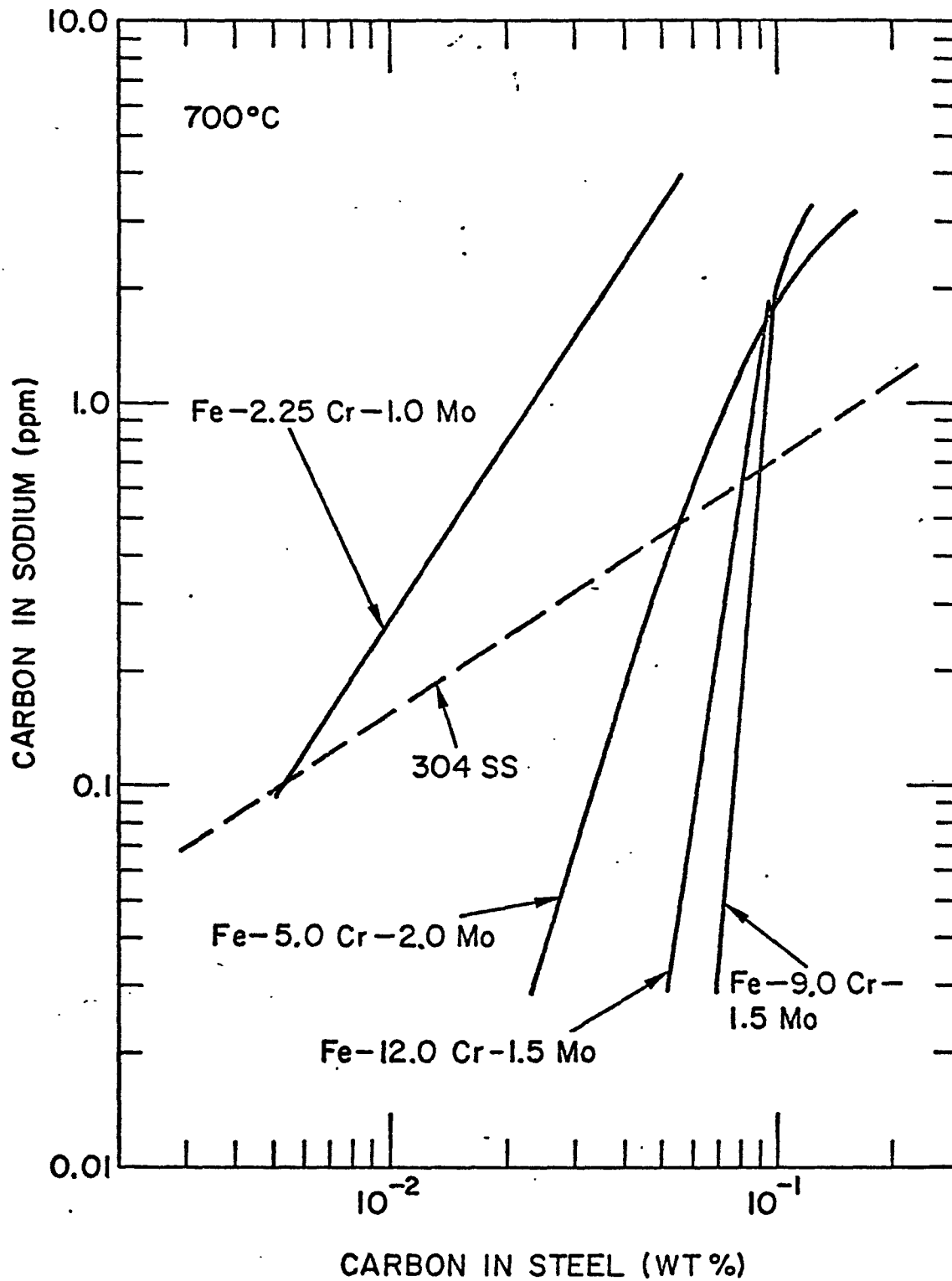
CARBON ACTIVITY-CONCENTRATION RELATIONSHIP FOR Fe-2Cr-Mo
STEEL AT 700°C.



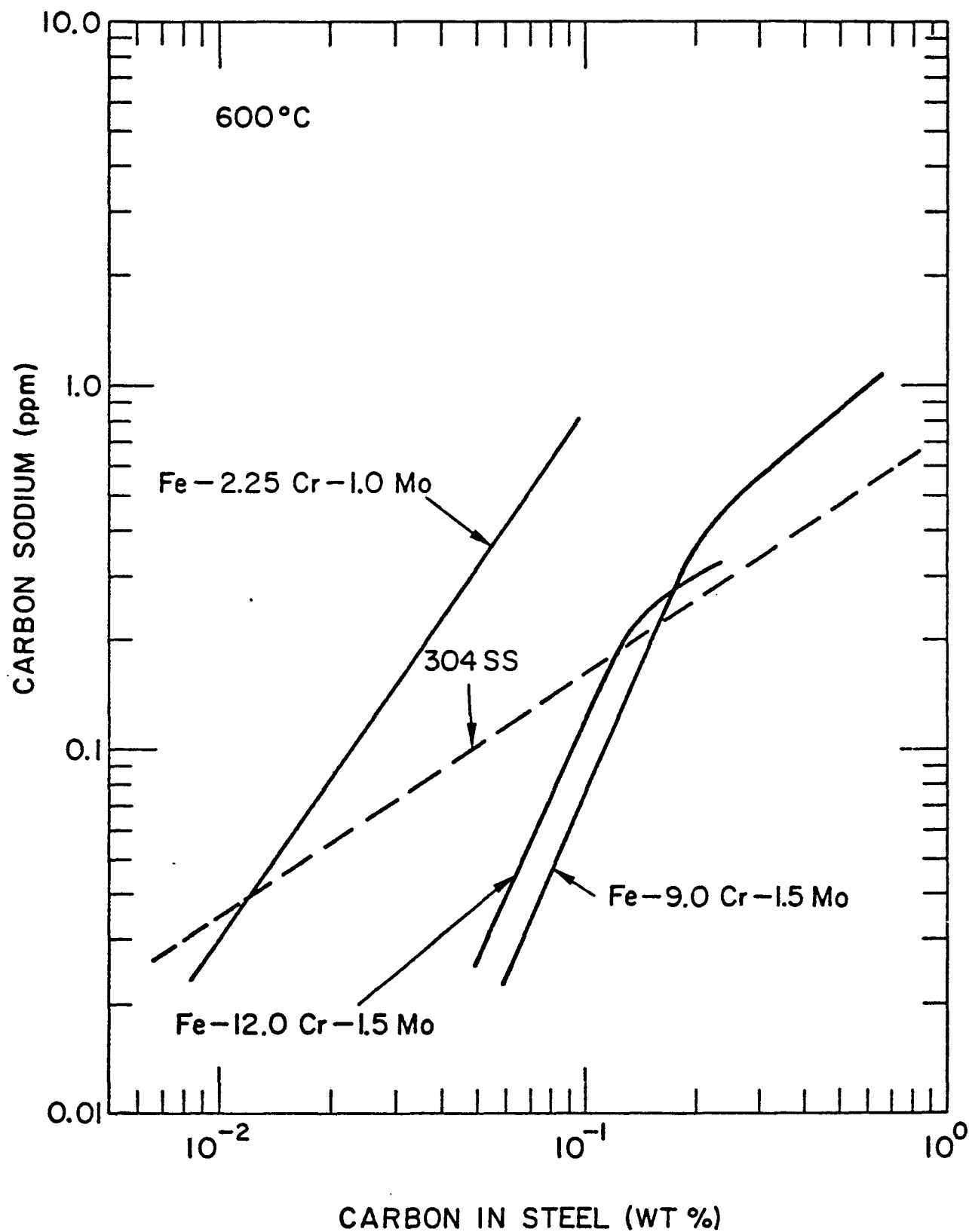
CARBON ACTIVITY-CONCENTRATION RELATIONSHIP FOR Fe-5Cr-Mo STEEL AT 700°C.



CARBON ACTIVITY-CONCENTRATION RELATIONSHIP FOR Fe-9Cr-Mo
AND Fe-12Cr-Mo STEEL AT 700°C.



RELATIONSHIP BETWEEN CARBON CONCENTRATION IN STEEL AND CARBON CONCENTRATION IN SODIUM AT 700°C.



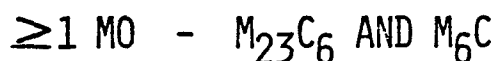
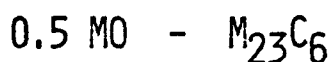
RELATIONSHIP BETWEEN CARBON CONCENTRATION IN STEEL AND
CARBON CONCENTRATION IN SODIUM AT 600°C

SUMMARY OF RESULTS

TEMPERATURE: 700°C

CARBON ACTIVITY $\lesssim 0.1$

1. ADDITION OF MOLYBDENUM TO FE-CR FERRITIC STEELS STABILIZES THE CARBIDE STRUCTURE, I.E., EQUILIBRIUM CARBON CONCENTRATION IN THE STEEL INCREASES WITH INCREASE IN MOLYBDENUM CONTENT.
2. THIS EFFECT IS GREATER IN STEELS CONTAINING 2 OR 5 WT % CHROMIUM.
3. EQUILIBRIUM CARBON CONCENTRATION IN FE-MO STEELS INCREASES WITH INCREASE IN CHROMIUM CONTENT, UP TO 9 WT %.
4. EQUILIBRIUM CARBIDE PHASE IN FE-CR STEELS CONTAINING



CARBON ACTIVITY $\gtrsim 0.1$

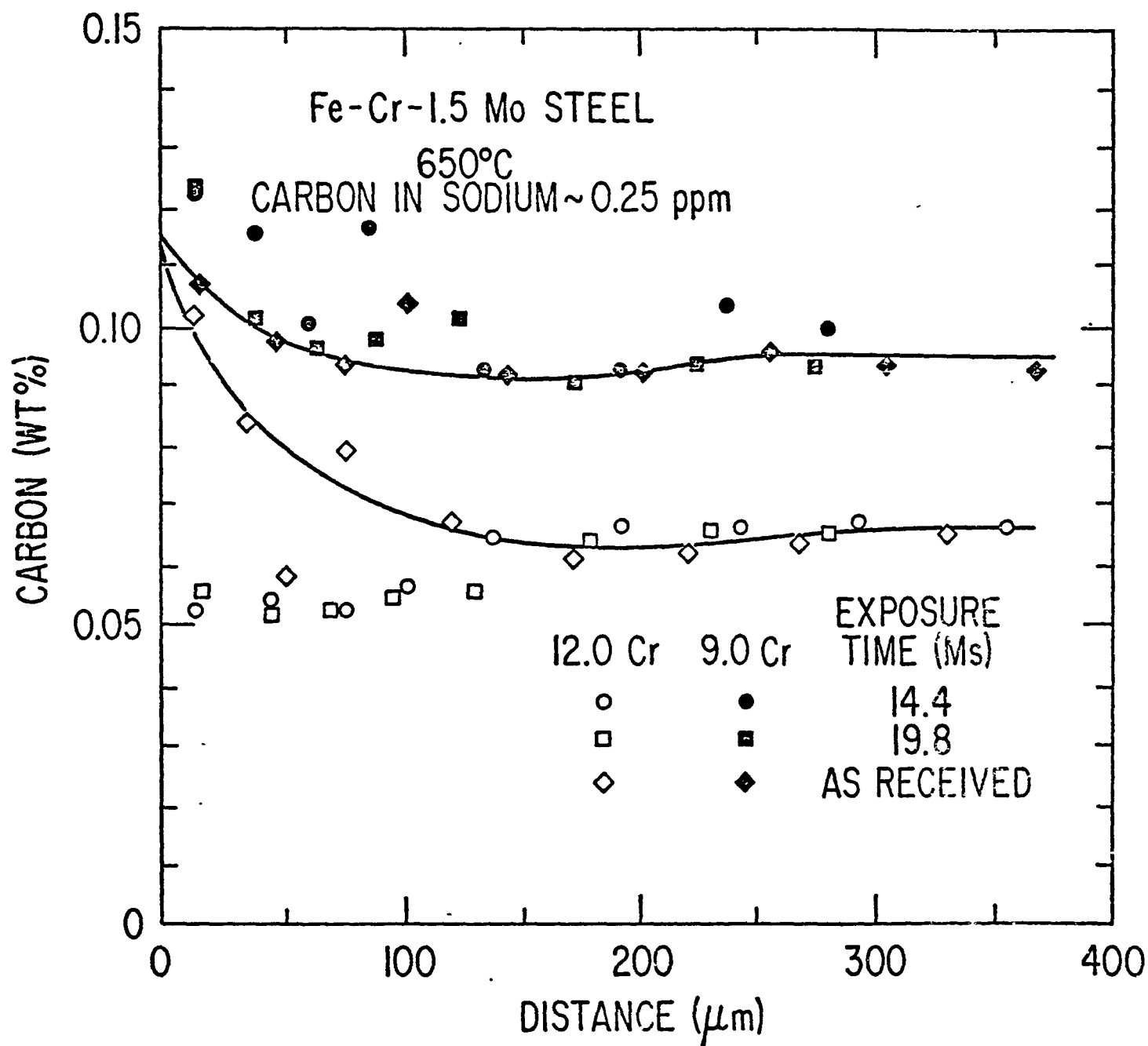
1. INFLUENCE OF CHROMIUM AND MOLYBDENUM ON THE EQUILIBRIUM CARBON ACTIVITY-CONCENTRATION RELATIONSHIP IS SMALL.

Sodium-exposure Time (in 1000 h) for Fe-Cr-Mo Ferritic Steels.
Carbon concentration in sodium 0.25 ppm.

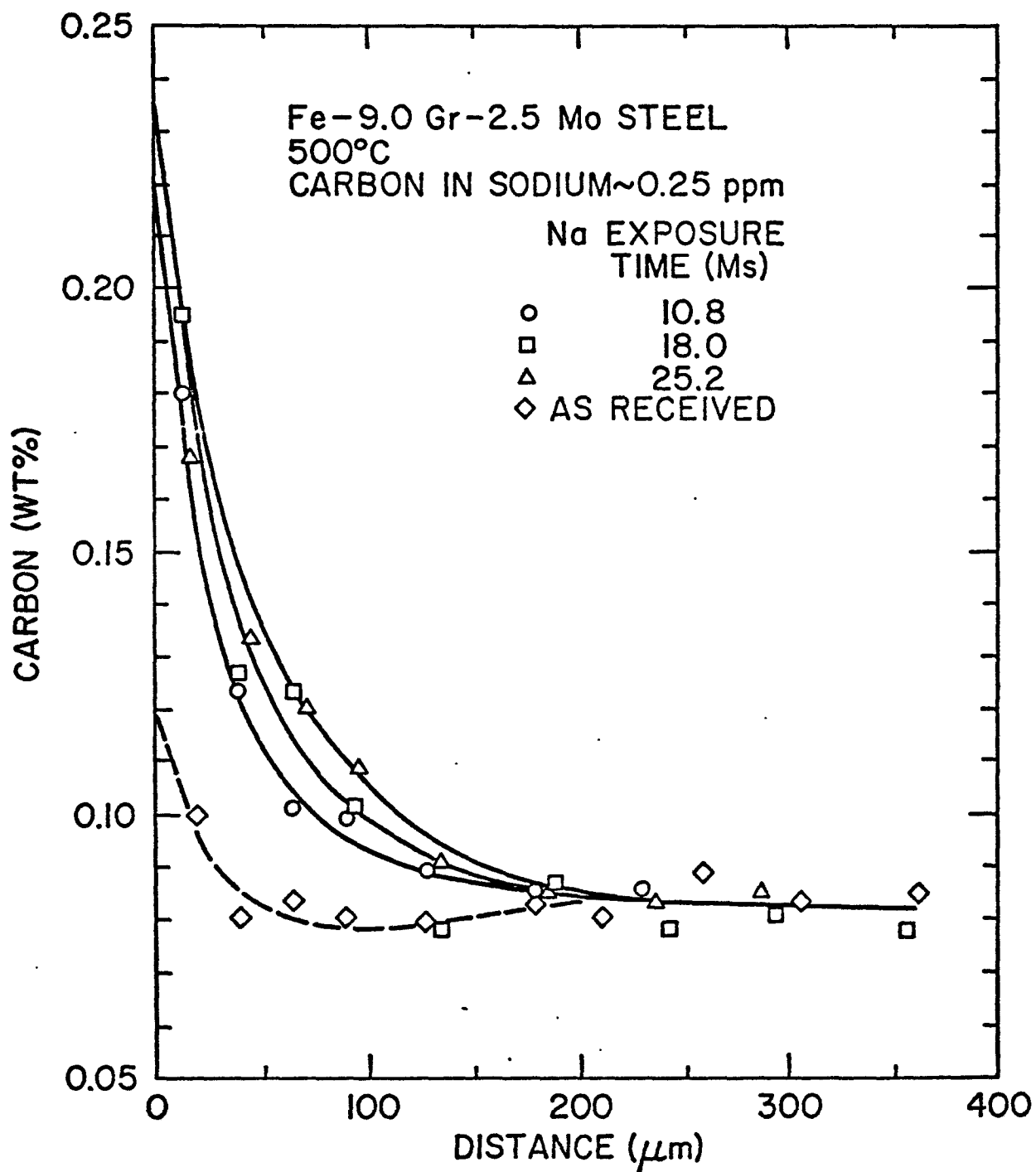
Alloy	Temperature (°C)				
	500	550	600 ^b	650	700
H1	3,5,7,10 ^a	2,4,6	2,4,6 ^a	1,2,4,5.5	-
H2	↓	↓	↓	↓	↓
H6					
H7					
H8					
H9					
H10					
H11	↓	↓	↓	↓	↓
Sandvik HT9	-	2,3	1,2,4	0.5,1,2	0.5,1,2
Vallourec EM12	-	2,3,4.5,6	1,2,4.5,6.5	0.5,1,2,3	0.5,1,2,3
C.E. ESRXA 3089	-	2,3,4.5,6	1,2,4.5,6.5	0.5,1,2,3	0.5,1,2,3
C.E. ESRXA 3177	3,5,7,10 ^a	2,4,6	2,4,6 ^a	1,2,4,5.5	-
Japan HCM9M	3,5,7,10 ^a	2,4,6	2,4,6 ^a	1,2,4,5.5	-

^aExposure not completed.

^bAlso exposed to sodium containing ~0.05 ppm carbon.



CARBON CONCENTRATION-DISTANCE PROFILES IN Fe-9Cr-1-1/2Mo AND Fe-12Cr-1-1/2Mo STEEL AFTER EXPOSURE TO FLOWING SODIUM AT 650°C.



CARBON CONCENTRATION-DISTANCE PROFILES IN Fe-9Cr-2-1/2Mo STEEL
AFTER EXPOSURE TO FLOWING SODIUM AT 500°C.

$$\frac{M_T}{M_\infty} = \frac{4}{\sqrt{\pi}} \left(\frac{DT}{A^2} \right)^{1/2} = K_T^{1/2}$$

M_T = MASS OF CARBON GAIN PER UNIT SURFACE AREA AT TIME T .

M_∞ = TOTAL MASS OF CARBON GAIN PER UNIT SURFACE AREA.

A = RADIUS OF THE SPECIMEN.

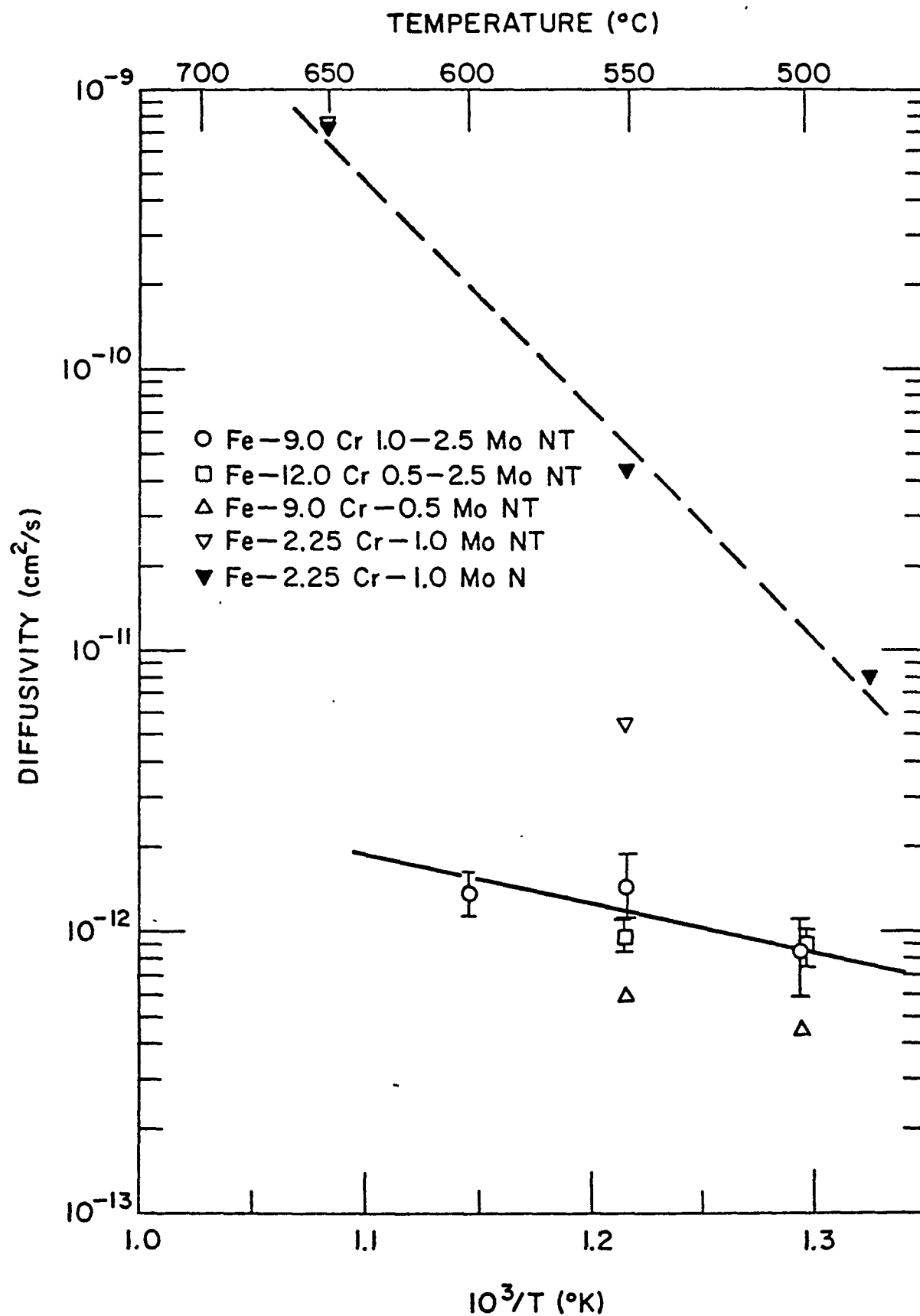
K = RATE CONSTANT.

D = DIFFUSION COEFFICIENT.

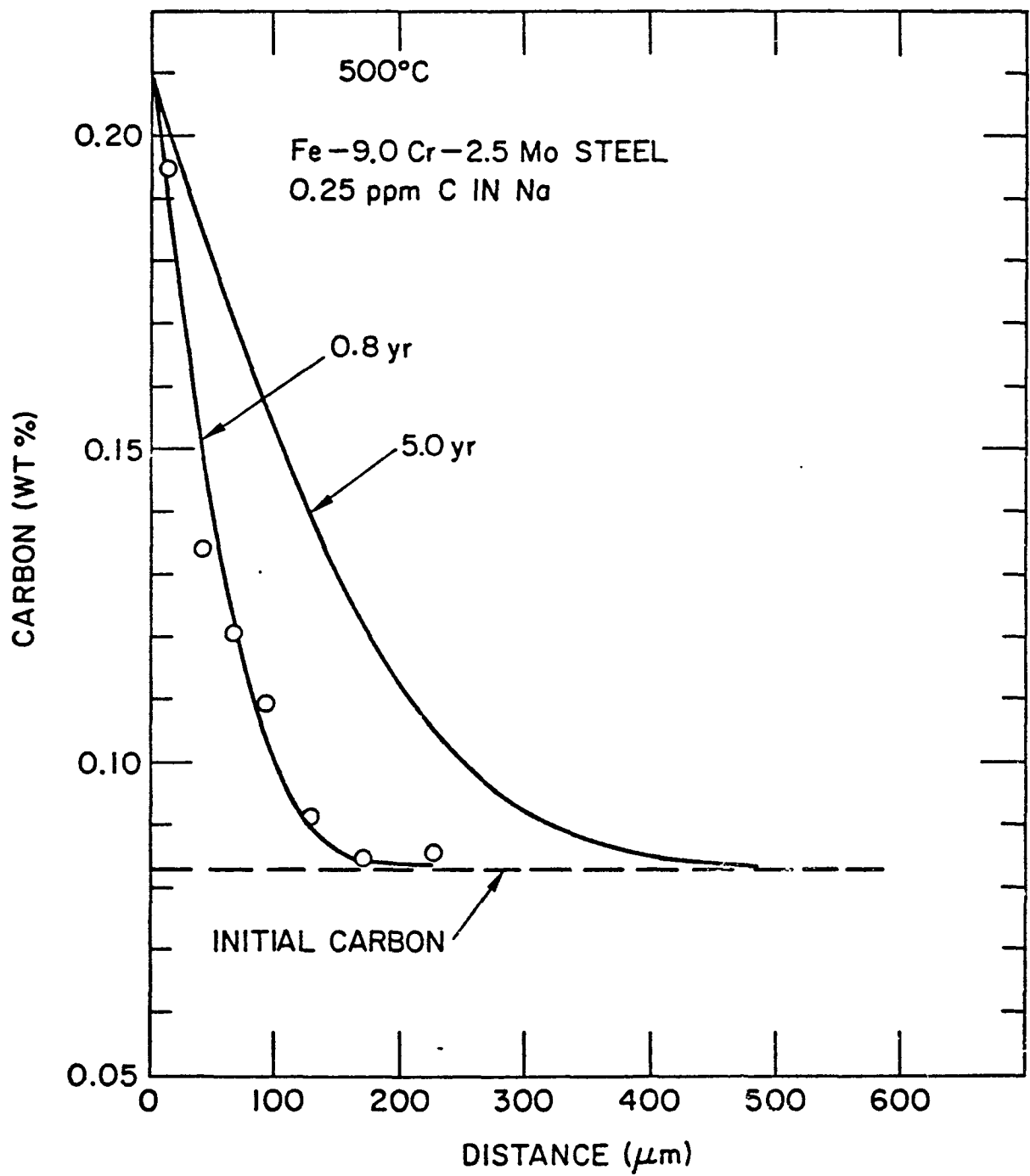
Kinetics of Carburization of Ferritic Steels in Sodium at 550°C Containing
0.25 ppm Carbon

Steel	Surface Carbon (ppm)	Carbon Gain M_t (10^{-4} kg/m ²)			Fraction Carbon Gain M_t/M_α (10^{-2})			Rate Constant K (10^{-6} s ^{-1/2})
		Exposure Time (Ms)			Exposure Time (Ms)			
		7.2	14.4	16.2	7.2	14.4	16.2	
Fe-9Cr- $\frac{1}{2}$ Mo	2600	2.28	5.08		1.09	2.42		5.21±1.65
Fe-9Cr-1 $\frac{1}{2}$ Mo	2800	5.13	8.80		1.85	3.17		8.57±1.55
Fe-9Cr-2 $\frac{1}{2}$ Mo	2000	3.85	4.26		2.41	2.67		↓
Fe-9Cr-2Mo (J)	2000	3.80	6.71		1.90	3.35		
Fe-9Cr-1Mo (C)	1800	4.29	5.53		2.99	3.88		
Fe-9Cr-2Mo (A)*	3500			9.20			3.08	
Fe-9Cr-2Mo (B)*	3200			6.82			2.91	
Fe-12Cr- $\frac{1}{2}$ Mo	2500	3.08	5.21		1.31	2.21		6.22±0.51
Fe-12Cr-1 $\frac{1}{2}$ Mo	2400	1.72	5.73		0.79	2.64		↓
Fe-12Cr-2 $\frac{1}{2}$ Mo	2200	3.73	5.05		1.66	2.25		

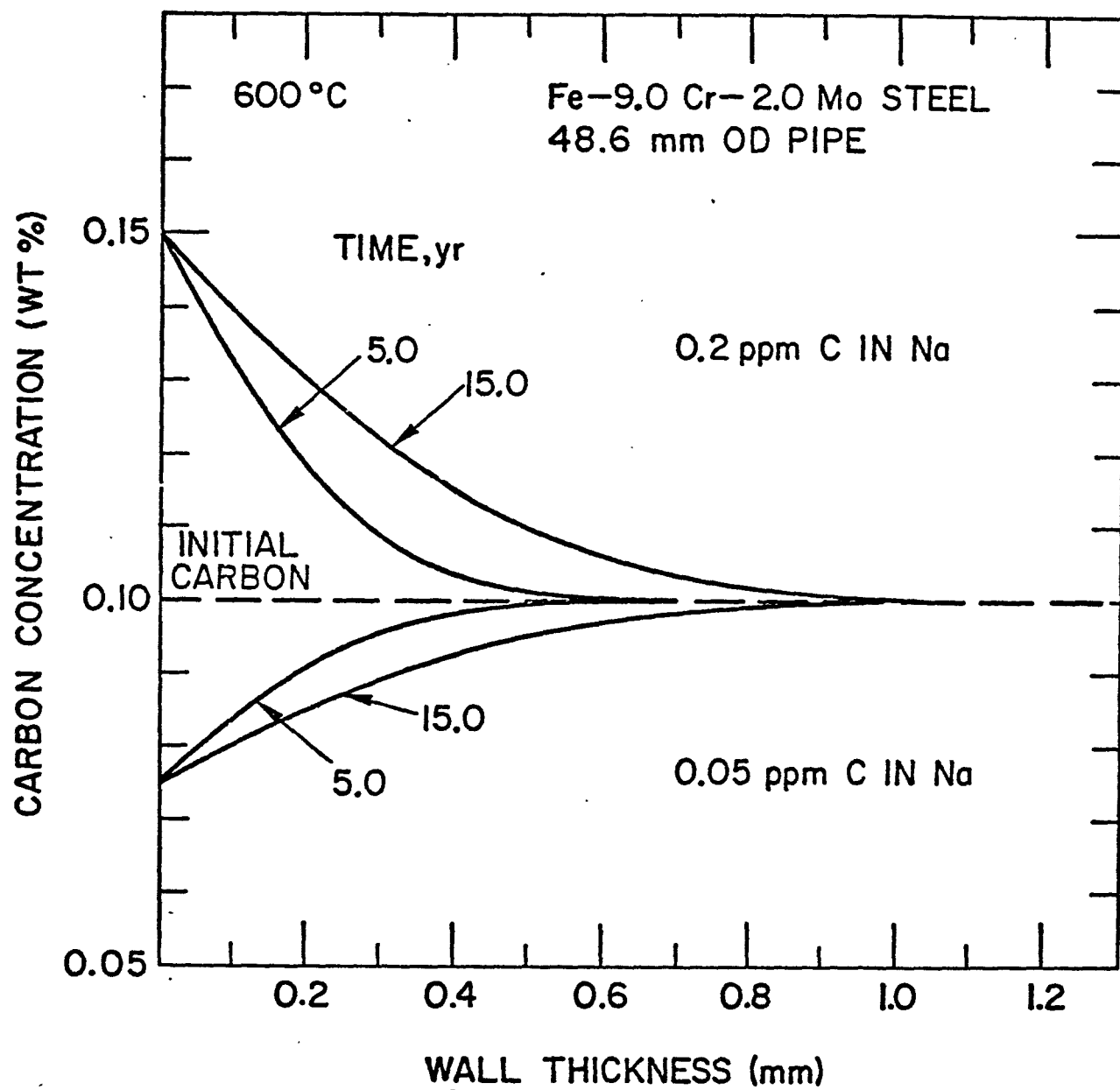
*Carbon in sodium 0.3 ppm.



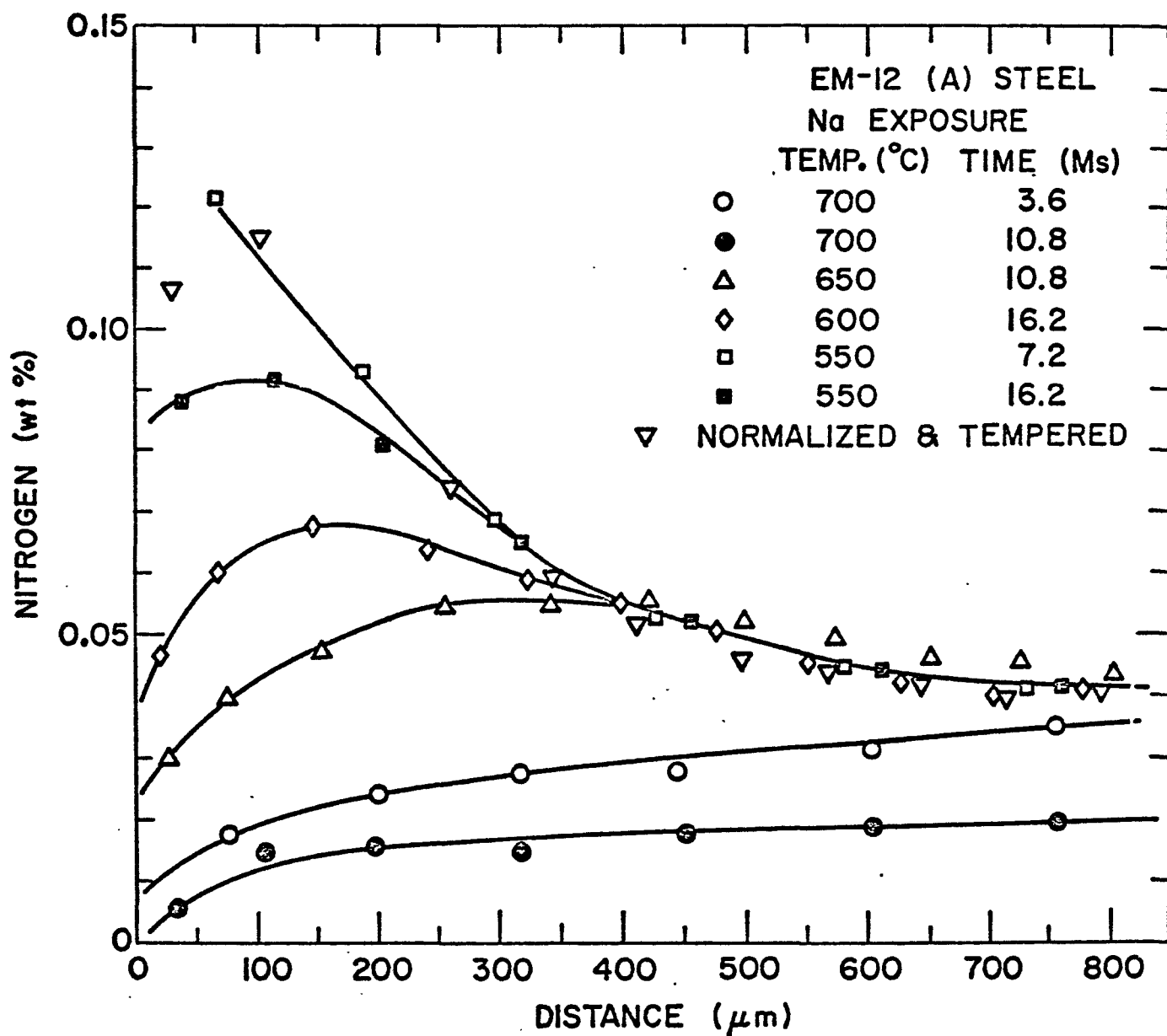
EFFECTIVE CARBON DIFFUSIVITY CALCULATED FROM THE CARBURIZATION/DECARBURIZATION RATE CONSTANTS FOR FERRITIC STEELS.



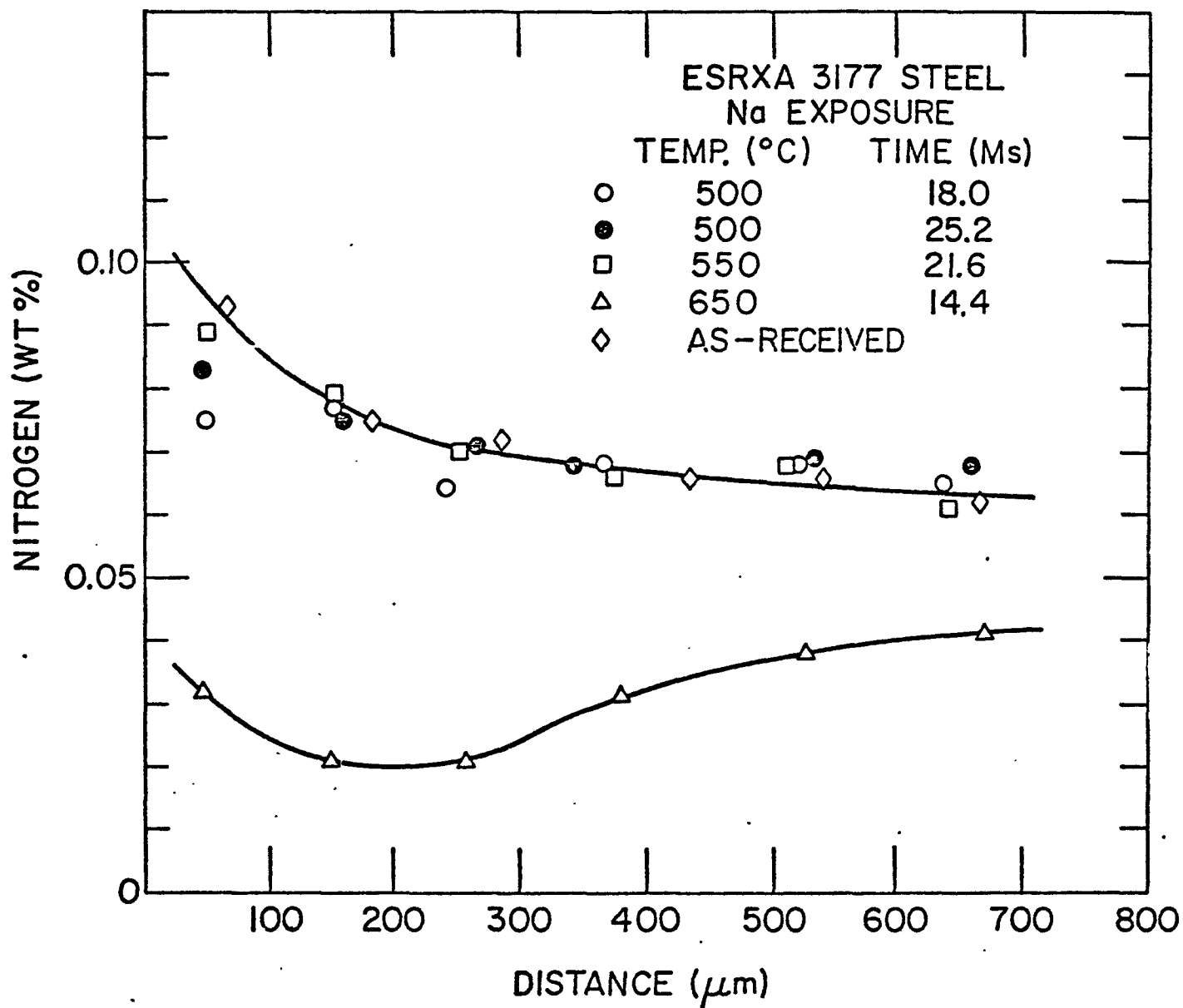
CARBURIZATION BEHAVIOR OF Fe-9Cr-2-1/2Mo STEEL AFTER EXPOSURE TO SODIUM CONTAINING 0.25 PPM CARBON AT 500°C.



CARBURIZATION BEHAVIOR OF Fe-9Cr-2Mo STEEL PIPING AFTER EXPOSURE TO SODIUM CONTAINING 0.2 AND 0.05 PPM CARBON AT 600°C.



NITROGEN CONCENTRATION-DISTANCE PROFILES IN FE-9Cr-1Mo STEEL
AFTER EXPOSURE TO FLOWING SODIUM AT TEMPERATURES BETWEEN
550 AND 700°C.



NITROGEN CONCENTRATION-DISTANCE PROFILES IN Fe-9Cr-1Mo STEEL
AFTER EXPOSURE TO FLOWING SODIUM AT TEMPERATURES BETWEEN
500 AND 650°C.

CONCLUSIONS

1. THE FE-9CR-MO FERRITIC STEEL CONTAINING 1 TO 2 WT % MOLYBDENUM SHOWS GOOD RESISTANCE AGAINST CARBON TRANSFER IN A HIGH-TEMPERATURE SODIUM ENVIRONMENT.
2. AT 600 AND 700°C, THE EQUILIBRIUM CARBON CONCENTRATION IN FE-9CR-MO STEEL IS HIGHER THAN THAT IN LOW-CHROMIUM FERRITIC STEELS OR TYPE 304 STAINLESS STEEL FOR CARBON ACTIVITIES $\lesssim 0.02$.
3. ESSENTIALLY NO LOSS OF NITROGEN OCCURS FROM FE-9CR-MO STEEL AT TEMPERATURES BELOW 550°C.
4. THE CARBURIZATION-DECARBURIZATION RATE CONSTANT FOR FE-9CR-MO STEEL IS SMALL COMPARED TO THAT FOR LOW-CHROMIUM FERRITIC STEELS OR STAINLESS STEELS.