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Review of Oxidation of Nb-1Zr

J. R. DiStefano

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ORNL/TM-10907

Metals and Ceramics Division

REVIEW OF OXIDATION OF Nb-1Zr

J. F. DiStefano

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REVIEW OF OXIDATION OF Nb-1Zr*

J. R. DiStefano

ABSTRACT

A major objective of the SP-100 Program Nuclear Assembly Test is to demonstrate the performance of a full-scale nuclear subsystem of a 100-kWe space nuclear power supply. The test will be run in a large vacuum chamber to protect the Nb-1Zr components from oxidation during operation. Much information about the oxidation of niobium and Nb-1Zr alloy already exists, and previous work in this area is reviewed. Oxidation of Nb-1Zr can proceed by solution, internal oxidation, and/or film formation. At temperatures up to about 650 K (377°C), oxidation generally follows a parabolic rate law because of the formation of protective oxide(s). At higher temperatures, oxidation becomes linear, but results are extremely sensitive to pressure and other system variables. Results obtained by several investigators could not be predicted using empirical equations developed by one investigator relating the increase in oxygen concentration to pressure, temperature, time, and specimen thickness. Additional data are required to provide more reliable guidelines for system operation that will protect against catastrophic effects.

INTRODUCTION

Nb-1Zr (Cb-1Zr) is very reactive in oxidizing atmospheres at high temperatures, and to avoid deterioration, it must be protected when used as a structural or containment material. Furthermore, under certain conditions, small quantities of oxygen in Nb-1Zr can lead to its rapid penetration by lithium, making protection even more important in applications such as SP-100. To prevent such harmful effects, the design specification for the Nuclear Assembly Test (NAT) calls for operation at pressures of $\leq 10^{-8}$ torr. However, even under these low-pressure conditions some oxidation will occur after long periods of time, and off-normal events may occur that could cause the pressure to temporarily rise. Thus, to be

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able to assess the consequences to Nb-1Zr components, it is important to determine the temperature-pressure-time relations for oxidation, especially if off-normal events occur.

One study of the effect of oxygen on the room-temperature tensile properties of Nb-1Zr is illustrated by the data in Table 1 (DiStefano, 1964). Oxidation of Nb-1Zr specimens at 1273 K (1000°C) resulted in a large increase in tensile strength and a corresponding decrease in ductility. However, when the samples were heat treated at 1873 K (1600°C) following oxidation, both strength and ductility were unaffected at oxygen concentrations up to 1360 ppm. Additions of up to 730 ppm during operation of a Nb-1Zr test loop [1373 K (1100°C)] did not have any appreciable effect on its tensile properties at either room temperature or 1373 K, as shown in Table 2 (Hoffman and Holowach, 1970). Resistance-heated samples of Nb-1Zr were contaminated to 490 ppm oxygen at 1523 K (1250°C) with little effect on their room-temperature properties (Jansen and Hoffman, 1964). However, when ~7000 ppm was added, the specimens broke during handling. In a similar study of the oxidation of resistance-heated Nb-1Zr at 1200 K (927°C), increases in strength and decreases in ductility were noted as shown in Table 3 (Lyon, 1971).

Table 4 illustrates the effect of oxygen in Nb-Zr alloys on resistance to attack by lithium. The corrosion protection obtained by heat treating at 1573 K (1300°C) is a function of both zirconium and oxygen concentrations. When the oxygen:zirconium atom ratio exceeds 2:1, no corrosion protection results, even after heat treatment. Other heat treatments, such as 1 h at 1873 K (1600°C) or 5 h at 1273 K (1000°C), were also found to be effective in suppressing corrosion of oxygen-contaminated Nb-1Zr. Because this ratio corresponds to the stoichiometry of ZrO_2, it has been postulated that corrosion protection results from the formation of this oxide. Internal friction studies indicated an oxygen-zirconium interaction peak in a Nb-1Zr specimen oxidized at 1273 K (1000°C) that could be subsequently suppressed by additional heat treating at 1273 K. The interpretation of this effect is that the interaction peak represents oxygen in a solution form, and the heat treatment that suppresses the peak precipitates oxygen, probably as ZrO_2. When samples were exposed to

Table 1. Effect of oxygen in Nb-1Zr alloy on its room-temperature tensile properties

Oxygen concentration (ppm)	Treatment	Strength (psi)		Elongation (%)
		Tensile	0.2% offset yield	
150	*a*	53,700	46,700	11.0
310	*a*	64,400	57,800	11.0
650	*a*	97,300	97,300	2.0
1200	*a*	125,200	125,200	0.0
2100	*a*	137,700	137,700	0.0
3260	*a*	119,900	119,900	0.0
100	*b*	38,700	35,600	14.0
290	*b*	37,300	33,300	10.0
560	*b*	38,800	33,200	11.0
860	*b*	35,700	33,100	11.0
1360	*b*	35,800	28,600	14.0

[a]Oxidation at 1273 K (1000°C) and $P_{O_2} = 9 \times 10^{-5}$ torr.

[b]Oxidation followed by heat treating in vacuum for 1 h at 1873 K (1600°C).

Source: Adapted from J. R. DiStefano, *Corrosion of Refractory Metals by Lithium*, ORNL-3551, March 1964, Table VII, p. 64.

Table 2. Results of tensile tests on Nb-1Zr tube tensile specimens taken from the sodium circuit of corrosion test loop

Specimen	Oxygen concentration (ppm)	Room temperature			1373 K (1100°C)		
		Yield strength (psi)	Ultimate tensile strength (psi)	Elongation (%)	Yield strength (psi)	Ultimate tensile strength (psi)	Elongation (%)
Before test	260	28,300	34,000	40	11,000	14,600	50.0
	260	19,100	37,400	34	11,700	16,800	42.0
Boiler inlet tube [1449 K (1176°C)]	36	18,500	31,100	38	10,800	15,700	47.0
	36	18,600	31,600	36	9,500	13,800	52.0
Boiler outlet tube [1360 K (1087°C)]	730	15,600	33,900	33	10,000	14,300	38.6
	730	16,900	32,800	36	10,300	15,000	51.5

Source: Adapted from E. E. Hoffman and J. Holowach, *Cb-1Zr Rankine System Corrosion Test Loop*, NASA CR 1509 (1970), General Electric, Cincinnati.

Table 3. Room-temperature tensile tests of Nb-1Zr test specimens

Oxygen concentration (ppm)	Ultimate tensile strength (ksi)	Yield strength 0.02% (ksi)	Yield strength 0.2% (ksi)	Elongation (%)
45	43.4	18.3	21.4	29.6
45	43.7	18.7	21.8	31.6
	43.6 Av	18.5 Av	21.6 Av	30.6 Av
45	49.8	17.6	24.0	28.6
45	49.5	49.5	20.5	32.4
	49.7 Av	19.1 Av	24.5 Av	30.5 Av
4430	81.0	47.5	54.1	17.7
4430	81.0	47.2	55.3	20.6
	81.0 Av	47.3 Av	54.7 Av	19.2 Av
4430	74.1	45.7	54.4	9.3
4430	82.1	42.0	55.0	16.8
	78.1 Av	43.9 Av	54.7 Av	13.1 Av
5990	122.0	78.0	87.5	15.4
5990	116.0	75.0	84.0	16.8
	119.0 Av	76.5 Av	85.8 Av	16.1 Av
5990	120.0	79.7	89.5	13.4
5990	115.0	72.2	85.5	14.0
	117.5 Av	76.0 Av	87.5 Av	13.7 Av
8460	133.0	*a*	129.0	2.0
8460	133.0	*a*	123.0	1.0
	133.0 Av		126.0 Av	1.5 Av
9670	111.0[b]	*a*	*a*	
9670	121.0	*a*	*a*	0.5
9670	117.0	*a*	*a*	
9670	84.7[b]	*a*	*a*	
4210	34.4	*a*	*a*	0.9
4210	46.1	34.9	46.1	1.4

[a]Failed before yield was obtained.

[b]Failed in pinhole.

Source: Adapted from T. F. Lyon, "Low-Pressure Oxidation of Cb-1Zr Alloy," *J. Vac. Sci.* **8**(6) [Suppl: *Proceedings of the Vacuum Metallurgy Conference Sponsored by the Vacuum Metallurgy Division of the American Vacuum Society*, 14-16 June 1971, New York, New York, VM48-VM58 (1971)], Table II, p. VM55.

Table 4. Depth of attack by lithium of Nb-Zr alloys as a function of zirconium concentration, oxygen concentration, and heat treatment[a]

Concentration (%)		Depth of attack (mils)	
Zirconium	Oxygen	After oxidation at 1273 K (1000°C)[b]	After heat treatment at 1573 K (1300°C)[c]
0.05	0.09	15	15[d]
0.05	0.18	25	25[d]
0.05	0.23	30[e]	30[d]
0.4	0.09	15	0
0.4	0.18	20	15[d]
0.4	0.23	30[e]	30[d]
0.6	0.09	10	0
0.6	0.18	20	0
0.6	0.23	30[e]	25[d]
0.9	0.09	10	0
0.9	0.18	20	0
0.9	0.23	30[e]	0
1.3	0.09	5	0
1.3	0.18	10	0
1.3	0.23	25	0

[a]Test conditions: 100 h at 1089 K (816°C).

[b]Specimen exposed to lithium after oxidation at 1273 K (1000°C).

[c]Specimen heat treated in vacuum for 2 h at 1573 K (1300°C) following oxidation and prior to exposure to lithium.

[d]Oxygen-to-zirconium atomic ratio was >2.

[e]Complete penetration of 60-mil-thick specimen.

Source: J. R. DiStefano, *Corrosion of Refractory Metals by Lithium*, ORNL-3551, March 1964, Table VI, p. 59.

lithium, those exhibiting an oxygen-zirconium peak were attacked, but those in which the peak had been suppressed by heat treating were not.

Another consideration in discussing oxidation effects on Nb-1Zr is the diffusion rate of oxygen. Generally, an Nb-1Zr component will be contaminated at its outside diameter (OD). A plot to determine the rate at which oxygen can be gettered from niobium by lithium is qualitatively useful in estimating the effect of temperature on the movement of oxygen from the OD to the inside diameter (ID) during or after oxidation (Fig. 1). At 773 K (500°C) the diffusion rate for oxygen is extremely slow, and significant amounts of oxygen would not be transferred to the ID except after a very long time. At temperatures approaching the NAT operating temperature, diffusion is rapid; it would be expected that contaminants on the OD would move relatively quickly into the wall. Whether the distribution of oxygen would be uniform throughout the wall depends upon the rate of formation of ZrO_2 and/or gettering of oxygen by lithium at the ID.

Results such as these indicate why it is important to understand the oxidation behavior of Nb-1Zr under conditions that could be encountered in SP-100 systems. This report reviews the results of previous studies of the oxidation behavior of niobium and Nb-1Zr to determine the need for further data for SP-100 and, in particular, the NAT. Although the reference list in this report is not extensive, several of the references cited contain their own literature review that refer the reader to many other studies conducted in this area.

REVIEW OF LITERATURE DATA

Oxidation of Nb-1Zr can proceed by solution, internal oxidation, and/or film formation. In general, Nb-1Zr exhibits a complex oxidation behavior that depends upon temperature, pressure, and microstructure. Past studies have been conducted in air, various pressures of oxygen, and residual gases present at low system pressures (high vacuum).

A study by Bridges and Fassell (1956) reviewed much of the previous data on oxidation of niobium. Bridges and Fassell developed theoretical equations for the oxidation of niobium above 800 K (527°C) at pressures of

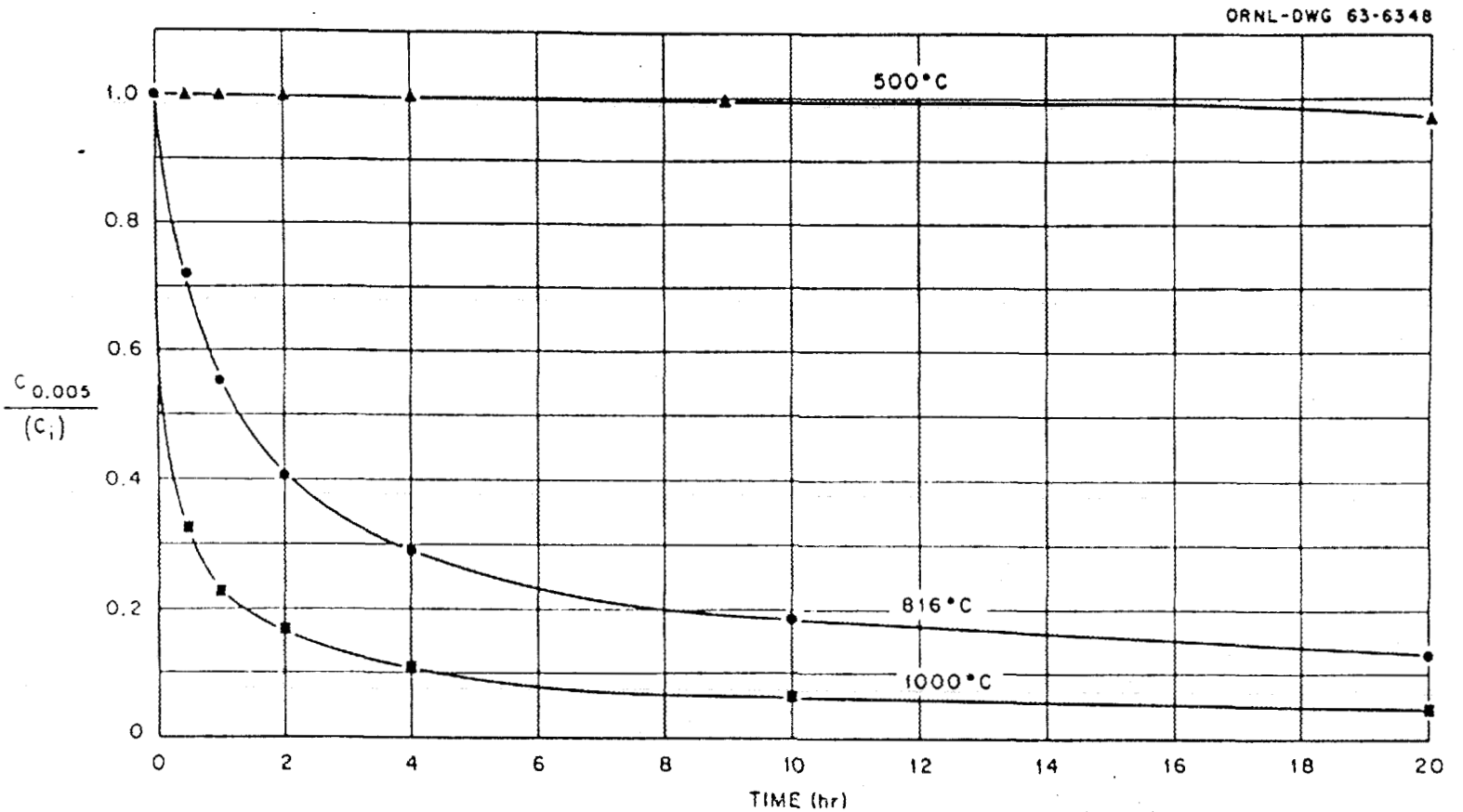


Fig. 1. Ratio of oxygen concentration 0.013 cm (0.005 in.) from surface to initial oxygen concentration in niobium as a function of diffusion time (based on assumption that diffusion is rate-controlling step in gettering of oxygen by lithium). In this plot, $c_x/c_i \propto 1/d^{1/2}$. *Source*: J. R. DiStefano, *Corrosion of Refractory Metals by Lithium*, ORNL-3551 (March 1964), Fig. 17, p. 42.

1 atm and higher. They noted that Fansteel Metallurgical Corporation had shown that the oxide formed on niobium in air at 473 K (200°C) is adherent and prevents further oxidation (Fansteel, 1945). They also referred to works that found that niobium obeys the parabolic rate law from 473 to 548 K (200–275°C) (Phelps et al., 1946; Gulbransen and Andrews, 1949; Gulbransen and Andrews, 1950). However, at 873 to 1473 K (600–1200°C), Klopp et al. (1957) subsequently reported a linear oxidation rate of niobium in pure oxygen.

Hurlen et al. (1959) made detailed studies of the oxidation of niobium at temperatures below 1073 K (800°C). At temperatures below about 773 K (500°C), they found that oxygen dissolution into the niobium preceded oxide scale formation. Both rate of oxidation and thickness of the oxide scale were dependent upon oxygen pressure. At 1 atm oxygen pressure, there was a decrease in the rate of oxidation (rate reversal) when increasing the temperature from 873 K (600°C) to 973 K (700°C) (Fig. 2). The nature and composition of the oxide scales were dependent upon temperature, oxygen pressure, and time.

In a continuation of the work of Hurlen et al., Kofstad et al. (1960) studied the oxidation behavior of niobium from 773 to 1473 K (500–1200°C). Reversals in the temperature coefficient of oxidation were found in two temperature regions [873 and 1073 K (600 and 800°C)] depending upon oxygen pressure (Figs. 3 and 4). This behavior was suggested to be due to different Nb_2O_5 modifications in different temperature regions and to the ability of the oxide to deform plastically and form more protective scales with decreasing oxygen pressure.

In 1962, Delgrosso et al. reported results of oxidation of Nb-1Zr in air from 477 to 1366 K (204–1093°C). Up to 589 K (316°C) plots of weight change versus time were parabolic with no change to linear kinetics out to 100 h. [Interestingly, at 533 K (260°C), no measurable weight change was found out to 1515 h.] At 644 K (371°C) the reaction rate was initially high (<5 h) and then became protective out to 60 h (Fig. 5). At about 700 K (427°C) the oxidation rates became linear after a brief parabolic period, and above 1144 K (871°C) oxidation was reported to be linear and nearly independent of temperature (Fig. 6). Internal oxidation of Nb-1Zr

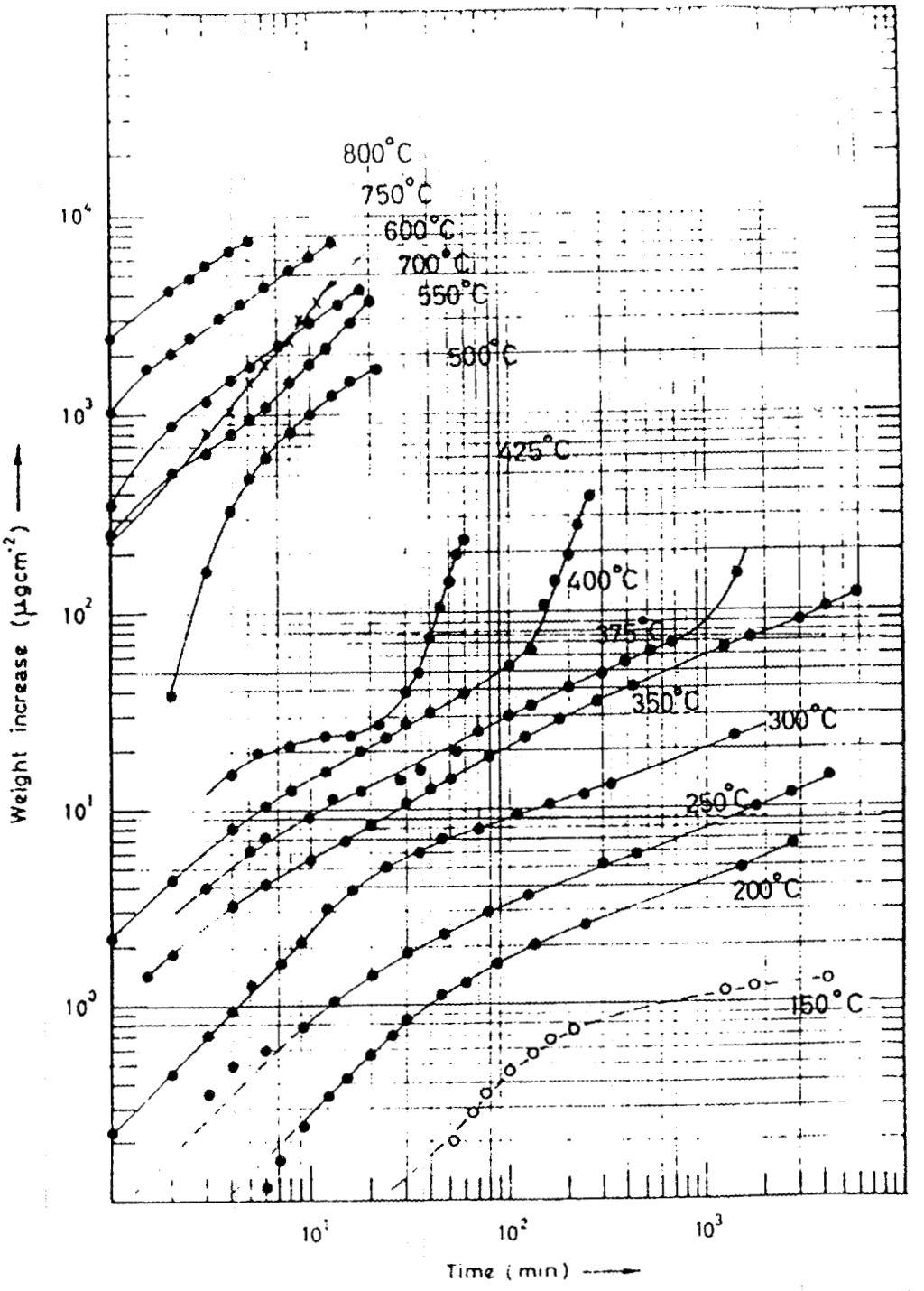


Fig. 2. Oxidation-time curves for niobium at 760 torr (1 atm) oxygen. *Source*: T. Hurlen, H. Kjollesdal, J. Markali, and N. Norman, *Oxidation of Niobium*, Technical (Scientific) Note No. 1, Central Institute For Industrial Research, Blindern-Oslo-Norway, April 1959, diagram 1.

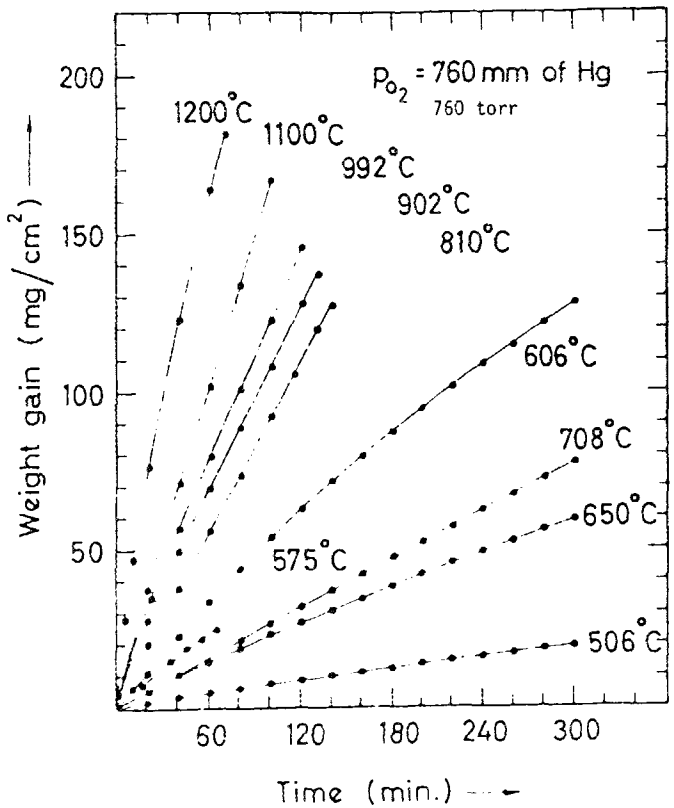
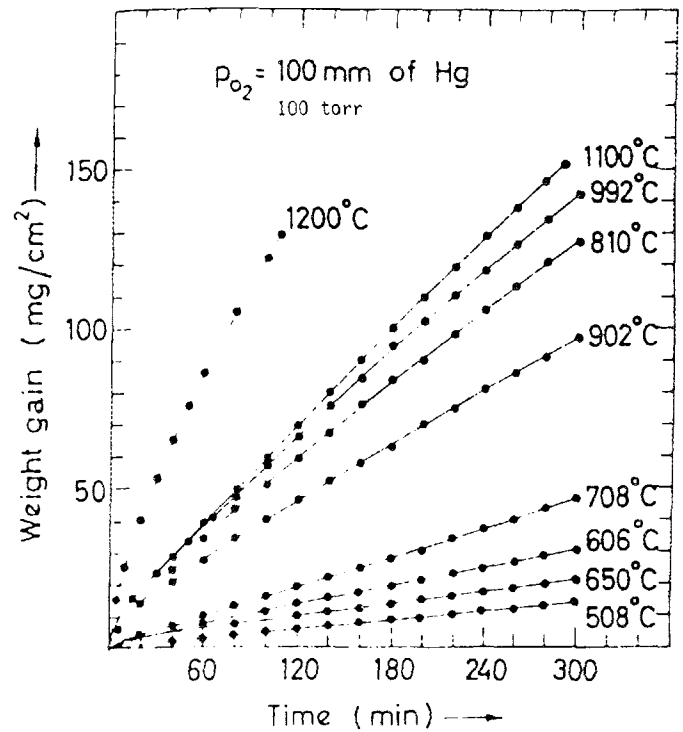


Fig. 3. Oxidation of niobium in the temperature range 773–1473 K (500–1200°C) at 760 torr (1 atm) oxygen. *Source*: P. Kofstad, H. Kjollesdal, J. Markali, and N. Norman, *High-Temperature Oxidation of Niobium*, Technical (Scientific) Note No. 2, Central Institute For Industrial Research, Blindern-Oslo-Norway, April 1960, Fig. 2



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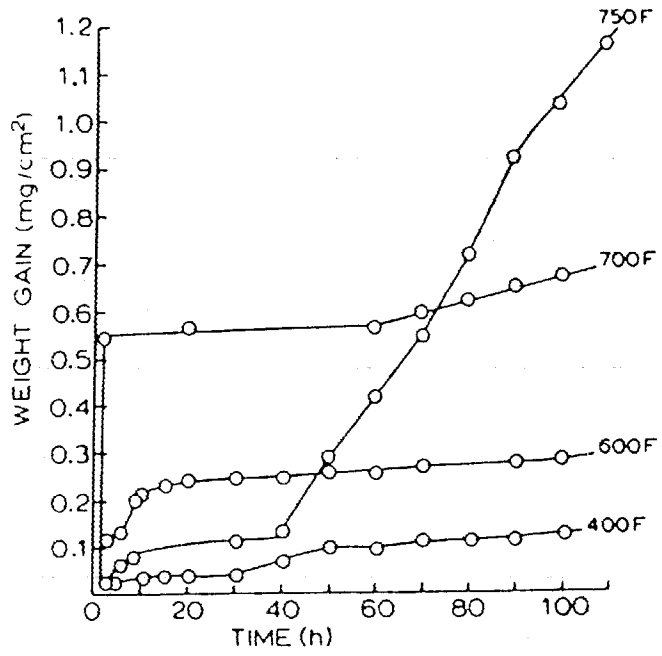

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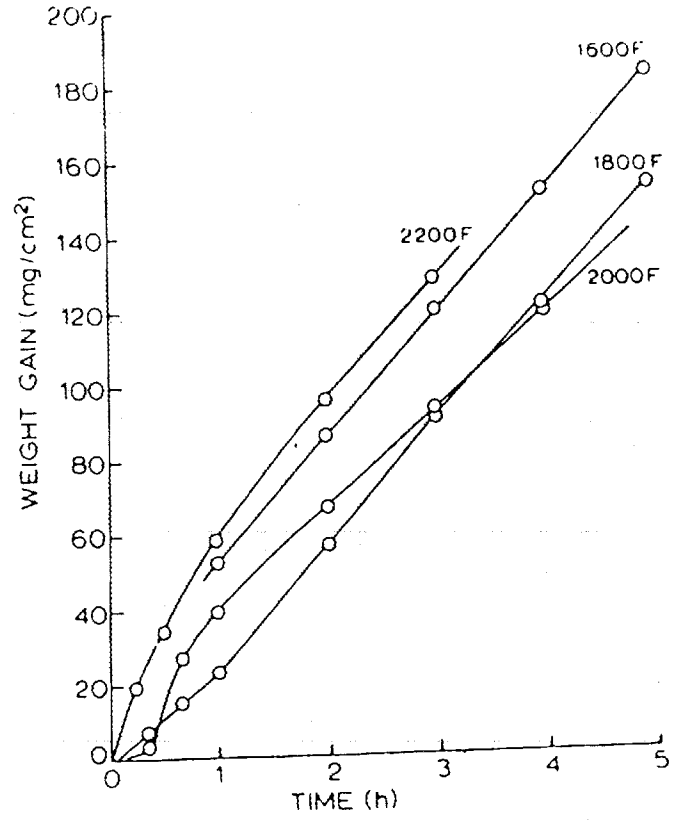

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was quite low below 673 K (400°C) but increased rapidly between 673 and 755 K (400 and 482°C). In addition to tests in air, some testing was done in air-argon mixtures containing 1 and 5% oxygen. Results at 922 K (649°C) are summarized in Fig. 7, which shows an order-of-magnitude reduction in oxidation rate in the lower-pressure oxygen. Data comparing the air oxidation rates of Nb-1Zr with niobium were presented. Agreement was fair, with differences depending upon temperature [greatest difference at about 810 K (537°C)] and microstructure (better agreement with recrystallized material than swaged material).

In 1964 Harrison and Delgrosso completed a study of the oxidation of Nb-1Zr from 810 to 1144 K (537–871°C) at oxygen pressures from 1×10^{-3} to 1×10^{-5} torr. At 810 K (537°C) oxidation rates were lower than those at the higher temperatures for all pressures studied. However, at 922 and 1144 K (649 and 871°C), depending upon the pressure, the oxidation rates at the lower temperature were sometimes greater than at the higher temperature. Also, at both 922 and 1144 K (649 and 871°C), oxidation-rate reversals occurred in going from a lower pressure to a higher pressure (Figs. 8 and 9). The authors conclude as follows:

> The following reactions occurred sequentially: adsorption and solution of oxygen creating a dispersed ZrO_2 subscale by internal oxidation, formation of orientation dependent CbO, oxidation of CbO to CbO_2 and subsequent establishment of a continuous CbO_2 layer. This CbO_2 layer caused protective oxidation and directly affected the total weight gain and degree of oxygen penetration . . .
>
> Within the pressure ranges investigated, some of the most severe contamination occurred at the lowest pressures when CbO_2 scale was not produced.

In summary, they stated:

> A knowledge of reaction characteristics in respect to rate of weight gain, oxygen penetration, and oxides formed as a function of pressure, temperature, and time must be acquired before valid engineering recommendations can be made.

Inouye (1964) reported on the reaction of interstitial impurities with Nb-1Zr at pressures between 10^{-6} and 10^{-8} torr (residual gases) at

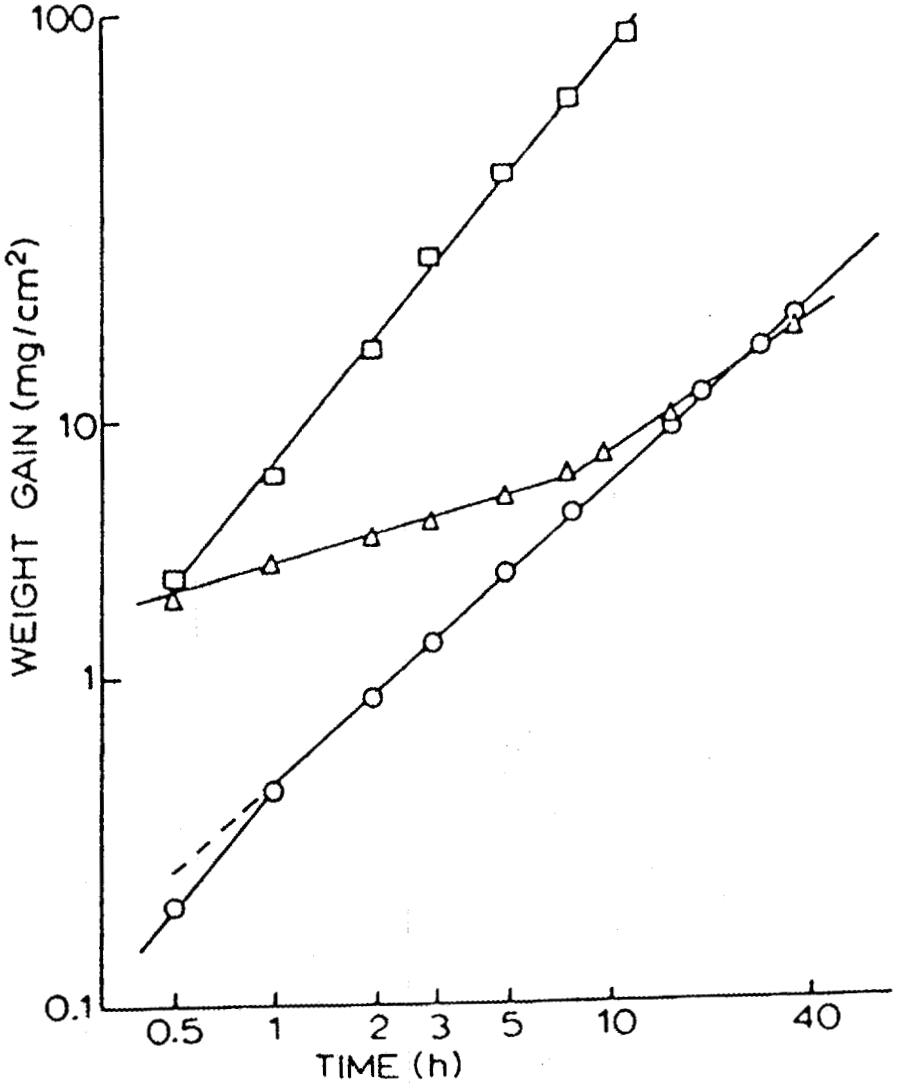

Fig. 7. Weight gain of Nb-1Zr at 1473 K (1200°F) in 760 torr (1 atm) air, 1% and 5% oxygen containing air-argon atmospheres. □ Atmosphere air; △ 5% oxygen; ○ 1% oxygen. *Source*: E. J. Delgrosso, R. C. Krutenat, C. E. Carlson, and J. S. Carta, "The Oxidation Characteristics of Niobium-1 Zirconium Alloy," *J. Less-Common Metals* 5, 57–77 (1963), Fig. 9, p. 68.

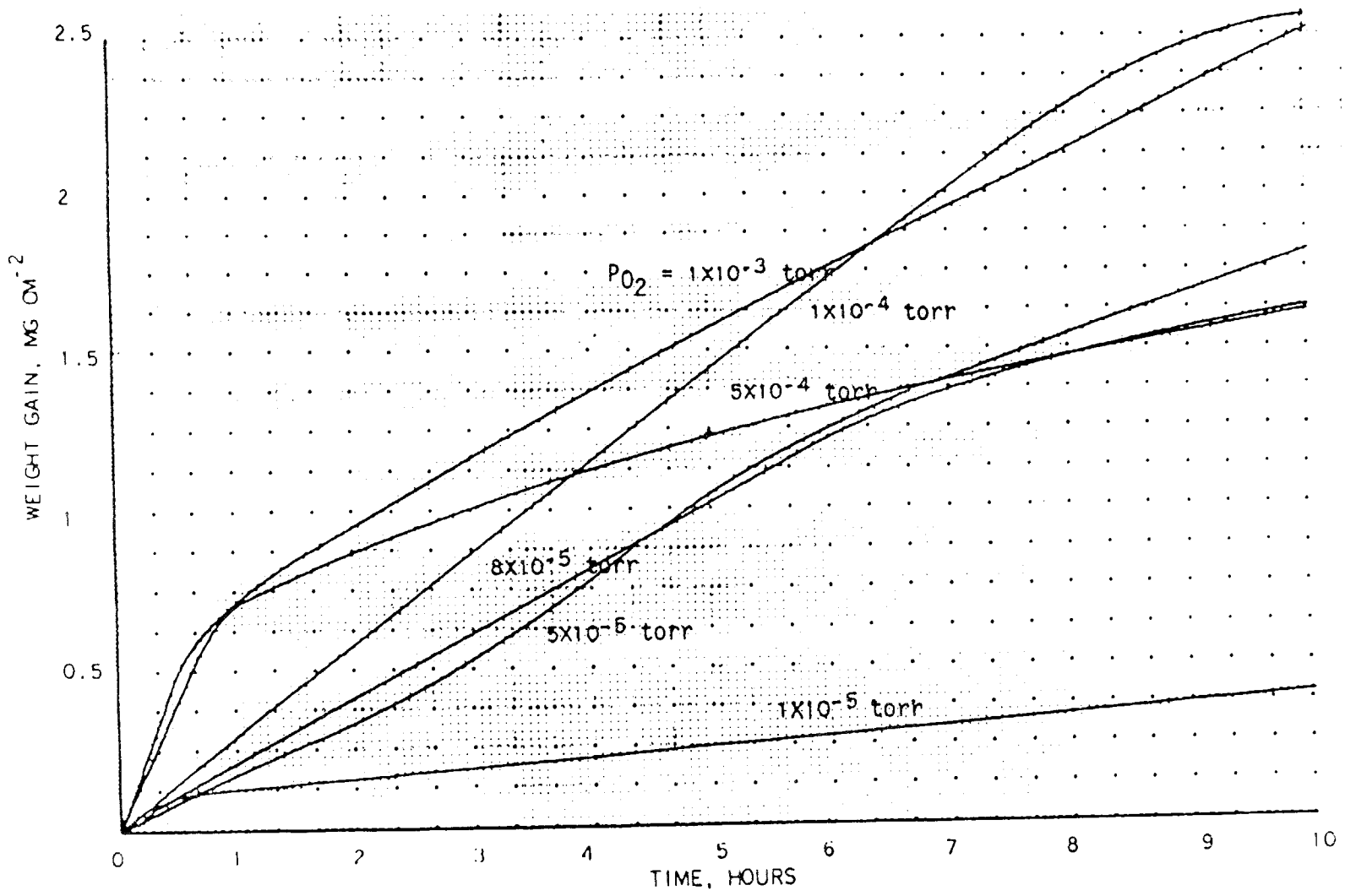

Fig. 8. Odixation of Nb-1Zr at 1033 K (1400°F). *Source*: R. W. Harrison and E. J. Delgross, *Low-Pressure Oxidation of Columbium-1 Zirconium*, CNLM-5351, Pratt & Whitney Aircraft, Middletown, Conn., April 1964, Fig. 6, p. 15.

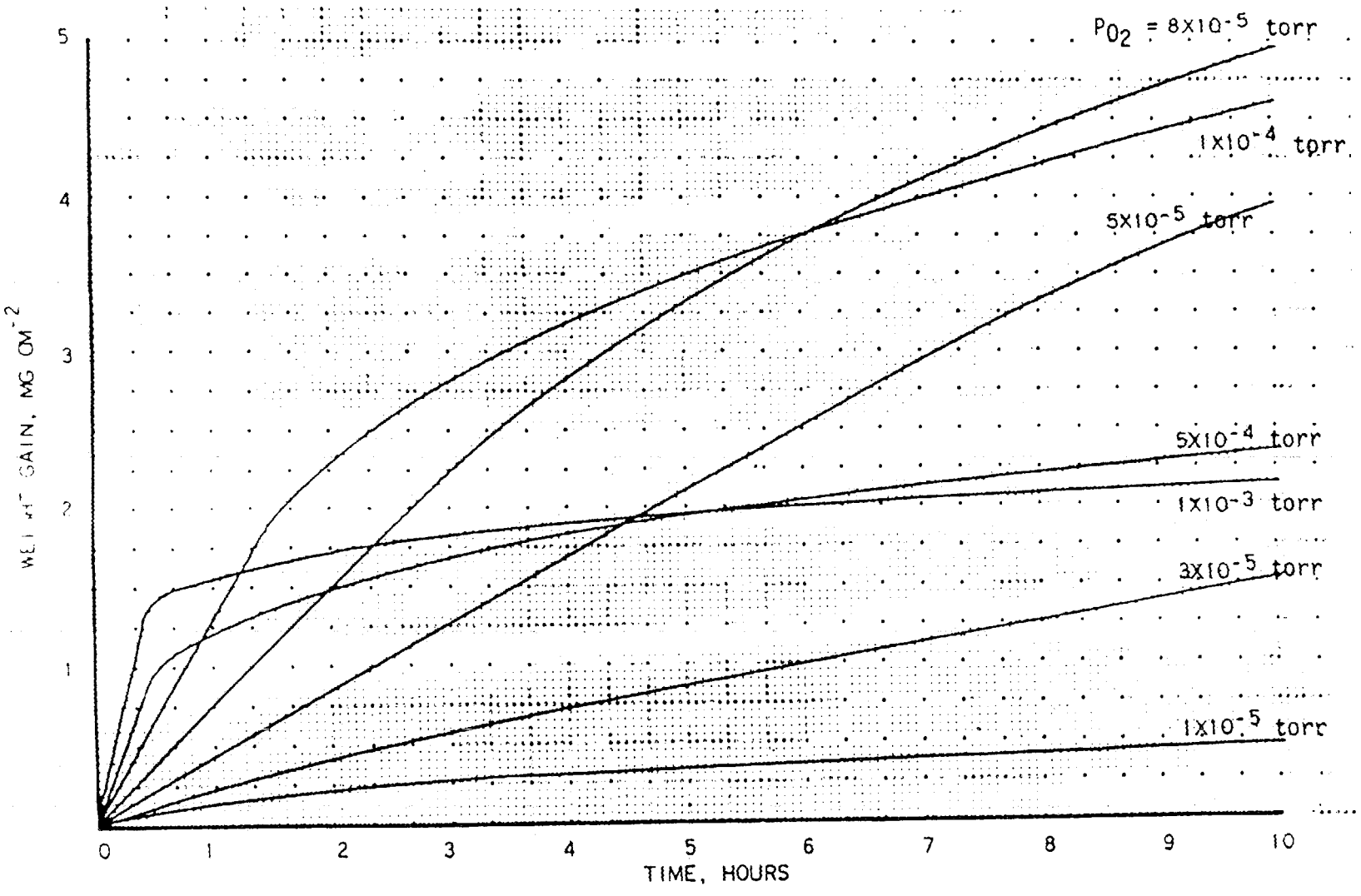

Fig. 9. Oxidation of Nb-1Zr at 1144 K (1600°F). *Source*: R. W. Harrison and E. J. Delgrosso, *Low-Pressure Oxidation of Columbium-1 Zirconium*, CNLM-5351, Pratt & Whitney Aircraft, Middleton, Conn., April 1964, Fig. 2, p. 11.

temperatures from 851 to 1473 K (578–1200°C). The system was cold trapped with liquid nitrogen and pumped by a glass oil diffusion pump backed by a metal diffusion pump and a mechanical pump. The composition of the residual gases in this system was determined as a function of total system pressure; the results are shown in Table 5. Although these results were considered to be approximate, they do indicate that the major components were H_2, H_2O, and nitrogen plus CO. Although oxygen was ≤1% of the residual gas, the H_2O and CO levels reported could have resulted from reactions that occur during ionization of oxygen in the residual gas analyzer. [By comparison, Lyon (1971) reported an oxygen partial pressure of 10^{-6} torr when the total system pressure was about 10^{-5} torr, and Hoffman and Holowach (1970) reported $<10^{-10}$ torr when the total pressure was about 10^{-8} torr.] Concentration changes (ppm) in Nb-1Zr after exposure for 1000 h at 2.7×10^{-7} torr are shown in Fig. 10. The total change corresponds closely with the increase in oxygen. Under these conditions, changes in nitrogen and hydrogen were negligible and changes in carbon were minor even at 1463 K (1190°C). Results also indicate that zirconium content may affect oxidation rate, especially at temperatures below 1145 K (872°C). Closer agreement between oxidation rates of niobium (0.1% Zr) and Nb-1Zr was previously reported by Delgrosso et al. (1963) from tests in air.

Oxidation rate data taken from Inouye (1964) are plotted as a function of system pressure in Fig. 11. Extrapolation indicates that 0.99-mm-thick (0.039-in.) samples contaminated from one side at 1323 K (1050°C) would pick up 500 ppm in 10,000 h at pressures of 10^{-7} to 10^{-8} torr. Other oxidation rate data reported by Rosenblum et al. (1966) are shown in Fig. 12. These data suggest that about 1 ppm oxygen would be picked up by a 19 to 25.4-mm-OD × 1.27-mm wall (0.75- to 1.0-in.-OD × 0.050-in.) sealed tube after 10,000 h at 1143 to 1373 K (870–1100°C) and 10^{-7} torr. In an Nb-1Zr loop test operated at 2×10^{-8} torr, Hoffman and Holowach (1970) reported much higher concentrations of oxygen (up to 790 ppm) in thin 0.05 mm (0.002 in.) foil insulation after 5000 h at 873 K (600°C).

To further determine the consistency among the various studies, calculations were made to compare the results of Inouye (1964) [(low pressure residual gas atmosphere, 0.5 to 1 mm (0.020- to 0.040-in.) specimens)

Table 5. Composition of residual gases in a vacuum system

Gas species	Composition (vol %)			Average
	1×10^{-5} torr[a]	1×10^{-6} torr[b]	1×10^{-7} torr[b]	
Hydrogen	44.0	61.0	4.8	37.0
CH_4	4.4	0.2	3.1	2.6
H_2O	18.0	7.3	13.7	13.0
Hydrocarbon	6.2	5.1	36.5	16.0
Nitrogen plus CO	21.4	24.0	34.0	26.0
Oxygen	1.0	0.16	0.8	0.65
CO_2	5.0	2.2	4.8	4.0

[a]Residual gases adsorbed on activated charcoal at 78 K (−195°C).

[b]Residual gases adsorbed on Linde 13X zeolite at 78 K (−195°C).

Source: Adapted from H. Inouye, *Contamination of Refractory Metals by Residual Gases in Vacuum Below 10^{-6} Torr*, ORNL-3674, September 1964, Table 1, p. 5.

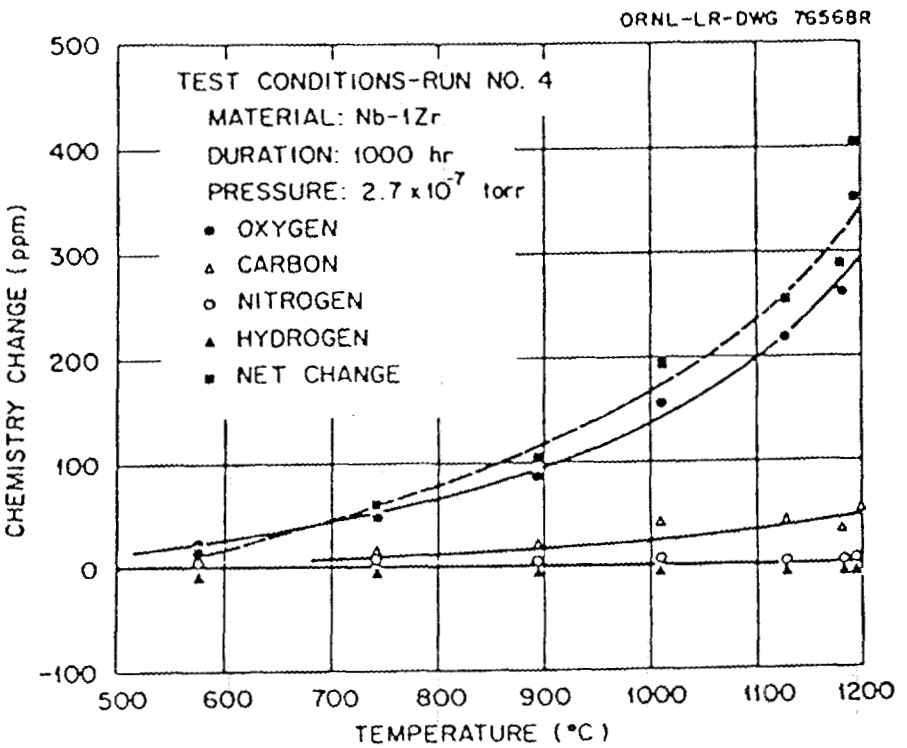

Fig. 10. Contamination of Nb-1Zr by O, C, H, and N at 2.7×10^{-7} torr. *Source*: H. Inouye, *Contamination of Refractory Metals By Residual Gases in Vacuum Below 10^{-6} Torr*, ORNL-3674, September 1964, Fig. 2, p. 9.

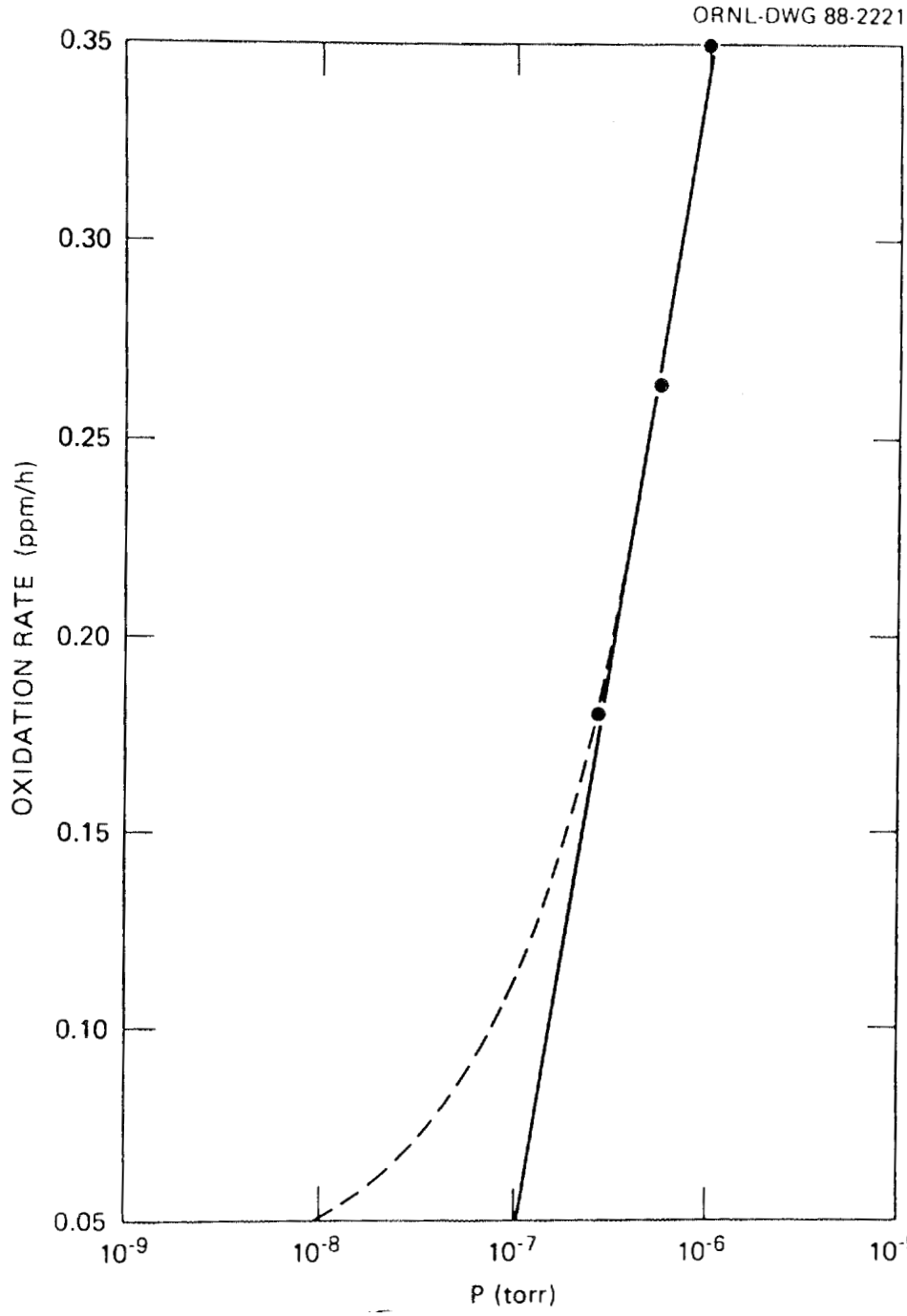

Fig. 11. Oxidation of Nb-1Zr [0.1 cm (0.034 in.)] at 1323 K (1050°C). *Source*: H. Inouye, *Contamination of Refractory Metals by Residual Gases in Vacuum Below 10^{-6} Torr*, ORNL-3674, September 1964

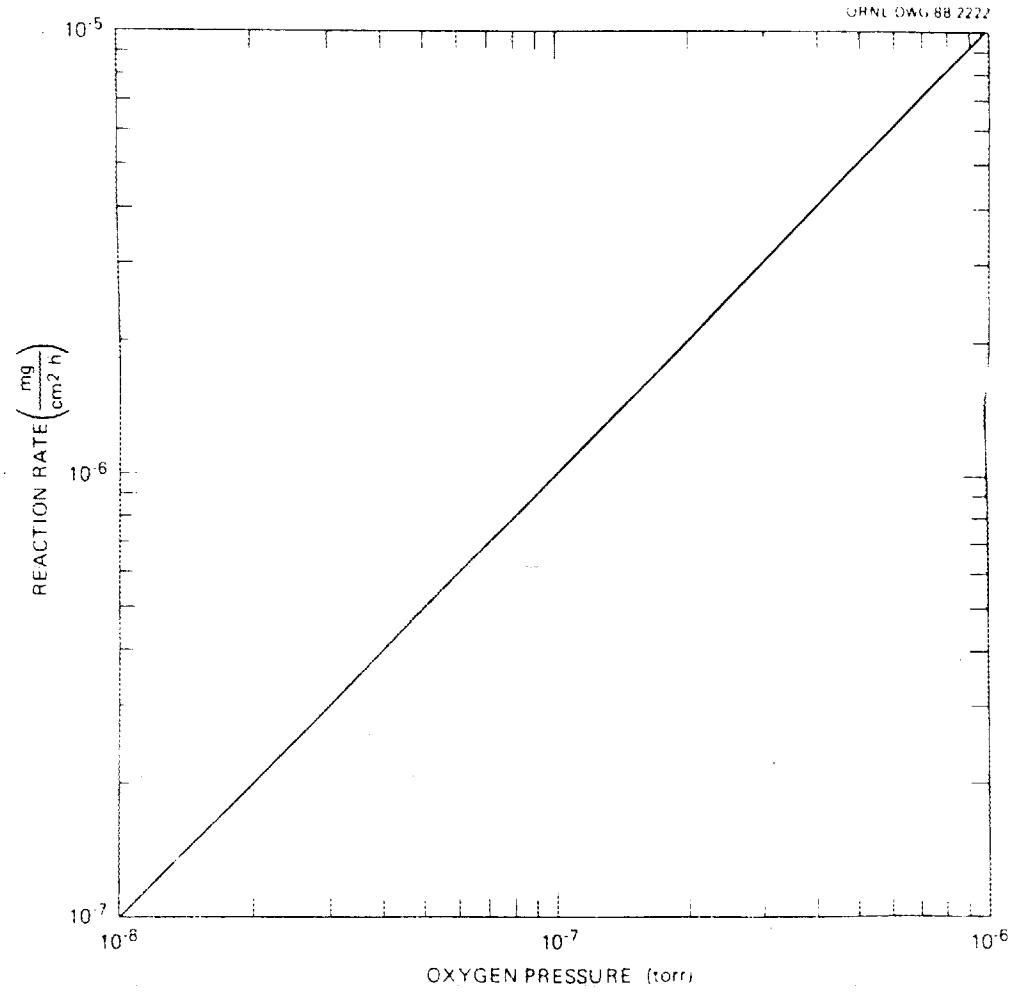

Fig. 12. Oxidation of Nb-1Zr at 1143–1373 K (870–1100°C). *Source*: adapted from L. Rosenblum et al., "Oxidation of Columbium, Tantalum, and Their Alloys," pp. 171–87 in *Proceedings of Space Power Systems Advanced Technology Conference, Lewis Research Center, Cleveland, Aug. 23–24, 1966*, NASA-SP-131.

with those of other investigators. Inouye (1964) derived the following equation from kinetic theory, assuming internal oxidation to be controlled by the arrival rate of the gas at the metal surface:

$$\Delta C = [82.5 \alpha P (M/T)^{1/2} t/x\rho] \times 10^6 \text{ ppm} ,$$

where

P = gas pressure (torr),
M = molecular weight of gas (g),
t = time (h),
x = wall thickness (in.),
α = sticking probability,
ρ = alloy density (g/cm^3),
T = temperature (K).

For a Nb-1Zr tube of fixed thickness exposed to a particular gas at a particular temperature,

$$\Delta C \text{ (ppm)} = k P t/x ;$$

i.e., ΔC should have a first order dependence on both P and t. To determine the adequacy of this equation, Inouye carried out experiments that did not confirm this relation, but rather yielded the following equation in which concentration depends upon the square root of the pressure:

$$\Delta C \text{ (ppm)} = k t (P)^{1/2}/x .$$

This finding then led to the following empirical equations for exposure of Nb-1Zr to the residual gases present in his system:

$$\Delta C \text{ (1023–1273 K)} = 90.6 t (P)^{1/2} \exp - 5500/RT/x ,$$

and

$$\Delta C \text{ (1273–1473 K)} = 6.89 \times 10^4 t (P)^{1/2} \exp - 22{,}400 RT/x .$$

No limits were stated for pressure, but it should be remembered that Inouye conducted these experiments at $\leq 10^{-6}$ torr.

Comparison of oxygen contamination levels that would be predicted using Inouye's empirical equations with values determined experimentally are shown in Table 6. Except for the results reported by Jansen and Hoffman (1964), experimental results are one to two orders of magnitude greater than would have been predicted. Inouye (1964) also conducted experiments to compare the oxidation of niobium in air at 5×10^{-4} torr (oxygen partial pressure = 1×10^{-4} torr) with that in pure oxygen at 1×10^{-4} torr, and the oxidation rate in air was a factor of ten lower at 1273 K (1000°C). He assumed that nitrogen might be inhibiting oxidation, but further experiments in which nitrogen was added to a residual gas atmosphere at 2×10^{-7} torr did not show any decrease in oxidation rate. Thus, he concluded that the 10^{-4} torr effect could not be extrapolated to lower pressures. These comparisons indicate that Inouye's empirical equations may be limited to a specific set of conditions in terms of pressure, gas composition, and geometery.

Another factor in the contamination rate of Nb-1Zr is the reproducibility of the sticking probability for oxygen. Hogan et al. (1965) had compared values obtained by various investigators as a function of pressure as shown in Table 7. However, they generally found higher values of the coefficient in their own study at 1373 K (1100°C) (0.42 at 5×10^{-5} torr and 0.74 at 8×10^{-7} torr oxygen pressure). Lyon (1971) found values of 0.16 to 0.65 at 1200 K (927°C) at about 10^{-6} torr that depended upon whether the specimen had an oxide film (exposed to room-temperature air for several days before testing) or was clean, respectively.

SUMMARY AND CONCLUSIONS

There have been numerous oxidation studies conducted on niobium and Nb-1Zr alloy. Conditions have ranged from air at low temperatures to a dynamic vacuum at high temperatures. When Nb/Nb-1Zr is exposed to oxidative atmospheres, reactions will occur that quantitatively and qualitatively depend upon the particular conditions that are present.

At low temperatures in air and relatively high oxygen partial pressures, protective oxide films form, resulting in negligible reaction

Table 6. Comparison of predicted increase in oxygen with experimental determinations

Temperature K	Temperature °C	Pressure (torr)	Time (h)	Oxygen increase (ppm) Predicted	Oxygen increase (ppm) Experimental	
1144	870	1×10^{-3} [a]	5	3	1,000	(Harrison and Delgrosso, 1984)
1265	992	1×10^{-1} [a]	5	400	23,000	(Kafstad et al., 1960)
1523	1250	1×10^{-4} [b]	150	3,150	10,000	(Jansen and Hoffman, 1966)
1523	1250	1×10^{-6} [b]	300	630	350	(Jansen and Hoffman, 1966)
1366	1093	2×10^{-5} [a]	1	6	2,500	(J. F. Hagan et al., 1965)
1200	927	1.3×10^{-7} [b]	274	180	4,400	(T. F. Lyon, 1971)

[a]Oxygen.

[b]Residual gas environment in system.

Table 7. Sticking probability for oxygen

Material	Pressure	Temperature	Sticking probability	Reaction rate ($mg/cm^2/h$)	Reference
Nb-1Zr	1.7×10^{-8}	1273	0.087	1×10^{-4}	(H. Inouye, 1964)
Nb	4×10^{-8}	1366	0.16	4.3×10^{-4}	(R. A. Pasternak, 1964)
Nb	2×10^{-7}	1366	0.13	1.7×10^{-3}	(R. A. Pasternak, 1964)
Nb-1Zr	6×10^{-7}	1253–1383	0.01	4×10^{-4}	(G. A. Barrett and L. Rosenblum, 1964)
Nb-1Zr	2.5×10^{-6}	1253–1383	0.01	2×10^{-3}	(G. A. Barrett and L. Rosenblum, 1964)
Nb-1Zr	2×10^{-5}	1253–1383	0.01	1.8×10^{-2}	(G. A. Barrett and L. Rosenblum, 1964)
Nb	3×10^{-5}	1123–1473	0.03	6×10^{-2}	(H. Inouye, 1961)
Nb	1×10^{-4}	1123–1473	0.03	2×10^{-1}	(H. Inouye, 1961)
Nb	2×10^{-4}	1123–1473	0.04	5×10^{-1}	(H. Inouye, 1961)

Source: Adapted from J. F. Hogan et al., *Reaction Rate of Columbium-1 Zirconium Alloy with Oyxgen at Low Pressures*, PWAC TIM 901, 1965, Pratt & Whitney Aircraft, CANEL, Middletown, Conn.

rates below 473 K (200°C) and slow parabolic rates up to 600 to 650 K (327–377°C); i.e., $x^2 = kt + C$, where x is the measure of oxidation, and t is the time. Lowering the oxygen pressure reduces the oxidation rate somewhat, but the effect is not extremely large. Above 700 K (427°C), linear rates generally occur even at low oxygen pressures; i.e., $x = k't + C'$. At the higher temperatures, oxidation rate is generally more sensitive to changes in pressure than at low temperatures.

In some temperature regions [around 800 and around 1000 K (527 and 727°C)], depending upon the pressure, reaction-rate decreases have been noted as the temperature is increased; and, in some cases, oxidation rate decreases as pressure is increased. These relationships have also been attributed to formation of protective oxide layers such as NbO_2.

Results such as those cited above complicate the development of quantitative relations that can predict the oxidation behavior of Nb-Zr. One investigator (Inouye) attempted to relate reaction rate to temperature, pressure, and time. He experimentally found that, for his conditions,

$$\Delta C = k\ P^{1/2}\ t/x \text{ (with symbols as previously defined)},$$

which led to two empirical equations covering the temperature range 1023 to 1473 K (750–1200°C). However, in general these equations did not successfully predict the data from other experiments. In addition to factors such as type of oxide formed, sticking probability variations, and residual gas composition, variables, such as surface area of specimen to volume flow rate of gas, location of pressure measurement, etc., could also be factors in the differences observed.

For the NAT, proximity of a component to the contaminant source should be particularly considered, especially if an off-normal event did occur. For this purpose, some type of oxygen pickup meter that could be positioned within the NAT vacuum vessel would be very desirable. In addition, further data should be obtained on oxidation with lithium inside a Nb-1Zr tube so that prototypic data are generated that involve oxidation rate, diffusion of oxygen, precipitation of ZrO gettering of oxygen by lithium, and possible lithium attack. Although it may not be possible to provide

quantitative oxidation-rate relations that cover all ranges of conditions, the data should allow determining boundary conditions that would provide guidelines for system operation that protect against catastrophic effects.

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