Dr-492

231
5-18-76
UC-79b Plus
UK, Germany &
Japan

HEDL-TME 76-20
UC-79b

EFFECT OF COMPOSITION ON THE CORROSION BEHAVIOR OF 316 STAINLESS STEEL IN FLOWING SODIUM

MASTER

HANFORD ENGINEERING DEVELOPMENT LABORATORY
Operated by Westinghouse Hanford Company
A Subsidiary of Westinghouse Electric Corporation

P.O. Box 1970 Richland, WA 99352

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Prepared for the U.S. Energy Research and Development Administration under Contract No. E(45-1)-2170

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the U.S. ERDA, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy $ ~~5.00~~; Microfiche $2.25
4.00

HEDL-TME 76-20
UC-79b

EFFECT OF COMPOSITION ON THE CORROSION BEHAVIOR OF 316 STAINLESS STEEL IN FLOWING SODIUM

J. F. Bates
W. F. Brehm

March, 1976

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Hanford Engineering Development Laboratory

Operated by the
Westinghouse Hanford Company

A Subsidiary of
Westinghouse Electric Corporation

for the United States
Energy Research and
Development Administration
Contract No. E(45-1)2170

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Blank Page

EFFECT OF COMPOSITION ON THE CORROSION BEHAVIOR OF 316 STAINLESS STEEL IN FLOWING SODIUM

J. F. Bates and W. F. Brehm

ABSTRACT

Type 316 stainless steel specimens irradiated and non-irradiated, with minor variations in C, N, Cr, Ni, Si, and Mn content, were exposed to flowing sodium in the Source Term Control Loop-1 facility. Test conditions of 604°C (1120°F), a sodium velocity of 6.7 m/s (22 ft/sec), and an oxygen content of 0.5 and 2.5 ppm were used to ascertain the effect of these compositional variations on the corrosion rate and on the ^{54}*Mn release rate.*

Variations in C, N, and Mn had no significant effect on the corrosion rate. The corrosion rate increased somewhat as the Ni and Si content of the steel was increased, and decreased with an increase in Cr content. Microprobe examination showed preferential leaching of Mn, Si, Cr, and Ni to depths of up to 10μm (0.4 mil) after exposure times ranging from 5000-8000 hours.

Variations in natural (^{55}*Mn) content did not affect release rates of* ^{54}*Mn [generated by* $^{54}Fe(n,p)^{54}Mn$*].*

Blank Page

CONTENTS

FIGURES

TABLES

INTRODUCTION

Corrosion resistance in flowing sodium and resistance to irradiation-induced swelling are fundamental requirements for material designed for cladding and duct applications in Liquid-Metal-Cooled Fast Breeder Reactors (LMFBRs). It has been shown that minor alloy modifications of 316 stainless steel result in improved swelling resistance.(1,2) One purpose of this work was to determine the effect of similar alloy modifications on the corrosion behavior of 316 stainless steel.

Another corrosion-related problem is the diffusive loss of ^{54}Mn from core components. ^{54}Mn is a major contributor to radiation levels in maintenance regions near LMFBR heat transport system components(3,4), and any means of reducing this release rate would be beneficial. ^{54}Mn arises from an (n,p) reaction with ^{54}Fe in the steel and not from nonradioactive manganese initially in the stainless steel (^{55}Mn). A higher manganese content may therefore mean that additional manganese produced by irradiation (^{54}Mn) would have a greater tendency to cluster or precipitate in another phase than to remain in the matrix as soluble manganese. Also, a very low manganese content may reduce the driving force for ^{54}Mn from the cladding to the sodium. An investigation was undertaken to determine if the initial level of manganese in a nominal 316 stainless steel base alloy could reduce this release rate of ^{54}Mn.

EXPERIMENTAL PROCEDURE

Several of the alloys used in swelling and mechanical properties studies were exposed to flowing sodium in the Source Term Control Loop #1 (STCL-1) at the Hanford Engineering Development Laboratory to determine the effect of minor alloy modifications on the corrosion behavior of 316 stainless steel. The specimens received up to 8000 hours exposure in sodium at 604°C (1120°F).

The specimens used in this experiment were tubes, produced by center-drilling bar stock. Approximate specimen dimensions were 13 mm long, 5.84 mm OD x 5.08 mm ID (1/2" long, 0.230" OD, 0.200" ID). Composition of the specimens is shown in Table 1. The specimens designated 16B, 17B, 18B,

TABLE I

SPECIMEN COMPOSITION, WEIGHT PER CENT

(All Others Except Iron Remained at AISI 316 Specification)

Specimen No.	C	N	Si	Mn	Cr	Ni
1	0.003	0.007	0.4	0.92	16.95	12.01
3[a]	0.047	0.05	0.39	0.94	17.0	12.05
5	0.128	0.111	0.43	0.97	17.0	12.10
25	0.046	0.052	<0.01	0.95	16.88	11.98
29	0.045	0.050	1.96	0.94	17.13	12.39
40	0.045	0.05	0.40	0.95	14.86	9.96
41	0.046	0.052	0.38	0.96	14.89	12.01
44	0.046	0.049	0.41	0.90	18.97	12.11
16B[+]	0.045	0.047	0.43	<0.01	16.92	12.15
17B[+]	0.046	0.052	0.38	0.92	17.0	12.07
18B[+]	0.047	0.054	0.38	2.04	17.17	11.91
19B[+]	0.044	0.056	0.37	3.89	17.03	11.98
"D"[+][b]	∿0.05	∿0.02	∿0.4	1.49	17.05	13.8
"B"[+][b]	∿0.05	∿0.02	∿0.4	1.52	16.9	13.9

a = 316 nominal composition

\+ = irradiated

b = irradiated fuel cladding specimens used in radioactive mass transport program and 19B were included to measure the effect of nonradioactive Mn in the steel upon corrosion and ^{54}Mn release. These specimens were irradiated to a fluence of ∿2 x 10^{22} n/cm^2 (E >0.1 MeV) prior to exposure in the loop.

These specimens were slightly smaller than the standard size specimens, having an OD of 5.59 mm (0.220") and an ID of 4.82 mm (0.190"). A tapered adapter was used on the specimen holder to ensure a smooth transition along the line of specimens. Schematic drawings of the test loop and the specimen holder are shown in Figures 1 and 2, respectively. The test loop is a pumped, non-isothermal facility, with equipment for continuous purification and monitoring of the oxygen level of the sodium by standard techniques. Details of these techniques and of the operation of the loop are given in Reference 3.

The specimen environment was as follows:

Specimen temperature:	604°C (1120 ±3°F)
Main line minimum temperature:	427°C (800 ±5°F)
Flow rate:	0.457 m^3/hr (2 gal/min)
Velocity past specimens:	6.7 to 7.6 m/sec (22 to 25 ft/sec)
Reynolds number at specimen surface:	47,500 ±2500

The Reynolds number was determined from:

$$N_{Re} = \frac{4R_h\ V\ \rho}{\eta} \qquad (1)$$

where R_h = hydraulic radius of test section =(area/wetted perimeter),
V = Velocity of sodium,
ρ = density of sodium, and
η = viscosity of sodium.

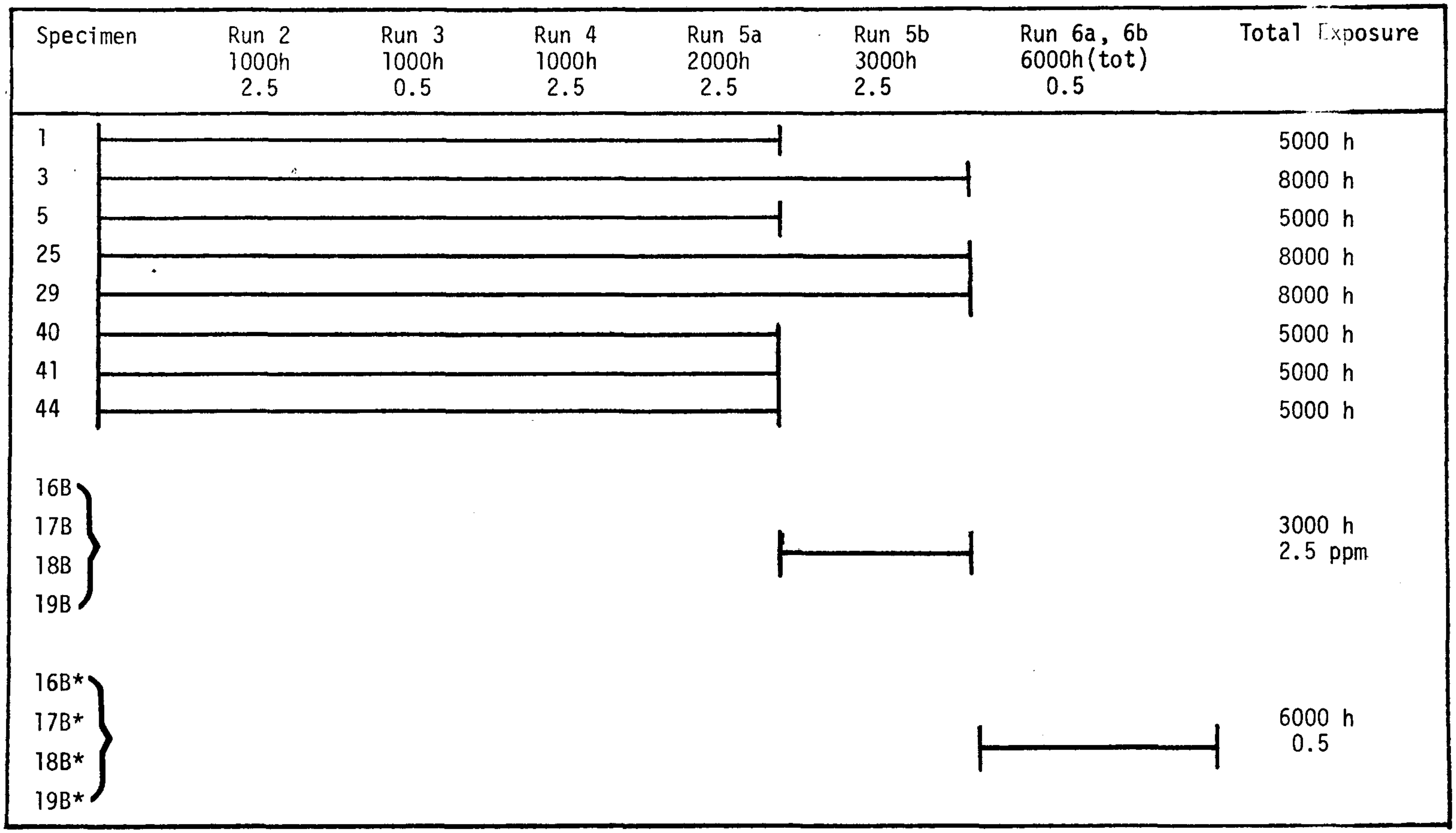
Oxygen levels in the sodium were controlled by changing the cold trap temperature and were monitored continuously by electrolytic oxygen meters, which in turn were calibrated with a standard technique(4) by exposure of a vanadium wire to loop sodium.

The STCL-1 loop is used to determine the effect of the oxygen level in sodium upon the release of radioactive species from irradiated 316 SS

TABLE 2

SPECIMEN EXPOSURE

STCL-1 RUN NUMBER AND OXYGEN LEVEL IN PPM



*The "depleted zone" was removed and analyzed by an incremental analysis electropolishing technique from these specimens after the first exposure.(5) After polishing and analysis, the specimens were re-inserted in the loop.

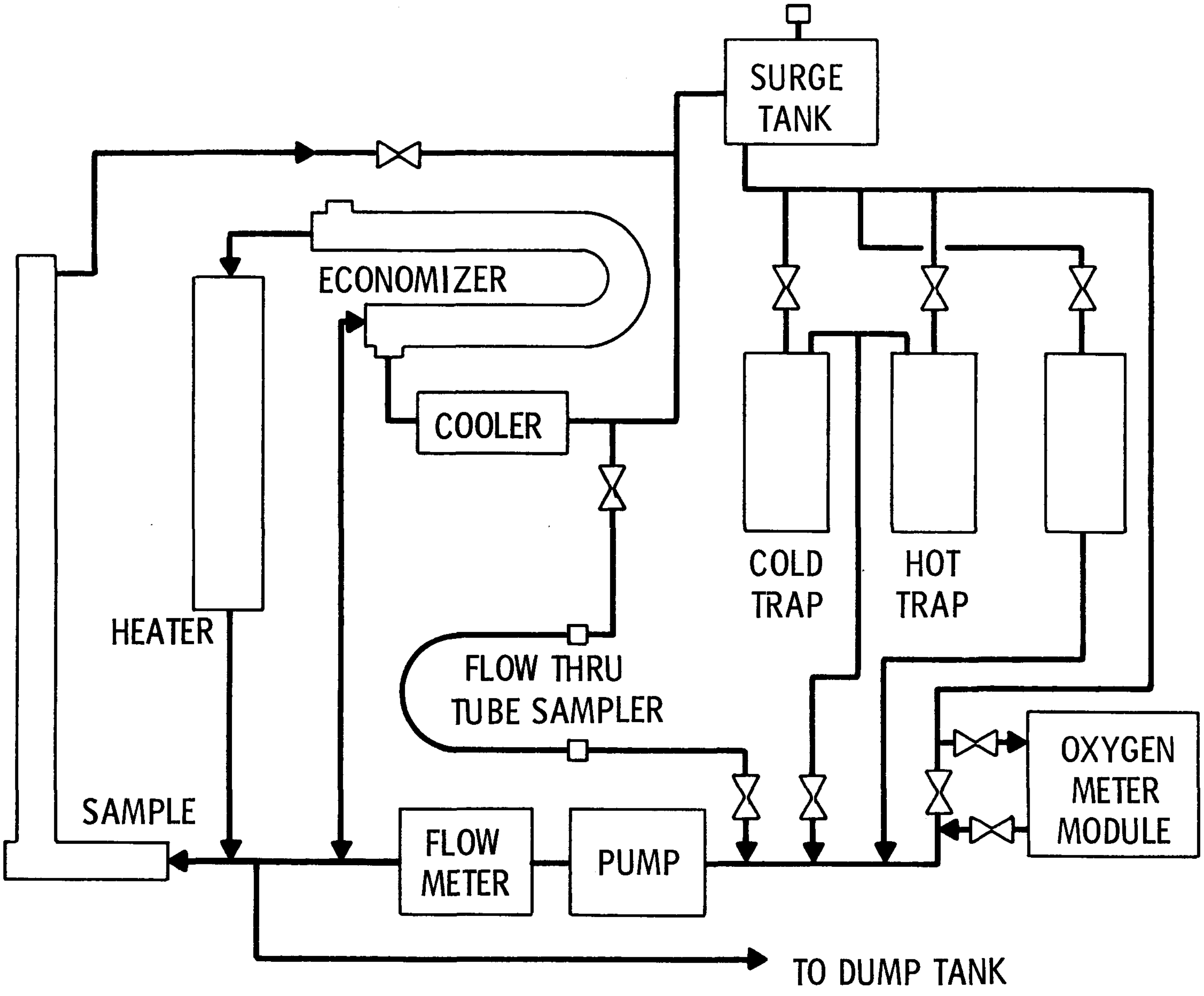


FIGURE 1. Source Term Control Loop.

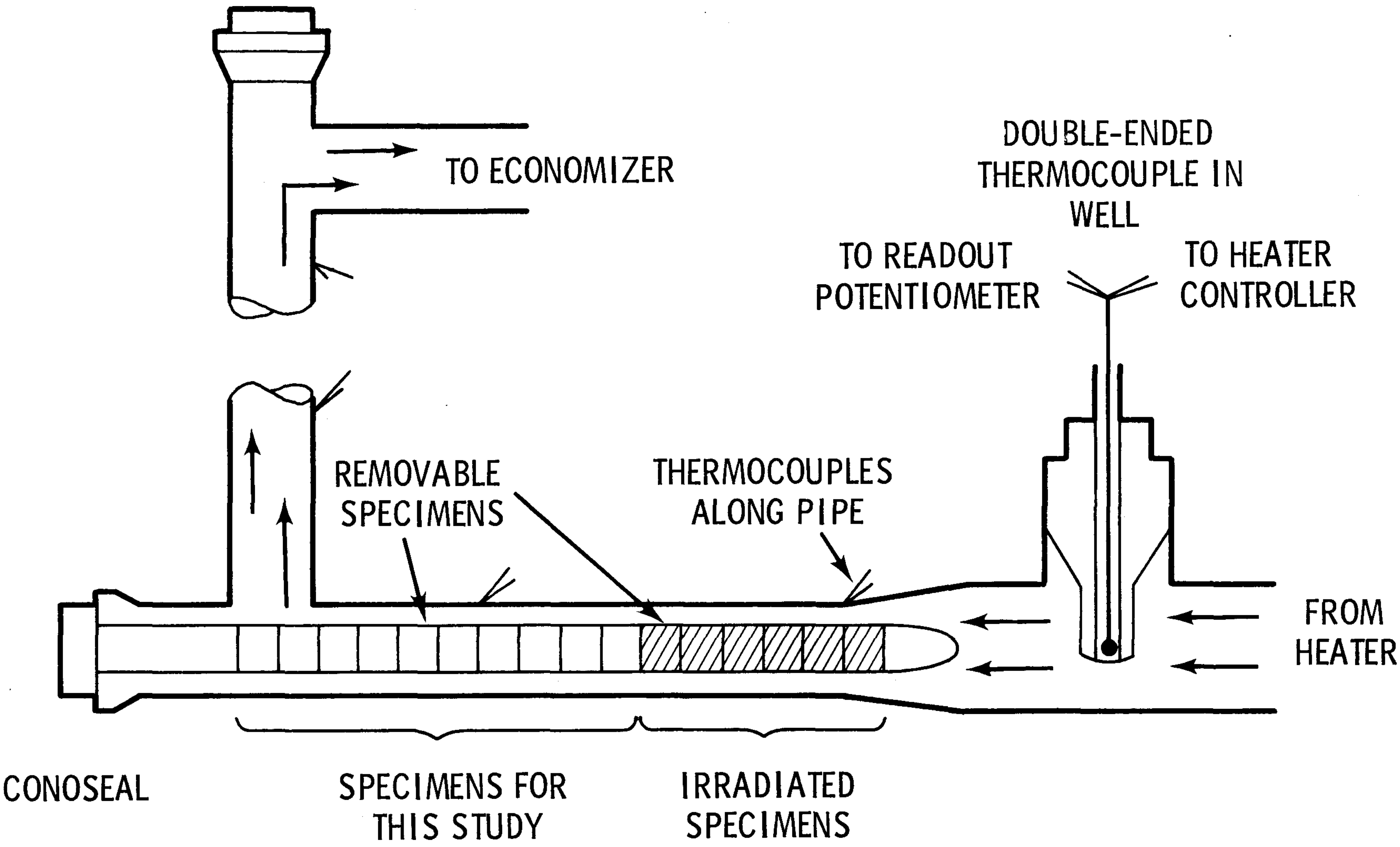


FIGURE 2. Schematic of Specimen Chamber Heated Along Length to Maintain Isothermal Conditions.

cladding.(5) Consequently, the specimens were exposed at two different oxygen levels. Oxygen levels of 2.5 ppm and 0.5 ppm were maintained for testing, with corresponding cold trap temperatures of 154°C (310°F) and 115°C (240°F). Temperature control of the cold trap was maintained at ±1°C. Table 2 shows the exposure history of each specimen at the two different oxygen levels.

After exposure, specimens were removed from the loop, and adherent sodium was removed by alcohol and deionized water rinses, followed by drying at 80°C (175°F) in a vacuum oven. The periodic weight changes were measured on microbalances sensitive to 10^{-6} gram.

Following the last exposure, composition gradients in the specimen material in samples 3, 29, 41 and 44 were determined by electron microprobe. In addition, gradients of both radioactive and nonradioactive species in the (irradiated) 16B-19B specimens were established by sequentially electropolishing 0.2 μm layers from the specimen surface and chemically and radiochemically analyzing the polishing solutions from each increment.(6)

RESULTS

The weight change data are shown in Table 3. A general scan of the data shows that, under these experimental conditions, the corrosion rates are quite modest, and none of the alloys exhibit corrosion rates which would prohibit their use in LMFBRs. The average corrosion rate of all specimens (except the 16B-19B series at 0.5 ppm oxygen) was 2.54 μm (0.10 mil) per year. By comparison, the Bagnall-Jacobs correlation(7) predicts a corrosion rate of 4.5 μm (0.18 mil) per year at 2.5 ppm oxygen.

A similar investigation of the effect of manganese on the corrosion rate and ^{54}Mn release rate from 316 stainless steel was also conducted. The specimens used in this study were the 16B-19B series. The average corrosion rate of the manganese series at 0.5 ppm oxygen was 1.5 μm (0.059 mil) per year, compared with a prediction of 0.9 μm (0.035 mil) per year from the Bagnall-Jacobs correlation;(7) and 1.27 μm (0.05 mil) per year in specimens of different heats of irradiated AISI Type 316

TABLE III

SPECIMEN WEIGHT LOSS

	Weight Loss $\mu g/mm^2$					Equivalent Corrosion Rate[α]	
Specimen No.	1000h	2000h	3000h	5000h	8000h	μm/yr	mils/yr
1	2.88	6.09	7.99	13.1		2.92	0.115
3	2.99	6.37	8.44	13.0	18.6	2.59	0.102
5	2.83	6.39	7.77	12.9		2.87	0.113
25	3.31	6.84	8.49	13.1	18.5	2.59	0.102
29	3.98	8.19	8.75	14.8	20.1	2.81	0.111
40	1.86	5.01	5.40	10.8		2.44	0.096
41	2.79	6.6	7.75	13.8		3.10	0.122
44	1 .88	4.86	6.09	12.0		2.66	0.105

[α] Based upon weight loss at longest exposure time. Not corrected for preferential subsurface leaching of Cr, Ni, Mn, Si.

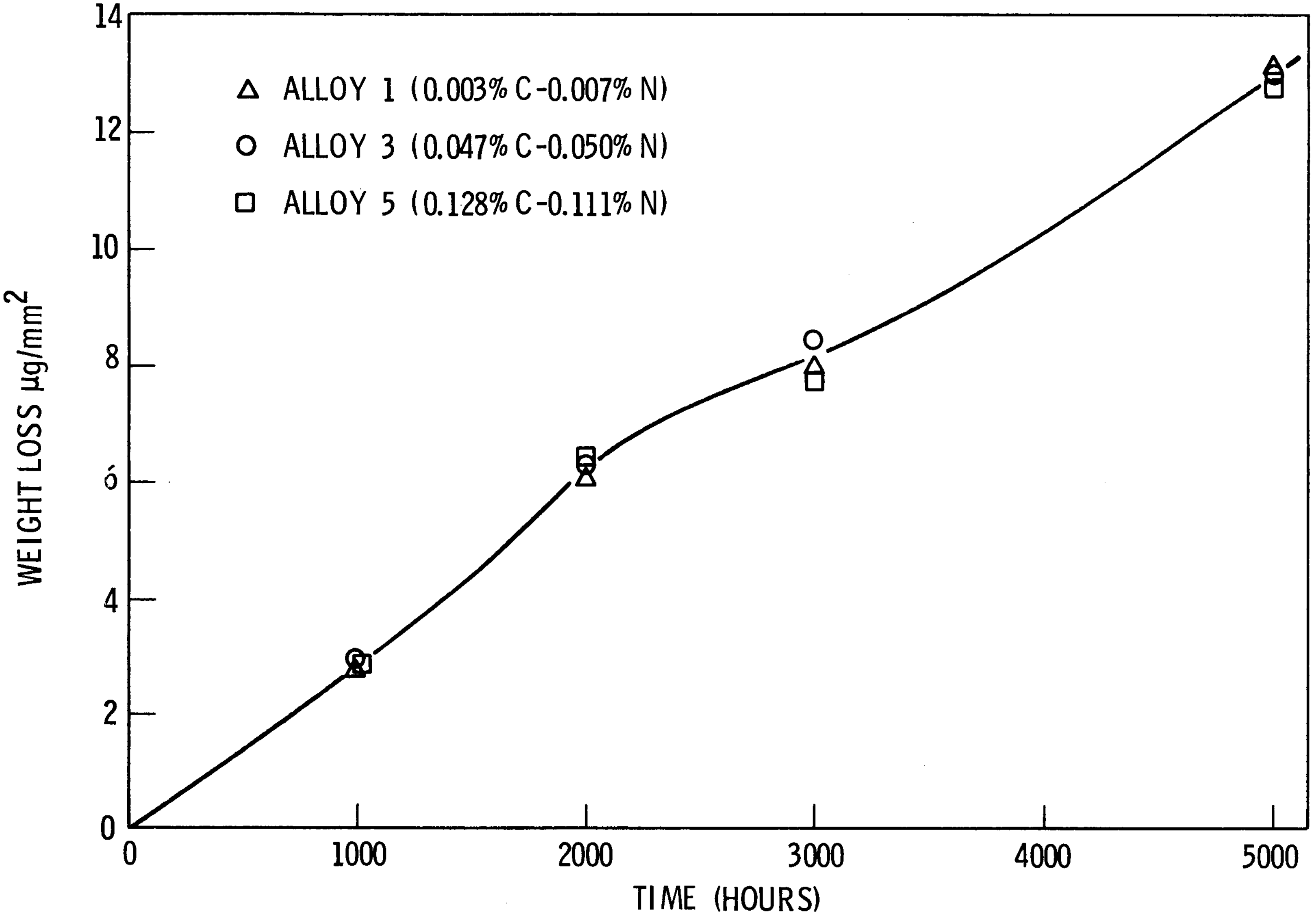


FIGURE 3. Effect of Carbon-Nitrogen Variations on the Corrosion Behavior of Stainless Steel in Flowing Sodium.

stainless steel which were exposed under these same conditions.(4) The weight change and ^{54}Mn release data for the 16B-19B series are shown in Table 3.

DISCUSSION

Carbon and Nitrogen

Simultaneous variations in carbon and nitrogen were found to have virtually no effect on the corrosion rate. Weight change data are shown plotted versus time in Figure 3 for specimens with the chemical variations shown in Table 1. These data do not imply that the carbon level has no effect on other physical and mechanical properties of the steel.

Silicon

Increasing the silicon content from 0.01 to 0.4 wt % was found to have little effect on the corrosion rate. A further increase in the silicon content to 2% resulted in an increased corrosion rate, as shown in Figure 4. An electron microprobe examination showed that silicon had been preferentially leached from both the 0.4% and the 2% silicon specimens to a depth of about 10 μm (0.4 mils) after 8000-hours exposure, as shown in Figure 5.

The local decrease in the Si concentration of the 2% Si specimen observed between 5 and 8 μm distance, as shown in Figure 5, could be caused by the microprobe scan traversing a grain boundary; faster outward diffusion of silicon would be expected in the grain boundary region. Another possibility is the local depletion of silicon because of the presence of a precipitate which forms in the Si-rich alloys.

The overall thickness of the Si-depleted zone (about 10 μm or 0.4 mils) is in good agreement with depleted zone thicknesses of other substitutional alloying elements (e.g., Cr, Ni, Mn) observed in other specimens exposed to sodium for comparable times and temperatures(4).

The overall effect of the Si addition is thus seen to be minimal under these test conditions. However, it must be remembered that "depleted

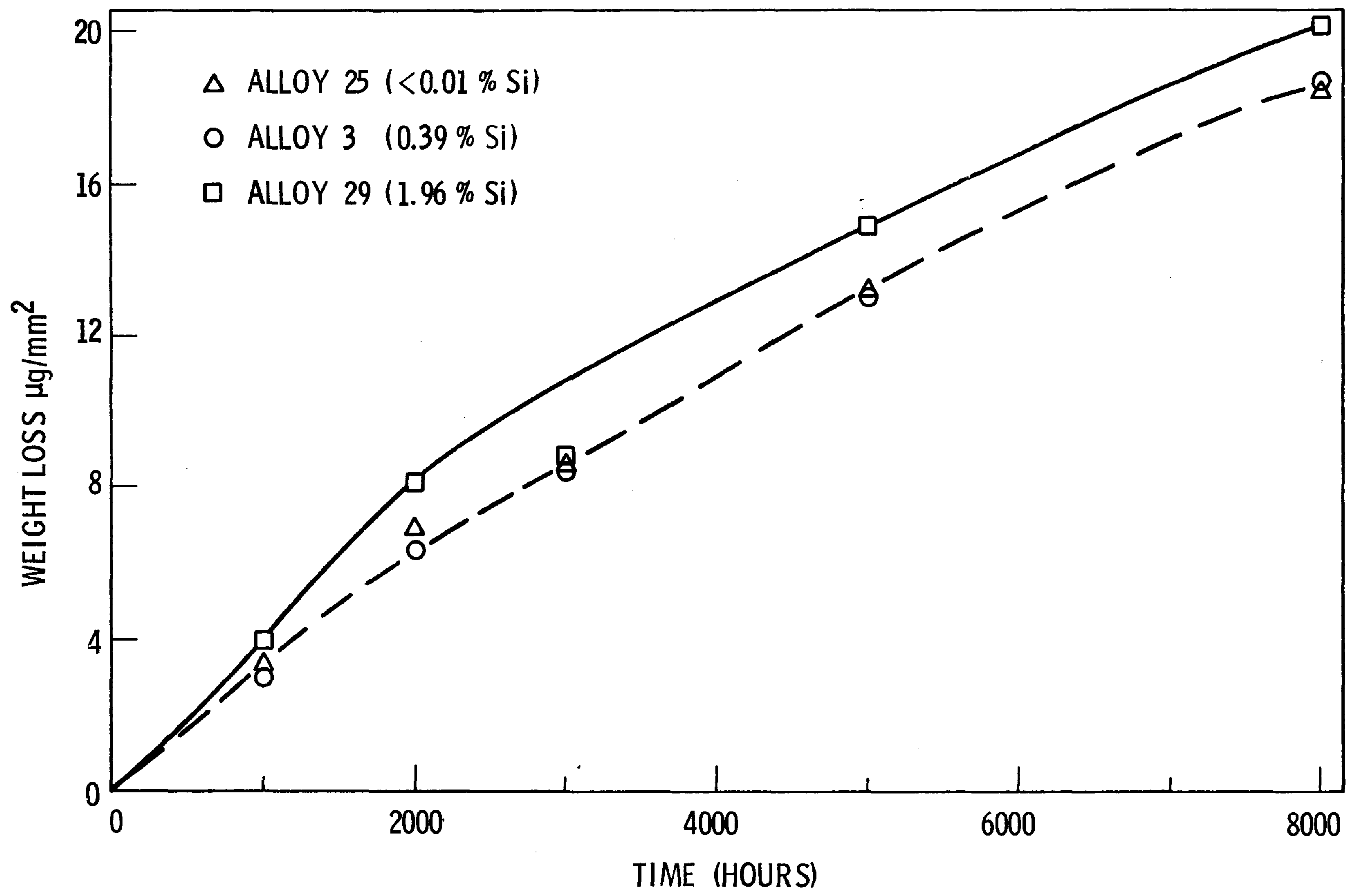


FIGURE 4. Effect of Silicon Variations on the Corrosion Behavior of Stainless Steel in Flowing Sodium.

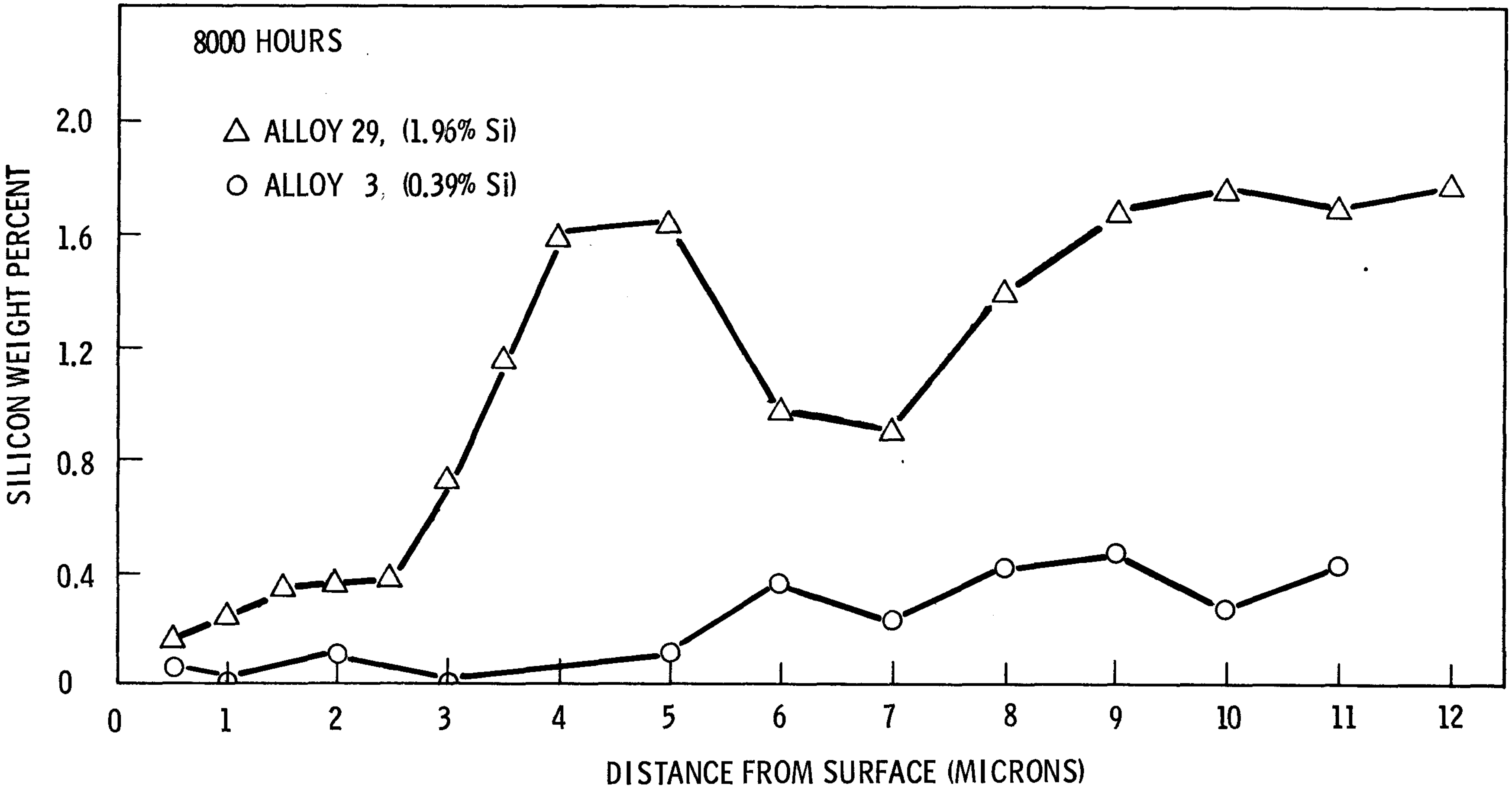


FIGURE 5. Silicon Diffusion from Stainless Steel Samples.

zones" of up to 50 μm (2 mils) thick in other substitutional alloys have been observed after 10,000 hours exposure at 700°C (1292°F).(8) Thus the swelling resistance through the cross section of an alloy may be altered as a result of preferential chemical corrosion.

Nickel

The results shown in Table 2 and plotted in Figure 6 reflect a lower corrosion rate in a specimen with nickel content lowered from 12% to 10%. Nickel is thought to be released by an atomic dissolution process, independent of oxygen activity. Hence, increasing the nickel content increases the driving force for dissolution of nickel at the metal surface. Electron microprobe analysis showed that nickel was indeed preferentially removed at the surface. This result is in general agreement with previous observations that nickel is preferentially removed from stainless steel by sodium and that some high-nickel alloys show higher corrosion rates than iron base alloys in sodium.(8,9)

The observed weight loss differences (about 25%) at the two nickel concentrations are not in agreement with observed corrosion rate differences between 304 stainless steel (8-12% Ni) and 316 stainless steel (10-14% Ni).(10) In fact, Baque et al.(10) report that 304L and 316 stainless steels containing 10% Ni corroded much more than 316L and 316 Ti steels containing 12% Ni. However, there are other gross compositional differences between 304, 316 and 321 stainless steels, whereas the alloys used in this study represent a variation of nickel and iron only. Therefore, at a constant molybedenum content (∿2.3 w/o), lowering the nickel content did have the effect of reducing the corrosion.

Chromium

The corrosion rate of 316 stainless steel was unaffected by changing the chromium content from 15 to 17%. However, a decrease in corrosion rate was observed upon further increasing the chromium content to 19%, as shown in Figure 7. Microprobe examination of the specimens showed a significantly smaller "depleted zone" in the 19% Cr specimen than in the other alloys, as shown in Figure 8. The smaller depleted zone indicates

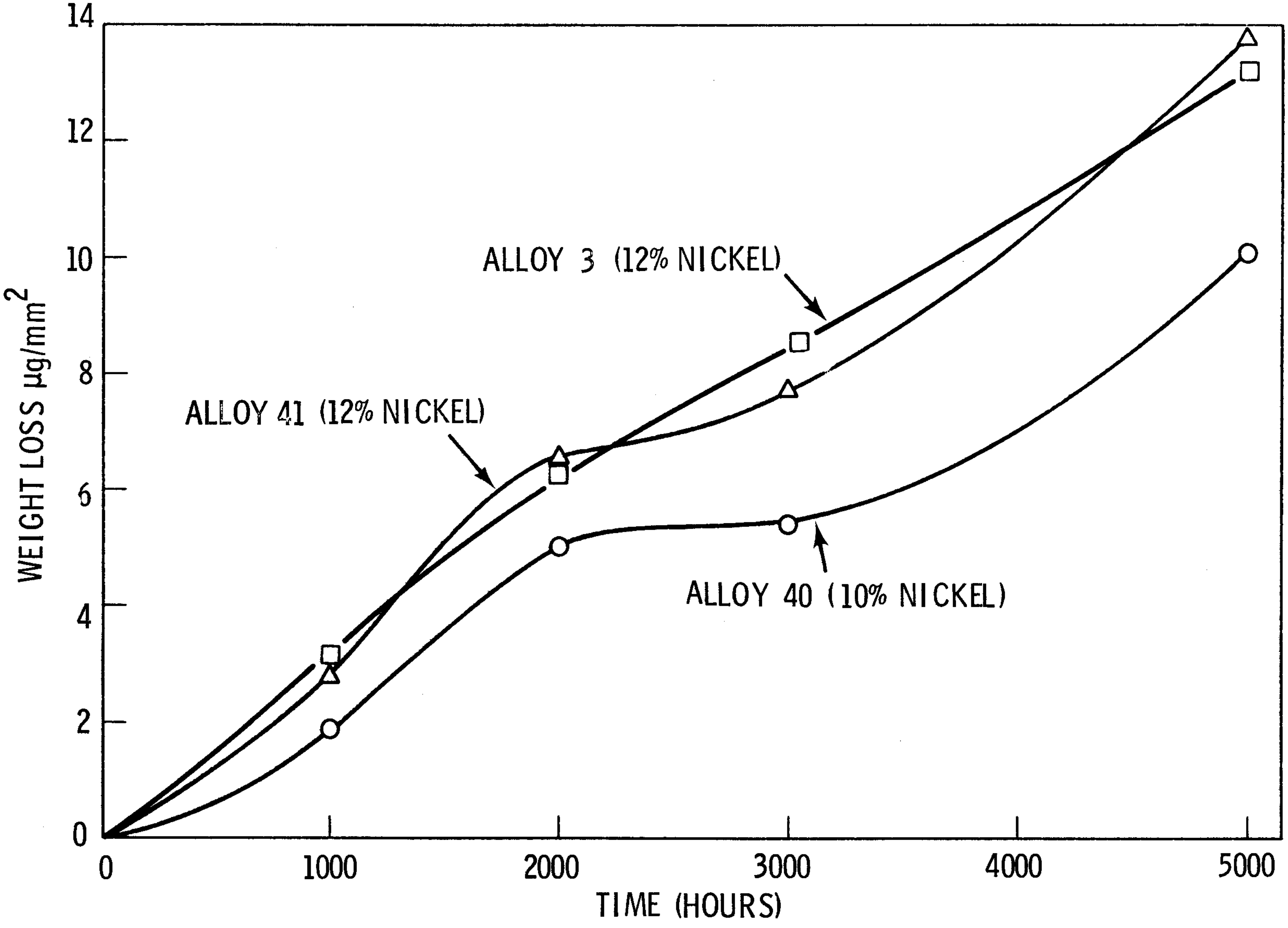


FIGURE 6. Effect of Nickel Variations on the Corrosion Behavior of Stainless Steel in Flowing Sodium.

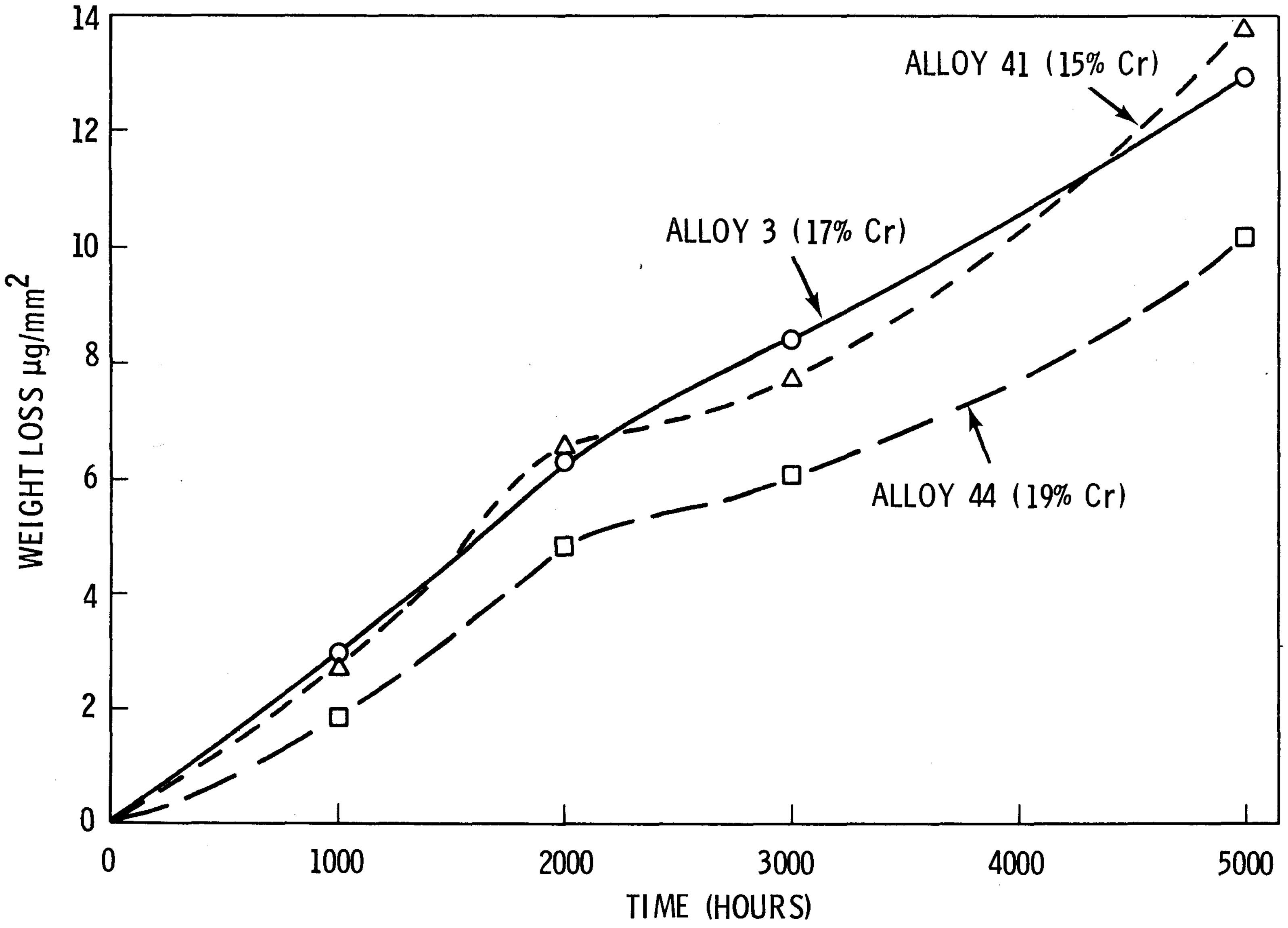


FIGURE 7. Effect of Chromium Variations on the Corrosion Behavior of Stainless Steel in Flowing Sodium.

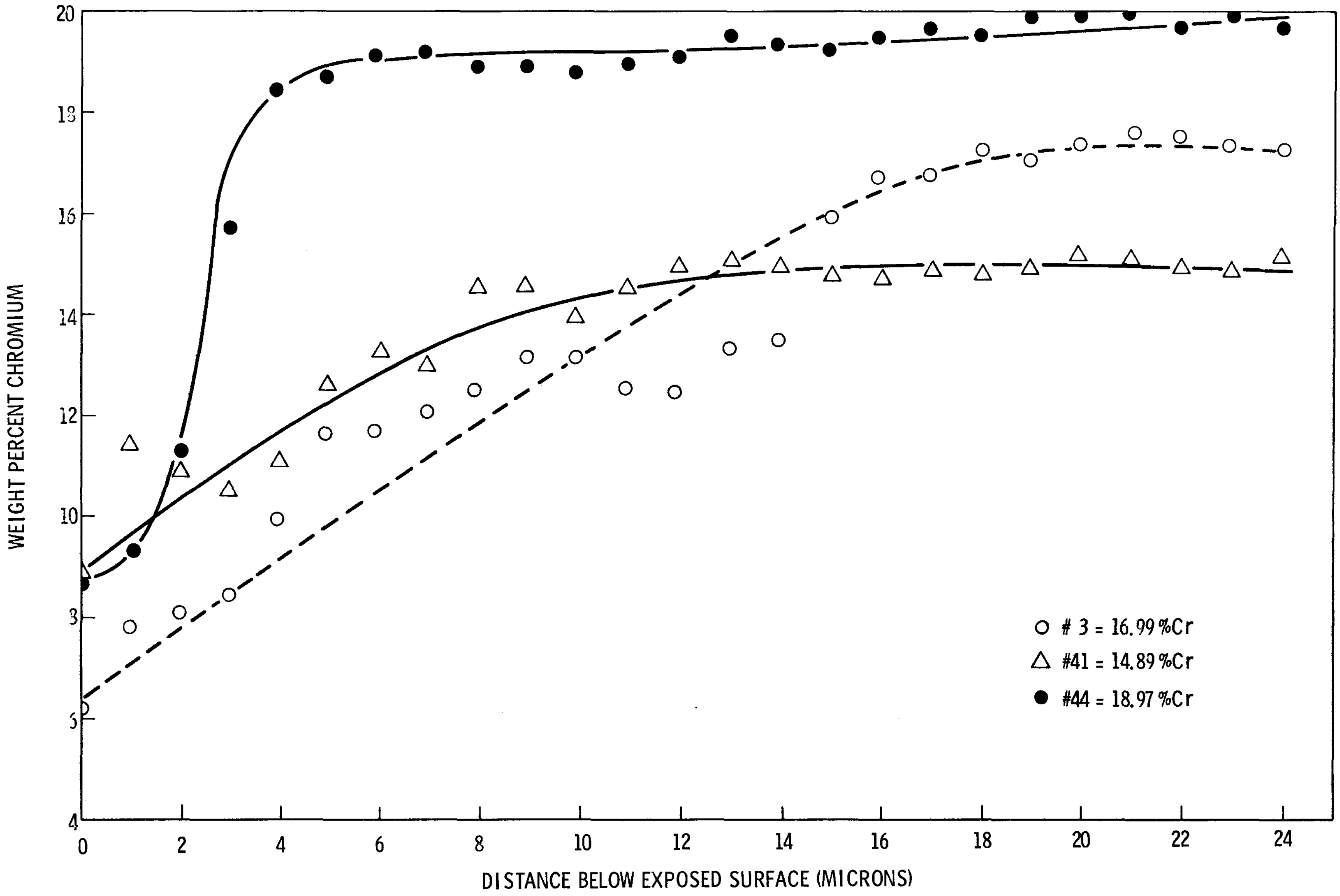


FIGURE 8. Effect of Chromium Content on the Surface Depletion Zone in 316 Stainless Steel.

a much smaller effective diffusion coefficient for Cr in the 19% Cr alloy since the surface concentrations were roughly equivalent. The smaller diffusion release of Cr from the 19% Cr alloy can account for the difference in weight loss. It is not apparent that a surface reaction could cause the effective diffusion coefficient for Cr to differ so widely in the 19% Cr alloy from that for the 17% Cr alloys. The surface concentration of Cr is similar for all alloys.

Manganese

No significant differences in corrosion rate as a function of Mn content were observed, as shown in Figure 9, for the specimens exposed at 0.5 ppm oxygen content. In addition, the ^{54}Mn diffusive release was not changed by the variation in the natural (^{55}Mn) content of the alloys. The overall weight loss of the irradiated specimens was slightly less than that of the unirradiated material. Figure 9 shows the normalized ^{54}Mn diffusion profiles in the 16B-19B series. It can be seen that the diffusion profiles did not differ significantly from each other or from the "D" and "B" specimens (irradiated 316 SS) which are shown for comparison.

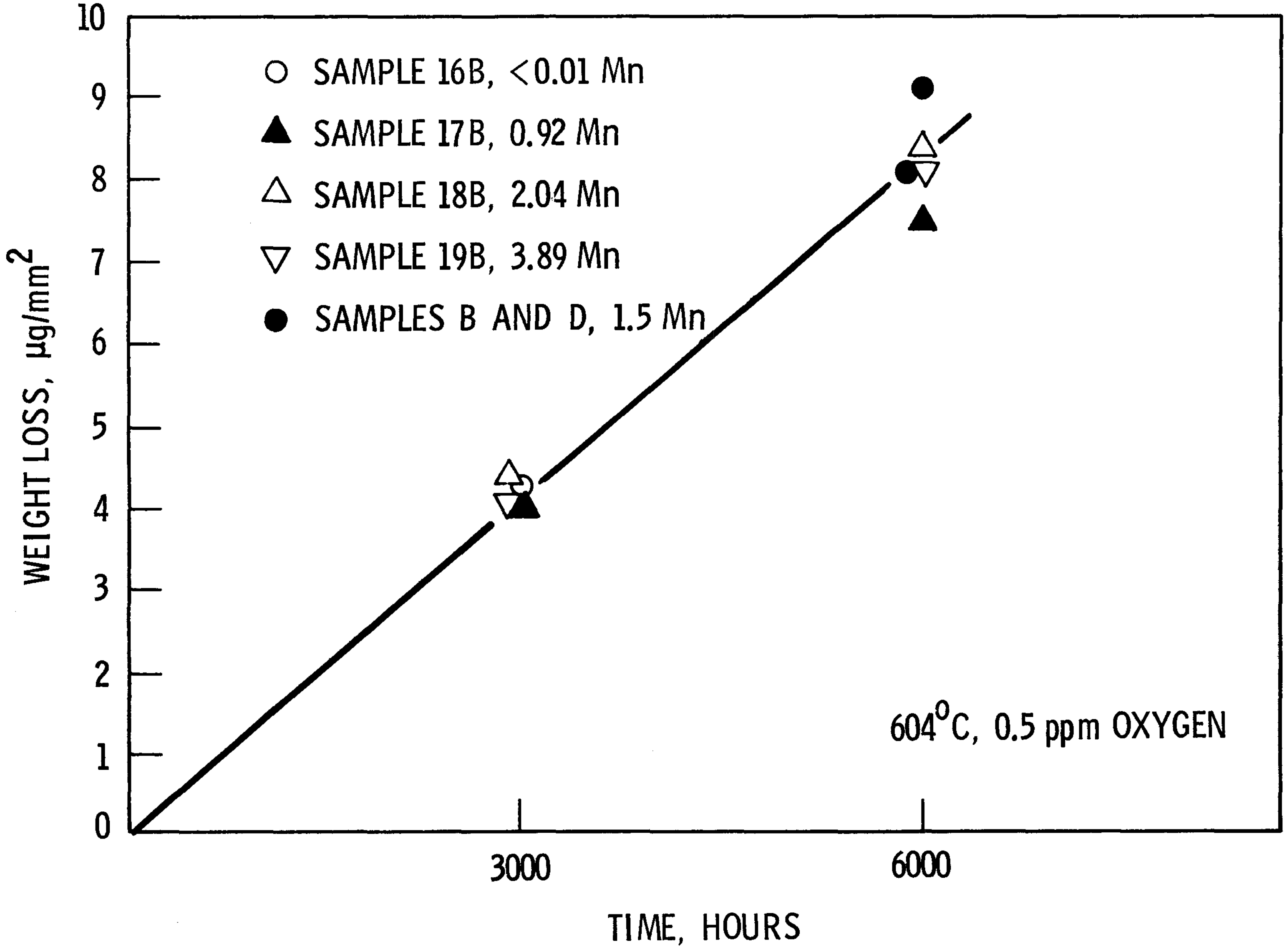


FIGURE 9. Effect of Manganese Content on Corrosion Rate.

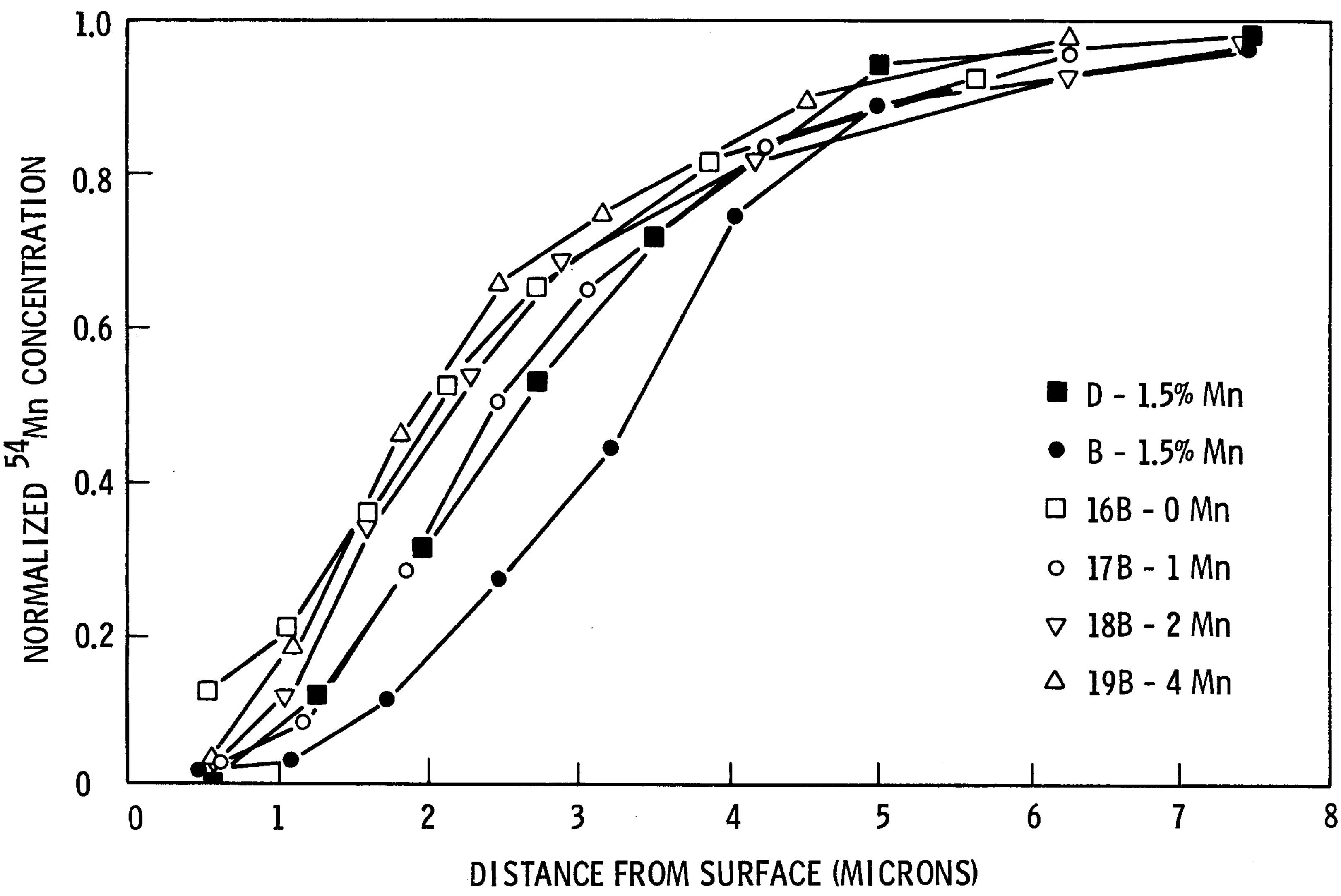


FIGURE 10. Effect of Manganese Content on ^{54}Mn Diffusion Rate.

TABLE IV

EFFECT OF VARIATIONS IN Mn CONTENT UPON ^{54}Mn RELEASE AND SPECIMEN WEIGHT LOSS

Oxygen Content of Na	Specimen Number	^{54}Mn Release, Percent of Total Specimen Activity		Weight Loss, $\mu g/mm^2$		Equivalent Corrosion Rate	
		3000 Hours	6000 Hours	3000 Hours	6000 Hours	µm/yr	mils/yr
2.5 ppm	16B	0.70		5.0		1.82	0.072
2.5 ppm	17B	0.70		5.9		2.16	0.085
2.5 ppm	18B	0.78		6.1		2.23	0.088
2.5 ppm	19B	0.75		7.0		2.54	0.10
0.5 ppm	16B		0.81 (estimated)	4.3	-	1.58	0.062
0.5 ppm	17B		0.93	4.1	7.5	1.38	0.054
0.5 ppm	18B		1.15	4.4	8.4	1.52	0.060
0.5 ppm	19B		0.84	4.2	8.2	1.49	0.059
0.5 ppm	"B"		1.19		9.1	1.68	0.066
0.5 ppm	"D"		0.96		8.1	1.50	0.059

CONCLUSION

The results shown above represent variations of less than 30% in the observed corrosion rates evaluated over 5000 to 8000 hours exposure with several intermediate examinations. It is not surprising that small variations in alloying elements can produce changes in corrosion rates, since significant changes in swelling resistance and mechanical properties behavior are caused by these same small alloy variations. None of the alloys tested, however, had corrosion rates high enough to cause concern over their use in a fast reactor core.

ACKNOWLEDGEMENTS

The authors acknowledge the assistance of the following persons: Barbara Whitten and Linda Hetrick for typing the manuscript; L. E. Chulos, E. R. Wood, and J. L. Bevan for test loop operations; W. I. Clark, A. C. Leaf, and R. F. Keough for chemical and radiochemical analyses; and M. E. Freed and R. L. McDowell for weight-change measurements.

REFERENCES

1. J. F. Bates, "Irradiation-Induced Swelling Variations Resulting from Compositional Modifications of 316 Stainless Steel", ASTM Symposium, Gatlinburg, Tennessee, June 11-13, 1974, ASTM-STP-570.
2. J. F. Bates and G. L. Guthrie, "A Relationship Between Equivalent Chromium Content and Irradiation-Induced Swelling in 316 Stainless Steel", Nucl. Tech., Vol. 27, 2 (October 1975).
3. W. F. Brehm and G. L. Grandy, "Mass Transport of Radioactive Material in Flowing Sodium", presented at NACE Meeting, Chicago, March 1974, HEDL-SA-658.
4. RDT Standard F-3-40, "Methods for the Analysis of Sodium and Cover Gas", January 1973.
5. W. F. Brehm, "Effect of Oxygen in Sodium Upon Radionuclide Release from Austenitic Stainless Steel", presented at IAEA Specialists Meeting on Fission and Corrosion Products in Primary Systems of LMFBR's. Dimitrovgrad, USSR, September 1975, HEDL-SA-985.
6. W. F. Brehm, et al., "Techniques for Studying Corrosion and Deposition of Radioactive Materials in Sodium Loops", presented at IAEA Specialists' Meeting, Dimitrovgrad, USSR, September 1975, HEDL-SA-986.
7. C. Bagnall and D. C. Jacobs, "Relationships for Corrosion of Type 316 Stainless Steel in Sodium", Westinghouse-Advanced Reactors Division, May 1975, WARD-NA-3045-23.
8. G. A. Whitlow, et al., "Sodium Corrosion Behavior of Alloys for Fast Reactor Applications", in Chemical Aspects of Corrosion and Mass Transfer in Liquid Sodium, S. A. Jansson (ed.), AIME, 1972 (Proceedings of TMS-AIME Symposium, Detroit, 1971).
9. G. P. Wozaldo and C. N. Spalaris, "Corrosion of Stainless Steel and Deposition of Particulates in Flowing Sodium Systems", General Electric Company, GEAP-13544 (1969).
10. P. Baque, et al., "Some Aspects of the Corrosion of Austenitic Stainless Steels in Sodium", in Liquid Alkali Metals, published for British Nuclear Energy Society by Thomas Telford LTD, London, 1973.
11. P. Roy, G. P. Wozaldo, and F. A. Comprelli, Argonne Laboratory Report ANL-7520, Pt.1, pp. 131-142 (November 9, 1968).
12. A. H. Fleitman and H. S. Isaacs, "The Corrosion and Mass Transfer of Pure Iron, Nickel, Chromium, and Cobalt in 660°-760°C Sodium", in Corrosion By Liquid Metals, Draley and Weeks (eds.), Plenum Press, New York (1970).

DISTRIBUTION

UC-79 (188)

UC-79b (43)

ERDA-RL (2)

A.G. Fremling
R.E. Constant

FFTFPO (5)

R.L. Ferguson

RDD-HQ (2)

Director

HEDL (28)

J.M. Atwood
J.L. Ballif
J.F. Bates (2)
D.W. Bennett
T.K. Bierlein
R.R. Borisch
W.F. Brehm (2)
W.H. Caplinger
R.J. Cash
L.E. Chulos
T.T. Claudson
R.P. Colburn
C.M. Cox
J.E. Hanson
M.K. Korenko
W.L. Kuhn
J.J. Laidler
J.J. McCown
J.C. McGuire
Central Records and Files (5)
Publications Services (2)