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CORROSION AND CREEP BEHAVIOR OF
TANTALUM IN FLOWING SODIUM

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CORROSION AND CREEP BEHAVIOR OF TANTALUM IN FLOWING SODIUM

Gilbert E. Raines, C. Vernon Weaver, and John H. Stang

The corrosion behavior of commercial tantalum in high-purity flowing sodium from 700 to 1200 F and the effect of sodium exposure on the creep strength of tantalum at 1200 F have been investigated. The tests were conducted in forced-convection flow loops constructed of Type 316 stainless steel.

With continuously gettered sodium systems (probably containing less than 10 ppm oxygen) operating for periods up to 50 days, weight losses sustained by 1200 F specimens corresponded to only about 0.1 mil of metal removed per year. Maximum weight losses, encountered with a continuously cold-trapped (about 40 ppm oxygen) sodium system, were equivalent to about 3 mils per year for 1200 F specimens. For the most part, metallographic examinations revealed no deleterious corrosion effects; however, one particular group of arc-cast tubing specimens suffered severe intergranular attack in sodium with about 80 ppm oxygen.

In addition to the corrosion findings, the corrosion tests yielded information about the partition of interstitials, particularly oxygen, in the sodium-tantalum system. Oxygen, for example, showed a tendency for migration from tantalum to high-purity sodium considerably stronger than would be predicted from limited thermodynamic data available.

In the creep experiments, the oxygen content of the sodium was maintained at the <10 ppm level by continuous gettering. In general, the results demonstrated that sodium exposure at 1200 F had very little, if any, effect on tantalum creep strength. Baseline data necessary to establish this were obtained in supplementary helium-atmosphere creep tests.

INTRODUCTION

The research described in this report was performed under the auspices of Los Alamos Scientific Laboratory and includes two investigations dealing with commercial grades of tantalum. The first is concerned with tantalum corrosion by high-temperature sodium and the second deals with the effects of sodium exposure on the creep properties of tantalum. These studies are important in the concept of the LAMPRE (Los Alamos Molten Plutonium Reactor Experiment) reactors now under study and development at LASL. In these systems, molten plutonium-alloy fuel is to be contained in a small core cooled by flowing sodium; tantalum is being considered as the material for core construction. The peak sodium temperature in the system will probably be of the order of 1200 F.

The corrosion studies consisted of experiments in which tantalum specimens were suspended for periods ranging from 8 to 50 days in the heated legs of small polythermal forced-convection loops containing high-purity sodium circulating under an argon atmosphere. The peak fluid temperature was 1200 F, the increase through the heated-leg

specimen zones being about 500 F. The loops were constructed of Type 316 stainless steel; each was equipped with a cold trap, a zirconium-foil-filled gettering trap, and a plugging indicator for control and monitoring of the oxygen levels in the sodium. Regulation of the oxygen level was important because the sodium coolant in LAMPRE systems must be very pure to prevent contamination of the fuel owing to migration of impurities to it through the container wall. The thermodynamic conditions for this migration appear to be favorable, since plutonium-base mixtures are much more powerful getters for impurities than either sodium or tantalum.

After exposure, the specimens were examined for weight changes and were subjected to thorough metallographic examinations. It is believed that the experimental corrosion effects are similar to those that can be expected in LAMPRE systems. This is because of simulation of corrosion-governing factors such as sodium purity and specimen-exposure temperature, use of Type 316 stainless steel as a basic construction material (a like material probably will be used in actual service for heat-exchanger-circuit construction), and system geometry including specimen surface-to-fluid volume ratio. Also, practical fluid temperature cycles were maintained, although this made relatively low sodium flow velocities essential owing to heat-transfer limitations.

In addition to corrosion effects, certain tendencies were demonstrated regarding the migration of interstitial elements (carbon, hydrogen, nitrogen, and oxygen) in the tantalum-sodium system. These observations, which were based primarily on evaluations of contamination levels in the tantalum specimens before and after the sodium exposures, cannot be applied directly to the reactor situation inasmuch as the powerful influence of the plutonium-alloy fuel was absent.

Experiments to evaluate creep behavior were conducted with loop systems similar in many respects to those used for corrosion experiments. However, each creep loop was provided with accessories necessary to apply a tensile load and monitor the creep of a stressed tantalum specimen immersed in 1200 F flowing sodium. In all of the creep tests, the oxygen content of the sodium charge was maintained at a very low level (<10 ppm) by continuous gettering with zirconium foil. The experiments were conducted for approximately 1000 hr; control tests were conducted in a helium atmosphere to establish baseline data.

CORROSION BEHAVIOR OF TANTALUM DURING EXPOSURE TO HIGH-TEMPERATURE SODIUM

Apparatus

Figure 1 shows details of the forced-convection loop system developed for the corrosion studies. As indicated previously, the basic loop was constructed of Type 316 stainless steel. All components were joined by inert-gas arc welding except the electromagnetic pump cell which, for convenience, was attached by Swagelok fittings.

FIGURE 1. FORCED-CONVECTION POLYTHERMAL FLOW LOOP FOR SODIUM-TANTALUM CORROSION

Following is a brief description of the major loop components.

Pump and Flowmeter. Each loop was equipped with a small d-c electromagnetic pump, the basic design of which was furnished by the Argonne National Laboratory. The sodium flow rate, which normally was of the order of 0.1 gpm, or about 11 fpm past the tantalum specimens, was measured by an electromagnetic flowmeter.

Purification Devices. Each loop was provided with a cold trap and a gettering trap for removal of oxygen from the sodium. These devices were located in individual flow paths parallel to the main flow circuit and, when not in use, were cut off by frozen sodium plugs. The cold traps were filled with stainless steel mesh which entrapped and contained oxides precipitated from the fluid at reduced temperature. Solubility-temperature relations established at Knolls Atomic Power Laboratory⁽¹⁾ were utilized to select cold-trap temperatures. The gettering traps were filled with alternate layers of flat and corrugated zirconium foil wound into a coil. While this configuration provided considerable surface for gettering, its open cross section offered little resistance to flow.

Each loop was equipped with a conventional perforated-disk plugging indicator for monitoring the oxygen level. It is estimated that the sensitivity of determinations above 20 ppm oxygen was about ± 20 ppm. Below this, plugging-indicator measurements in sodium systems are difficult to interpret.

Heat-Transfer Components. Fluid heating and cooling was accomplished in the two vertical legs of the apparatus. The main heating furnace employed ten symmetrically arranged General Electric quartz infrared lamps, each rated at 500 w. Heat for the sodium-purification traps was supplied by auxiliary clamshell-type furnaces. While most of the cooling was effected by radiation from the unheated vertical leg, some, resulting from forced-air cooling of heater-element terminals, occurred at the hot leg just above and below the furnace zone.

Instrumentation. Control of peak fluid temperature within ± 20 F (at 1200 F) was achieved by on-off regulation of the main furnace, governed by the response of a thermocouple located in the annular space between the furnace elements and the hot leg. The peak fluid temperature itself was measured by a thermocouple in a deep well positioned in the hot leg. Fluid temperatures elsewhere in the system were estimated from measured temperatures of the outside surfaces of the flow circuit.

Specimens

As indicated in Figure 1, the tantalum specimens were suspended within the heated vertical leg of the loop system. With one exception, they consisted of a stack of

(1) References at end of text.

eight 1-in. -long sections of 1/2-in. -OD thin-walled tubing or similar sections made from 10 to 15-mil sheet. In the one exception, the specimens consisted of six finished creep specimens which were exposed to lower their oxygen content for subsequent inert-gas creep tests.⁽²⁾ Table 1 gives descriptions of the commercial annealed sintered and annealed arc-cast materials that were evaluated. The annealing treatment, which consisted of an 8-min high-vacuum exposure at 2650 F, produced a fairly fine-grained material (average grain diameter 1/2 to 1 mil).

Procedure

Loop Operation

After final assembly, including installation of the tantalum specimens (on a carriage) in the upper extension of the hot leg, each loop system was leak checked by helium mass spectrometer and evacuated. After being charged with a measured amount of sodium (all charges were taken from a single shipping container), the system was pressurized to 3 to 5 psi with argon and the charge was purified to the desired oxygen level as described below.

To initiate an experiment, the specimen carriage was lowered into the flowing sodium by an external electromagnet. The specimens were arranged on the carriage so that sodium could flow both around and through them. The one at the top of the stack was exposed to sodium as it reached its peak temperature, 1200 F, while the bottom one was exposed to relatively cool (normally about 700 F) fluid entering the heating zone. Temperatures of the intermediate specimens were estimated from wall temperatures. As might be expected, the gradient from specimen to specimen decreased in the direction of flow.

Table 2 summarizes principal conditions of the experiments. Procedures used to achieve various oxygen levels are outlined below.

- (1) Prior to Tests 1 and 5, cold trapping with a trap temperature of 250 F was followed by a 3 to 5-day high-temperature gettering period. Both purification facilities were frozen out of the system during the actual corrosion run. The nominal oxygen level with this sequence was estimated from plugging-indicator data to be ~10 ppm.
- (2) Tests 2, 7, 8, and 9 were experiments in which the nominal oxygen level in the sodium was relatively high. Cold-trap operation was maintained both prior to and during the specimen-exposure period.
- (3) Tests 3, 4, and 6 were similar in that the test sodium was gettered both prior to and throughout the specimen-exposure period. The nominal oxygen level listed for these tests (<10 ppm) is lower than that listed for Tests 1 and 5 (~10 ppm) although plugging-indicator estimates were essentially the same. The presumed difference is based on the observation that, during each corrosion exposure, oxygen migrated from the tantalum specimens to the sodium. The quantities of oxygen involved were minute, and there was no opportunity to remove them without continuous gettering.

TABLE 1. DESCRIPTION OF TANTALUM SPECIMEN MATERIALS PRIOR TO EXPOSURE TO SODIUM

Material ^(a)	Code Designation in Table 3	Test	Concentration of Interstitial Elements ^(b) , ppm				Hardness, VHN	Comments
			Oxygen	Hydrogen	Nitrogen	Carbon		
Unannealed sintered tubing	I	1	118, 88	1.7, 2.4	40	40	211	Analyses determined for as-received material
Annealed sintered tubing	II	2, 3, 5, 6, 7, 9	(150-200)	(2)	(30-60)	(10-50)	(120-150)	
Annealed sintered sheet	III	4	(240-300)	(1.6)	(130-160)	(20)	169-171	
Annealed arc-cast sheet	IV	2, 3, 5, 6, 7, 8, 9	(150-200)	(2)	(90-120)	(180-210)	155-180	
Annealed sintered tubing	V	8	344, 530	0.9, 1.1	--	--	172-215	Control-specimen analysis shown; relatively high oxygen content attributed to contaminated annealing atmosphere
Annealed arc-cast tubing	VI	9	390	<1/2	30	70	191	Control-specimen analysis shown
Annealed arc-cast tubing	VII	8	--	--	--	--	115-125	Analyses of specimens from other annealing groups of this material show oxygen levels of 390-560 ppm and VHN of 160-200 (for example Group VI above); however, the hardness listed indicates a much lower interstitial level

(a) Annealing was accomplished by an 8-min treatment in vacuum at 2650 F.

(b) Parentheses designate estimates based on (1) original batch analyses and (2) analyses of various similar materials determined after annealing runs. Minor variations in the interstitial levels owing to the annealing treatment occurred.

TABLE 2. SUMMARY OF PRINCIPAL TEST CONDITIONS FOR CORROSION STUDIES OF TANTALUM SPECIMENS IN SODIUM FLOW LOOPS

	Test								
	1	2	3	4(a)	5	6(b)	7	8	9
Length of Exposure, days	15	11	8	33	43	50	34	38	20
Peak Sodium Temperature, F	1200	1200	1200	1200	1200	1200	1200	1200	1200
Nominal Sodium Temperature Cycle, F	700	500	500	200	500	500	500	500	500
Cold-Trapping and Gettering Procedures									
Prior to Immersion of Specimens Into Sodium									
Cold Trapping Employed	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Cold Trapping Temperature, F	250	500	250	250	250	250	350	500	500
Length of Gettering Period, days	3	None	4	5	5	3	None	None	None
Gettering Temperature, F	1250	--	1100	1200	1200	1200	--	--	--
During Specimen-Exposure Period									
Cold Trap Operating Continuously	No	Yes	No	No	No	No	Yes	Yes	Yes
Cold Trapping Temperature, F	--	500	--	--	--	--	350	500	500
Gettering Trap Operating Continuously	No	No	Yes	Yes	No	Yes	No	No	No
Gettering Temperature, F	--	--	950	1000	--	1000	--	--	--
Nominal Oxygen Content in Sodium From Plugging-Indicator Determinations, ppm									
Before Immersion of Tantalum Specimens Into Sodium	~10	80	<10	<10	~10	<10	20	80	80
At End of Run(c)	~10	80	<10	<10	~10	70	40	80	80

(a) Special experiment in which finished creep specimens were exposed.

(b) It is suspected that the high final oxygen level for this experiment is attributable to a leak at the O-ring gas seal. Since the corrosion data correlate well with those from other <10 ppm runs, the leak probably did not occur until the run was nearly completed.

(c) Spot checks of posttest oxygen levels were made in a mercury-amalgamation apparatus available at Battelle with the following results: Test 1, 7 ppm; Test 6, 61 ppm; Test 7, 62 ppm.

Evaluation of Specimen Behavior

As indicated previously, this investigation dealt principally with the corrosion behavior of tantalum but certain of the findings pertained to the migration of interstitial elements in the tantalum-sodium system. Corrosion was judged by weight-change data and by metallographic examinations of exposed specimens. Information about the migration of interstitials was based largely on pretest and posttest analyses of the specimens. Oxygen and hydrogen analyses were made by a vacuum-fusion process having a calculated sensitivity of ± 4 ppm oxygen and ± 0.5 ppm hydrogen (for the 2-g sample used). Nitrogen was determined by the micro-Kjeldahl technique after the tantalum was brought into solution using HF, H₂SO₄, and H₂O₂. Carbon content was established by the Leco conductimetric technique.

Results and Discussion

Corrosion Behavior

According to specimen-weight-change data, tantalum has excellent resistance to corrosion attack by high-temperature sodium. The data obtained are presented in Table 3 and are depicted in Figure 2 in terms of rate of metal removed from the exposed specimen surfaces. With a lone exception, evidence of intergranular corrosion was not found metallographically. The exception occurred in the case of arc-cast-tubing specimens exposed, together with arc-cast-sheet and sintered-tubing specimens, in Test 9. To illustrate this situation, photomicrographs of typical sections of specimens from this run are shown in Figure 3. The susceptibility of the arc-cast tubing to intergranular corrosion may clearly be seen; on the other hand, the sintered tubing, which had original surface defects comparable with those present on the arc-cast tubing, was virtually unchanged. The posttest section of arc-cast sheet has the typical clean appearance of a specimen which did not suffer visible attack. As indicated in Table 3, the only marked difference in the composition of these three materials was the unusually high original oxygen level (390 ppm) of the arc-cast tubing. It seems reasonable that this high contamination played an important contributing role in a process which led to the aggravated corrosion observed.

As can be seen in Figure 2, the specimen weight losses, although low, were influenced by exposure temperature and oxygen level in the sodium. The dependency noted may be regarded as normal for materials exposed to sodium, since both increased temperature and increased oxygen level can lead to an increased tendency for sodium to dissolve tantalum. Even so, it appears that the rate of solution, in the case of the gettered experiments, was low enough to be the limiting factor in the corrosion rate; as will be shown subsequently, this was probably not the case for the cold-trapped systems.

The fact that the rates of attack when continuous gettering was employed were consistently lower than rates observed when gettering was confined to a pretest period points to the effectiveness of the continuous gettering in removing minute amounts of oxygen. One source of the trace oxygen was the tantalum specimens themselves since, as will be discussed later, a major fraction of the interstitial oxygen they originally contained migrated into the sodium.

TABLE 3. RESULTS OF EXPOSURE OF TANTALUM SPECIMENS TO SODIUM

Specimen	Type of Tantalum (Refer to Table 1)	Estimated Average Specimen- Exposure Temperature, F	Posttest Examination Data						
			Concentration of Interstitial Elements,				Hardness, VHN	Weight Loss	
			ppm					Mg/(In. ²)(Month)	Equivalent Mils per Yr
			O ₂	H ₂	N ₂	C			
<u>Test 1</u>									
A-8	I	1200	(a)	(a)	(a)	(a)	(a)	8.2	0.35
A-7	I	1200	94	1.7	220	230	161	6.4	0.27
A-6	I	1150	32	1.7	(a)	(a)	205	7.6	0.32
A-5	I	1100	36	1.8	(a)	(a)	214	8.2	0.35
A-4	I	1000	28	7.7	(a)	(a)	173	11.4	0.48
A-3	I	600	74	5.4	(a)	(a)	249	5.5	0.23
A-2	I	500	88	8.5	(a)	(a)	205	0.5	0.02
<u>Test 2</u>									
B-8	IV	1200	31	28	170	160	135	30.3	1.28
B-7	II	1200	48	11	(a)	(a)	105	28.6	1.21
B-6	II	1150	27	11	(a)	(a)	119	29.2	1.23
B-5	II	1100	46	6.9	80	80	106	18.6	0.79
B-4	II	900	52	7.9	50	100	108	4.4	0.19
B-3	II	800	(a)	(a)	(a)	(a)	(a)	5.5	0.23
B-2	II	750	66	8.5	60	40	107	5.5	0.23
<u>Test 3</u>									
D-7	II	1200	(a)	(a)	(a)	(a)	(a)	0.75	0.03
D-6	II	1200	22	3.9	(a)	(a)	135	0.75	0.03
D-5	II	1150	(a)	(a)	(a)	(a)	135	0.75	0.03
D-4	II	1100	64	3.5	40	40	114	0.75	0.03
D-8	IV	1050	16	6.2	90	190	156	3.75	0.16
D-3	II	1000	90	6.3	(a)	(a)	149	0.75	0.03
D-2	II	800	120	10	(a)	(a)	152	6.0	0.25
<u>Test 4</u>									
Six specimens	III	1200	--	--	--	--	130-132	2.3-2.6	0.11
5-4	III	1200	33	6	160, 270, 130	10	130	2.4	0.11
<u>Test 5</u>									
C-7	II	1200	(a)	(a)	(a)	(a)	(a)	9.9	0.42
C-8	IV	1200	12	3.8	230	280	158	8.2	0.35
C-6	II	1150	20	3.0	(a)	(a)	125	8.7	0.37
C-5	II	1100	25	2.7	110	60	107	7.4	0.31
C-4	II	1050	24	4.7	(a)	(a)	118	6.5	0.27
C-3	II	1000	9	3.6	(a)	(a)	122	5.8	0.25
C-2	II	800	61	5.6	50	40	121	Gain (1.0)	--
<u>Test 6</u>									
F-7	II	1200	(a)	(a)	(a)	(a)	(a)	1.3	0.06
F-6	II	1200	16	17	50	40	116	2.2	0.09
F-5	II	1150	5	5.5	(a)	(a)	125	2.3	0.10
F-8	IV	1100	14	2.7	140	230	149	1.6	0.07
F-4	II	1050	24	5.4	(a)	(a)	120	1.8	0.08
F-3	II	1000	24	6.0	(a)	(a)	125	1.1	0.05
F-2	II	800	23	5.0	60	10	111	0.8	0.03

TABLE 3. (Continued)

Specimen	Type of Tantalum (Refer to Table 1)	Estimated Average Specimen- Exposure Temperature, F	Posttest Examination Data						
			Concentration of Interstitial Elements,				Hardness, VHN	Weight Loss	
			ppm					Mg/(In. ²)(Month)	Equivalent Mils per Yr
			O ₂	H ₂	N ₂	C			
<u>Test 7</u>									
E-7	II	1200	21	4	(a)	(a)	131	65.1	2.76
E-6	II	1200	(a)	(a)	(a)	(a)	(a)	72.0	3.05
E-8	IV	1150	44	5.9	190	230	137	50.1	2.12
E-5	II	1100	29	37	(a)	(a)	125	53.7	2.27
E-4	II	1050	38	8.7	90	30	110	23.6	1.00
E-3	II	1000	70	51	(a)	(a)	135	6.0	0.25
E-2	II	800	242	17	50	20	122	Gain (0.1)	--
<u>Test 8</u>									
G-1	V	1200	360	10, 12 483	100	130	99	35.9	1.52
G-9	VII	1200	12, 16	8, 9	110	130	105	44.2	1.87
G-7	IV	1150	74, 17	9, 11	150	230	125	30.8	1.30
G-2	V	1100	510	17, 2 530	(a)	(a)	112	17.5	0.74
G-5	VII	1050	95, 47	21, 20	60	60	108	5.5	0.23
G-8	IV	1000	26, 30	22, 25	90	220	142	0.1	Nil
G-6	VII	800	67, 73	28, 30	50	40	112	Gain (0.1)	--
<u>Test 9</u>									
H-4	II	1200	22	5.7	170	110	96	60.6	2.57
H-7(b)	VI	1200	(a)	(a)	140	100	90	69.9	2.96
H-9	IV	1150	348	4.1	210	260	129	40.6	1.72
H-5	II	1100	46	7.0	90	100	97	26.7	1.13
H-8(b)	VI	1050	492	8.9	40	80	99	Gain (0.1)	--
H-10	IV	1000	48	6.2	110	190	136	Gain (1.9)	--
H-11(b)	VI	800	645	13.0	40	100	97	3.5	0.15

(a) Not obtained.

(b) These specimens exhibited marked intergranular attack as discussed in the text.

FIGURE 2. EFFECTS OF TEMPERATURE AND OXYGEN CONTENT OF THE SODIUM IN ITS ATTACK ON TANTALUM

500X

BEFORE EXPOSURE

N41733

500X

AFTER EXPOSURE
AT 1200 F

N50173

SINTERED BAR

522X

BEFORE EXPOSURE

N42331

500X

AFTER EXPOSURE
AT 1050 F

N50177

ARC-CAST TUBING

500X

BEFORE EXPOSURE

N41732

500X

AFTER EXPOSURE
AT 1150 F

N50179

ARC-CAST SHEET

ETCHANT: 30 LATIC ACID-10HNO₃-10HF

FIGURE 3. PHOTOMICROGRAPHS OF VARIOUS TYPES OF TANTALUM BEFORE AND AFTER EXPOSURE TO SODIUM (80 PPM OXYGEN) FOR 34 DAYS

Specimens were transverse sections.

The higher corrosion rates above about 1000 F for the continuously cold-trapped systems appear to reflect the effect of both oxygen level and cold-trap temperature. Although such rates might be expected from a consideration of system oxygen level alone, it should be noted that the rate at the 40 ppm level was consistently higher than that at 80 ppm. It is believed that an explanation for this particular behavior can be based on the difference in cold-trap temperatures required to produce these levels (350 F for 40 ppm and 500 F for 80 ppm). It is reasonable because of the decrease of solubility with reduced temperature that the opportunity for mass transfer in the 40-ppm system was relatively high and, in fact, sparse tantalum deposits were found in the cold trap. Since such deposition would act to lower the concentration of the tantalum in the sodium, it is plausible that the direct result would be an increased potential for attack in the hot-zone areas. This is the basic situation that would be predicted for polythermal liquid-metal systems where solubility is the mechanism of attack and cold-zone precipitation is the rate-controlling step. It is probable that the higher oxygen level systems discussed here fall into this category, since the increased aggressiveness of the sodium owing to contamination would reduce the possibility that rate of solution was the slow step.

When interpreted in terms of a practical reactor system required to operate for thousands of hours, these concepts assume importance, since it would certainly be desirable to minimize the opportunity for hot-zone corrosion. This would be achieved only if the system oxygen level is such that rate of solution controls the corrosion rate. One way of maintaining the low contamination level required to insure this is through the use of continuous or semicontinuous high-temperature gettering.

Oxygen Partition in Tantalum-Sodium Systems

A rather pronounced reduction of the oxygen content of the exposed tantalum specimens was observed, particularly at higher temperatures. Figure 4 shows a plot of pertinent data from the long-term runs, where oxygen equilibrium is most likely to have been reached. It is of interest to note that the tendency found for oxygen migration toward the sodium is considerably stronger than that which was predicted thermodynamically. Differences in calculated behavior assuming equilibrium and experimental behavior are shown in Figure 5. To obtain the three experimental curves in this plot, nominal oxygen-in-sodium values of 1, 10, and 40 ppm were assigned to the experiments involved and the oxygen-in-tantalum values were taken from Figure 4.

While a large difference obviously exists between the experimental and the predicted oxygen behavior, some of the disagreement probably can be attributed to the dearth of basic solubility data. This made it necessary, for example, to use data for the solubility of oxygen in sodium extrapolated above 1000 F; MSA solubility data⁽³⁾ were employed to obtain the predicted values included in Figure 5.* It was found that data from other sources^(1,4) yielded comparable ranges which were displaced slightly farther away from the experimental situation. In addition, it was necessary to use data extrapolated below 1340 F for the solubility of oxygen in tantalum. The data which were extrapolated were given in a paper by Gebhardt and Preisendanz⁽⁵⁾, the only source found that included temperature as a variable.

*The method of calculation involved is outlined in the Appendix of this report.

FIGURE 4. REDUCING EFFECT OF SODIUM ON TANTALUM SPECIMENS IN FORCED-CIRCULATION POLYTHERMAL LOOPS

FIGURE 5. PARTITION OF OXYGEN BETWEEN TANTALUM AND SODIUM

Nitrogen and Carbon Behavior

Except in the case of Test 1, the carbon and nitrogen contents of the tantalum specimens remained approximately constant during the various exposures. The increases in nitrogen exhibited by the specimens from Test 1 probably stemmed from the physical entrapment of nitrogen (the original cover gas for sodium shipping containers) in the test charge of sodium. For subsequent runs, the nitrogen had an opportunity to be evolved during repeated meltings of the sodium in the shipping vessel. The carbon pickup noted after Test 1 may be attributed to acetone contamination. Acetone was used in this system as a volume-calibrating fluid and trace amounts of it probably remained after the pretest cleaning operations.

Hydrogen Behavior

The hydrogen content in tantalum increases consistently (although in very low concentrations) during sodium exposure. This can probably be related to the NaOH impurity in the fluid. It was noted that the hydrogen pickup during the gettered experiments was less than those in the cold-trapped runs, indicating some ability of the getters to remove hydrogen.

Hardness Correlation

The carbon, hydrogen, nitrogen, and oxygen contents of tantalum affect its hardness. It was found in this investigation that the interstitial levels which, in the majority of cases, were below 1/2 a/o, could be related to the specimen hardness by the following empirical equation:

$$\text{VHN} = 75 + 0.20 (\text{O}) + 0.18 (\text{N}) \\ + 0.2 (\text{H}) + 0.15 (\text{C}),$$

where VHN is Vickers hardness and the carbon, hydrogen, nitrogen, and oxygen levels are in ppm. This equation has a probable error of ± 10 VHN, a standard deviation of ± 15 VHN, and actual deviations of ± 30 VHN for the 29 specimen analyses used.

Perkins⁽⁶⁾ at Los Alamos investigated in considerable detail variations in hardness of tantalum with hydrogen, nitrogen, and oxygen levels. His procedure was to start with a thoroughly degassed material and to add to it controlled amounts of single gases. In the impurity range common to the two investigations, there is fair agreement among the data. For higher ranges, Perkins found a departure from the linear relations depicted by the above equation.

EFFECT OF SODIUM EXPOSURE ON THE CREEP BEHAVIOR OF TANTALUM

Apparatus

The forced-convection polythermal flow loop made of Type 316 stainless steel and designed for creep tests of tantalum specimens in high-temperature flowing sodium is shown in Figure 6. Several features of the system dictated by the special test conditions demanded are described below.

Specimen Environment

It was necessary to separate the specimen chamber from the fluid heating zone, since it was mandatory that the bath surrounding the stressed specimen be isothermal. To provide an efficient heating zone, a tube-and-shell heat exchanger was incorporated into the loop circuit. The sodium passed through the baffled shell and heat was supplied by six 1250-w quartz infrared lamps, one inserted into each of the six tubes present. The specimen chamber, which was located just beyond the furnace so that the specimen itself was exposed to sodium at the peak temperature, was well insulated to minimize heat losses. In addition, the sodium flow rate through the specimen zone was maintained at about 30 fpm, thus minimizing the opportunity for temperature variation along the 3-1/2-in. specimen length.

It was also necessary that the fluid-temperature level in the specimen zone be controlled within stringent limits. To achieve the control desired, about 80 per cent of the furnace capacity was utilized continuously during a run, and the remaining 20 per cent was operated on-off by a time-proportioning controller. The sensing thermocouple was welded into the insulated specimen-chamber wall. This scheme provided temperature control within ± 10 F at 1200 F in the specimen zone. To avoid specimen overheating during an apparatus malfunction, an auxiliary switch was provided to shut the system down when the fluid temperature reached 1230 F.

It was not convenient in these loop systems to achieve high-fluid-temperature cycles because the volumes of fluid circulated were relatively large. However, a thermal cycle of 80 F could be achieved by blowing air across the external flow circuit. If fins were added, a cycle of 160 F could be attained.

Sodium Purification

Since it was desired to maintain a high level of sodium purity (<10 ppm oxygen), a zirconium-foil-filled gettering chamber was located in series with the main flow circuit. This provided continuous purification after the system was charged with test sodium which had been prepurified in an auxiliary system and transferred directly into the loop by gas pressure. The auxiliary system, which contained a sodium shipping vessel as an integral part, was equipped with pumping and heating facilities, a cold trap, a zirconium-foil-filled gettering trap, and a plugging indicator.

FIGURE 6. FORCED-CONVECTION POLYTHERMAL LOOP FOR STUDIES OF CREEP BEHAVIOR OF TANTALUM DURING EXPOSURE TO SODIUM

Specimen Loading and Creep Monitoring

Conventionally shaped specimens fabricated of arc-cast tantalum sheet were employed in this investigation. The specimen dimensions are shown in Figure 7.

FIGURE 7. TANTALUM CREEP-SPECIMEN CONFIGURATION

The loading system employed was adopted from an ORNL design⁽⁷⁾ developed for studies of structural materials in static sodium baths. In essence, in this design, a dead weight suspended from an external lever arm transmits a tensile load to the fluid-immersed specimen through a pull rod which enters the specimen-containing system through a bellows seal. The internal holder to which the specimen is fastened is anchored in such a way that it is in compression when the specimen is in tension. Sturdy load-carrying members fabricated from Type 316 stainless steel were used in this investigation, even though actual applied loads were low, to minimize support-structure deformations.

Specimen deformations were indicated by a dial gage in contact with an external section of the load rod. The strain thus registered was the combined gage-section deformation, grip-portion deformation, and pin-hole elongation. In early runs, the triple-thickness grips shown in Figure 7 were not used and the end-deformation effects were large. As a result, it was difficult to interpret gage-section behavior and, consequently, these early tests are not reported. After the strengthened grips were adopted, the grip-portion deformation was minimized and pin movement with respect to the holes was confined largely to a short pin-seating period after loading. In addition, some calibration data were obtained from an inert-atmosphere creep run instrumented with internal extensometers and an external dial gage.

Blanket-Gas System

High-purity argon was employed as the system blanket gas. Since pressure fluctuations which would act against the load-rod bellows seal and vary the specimen load could not be tolerated, a static gas system could not be utilized. Instead, a low continuous flow was maintained and, in exiting from the system, was allowed to bubble through a mineral-oil trap. An intermediate empty trap prevented drawing mineral oil

back into the sodium. In computing the specimen loads, allowances were made for the 2-in. head of mineral oil in the exit trap.

Procedure

The test sodium was treated in the auxiliary prepurification system by cold trapping at approximately 300 F and subsequent gettering for about 4 days at 1000 F with the cold trap frozen. After a loop system was evacuated hot, it was filled with blanket gas and a flush charge was pumped in and circulated at 1200 F for at least 48 hr. After the flush was drained (at about 1000 F), the test charge was introduced and allowed to freeze. It was necessary at this point to open the system at the O-ring closure and position the tantalum specimen assembly (and the gettering foil). This was readily accomplished since the level of the frozen sodium was well below the specimen zone*; the contamination incurred during these steps was considered to be negligible since the atmosphere-exposed area of frozen sodium was not large. After resealing and re-evacuating, argon was again introduced. Following an adequate heating period, the EM pump was started and, when the proper flow and temperature conditions were achieved, the specimen was loaded and the creep test started. After the run, the specimens were examined metallographically to determine corrosion effects; weight-changes were also noted.

As indicated previously, specimen creep during the run was obtained by dial-gage readings. These data were compared with those obtained from comparable inert-atmosphere (helium) control experiments to ascertain differences in creep behavior that might be attributed to sodium exposure. The specimens utilized for the helium runs were identical with those employed for the sodium runs.

Results and Discussion

In this phase of the research, the following types of experiments were conducted (all experiments were terminated before the onset of third-stage creep):

- (1) Standard creep experiments in which stress was applied to the specimen immediately after the peak temperature of the sodium reached 1200 F.
- (2) A special creep experiment in which the tantalum specimen was exposed for 455 hr to 1200 F flowing sodium prior to application of specimen load. This was done to evaluate a specimen which had a relatively low oxygen level.
- (3) Control creep experiments in a helium atmosphere; in one of these, creep was monitored by both an externally mounted dial gage and by internal extensometers attached to the gage section.

*During the test period, the specimen was completely immersed in sodium. As indicated above, the room-temperature sodium level was purposely made low to facilitate assembly. To achieve the levels desired in the two cases, it was necessary to design system-component volumes on the basis of sodium thermal-expansion characteristics.

TABLE 4. CREEP DATA FOR ARC-CAST TANTALUM SPECIMENS^(a) EXPOSED TO 1200 F SODIUM

Stress, psi	Length of Test, hr	Time to Reach Indicated Percentage Deformation, hr				Total Deformation, per cent	Minimum Creep Rate, per cent per hr
		0.1	0.2	0.5	1.0		
<u>Standard In-Sodium Exposures^(b)</u>							
20,000 ^(c)	258	2	5	--	--	0.40	<0.0001
22,000	1100	4	240	--	--	0.43	<0.0001
26,000	1090	<1	3	12	264	1.74	0.0007
26,000	934	<1	1.8	7	18	2.00	0.0004
26,000 ^(c)	998	<1	<1	4	130	4.36 ^(d)	0.0012
<u>Special In-Sodium Exposure^(e)</u>							
26,000	1200	<1	<1	<1	7	2.25	0.0003
<u>Control Exposures in Helium</u>							
26,000	600	<1	14	300	--	0.64	0.0003 ^(f)
26,000	547	{ (g)	525	--	--	0.20	0.00006 ^(f)
		{ (g)	(g)	(g)	<1	1.80	0.0005

(a) A control specimen from this group had the following analysis and hardness:

Analysis	
Oxygen	236 ppm
Hydrogen	0.8 ppm
Nitrogen	230 ppm
Carbon	40 ppm
Hardness	
Gage section	Approximately 195 VHN
Grip section	Approximately 170 VHN

(b) Load applied at start of exposure.

(c) The fluid-temperature cycle in these experiments was 160 F. In other sodium tests, it was 80 F.

(d) Part of this relatively high total deformation was incurred during startup periods following power-failure shutdowns.

(e) Load applied after 455 hr to reduce oxygen content of the test piece prior to initial loading.

(f) These creep data obtained by reading internal extensometers attached directly to the gage section of the specimens. All other creep data obtained by reading externally mounted dial gages.

(g) These indicated deformations surpassed during initial loading.

The test material for these experiments was commercial arc-cast tantalum from a single annealing lot; the specimens used had grip portions strengthened as shown in Figure 7. Because of the unusual configuration presented by the grips, it was not possible with the induction annealing equipment available to obtain uniform heating along the entire specimen length. As a result, the specimen gage sections were not completely annealed and, consequently, the specimens displayed higher over-all strength properties than found in Battelle inert-atmosphere creep studies of fully annealed arc-cast tantalum with comparable interstitial contaminant levels.⁽⁸⁾

Table 4 presents creep data from the various experiments indicated above. The most important conclusion indicated by the data is that low-oxygen-level sodium exposure does not have a deleterious effect on the creep behavior of tantalum at the 1200 F level. The data which illustrate this most pointedly are those from the directly comparable 26,000-psi runs in sodium and in inert atmosphere; minimum creep rates for these runs are not significantly different. The conclusion is also confirmed by the fact that posttest inspections of the specimens failed to reveal any unusual corrosion effects which would be expected if the tantalum were susceptible to stress-aggravated corrosion.

In the special sodium exposure, the minimum creep rate was comparable to that observed in the corresponding standard exposures. Since it is certain, in view of the oxygen-partition findings discussed earlier, that the specimen involved had a relatively low oxygen content throughout the stressing period, this result by itself would indicate that interstitial oxygen does not have an important strengthening effect in tantalum. It should be mentioned that the findings⁽²⁾ of the inert-atmosphere creep tests of low-oxygen tantalum which had been pre-exposed to high-purity sodium were similar, in that the minimum-creep-rate values fell nearly within the band established for the original (ungettered) material.

As may be seen from the values listed in Table 4, indicated first-stage creep (and, consequently, total indicated final deformations) of the sodium-exposed specimens was consistently quite high. It should be pointed out that this does not reflect specimen creep behavior but rather is traceable to pin movement upon seating, as referred to previously. Most of the movement generally occurred during a short period at the start of the test, presumably because the pin hole quickly deformed to accommodate the pin, and, consequently, local stresses were lowered to a level which retarded further distortion. Hence, the gross effect was largely confined to first-stage creep. However, since there was a difference between minimum creep rates determined simultaneously by extensometer and by dial gage, it appears that some deformation of the specimen grips and possibly elongation of the pin holes continued as the experiments progressed. Thus, the strengthened grip portions, while drastically reducing false deformations, did not completely eliminate them.

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APPENDIX

CALCULATION OF THE OXYGEN PARTITION
IN TANTALUM-SODIUM SYSTEMS

APPENDIX

CALCULATION OF THE OXYGEN PARTITION
IN TANTALUM-SODIUM SYSTEMS

Several approaches may be used in the calculation of oxygen equilibria. Outlined in this section is the one used to calculate the partition of oxygen in the tantalum-sodium system. This method consists essentially of (1) utilizing data on the solubility of oxygen in sodium and in tantalum to determine activity coefficients for oxygen in both metals, (2) calculating free-energy changes for reactions and hence the equilibrium constants from established free-energy data, and (3) substitution of these values in the proper equation to obtain equilibrium ratios.

Consider the following reaction:

For Reaction (A-1) the standard free energy may be written:

$$\Delta F^\circ = 1/5 (\Delta F_{f\text{Ta}_2\text{O}_5}^\circ) - (\Delta F_{f\text{Na}_2\text{O}}^\circ) \quad , \quad (\text{A-2})$$

$$\Delta F^\circ = -RT \ln K_a, \quad K_a = e^{\frac{-\Delta F^\circ}{RT}} \quad (K_a = \text{activity equilibrium constant}) \quad . \quad (\text{A-3})$$

Making the assumption which generally applies to metal-oxygen systems that oxygen dissolves monatomically in the metals, then Reaction (A-1) so far as activities are concerned may be written:

From this,

$$K_a = \frac{(a_{\text{Na}})^x (a_{\text{O in Ta}})}{(a_{\text{O in Na}}) (a_{\text{Ta}})^y} \quad . \quad (\text{A-5})$$

Assuming Raoult's law and Henry's law to apply:

$$a_{\text{Na}} = X_{\text{Na}} \approx 1 \quad (\text{A-6})$$

$$a_{\text{Ta}} = X_{\text{Ta}} \approx 1 \quad (\text{A-7})$$

$$a_{\text{O in Ta}} = (\gamma_{\text{O in Ta}}) (X_{\text{O in Ta}}) \quad (\text{A-8})$$

$$a_{\text{O in Na}} = (\gamma_{\text{O in Na}}) (X_{\text{O in Na}}) \quad , \quad (\text{A-9})$$

where $(\gamma_{\text{O in Ta}})$ and $(\gamma_{\text{O in Na}})$ are the activity coefficients (Henry's law constants). These constants may be evaluated by the use of data for oxygen solubility in sodium and tantalum. With an oxygen content above or equal to the saturation level for either metal at any given temperature, the oxygen is precipitated as an oxide in the form of a crystalline solid. Since the activity of the oxygen in the oxide phase (crystalline solid) is unity, it must also be unity for the dissolved oxygen if the system is at equilibrium.

Then by substituting atomic fractions at the saturation level into $a = 1 = \gamma X_{\text{O in metal, sat.}}$, an expression for γ is obtained:

$$\gamma = 1/X_{\text{O in metal, sat.}} \quad (A-10)$$

Substituting the values of Equations (A-6), (A-7), (A-8), and (A-9) into Equation (A-5) yields:

$$K_a = \frac{(\gamma_{\text{O in Ta}})(X_{\text{O in Ta}})}{(\gamma_{\text{O in Na}})(X_{\text{O in Na}})} \quad (A-11)$$

Then below saturation, the equilibrium ratio would be

$$\frac{X_{\text{O in Ta}}}{X_{\text{O in Na}}} = \frac{(K_a)(\gamma_{\text{O in Na}})}{\gamma_{\text{O in Ta}}} \quad (A-12)$$

Since 1 ppm oxygen in sodium is equivalent to $X_{\text{O in Na}}$ of 1.437×10^{-6} and 1 ppm oxygen in tantalum is equivalent to $X_{\text{O in Ta}}$ of 1.136×10^{-5} , then to convert to a weight basis,

$$\frac{\text{ppm O in Ta}}{\text{ppm O in Na}} = \frac{K_a(\gamma_{\text{O in Na}})(1.437 \times 10^{-6})}{(1.136 \times 10^{-5})(\gamma_{\text{O in Ta}})} = \frac{K_a(\gamma_{\text{O in Na}})(0.1262)}{(\gamma_{\text{O in Ta}})} \quad (A-13)$$

Tables A-1, A-2, and A-3 present calculated values for K_a , γ_{O} , and equilibrium ratios; the latter values are presented in Figure 5 in the text.

A-3 and A-4

TABLE A-1. CALCULATED VALUES OF K_a FOR TANTALUM-OXYGEN-SODIUM SYSTEMS FROM EQUATIONS (A-2) AND (A-3)

Temperature		Standard Free-Energy of Formation, ΔF_f° , cal per mole		Standard Free-Energy Change, ΔF° , cal			Activity Equilibrium Constant, K_a		
K	F	Ta ₂ O ₅ , ± 650	Na ₂ O, ± 1900	Maximum	Nominal	Minimum	Maximum	Nominal	Minimum
700	801	-414,050	-75,900	-8,940	-6,910	-4880	610	147	33
800	981	-403,750	-72,400	-10,380	-8,350	-6320	690	191	53
900	1161	-393,600	-69,000	-11,750	-9,720	-7690	720	230	74
1000	1341	-383,550	-65,500	-13,240	-11,210	-9180	780	284	101

(a) All ΔF_f° data are from Reference (9). Three values of K_a (maximum, nominal, and minimum) are calculated to allow for the uncertainties established for the ΔF_f° data in Reference (9).

TABLE A-2. CALCULATED VALUES OF y_O FOR TANTALUM-OXYGEN-SODIUM SYSTEMS FROM EQUATION (A-10)

Temperature		X_O in Ta, sat. (a), atomic fraction	y_O in Ta	X_O in Na, sat. (b), atomic fraction	O in Na
K	F				
700	801	0.005	200	0.00105	952
800	981	0.008	125	0.0026	385
900	1161	0.011	90.9	0.0055	181.8
1000	1341	0.014	71.4	0.0100	100.0

(a) From Reference (5), all values extrapolated.

(b) From Reference (3), values for 900 and 1000 K extrapolated.

TABLE A-3. CALCULATED VALUES OF EQUILIBRIUM RATIOS FOR TANTALUM-OXYGEN-SODIUM SYSTEMS FROM EQUATION (A-13)

Temperature		Activity Equilibrium Constant, K_a	Activity Coefficient		Equilibrium Ratio, ppm O in Ta/ppm O in Na
K	F		y_O in Na	y_O in Ta	
700	801	610	952	200	357
		147			88.4
		33			19.8
800	981	690	385	125	268
		191			74.4
		53			20.6
900	1161	720	181.8	90.9	182
		230			58.2
		74			18.7
1000	1341	780	100.0	71.4	138
		284			50.2
		101			17.8