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INVESTIGATION OF SOLUBILITY AND DIFFUSION OF OXYGEN IN REFRACTORY METALS

THIRD QUARTERLY REPORT

by

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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THIRD QUARTERLY REPORT

(January - March 1966)

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ABSTRACT

Electrical resistivity measurements are being used to determine the solubility limits and diffusion constants of oxygen in tantalum, Ta-10W, alloy T222, columbium, Cb-1% Zr, and alloy FS-85.

Tentative solubility limits have been established for tantalum in the range 600 to 920°C. The limits of solubility range from 770 ppm at 598°C to 2265 ppm at 918°C.

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I. INTRODUCTION

This investigation concerns oxygen diffusion and solubility in commercially pure refractory metals and in advanced alloys for space power system components. Oxygen contamination of refractory metals reduces their resistance to alkali metal corrosion. Accurate knowledge of oxygen diffusion constants and solubility limits are required in order to establish realistic engineering and environmental specifications.

This investigation is divided into two phases:

Phase I. A determination of the limits of oxygen solubility in commercially pure tantalum and columbium and in the alloys Cb-1Zr, Ta-10W, FS-85 (Cb-28Ta-10.5W-0.9Zr) and T222 (Ta-9.8W-2.4Hf-0.01C), at five temperatures in the temperature range of 1000°F to 2400°F.

Phase II. Average diffusion constants will be determined from electrical resistivity data using commercially obtainable wires for specimen samples. Absolute oxygen contents shall be determined by neutron activation analysis. Other methods of analysis such as electron microprobe analysis, X-ray diffraction analysis, microhardness and conventional chemical analysis will be employed for obtaining corroborating data.

It is expected that the data obtained on the pure metals will confirm the previously reported data in the

literature and provide the required confidence level to pursue alloy solubility data.

II. SUMMARY

A series of five oxygen calibration runs was completed and specimens were then submitted for neutron activation analysis. The results were used to construct an oxygen calibration curve to relate the change in resistance at constant temperature to the additive oxygen content in ppm.

A series of six iso-thermal solubility runs was completed. The data from these runs was used in conjunction with the oxygen calibration curve to yield the (tentative) solubility limits for oxygen in tantalum in the range 600°C to 920°C.

Two of the iso-thermal runs together with an iso-concentration run were conducted at extended time schedules to explore the time dependence of the data obtained from the two techniques.

III. APPARATUS

The apparatus employed in the solubility determination phase of this program is described in the 1st and 2nd quarterly reports.

A. Double Vacuum Furnace

A double wall vacuum furnace was built during the last quarterly period to supplement the air furnace used for the lower temperature range solubility runs. Early in this quarter the furnace proper (independent from the solubility determination apparatus) was pumped down and the heating elements powered.

Under power the tungsten heaters (0.050 diameter hairpin filaments) twisted and were in jeopardy of shorting out through the weights hung from the filament loops. A ceramic guard ring was installed to correct this tendency.

B. Dense Alumina Reaction Tubes

Four dense alumina tubes were purchased to supplement the quartz reaction tubes, in use with the lower-temperature range air furnace. Of these, one was porous at the closed end, two were cracked during cutting operations and a fourth was metallized and brazed into a flange but developed a leak across the metallized area. The porous tube was returned to the vendor; the two tubes with cracks on the' open end have been re-cut below cracks and will be metallized* with a metallizing paint which will be specifically

*Morganite ARR Alumina has not previously been metallized by us.

developed for this low silica ceramic body.

The ceramic tube in the flange has only a low order leak so it can be used in the double vacuum oven as there is sufficient pumping speed in the guard vacuum to protect the heater filaments.

IV. EXPERIMENTAL PROCEDURES

A. General

The experimental procedures employed in the work during this quarter were discussed in detail in the 2nd Quarterly Report.

The chemical cleaning procedure used on tantalum specimens is described in Table I.

Special procedures specific to individual runs or run categories are discussed more appropriately in the results section.

B. Vacuum Bake-out of Solubility Apparatus

The entire vacuum system of the oxygen solubility determination apparatus can be baked out and a base pressure of 1×10^{-9} achieved before starting each experimental run. This practice is not required, however, since the first charge will be adsorbed on the walls, sample holder, etc. and will make it impossible to regain a high vacuum without a long vacuum bake-out. Further, the oxygen adsorbed by the clean walls, etc. is diverted from the specimen so that the amount of oxygen accepted by the specimen varies

TABLE I

CLEANING PROCEDURE FOR Ta SPECIMENS
1. Vapor degrease (Trichlorethylene)
2. Rinse, de-ionized water
3. Immerse in acid mixture for 5 seconds (10% HF, 90% HNO_3 by volume)
4. Rinse, de-ionized water
5. Rinse, C.P. ethanol
6. Static air dry

over the first few charges even though the charges admitted may be identical and the sorption capacity constant. It was therefore deemed the preferable procedure to allow the walls, etc. of the apparatus to become and remain saturated with oxygen.

C. Time Correlation During Experimental Runs

A Moseley 680 "Autograph" recorder has been connected to the output of the "Millitorr" ionization gage (1 to 1 x 10^{-6} torr). The pressure-time profile provides a means of monitoring the engassing charge cycle; an event marker pen provides temporal correlation between the engassing cycle and the resistance-measurements taken on the Kelvin bridge.

V. EXPERIMENTAL RESULTS

A. General

A total of 13 experimental runs were conducted in this quarter. Five runs comprised an "oxygen calibration" series; six were oxygen solubility runs employing the iso-thermal technique; one run employed the iso-concentration technique; one iso-thermal run was completed with a Ta-10W specimen.

The iso-thermal and iso-concentration techniques have been discussed previously in the first and second quarterly reports.

B. Iso-Thermal Solubility Runs

A series of 5 iso-thermal runs were conducted to

determine the solubility limit of oxygen in Ta over the range 600°C to 950°C. The sample arrangement is as depicted in Figure 1. A photograph of an actual specimen is shown in Figure 4 of the Second Quarterly Report together with details of sample preparation. The iso-thermal technique requires that the solubility limit be indicated by a break in the resistance vs oxygen charge curve.

Experimental runs TA 05 through TA 09 employed the iso-thermal technique. The pre-treatment of the sample consisted of chemically cleaning the recrystallized wire as outlined in Table I and a vacuum bake-out at 900°C for a minimum of 12 hours unless noted otherwise in the text. Engassing was accomplished by trapping an oxygen charge in a 300cc volume at reduced pressure, pumping out the balance of the oxygen feed system and then admitting the charge to the reaction tube of the furnace through valve V^5 (See Figure 2). Each charge cycle consisted of a 3-3/4 minute period during which the oxygen charge was admitted to the specimen and a second 3 - 3/4 minute period during which the reaction tube was pumped out and the specimen was allowed to homogenize. Resistance measurements were made during this second half of the 7 - 1/2 minute cycle.

The specimen weights, constant engassing temperatures and size of oxygen charge was varied from run to run as noted.

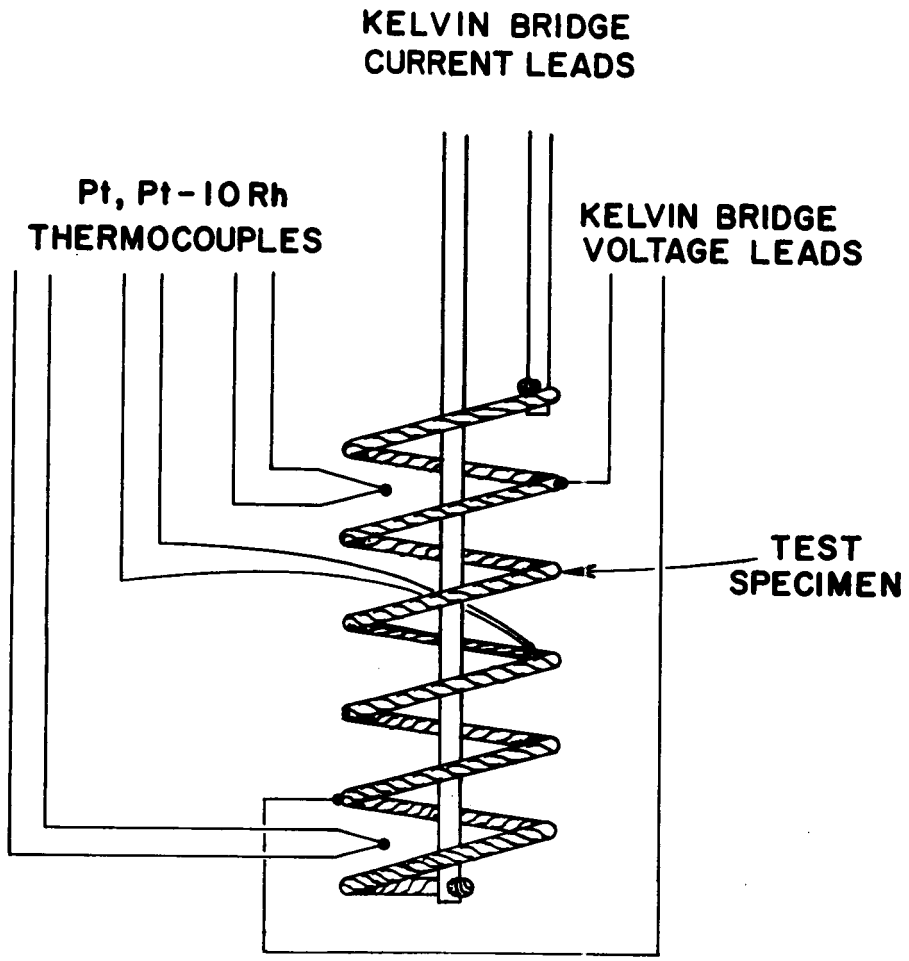
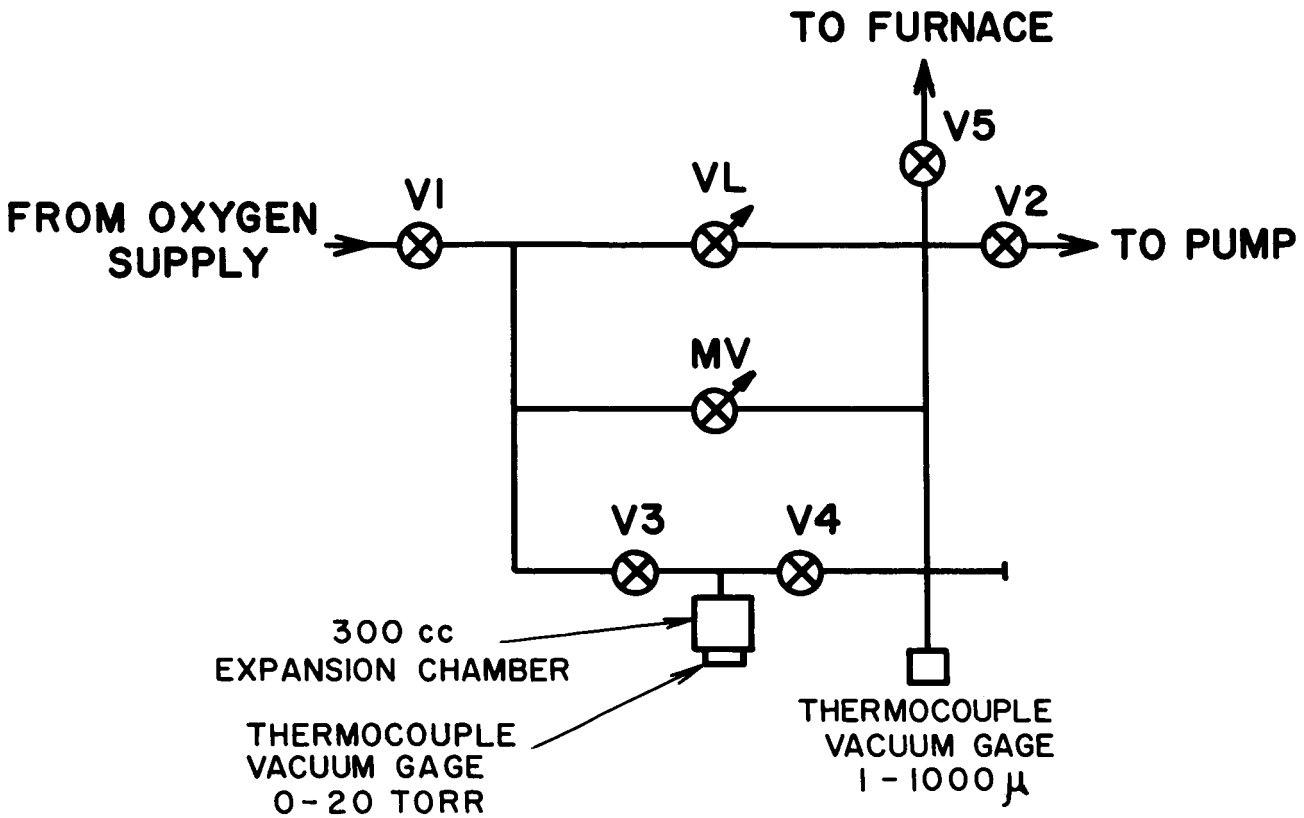


FIGURE 1. Schematic of Test Specimen showing placement of current and voltage leads and thermocouples.



MV : Micrometer metering valve
VL : Granville - Phillips variable leak
V : High vacuum bakable valves

FIGURE 2. Schematic of Oxygen Feed System.

Experimental Run TA 05

TA 05 was conducted at a constant temperature of 780°C. A total of 44 oxygen charges (300 cc at 1000μ per charge) were admitted to the reaction tube. There were two procedural errors, occurring in the 2nd and 3rd cycle which were easily corrected during reduction of the data. The data are reported in Table II and the resistance vs oxygen charges admitted is plotted in Figure 3. Intersection of the initial and final linear portions of the curve occurs at approximately $R/R_O = 1.205$ when correction is made for procedural errors. (The procedural errors such as to cause a deprivation of oxygen can be adjusted for by shifting the curve to the left by an appropriate amount. This correction does not effect R_S/R_O, however.)

Experimental Run TA 06

TA 06 was conducted at a constant temperature of 881°C. A total of 33 oxygen charges were admitted to the reaction tube. The charge size was 300 cc at 2000μ. This is double the charge size employed in the preliminary Run TA 05 and has been adopted as a "unit charge" hereafter. The solubility limit is indicated at $R/R_O = 1.249$. (See Table III)

Experimental Run TA 07

TA 07 was conducted at a constant temperature of 598°C. A total of twenty-five 1000μ charges was admitted to

TABLE NO. II

Resistance Data From Run TA 05

Oxygen Charge No.	R (Ohms)	Normalized R R/Ro	Oxygen Charge No.	R (Ohms)	Normalized R R/Ro
0	.1912	1.000	23	.2237	1.170
1	.1919	1.037	24	.2249	1.176
2	.1920	1.004	25	.2259	1.181
3	.1932	1.011	26	.2269	1.187
4	.1947	1.018	27	.2280	1.192
5	.1962	1.026	28	.2290	1.198
6	.1978	1.035	29	.2299	1.202
7*	.1982	1.037	30	.2308	1.207
8	.2000	1.046	31	.2316	1.211
9	.2016	1.054	32	.2324	1.215
10	.2034	1.063	33	.2330	1.219
11	.2052	1.073	34	.2337	1.222
12	.2069	1.082	35	.2343	1.223
13	.2087	1.092	36	.2348	1.228
14	.2104	1.100	37	.2353	1.231
15	.2120	1.109	38	.2358	1.233
16	.2136	1.117	39	.2361	1.234
17	.2152	1.126	40	.2366	1.237
18	.2167	1.133	41	.2370	1.240
19	.2182	1.141	42	.2373	1.241
20	.2196	1.149	43	.2377	1.243
21	.2210	1.156	44	.2380	1.245
22	.2223	1.162			

*Operational Error (Incomplete oxygen charge)

Specimen Temperature	780°C
Point of Saturation (Rs)	Rs = .2310, $^{Rs}/_{Ro}$ = 1.205
Charge Size	300 cc at 1000μ pressure
Specimen Mass	3.689 grams
Engassing Schedule	3 3/4 min. engassing time followed by 3 3/4 min. homogenize time
Sample Preparation	Std procedure except for omission of 1450°C bake out

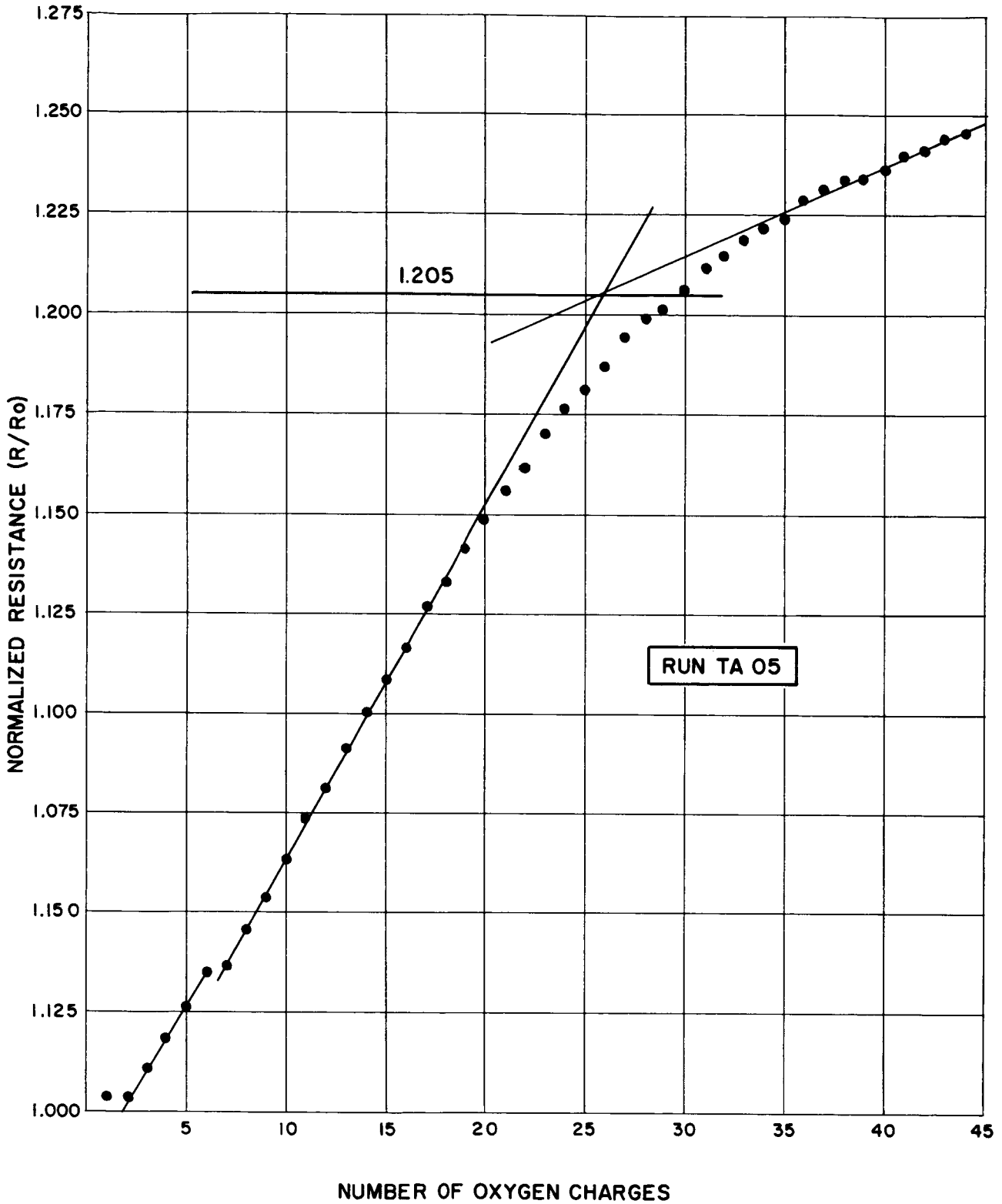


FIGURE 3. Plot of Normalized Resistance (R/Ro) versus number of oxygen changes for Run TA 05. The Run was at 780°C. See Table II and Text for additional details.

TABLE NO. III

Resistance Data From Run TA 06

Oxygen Charge No.	R (Ohms)	Normalized R R/Ro	Oxygen Charge No.	R (Ohms)	Normalized R R/Ro
0 (Ro)	.2468	1.00	17	.3052	1.237
1	.2503	1.015	18	.3067	1.243
2	.2544	1.031	19	.3079	1.248
3	.2587	1.048	20	.3089	1.252
4	.2631	1.066	21	.3100	1.256
5	.2676	1.084	22	.3108	1.259
6	.2719	1.102	23	.3116	1.263
7	.2758	1.118	24	.3124	1.266
8	.2798	1.134	25	.3130	1.268
9	.2836	1.149	26	.3137	1.271
10	.2871	1.163	27	.3141	1.273
11	.2906	1.177	28	.3147	1.275
12	.2940	1.191	29	.3153	1.278
13	.2969	1.203	30	.3158	1.280
14	.2995	1.214	31	.3161	1.281
15	.3017	1.222	32	.3166	1.283
16	.3036	1.230	33	.3171	1.285

Specimen Temperature	881°C
Point of Saturation	Rs = .3082 Rs/Ro = 1.249
Charge Size	300cc at 2000u pressure
Specimen Mass	4.2314 grams
Engassing Schedule	3 1/3 min. engassing time followed by 3 1/2 min homogenize time
Specimen Preparation	Std procedure

the reaction tube. An intersection was observed in the resistance vs. oxygen charge plot at approximately $R/Ro = 1.049$. Though the size of the oxygen charge was reduced to 1/2 the standard unit charge for this run, it was still too large in view of the low limit of solubility at this low temperature. See Table IV.

Experimental Run TA 08

TA 08 was conducted at the constant temperature of 918°C. The specimen was given an additional pre-treatment of 1 hour at 1450°C in vacuum. A total of 37 unit charges of oxygen were admitted to the reaction tube. An intersection was observed in the resistance vs. oxygen charge plot at approximately $R/Ro = 1.272$. See Table V.

Experimental Run TA 09

TA 09 was terminated before completion due to equipment failure.

C. Oxygen-Calibration Runs (TA 10 through TA 14)

In the iso-thermal solubility determination technique the point of saturation for a given temperature is determined by monitoring the change in the specimen's electrical resistance as successive oxygen charges are admitted to the furnace reaction tube. The oxygen concentration corresponding to the ratio of initial resistance, at temperature, to the resistance at the point of saturation (Rs/Ro) must then be determined to yield the saturation limit (in ppm

TABLE NO. IV

Resistance Data From Run TA 07

Oxygen Charge No.	R (Ohms)	Normalized R R/Ro	Oxygen Charge No.	R (Ohms)	Normalized R R/Ro
0 (Ro)	.1838	1.000	13	.1942	1.059
1	.1847	1.005	14	.1952	1.062
2	.1859	1.011	15	.1960	1.066
3	.1872	1.018	16	.1965	1.069
4	.1885	1.026	17	.1969	1.071
5	.1895	1.031	18	.1974	1.073
6	.1906	1.037	19	.1979	1.077
7	.1912	1.040	20	.1983	1.079
8	.1920	1.045	21	.1987	1.081
9	.1924	1.047	22	.1992	1.084
10	.1931	1.051	23	.1997	1.087
11	.1937	1.054	24	.2002	1.089
12	.1942	1.057	25	.2006	1.091

Specimen Temperature	598°C
Point of Saturation	Rs = .1929, $^{Rs}/Ro$ = 1.049
Charge Size	300 cc at 1000u pressure
Specimen Mass	4.0131 grams
Engassing Schedule	3 3/4 min engassing time followed by 3 3/4 min. homogenize time
Specimen Preparation	Std procedure

TABLE NO. V

Resistance Data From Run TA 08

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
0 Ro*	.1706	1.000	19	.2186	1.281
1*	.1738	1.019	20	.2192	1.285
2	.1770	1.038	21	.2197	1.288
3	.1810	1.061	22	.2203	1.291
4	.1850	1.084	23	.2207	1.294
5	.1886	1.106	24	.2211	1.296
6	.1924	1.128	25	.2215	1.298
7	.1953	1.145	26	.2219	1.301
8	.1973	1.157	27	.2222	1.302
9	.2012	1.180	28	.2225	1.304
10**	.2039	1.195	29	.2229	1.307
11	.2067	1.212	30	.2233	1.309
12	.2089	1.225	31	.2237	1.311
13	.2110	1.237	32	.2240	1.313
14	.2129	1.248	33	.2244	1.315
15	.2145	1.257	34	.2247	1.317
16	.2158	1.265	35	.2250	1.389
17	.2169	1.271	36	.2254	1.321
18	.2178	1.278			

* Seven min. delay due to T.C. meter sticking
**Closed high vacuum valve with one min. early.

Specimen Temperature	918°C
Point of Saturation	Rs = .2171 $^{Rs}/_{Ro}$ = 1.272
Charge Size	300 cc at 1000μ pressure
Specimen Mass	3.4180 grams
Engassing Schedule	3 3/4 min. engassing followed by 3 3/4 min.
Specimen Preparation	Std procedure except for 1450°C bake out

of oxygen) for the particular temperature. Therefore a series of experimental runs was conducted to determine the relation between $^{R}/_{Ro}$ of a sample material and its oxygen content (im ppm) in the range below saturation.

Five oxygen calibration runs were conducted (TA 10 to TA 14) and the engassing data are reported in Tables VI through X. In each case the specimen was cleaned per standard procedure and vacuum baked overnight at 900°C. Four of the specimens were engassed (300 cc at 2000 μ of oxygen per charge, 7 - 1/2 minute cycle) to various values of $^{R}/_{Ro}$ in the range of interest; the fifth specimen (TA 13) was not engassed. These five specimens together with an "as received" sample of the Ta material and two specimens from previous runs were submitted for neutron activation analysis for oxygen content.

The report of the activation analysis service is tabulated in Table XI and is plotted against $^{R}/_{Ro}$ in Figure 4.

These results, although good, are not up to the expected accuracy; it had been hoped that 10 ppm accuracy would be obtained. The standard deviation is 50 ppm as determined from counting statistics. This discrepancy is perhaps due to the form of specimen, in that the wire did not fill the neutron activation analysis capsule volume. The inertia of the material kept it at the trailing end

TABLE NO. VI

Resistance Data From Run TA 10

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
0 (Ro)	.2081	1.000	4	.2236	1.075
1	.2113	1.016	5	.2277	1.095
2	.2154	1.036	6	.2321	1.116
3	.2195	1.055			

Specimen Temperature	899°C
Point of Saturation	NONE (0_2 Calibration Run)
Charge Size	300 cc at 2000μ pressure
Specimen Mass	3.6060 grams
Engassing Schedule	3 3/4 min. engassing followed by 3 3/4 min. homogenize time
Specimen Preparation	Std procedure

TABLE NO. VII

Resistance Data From Run TA 11

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
0 (Ro)	.2207	1.000	3	.2318	1.050
1	.2240	1.015			
2	.2279	1.003			

Specimen Temperature	901°C
Point of Saturation	NONE (0_2 Calibration Run)
Charge Size	300 cc at 2000μ pressure
Specimen Mass	3.9193 grams
Engassing Schedule	3 3/4 min. engassing followed by 3 3/4 min. homogenize time
Specimen Preparation	Std procedure

TABLE NO. VIII

Resistance Data From Run TA 12

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
0 (Ro)	.2271	1.000	6	.2517	1.108
1	.2305	1.015	7	.2558	1.126
2	.2344	1.032	8	.2598	1.144
3	.2386	1.051	9	.2637	1.161
4	.2429	1.070	10	.2678	1.179
5	.2473	1.089	11	.2680	1.180

Specimen Temperature	898°C
Point of Saturation	NONE (0_2 Calibration Run)
Charge Size	300cc at 2000u pressure
Specimen Mass	4.0417 grams
Engassing Schedule	3 3/4 min. engassing followed by 7 1/2 min homogenize time
Specimen Preparation	Std procedure

TABLE NO. IX

Resistance Data From Run TA 13

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
(NONE) Ro	.2238	1.000			

Specimen Temperature	901°C
Point of Saturation	NONE (No Engassing)
Charge Size	NONE
Specimen Size	4.0262 grams
Engassing Schedule	NONE
Specimen Preparation	Std procedure

TABLE NO. X

Resistance Data From Run TA 014

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
0 (Ro)	.2483	1.000	8	.2892	1.165
1	.2542	1.024	9	.2912	1.176
2	.2602	1.048	10	.2950	1.188
3	.2661	1.072	11	.2977	1.199
4	.2717	1.094	12	.2997	1.207
5	.2769	1.115	13	.3019	1.216
6	.2814	1.133	14	.3032	1.221
7	.2854	1.149	15	.3045	1.226

Specimen Temperature	900°C
Point of Saturation	NONE (0_2 Calibration Run)
Charge Size	300cc at 2000u pressure
Specimen Mass	4.0368 grams
Engassing Schedule	3 3/4 min. Engassing followed by 3 3/4 min. homogenize
Specimen Preparation	Std procedure

TABLE XI

Neutron Activation Analysis For Oxygen (ppm)					
SPECIMEN	WT (g)	R/R_o	Oxygen ppm 1st & 2nd Determination		Std. Dev.
As Received	3.1523	----	159	133	20
TA-13	2.6639	1.0000	206	225	20
TA-11	2.6425	1.0507	817	764	50
TA-10	2.4341	1.1163	1350	1300	50
TA-12	2.7401	1.1792	1640	1710	60
TA-14	2.6231	1.3035	2440	2490	50
TA-05**	2.5182	1.2447	4370	4370	40
TA-07**	2.8456	1.1147	2450	2430	10

**Included here for comparison

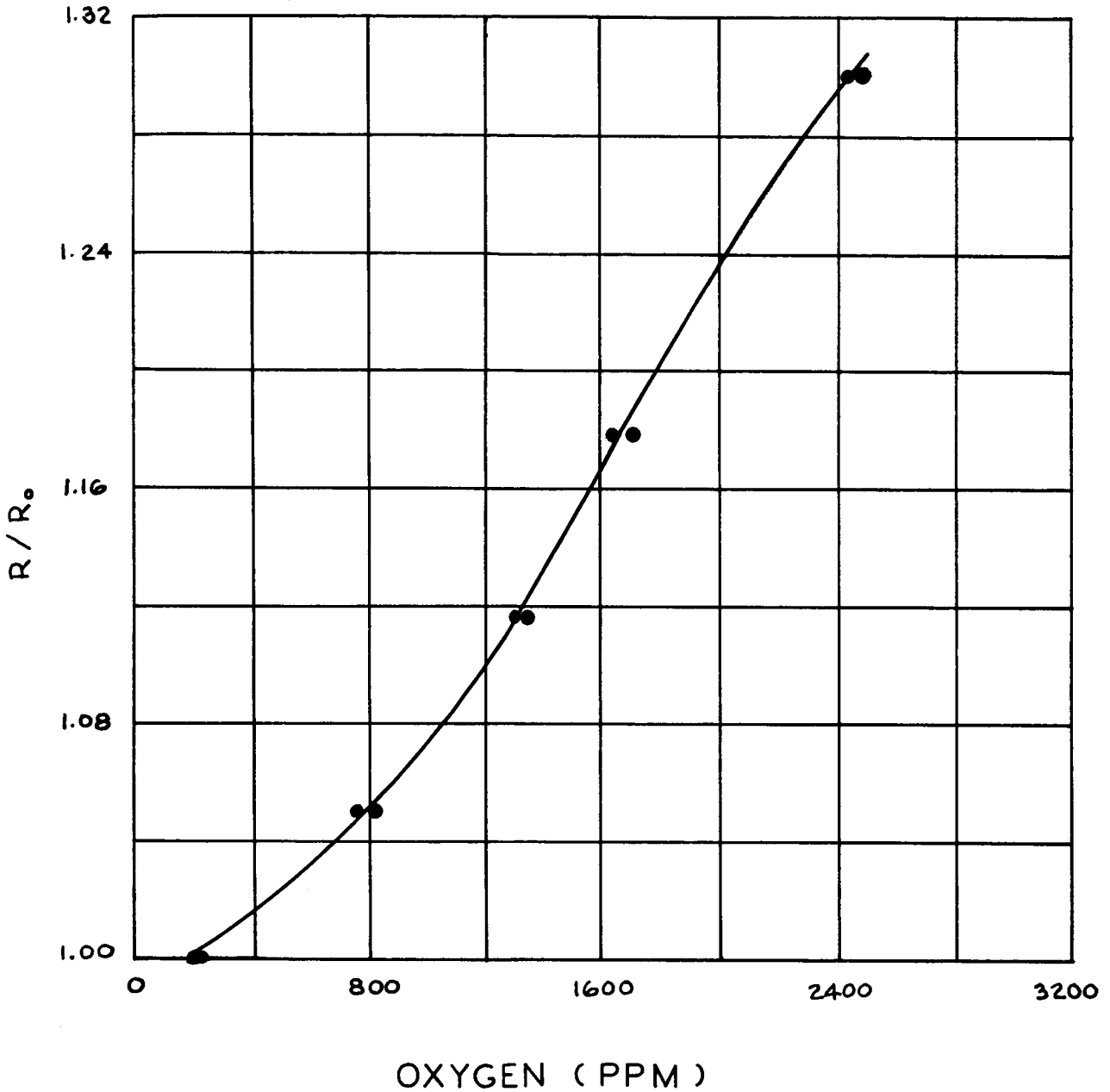


FIGURE 4. Calibration Curve for Oxygen in Tantalum in terms of normalized electrical resistance (R/Ro) of the tantalum. Samples were engassed at 900°C ± 2°C.

of the capsule as it was shot toward the neutron counters thereby passing the counters later than the leading end of the capsule. Further, specimens were deformed or fragmented by the 1st pass so that the geometry is different for the 2nd pass.

D. Extended Time Solubility Experiments

Three runs were completed whose main objective was to determine the effect of extending the length of the cycle in iso-thermal experiments (TA15, TA16) or employing a lower cooling rate in an iso-concentration experiment (TA17). All three specimens were heated in vacuum at 1450°C for one hour in addition to the standard pre-treatment of 900°C in vacuum overnight. This alteration in pre-treatment did not affect the final result significantly, (see later).

Iso-Thermal Runs TA 15 and TA 16

The iso-thermal experiments TA 05 to TA 09 employed either a 7 - 1/2 minute engassing cycle with a full "unit" (300 cc at 2000 μ) or a "half-unit" charge. Runs TA 15 and TA 16 employed a 30 minute cycle (3-3/4 minutes engassing time with 26-1/4 minutes for homogenization in vacuo at 780°C.) The specimens used in these runs were annealed at 1450°C for one hour, by self heating, before engassing.

Run TA 15 was terminated after 18 engassing cycles due to equipment failure.

Run TA 16 was carried to completion and a "curve

break" inflection occured at $^{R}/Ro$ = 1.198, Figure 5. Data are reported in Table XII.

Iso-Concentration Run TA 17

Previous iso-concentration runs reported in the 2nd Quarterly Report at average cooling rates of approximately 2°C/minute had failed to produce a discernable inflection. Run TA 17 was engassed using the standard 7-1/2 minute cycle and unit charges. This iso-concentration experimental run was then programmed to determine whether an inflection in the resistance vs temperature curve would occur if the average cooling rate were reduced to 0.83 C°/min. This was accomplished by manually lowering the specimen temperature in 25 C° steps every 30 minutes.

The resistance values obtained from this run were plotted. There was little or no change in resistance noted after reaching temperature for any given step. There was no discernable inflection in the resistance vs temperature curve. Data on the engassing schedule and the temperature cycle are repeated in Tables XIII and XIV.

Note on Equilibrium of Oxygen with Tantalum

Three resistance measurements were made during each engassing cycle during runs TA 15 and TA 16; one at approximately 4 minutes, after the pressure in the reaction tube had fallen back to the "base-pressure" level, another within a minute of the end of the 30 minute cycle; and one

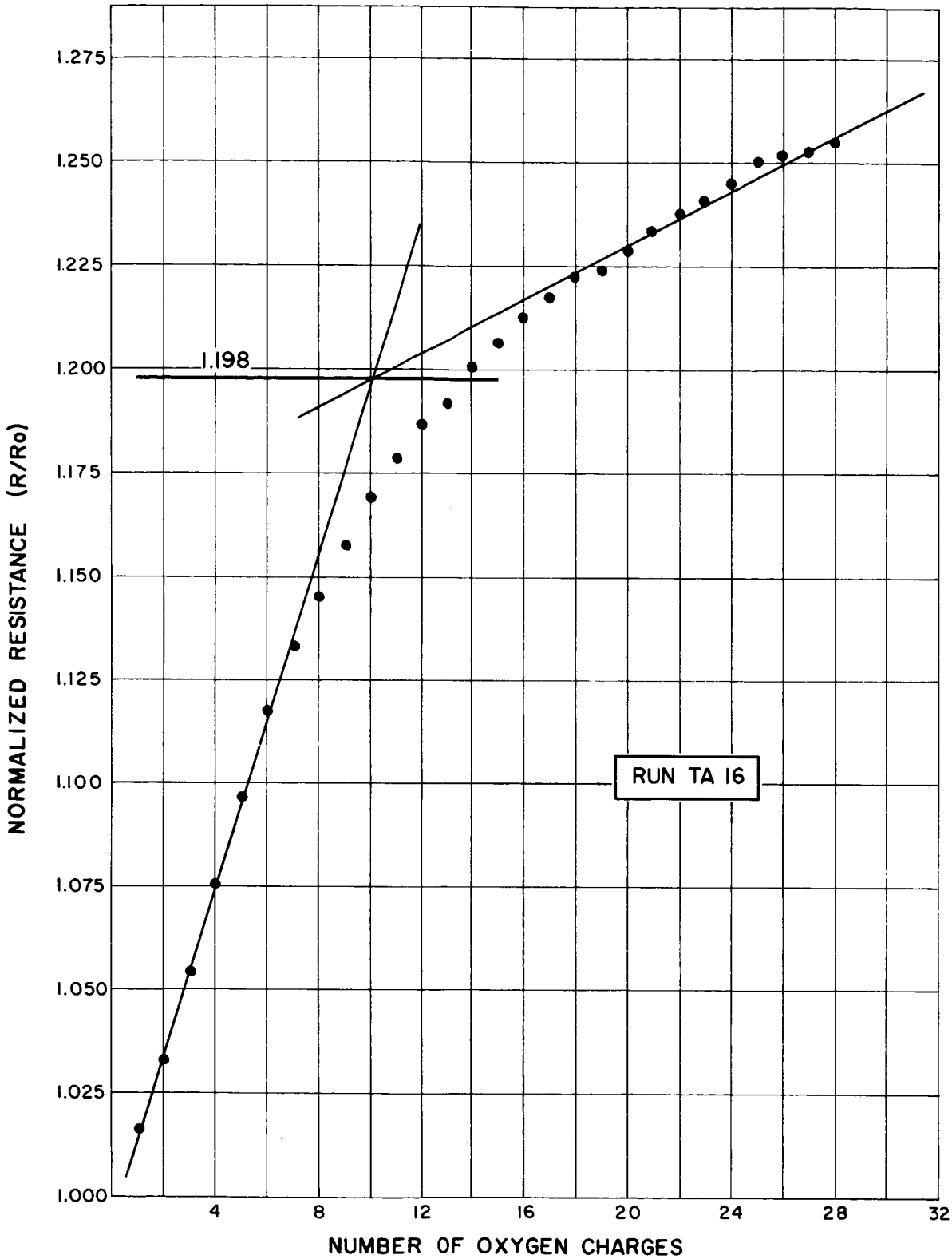


FIGURE 5. Plot of Normalized Resistance (R/Ro) versus Number of Oxygen Charges for Run TA 16. The Run was at 780°C with extended hold times between oxygen charges. See Table XII and Text for additional details.

TABLE NO. XII

Resistance Data From TA 16

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
0	.1578	1.000	15	.1904	1.207
1	.1598	1.017	16	.1914	1.213
2	.1630	1.033	17	.1922	1.218
3	.1665	1.055	18	.1930	1.223
4	.1698	1.076	19	.1932	1.224
5	.1731	1.097	20	.1940	1.229
6	.1764	1.118	21	.1947	1.234
7	.1790	1.134	22	.1954	1.238
8	.1807	1.145	23	.1959	1.241
9	.1828	1.158	24	.1964	1.245
10	.1844	1.169	25	.1971	1.250
11	.1860	1.179	26	.1975	1.252
12	.1873	1.187	27	.1978	1.253
13	.1883	1.193	28	.1982	1.256
14	.1895	1.201			

Specimen Temperature	780°C
Point of Saturation	Rs = 1.890 $^{Rs}/_{Ro}$ = 1.198
Charge Size	300 cc at 2000μ pressure
Specimen Mass	3.665 grams
Engassing Schedule	3 3/4 min. engassing time followed by 25 min. homo-genizing time.
Specimen Preparation	Std procedure except for 1450°C bake out.

TABLE NO. XIII

Resistance Data From Run TA 17

Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro	Oxygen Charge No.	R (Ohms)	Normal-ized R R/Ro
0(Ro)	.1995	1.000	7	.2314	1.160
1	.2077	1.041	8	.2352	1.179
2	.2093	1.049	9	.2394	1.198
3	.2151	1.078	10	.2429	1.218
4	.2213	1.109	11	.2455	1.231
5	.2246	1.126	12	.2487	1.247
6	.2283	1.144			

Specimen Temperature	901°C
Point of Saturation	NONE (Sample used for iso-concentration Run)See Table XIV
Charge Size:	300cc at 2000μ pressure
Specimen Mass:	3.655 grams
Engassing Schedule	3 3/4 min. engassing time followed by 3 3/4 min homo-genize time
Specimen Preparation	Std procedure except for 1450°C bake out

TABLE NO. XIV

Iso-Concentration Data From Run TA 17

Event No.	Specimen Temperature °C	Resistance After 30 Minute Hold
1	950	.2250
2	924.9	.2510
3	900.6	.2480
4	874.8	.2442
5	850.7	.2406
6	825.4	.2366
7	801.5	.2329
8	744.1	.2287
9	752.4	.2255
10	724.1	.2210
11	702.9	.2174

Cooling Rate:	250°C/300 min.
Charge Size:	NONE
Specimen Mass:	3.6551 grams
Specimen Preparation:	Std procedure except for 1450°C bake out

measurement between these two. There was a small difference between the three readings due to experimental procedure. There was a slight increase in resistance; at many engassing levels above saturation, the three readings are in agreement. Table XV shows typical values of the resistance fluctuation at various engassing levels (for TA 16).

E. Tentative Solubility Limits for Oxygen in Ta.

Figure 6 is a tentative plot of solubility limit vs temperature as determined from iso-thermal experimental runs TA 05, TA 06, TA 07, and TA 08 as well as from TA 16 (extended time iso-thermal run). No TA 17 data representing an iso-concentration run is presented since no readily discernable indication of solubility limit was obtained from TA 17 or from runs TA 01*, TA 03*, and TA 04*.

The values for oxygen in ppm were obtained by referencing the value of R_s/R_o for an individual run against the oxygen calibration curve (Figure 4). The error limits shown in Figure 4 are those associated with the neutron activation analysis alone. The error in temperature is estimated at less than $\pm$ 2C° and so is the lesser of the two** After oxygen analysis the second greatest source of error is that associated with the determination of the R/R_o value at saturation for each individual iso-thermal run; this is a graphical solution for the intersection of two straight line segments which themselves are a graphical approximation.

*Reported in Second Quarterly Report.
**$\Delta T = 1°C$ is equivalent to $\Delta 0_2 = 8$ ppm Max. from the graphical plot of the data.

TABLE XV

Resistance Variation As A Function Of Time

At Constant Oxygen Levels*

Oxygen Charge No.	Resistance (Ohms)			
	R_1	R_2	R_3	ΔR
1	.1598	.1599	.1600	+.0002
2	.1630	.1631	.1632	+.0002
3	.1665	.1667	.1667	+.0002
4	.1698	.1699	.1702	+.0004
5	.1731	.1732	.1732	+.0001
6	.1764	.1764	.1765	+.0001
7	.1790	.1790	.1790	.0000
8	.1807	.1809	.1810	+.0003
9	.1828	.1828	.1828	.0000
10	.1844	.1945	.1845	+.0001
11	.1860	.1860	.1860	.0000
12	.1873	.1873	.1873	.0000
13	.1881	.1883	.1883	+.0002
14	.1895	.1895	.1895	.0000
15	.1904	.1904	.1905	+.0001
16	.1914	.1914	.1914	.0000
17	.1921	.1922	.1922	+.0001
18	.1929	-----	.1930	+.0001
19	.1932	-----	.1932	.0000
20	-----	.1939	.1940	+.0001
21	-----	.1946	.1947	+.0001
22	-----	.1954	.1954	.0000
23	-----	-----	.1959	----
24	.1964	.1964	.1964	.0000
25	.1970	.1971	.1971	+.0001
26	-----	-----	.1975	-----
27	-----	-----	.1977	-----
28	-----	.1981	.1982	+.0001

R_1 Initial Resistance after Engassing

R_2 Resistance at Intermediate Point in Time

R_3 Resistance After 26 1/4 min. Homogenization

*DATA FROM EXTENDED TIME SOLUBILITY RUN TA 16

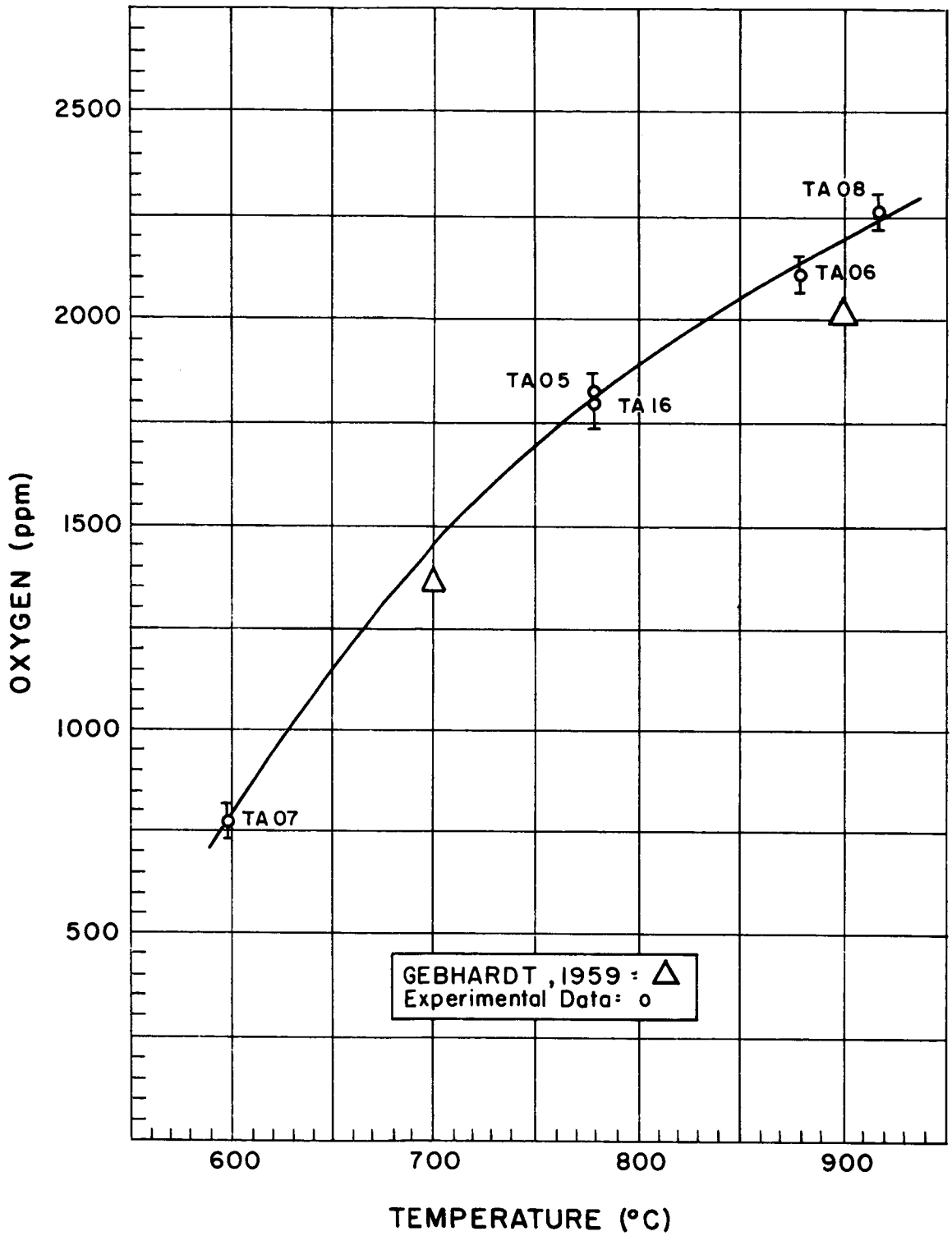


FIGURE 6. Plot of Oxygen Solubility versus Temperature for Tantalum (tentative).

Because neutron activation analysis is capable of a higher degree of accuracy than that realized herein and since the graphical error has not yet been evaluated, the solubility limits reported here will be considered tentative.

VI. DISCUSSIONS AND CONCLUSIONS

A. Extended time Solubility Runs

Iso-thermal run TA 05 indicated a saturation limit of 1835 ppm of oxygen at 780°C ($R/Ro = 1.204$) while iso-thermal run TA 16 (extended time cycle) indicated a saturation limit of 1795 ppm of oxygen at 781° ($R/Ro = 1.198$). Discounting the difference in (constant) temperature the values are within 40 ppm as compared to the neutron activation analysis standard deviation of ± 50 ppm at that range.

The longer engassing time should allow the Ta-O_2 system to more closely approach an equilibrium resistance value. It was therefore anticipated that Run TA 16 would indicate the same or a greater O_2 solubility, as compared to TA 05. The decrease in solubility with increased homogenizing time indicates that one of at least three things are happening.

1. Since the homogenization is taking place in high vacuum with a very low oxygen partial pressure, there is a net loss in oxygen during the hold time due to outgassing which increases with longer hold times.

2. A compositional or metallurgical change is taking place which affects the overall electrical resistivity of the specimen such as grain boundary oxide spherodization.

3. The temperature error is of an order of $\pm$ 2°C which would be about $\pm$ 16 ppm. In addition, the higher temperature anneal at 1450°C for TA 16 may have contributed to the difference.

Three resistance measurements were made during the homogenization portion (26-1/4 minutes) of each engassing cycle (See Table XV). Were the resistance values obtained from an iso-thermal run time dependent, the three values for each cycle would show a consistent trend; they do not.

The resistance fluctuation is attributed mainly to small ($\pm$ 2°C) temperature variations and possibly resistance measurement errors, the latter is extremely small. The effect of possible time dependence on the final value of R/R_o for the saturation point can best be determined when a computer program is available for evaluating iso-thermal data. (The data from TA -16 used in determining the tentative solubility limits reported above was obtained by using the third (final) resistance measurement from each engassing cycle. The failure of the iso-concentration method (run TA 17) to produce a graphically discernable inflection at the temperature corresponding to the saturation limit for the

dissolved oxygen level present, indicates that this technique is not feasible, at least for Ta, within the objectives and scope of this program. An additional continuous temperature rate programer is needed in order to pursue this technique further.

B. Computer Programs

Both the iso-thermal and the iso-concentration methods employed rely on graphical solutions to determine points of saturation; this dependence introduces a small systematic error. To obviate graphical solutions, it is desirable to develop computer programs to process the raw data and locate the saturation point.

Results to date with the iso-concentration technique yield no apparent indication of a saturation point in the plotted data. If, indeed, the dissolved oxygen is not totally "frozen-in" but does precipitate in some finite amount, then the saturation point can only be determined (for Ta, at least) by a statistical analysis. A simple single regression program was written and applied to the data from iso-concentration runs with unsatisfactory results to date. A multiple regression analysis would be more in order (e.g., an adaptation of the NASA SNAP 7094 Regression Analysis Program) and will be considered for future use.

In the case of the iso-thermal technique the indications of the point of saturation are real and easily discernable

from the plotted data. The tentative solubility limits reported above are derived from a graphical solution and are subject to an uncertain error. A computer program could be used to calculate the error in the extrapolation process and define the saturation point with less uncertainty. Preliminary work has begun in this area; a simple program has been written and applied to test cases.

VII. WORK PLANNED FOR NEXT QUARTER

1. Further analysis of the data from all trial runs, solubility determination runs and oxygen calibration runs.

2. Determination of solubility limits of oxygen in columbium in the range 580°C to 950°C.

3. Process additional alumina reaction tubes and place high temperature oxygen solubility furnace in operation. If the present tubes cannot be successfully metallized, order tubes from a second source known to have the capacity of being metallized. (AD-99 or AD995, Coors).

4. Continue design and construction of diffusion apparatus.

5. Develop computer program to determine saturation points from iso-thermal experimental data.