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**EFFECT OF OXYGEN, HEAT TREATMENT, AND
TEST TEMPERATURE ON THE COMPATIBILITY
OF SEVERAL ADVANCED REFRACTORY
ALLOYS WITH LITHIUM**

C. E. Sessions
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OAK RIDGE NATIONAL LABORATORY

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METALS AND CERAMICS DIVISION

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C. E. Sessions and J. H. DeVan

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APRIL 1971

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ABSTRACT

The niobium alloys D-43, B-66, FS-85, Cb-752, and Cb-753 and the tantalum alloy T-111 were tested in static lithium at 500 and 1000°C. The compatibility of the alloys with lithium was examined from the standpoint of the oxygen content and prior heat treatment of each alloy. Specimens of the alloys were internally oxidized at 1000°C under partial pressure of 9×10^{-5} torr O_2 to produce concentrations of 100 to 3000 ppm O. Some of these specimens were then heat treated in vacuum at 1000, 1300, and 1600°C. Oxygen-contaminated specimens exposed to lithium without prior heat treatment exhibited Widmanstätten precipitates at 500°C for high oxygen concentrations and heavy intergranular attack at 1000°C for all levels of oxygen contamination. The susceptibility to attack of these oxidized alloys that had not been heat treated was eliminated by a heat treatment at 1300 to 1600°C before exposure to lithium. We attribute the resistance to corrosion afforded by heat treating the contaminated alloys to homogenization and subsequent precipitation of the oxygen present as either hafnium or zirconium oxide. Corrosion induced by oxygen was greatest in the case of T-111, and the susceptibility of the niobium alloys increased in the order FS-85, B-66, D-43, Cb-752, and Cb-753.

Hydrogen embrittlement and cracking of the alloys was encountered during decontamination after testing when either water or alcohol was used to remove the residual lithium films from the test coupons. Samples that were recrystallized and exposed to lithium at 1000°C were more susceptible to hydrogen embrittlement than samples exposed to lithium at 500°C. Hydrogen embrittlement could be eliminated by removing the residual lithium by vacuum distilling or by organic solvents that react more slowly than alcohol.

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INTRODUCTION

Niobium and tantalum alloys show promise as construction materials for nuclear reactors that will operate at high temperatures, particularly for those being developed for space power applications. Alloys of both metals afford excellent strength at high temperature, fabricability, and thermal stability in vacuum. In addition, they are among the most corrosion-resistant materials available for heat-transfer circuits that contain alkali metals.

The corrosion of refractory metals by lithium has been studied for several years as part of the development of lithium-cooled nuclear power systems for space.¹ Early screening studies^{2,3} showed that niobium was quite resistant to dissolutive attack by lithium to at least 1000°C. The solubility of niobium in lithium increases with temperature between 760 and 1425°C (refs. 4-6), but does not exceed 10 ppm if the nitrogen content of the lithium is below about 100 ppm (ref. 5). However, the presence of oxygen as an interstitial impurity in either niobium or tantalum may lead to catastrophic attack in lithium above 200°C.

We evaluated the effects of oxygen contamination of niobium and tantalum alloys on their resistance to corrosion by lithium. Test variables included alloy composition, heat treatment, and test temperature.

¹E. M. Douthett, "The Snap-50/SPUR Program," pp. 541-560 in Space Power Systems Engineering, ed. by G. C. Szego and J. E. Taylor, vol. 16 in the series Progress in Astronautics and Aeronautics, Academic Press, New York, 1966.

²E. E. Hoffman, Corrosion of Materials by Lithium at Elevated Temperatures, ORNL-2924, pp. 3-8 (October 3, 1960).

³M. S. Freed and K. J. Kelly, Corrosion of Columbium Base and Other Structural Alloys in High Temperature Lithium, PWAC-355 (June 22, 1961).

⁴H. Leavenworth, R. E. Cleary, and W. D. Bratton, Solubility of Structural Metals in Lithium, PWAC-356 (1961).

⁵R. E. Cleary, S. S. Blecherman, and J. E. Corliss, Solubility of Refractory Metals in Lithium and Potassium, TIM-850 (October 1965).

⁶R. L. McKisson et al., Solubility Studies of Ultra Pure Transition Elements in Ultra Pure Alkali Metals - Final Report, AI-65-210 (March 21, 1966).

PREVIOUS STUDIES

When exposed to lithium above 800°C, all but the most reactive refractory metals lose oxygen rapidly to lithium, the rate depending on the exposure temperature. In the case of niobium and tantalum, the movement of oxygen out of the alloy may be accompanied by penetration of lithium into the alloy to form a complex oxide phase along grain boundaries and {110} crystallographic planes adjoining exposed surfaces.^{2,3,7} Lithium penetrates the alloy only when the oxygen concentration in the refractory metal exceeds a threshold level of 300 to 500 ppm; hence, attack occurs only during the time required to reduce the oxygen concentration below this level.

The addition of zirconium to niobium markedly affects the susceptibility of niobium to this oxygen-induced attack. One percent zirconium reduces the oxygen solubility of niobium from 6000 ppm (ref. 8) to 180 ppm (ref. 9) at 1200°C. Thus, the concentration of oxygen in solid solution in the Nb-1% Zr alloy can be controlled to a relatively low level by proper heat treatment. Generally, a 1-hr heat treatment at 1300 to 1600°C before exposure to lithium is adequate to precipitate dissolved oxygen as ZrC₂ and produce a corrosion-resistant alloy. Without this stabilizing heat treatment, attack by lithium can be induced by oxygen contamination during welding² or by adding oxygen to the alloy at 1000°C (ref. 7).

¹J. R. DiStefano, Corrosion of Refractory Metals by Lithium, ORNL-3551 (March 1964). M.S. Thesis, the University of Tennessee.

²A. V. Lenel and W. R. Hulsizer, The Strengthening of Columbium and Columbium Alloy by Interstitial Alloying Elements, AROD-2530-2 (July 31, 1963).

³V. C. Marcotte and W. L. Larsen, J. Less-Common Metals 10, 229-236 (1966).

The stoichiometry of the ZrO_2 oxide implies that 3300 ppm O could be tied up by 1% Zr in niobium. Studies^{7,10,11} in which oxygen was deliberately added to Nb-1% Zr verified that the alloy resists attack by lithium up to about 3000 ppm O but that it is attacked above this oxygen level. The status of the effect of alloying on the resistance of refractory alloys to corrosion in lithium was reviewed in 1967 by DeVan, Litman, DiStefano, and Sessions.¹²

Brehm, Gregg, and Li¹³ investigated the penetration of lithium into oxygen-doped bicrystals of niobium as a function of temperature (800 to 1050°C) and bicrystal tilt orientation (6 to 33°). They reported that the penetration of lithium into niobium (1) followed parabolic kinetics (i.e., square root of the exposure time), (2) yielded an activation energy of 70,000 cal/mole, and (3) was anisotropic with respect to the crystallographic orientation. These authors proposed that penetration represents the growth of a Li-Nb-O corrosion product within the niobium and that the rate of growth is controlled by the rate at which lithium diffuses through the corrosion product.

Klueh¹⁴ criticized the proposed diffusion model on the basis that it predicts a reduction in the penetration rate for increasing oxygen concentrations in the refractory metal, which is contrary to experimental

¹⁰C. E. Sessions, "Corrosion of Advanced Refractory Alloys in Lithium," pp. 143-148 in NASA-AEC Liquid Metals Information Meeting, held in Gatlinburg, Tennessee, April 21-23, 1965, CONF-650411 (September 1966).

¹¹R. E. Cleary, "Corrosion Studies of Refractory Metals in Lithium," AEC-NASA Liquid Metals Information Meeting, held in Gatlinburg, Tennessee, April 21-23, 1965, TID-22353 (Confidential).

¹²J. H. DeVan, A. P. Litman, J. R. DiStefano, and C. E. Sessions, "Lithium and Potassium Corrosion Studies with Refractory Metals," pp. 675-697 in Alkali Metal Coolants, International Atomic Energy Agency, Vienna, 1967.

¹³W. F. Brehm, J. L. Gregg, and Che-Yu Li, Trans. Met. Soc. AIME 242, 1205-1210 (1968).

¹⁴R. L. Klueh, Penetration of Refractory Metals by Alkali Metals, ORNL-TM-2836 (April 1970).

observations. In addition, the diffusion model is not in accord with the relatively rapid penetration rates observed at low temperatures (about 500°C). Klueh proposed an alternate model¹⁴ that also attributes penetration to a corrosion-product oxide but suggested that the growth rate is controlled by a mechanical wedging process. According to this model, lithium is supplied to the corrosion front either by capillary action along the penetration path or by suction due to a lower pressure at the corrosion front. This model is in accord with the observation that penetration depths increase with increasing oxygen content in the alloy and also accounts for the relatively fast penetration rates observed at lower temperature.

TEST PROCEDURE

The sources and compositions of the alloys used for this study are listed in Table 1. Generally, the alloys were stress-relieved sheet that we machined into test coupons about $1.5 \times 0.5 \times 0.030$ to 0.060 in. One coupon of each alloy was tested as received. Other coupons were doped with oxygen in a modified Sievert's apparatus by the procedure described in Appendix A. The coupons were doped in pairs, and one coupon from each pair was subsequently heat treated at 1300°C and 10^{-7} to 10^{-9} torr in the vacuum furnace shown in Fig. 1. Additional coupons of some alloys were similarly heat treated at 1600°C.

The lithium used for these tests was from a single batch that had been hot gettered¹⁵ to remove nitrogen and oxygen and then stored in type 347 stainless steel containers. Typical comparative analyses of the lithium before tests are given in Table 2.

Each test coupon was loaded into a capsule about 5 in. long $\times$ $3/4$ in. in diameter. The capsules were placed inside an argon-filled glove box, and sticks of lithium that had been cast into a copper chill block from a temperature of about 300°C were added until the capsule was about

¹⁵E. E. Hoffman, "Solubility of Nitrogen and Oxygen in Lithium and Methods of Lithium Purification," pp. 195-206 in Symposium on Newer Metals Spec. Tech. Publ. 272, American Society for Testing and Materials, Philadelphia, 1959.

Table 1. Chemical Composition of Refractory Alloys
Used in Studies of Lithium Corrosion

Alloy	Chemical Composition, wt %										
	Nb	Ta	W	Zr	Mo	V	Hf	C	O	N	H
D-43 ^a	Bal		9.4	0.95				0.093	0.0032	0.0032	0.0008
B-66 ^b	Bal			1.02	4.88	4.61		0.0045	0.018	0.0011	0.0008
FS-85 ^c	Bal	27.73	10.15	0.83				0.003	0.014	0.0039	0.0002
Cb-752 ^d	Bal		9.6	2.8				0.007	0.0071	0.0078	0.0004
Cb-753 ^d	Bal			1.1		5.1		0.004	0.0170	0.0076	0.0006
T-111 ^b		Bal	7.5				1.9	0.007	0.0053	0.0029	0.0004

^aMaterial supplied by E. I. du Pont de Nemours and Company.

^bMaterial supplied by Westinghouse Electric Corporation.

^cMaterial supplied by Fansteel Metallurgical Corporation.

^dMaterial supplied by Union Carbide Corporation.

Fig. 1. Induction-Heated Vacuum System Used for Heat Treating to 1600°C.

Table 2. Typical Analyses of Impurities in Lithium
Used for Capsule Tests

Element	Content, ppm	
	Vendors Analysis	ORNL Analysis After Purification ^a
Aluminum	5	4
Calcium		4
Chromium		57
Copper		9
Carbon ^b		~ 100
Iron		26
Magnesium		4
Manganese		26
Molybdenum		< 57
Niobium		< 167
Nitrogen ^c	120	25-75
Nickel		167
Oxygen ^d		300-500
Potassium ^e	600	
Silicon	10	35
Strontium		9
Sodium ^e	150	
Titanium		17
Zirconium		< 17

^aConcentration of most elements determined by semi-quantitative spectrophotographic analysis.

^bDetermined by colorimetric analysis of trapped C₂H₂.

^cDetermined by micro-Kjeldhal technique.

^dDetermined by thermal-neutron activation. [Ref. L. C. Bates, Nucleonics 21(7), 72-75 (1963).]

^eDetermined by flame photometry.

one-third full. The capsules were then sealed by gas tungsten-arc welding in the glove box under 1 atm of argon. The completed capsule assembly is shown schematically in Fig. 2.

We conducted tests of all of the niobium-base alloys in Nb-1% Zr capsules, since we knew this material would not introduce any significant interaction between dissimilar metals that might confuse the evaluation of the refractory-alloy test coupon. For the same reason, we tested T-111 in tantalum capsules. In order to protect the capsules from oxidation during testing, three or four individual capsules were wrapped with two layers of tantalum foil and sealed under argon in an Inconel outer container. The Inconel container was then heated in an air furnace at a constant temperature of either 500 or 1000°C for 100 hr. To avoid contact between the liquid lithium and the test coupon before the test temperature was reached, we inserted the capsules into a hot furnace in an inverted position. When the test temperature was reached, the Inconel container was withdrawn from the furnace, inverted so that the molten lithium came into contact with the test coupon, and then placed back into the furnace. When the test was completed the container was withdrawn from the furnace, inverted to drain the molten lithium from the test coupon, and allowed to cool in air. Residual lithium was removed from the capsule and coupon by placing the bottom half of the capsule, which contained the coupon, in water, ethyl alcohol, or butyl cellosolve. In a few tests, residual lithium was removed by vacuum distillation at 500 to 750°C.

The resistance of each alloy to corrosion by lithium was evaluated by measuring the change in the weight of the specimen, analyzing the specimen for oxygen, nitrogen, hydrogen, and lithium, and examining the specimen metallographically.

TEST RESULTS

Alloy B-66 (Nb-5% Mo-5% V-1% Zr)

Nine coupons of alloy B-66 were tested in lithium. The history before test, chemical analyses, and metallographic observations of these coupons are given in Table 3.

ORNL-DWG 70-7489

Fig. 2. Schematic of Static Capsule.

Table 3. Corrosion Results of Alloy B-66 in Lithium

Condition Before Test ^a	Oxygen Concentration, ppm		Lithium Concentration, ppm		Weight Change (mg/cm ²)	Metallographic Observation
	Before Test	After Test	Before Test	After Test		
<u>Exposed 100 hr at 500°C</u>						
Oxidized	1800	1200	< 5	< 10	+0.002	No attack
Oxidized, heat treated at 1300°C	2000	1100	< 5	< 10	+0.004	No attack
Oxidized	2700	2100	< 5	128	+0.103	0.003-in. platelet attack
Oxidized, heat treated at 1300°C	2700	2600	< 5	< 10	+0.031	No attack
<u>Exposed 100 hr at 1000°C</u>						
Oxidized	1800	250	< 5	39	-5.420	0.010-in. intergranular attack
Oxidized, heat treated at 1300°C	2000	1300	< 5	< 5	-1.391	No attack
Oxidized	2700	340	< 5	11	-3.518	0.015 to 0.020-in. intergranular attack
Oxidized, heat treated at 1300°C	2700	2100	< 5	< 10	-6.839	No attack
Cold worked	110	89	< 5	< 5	+0.074	No attack

^aOxidized coupons were heat treated 2 hr at 1600°C before oxidation.

Exposed to Lithium at 500°C

Oxidized. - No attack was found at the 1800 ppm O level [Fig. 3(a)]; however, Widmanstätten precipitates (i.e., corrosion attack) occurred to a depth of 0.003 in. in the specimen containing 2700 ppm O. All specimens lost oxygen as a result of the exposure to lithium. The lithium concentration of the specimens was negligible except in the specimens that were attacked.

Oxidized and Heat Treated. - No lithium attack or significant change in chemical composition was found at oxygen levels up to 2700 ppm for coupons that were heat treated 2 hr at 1300°C [Fig. 3(b)].

Exposed to Lithium at 1000°C

Cold Worked (No Oxygen Added). - No attack or significant change in interstitial chemistry was found. The received cold-worked structure was retained after exposure to lithium.

Oxidized. - Intergranular and platelet corrosion [Fig. 3(c)] occurred to a depth of 0.010 and 0.020 in. at the 1800 and 2700 ppm O levels, respectively. A large decrease in oxygen concentration and an increase in lithium concentration occurred for the corroded specimens.

Oxidized and Heat Treated. - No attack by lithium occurred at oxygen levels of 2000 or 2700 ppm O after heat treating at 1300°C. However, surface cracks developed as a consequence of hydrogen pickup during removal of lithium [Fig 3(d)].

Alloy D-43 (Nb-10% W-1% Zr-0.1% C)

The results for eight coupons of Alloy D-43 tested in lithium are summarized in Table 4. All D-43 coupons contained a large volume of carbide precipitates before test. Photomicrographs revealed the precipitates to have an acicular form [Fig. 4(a)], typical of specimens annealed above 1600°C (ref. 16).

¹⁶T. K. Roche, "Aging of Columbium Alloy D-43" paper presented at the Annual Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers, Chicago, Illinois, February 14-18, 1965.

Fig. 3. Effect of Oxygen on the Compatibility of Alloy B-66 with Lithium. (a) Sample tested at 500°C as oxidized (1300 ppm O). (b) Sample tested at 500°C, oxidized (2000 ppm O) and heat-treated 2 hr at 1300°C. (c) Sample tested at 1000°C as oxidized (2000 ppm O). (d) Sample tested at 1000°C, oxidized (2000 ppm O) and heat-treated 2 hr at 1300°C.

Table 4. Corrosion Results of Alloy D-43 in Lithium

Condition Before Test ^a	Oxygen Concentration, ppm		Weight Change (mg/cm ²)	Metallographic Observations
	Before Test	After Test		
<u>Exposed 100 hr at 500°C</u>				
Oxidized	1200	1000	-0.029	No attack
Oxidized, heat treated at 1300°C	1300	860	-0.029	No attack
Oxidized	1800	1800	-0.016	0.010-in. platelet attack
Oxidized, heat treated at 1300°C	2300	2000	-0.014	No attack
<u>Exposed 100 hr at 1000°C</u>				
Oxidized	990	380	-0.098	0.004-in. platelet attack
Oxidized, heat treated at 1300°C	1600	710	-0.058	No attack
Oxidized	2000	780	-0.450	0.012-in. platelet and intergranular attack
Oxidized, heat treated at 1300°C	2400	1800	-0.147	No attack

^aOxidized coupons were heat treated 2 hr at 1600°C before oxidation.

Fig. 4. Effect of Oxygen Contamination on Compatibility of Alloy L-43 with Lithium. (a) Coupon before test, oxidized to 2000 ppm O. (b) Coupon after testing 100 hr at 500°C in lithium. Oxygen content before and after exposure was 1800 ppm. (c) Coupon after testing 100 hr at 1000°C. Oxygen content decreased from 2000 ppm initially to 780 ppm after test. 200x.

Exposed to Lithium at 500°C

Oxidized. - No attack occurred at the 1200 ppm O level, but 0.010 in. of transgranular platelet attack was found in the sample that contained 1800 ppm O [Fig. 4(b)]. However, there was no significant loss of oxygen from this specimen.

Oxidized and Heat Treated. - No attack was found in samples that contained either 1300 or 2300 ppm O, but a loss of oxygen was noted.

Exposed to Lithium at 1000°C

Oxidized. - Transgranular attack was observed to a depth of 0.004 in. at the 990 ppm O level. The sample containing 2000 ppm O was attacked to a depth of 0.012 in. Exposure to lithium reduced the oxygen content of both oxidized samples.

Oxidized and Heat Treated. - Heat treatment suppressed attack at oxygen levels of 1600 and 2400 ppm. Both specimens lost oxygen, however.

Alloy Cb-752 (Nb-10% W-2.5% Zr)

The results for nine coupons of Cb-752 are given in Table 5. After test, all but one of the capsules were vacuum distilled to remove the excess lithium. After distillation, several translucent crystals (shown in Fig. 5) were found in the capsule in which the Cb-752 coupon that contained the highest oxygen concentration had been tested. We could not positively identify these minute crystals, but x-ray diffraction produced a pattern that matched some lines of the compounds Li_2O , LiNbO_3 , $\text{Nb}_2\text{O}_5 \cdot 6\text{ZrO}_2$, and LiOH . Although these particular compounds or complexes were not found in any of the other tests of corrosion of niobium-base alloys in lithium, indications are that they were water soluble and, thus, would normally have been lost in tests in which water and organic decontaminants had been used. Vacuum distillation was generally not used to remove lithium after test, because temperatures of about 700°C are needed to obtain reasonable rates of lithium distillation, and this temperature exceeds that of one of the corrosion tests.

Table 5. Corrosion Results of Alloy Ch-752 in Lithium

Conditions Before Test	Interstitial Content, wt %							Weight Change (mg/cm ²)	Metallographic Observations
	Before Test			After Test					
	O	N	H	O	N ^a	H	Li		
				<u>Exposed 100 hr at 500°C</u>					
Oxidized	1600	84	7	1300	440	100	< 10	0	No attack
Oxidized, heat treated at 1300°C	1900	84	7	1200	290	96	< 10	0	No attack
Oxidized	2100	87	4	2400	130	22	< 5	0	0.003 in. of platelet attack
Oxidized, heat treated at 1300°C	2500	97	4	2200	130	7	< 5	+0.23	No attack
				<u>Exposed 100 hr at 1000°C</u>					
Oxidized	1400	86	3	300	150	6	36	-0.34	0.003 to 0.005 in. of intergranular attack
Oxidized, heat treated at 1300°C	1000	84	5	1100	170	8	< 10	0	No attack
Oxidized	2500	86	4	730	120	6	< 10	-0.68	0.003 to 0.005 in. of intergranular attack
Oxidized, heat treated	3000	89	4	2200	620	70	< 5	0	0.010 to 0.015 in. of transgranular cracks ^b
Recrystallized at 1600°C	71	78	4	95	170	3	< 10	0	No attack

^aIncreases in nitrogen resulted from the presence of nitrogen in lithium.

^bResult of hydrogen embrittlement during lithium decontamination after test.

Fig. 5. Translucent Crystals from Vacuum Distillation of Lithium Residue of Cb-752 Test Coupon. About 35X.

The lithium used for testing alloy Cb-752 contained an unusually high nitrogen concentration, but x-ray diffraction did not reveal any nitrogen compounds in the crystals formed by distillation.

Exposed to Lithium at 500°C

Oxidized. - No attack or significant loss of oxygen occurred in the specimen that contained 1600 ppm O. The coupon that contained 2100 ppm O suffered 0.003 in. of transgranular platelet attack and did not lose oxygen.

Oxidized and Heat Treated. - No attack was found at either oxygen level for coupons heat treated at 1300°C, although the oxygen contents of the coupons decreased. The weight gain of 0.23 mg/cm² reported for the sample with higher oxygen content appears abnormally large and may reflect an error in weighing.

Exposed to Lithium at 1000°C

Oxidized. -- Intergranular attack to a depth of 0.003 to 0.005 in. occurred for samples with both 1400 and 2500 ppm O. Both samples lost weight and decreased in oxygen concentration.

Oxidized and Heat Treated. -- No attack occurred at either oxygen level for coupons heat treated at 1300°C. The sample with 3000 ppm O was embrittled as a consequence of hydrogen pickup during lithium decontamination after test and was severely cracked, as discussed below.

Alloy FS-85 (Nb-28% Ta-10% W-1% Zr)

Table 6 summarizes the corrosion results for eleven coupons of alloy FS-85 tested in lithium at 500 and 1000°C.

Exposed to Lithium at 500°C

Oxidized. -- No attack was observed in the sample that contained 1200 ppm O, but 0.005 to 0.010 in. of transgranular platelet attack occurred in the sample that contained 2100 ppm O (see Fig. 5). Both coupons lost about 300 ppm O during exposure to lithium.

Oxidized and Heat Treated at 1300°C. -- No attack or change in oxygen concentration was found up to 2100 ppm O.

Exposed to Lithium at 1000°C

As Received and Recrystallized. -- One coupon of alloy FS-85 was tested in the cold-worked condition, and another coupon was tested after recrystallization at 1600°C. Neither was attacked.

Oxidized. -- Intergranular attack was found to a depth of 0.005 to 0.010 in. and 0.015 in. for the coupons that contained 1200 and 1900 ppm O, respectively [see Fig. 6(b)]. A relatively large loss of oxygen and weight losses greater than 1 mg/cm² were recorded after the 100-hr exposure to lithium.

Table 6. Corrosion Results of Alloy FS-85 in Lithium

Condition Before Test	Oxygen Content Before Test (ppm)	Interstitial Content After Test, ppm				Weight Change (mg/cm ²)	Metallographic Observations
		O	N	H	Li		
<u>Exposed 100 hr at 500°C</u>							
Oxidized	1200	880	51	9	< 3	0	No attack
Oxidized, heat treated at 1300°C	1200	1000		19	< 3	0	No attack
Oxidized	2100	1900	43	10	64	+0.025	0.005 to 0.010 in. of platelet attack
Oxidized, heat treated at 1300°C	2100	2200	48	10	< 3	0	No attack
<u>Exposed 100 hr at 1000°C</u>							
Oxidized	1200	290		190	48	-1.503	0.005 to 0.010 in. of intergranular attack
Oxidized, heat treated at 1300°C	1200	1000	48	59	< 3	-0.025	No attack ^a
Oxidized, heat treated at 1600°C	1300	1100		160	< 3	0	No attack ^a
Oxidized	1900	620	62	21	180	-1.155	0.015 in. of inter- granular attack
Oxidized, heat treated at 1300°C	1900	930	54	70	18	-0.049	Intergranular attack on one end ^b
Cold worked	140	87	46	97	< 3	+0.176	No attack ^a
Recrystallized at 1600°C	140	170		140	< 3	+0.087	No attack ^a

^a Specimen exhibited a few transgranular cracks due to hydrogen embrittlement.

^b Attack probably the result of excessive oxygen concentration at this end which exceeded the ZrO₂ stoichiometry.

Fig. 6. Effect of Oxygen Contamination on Compatibility of Alloy FS-85 with Lithium. (a) Tested at 500°C as oxidized. Oxygen decreased from 1200 to 880 ppm. (b) Higher oxygen sample tested at 500°C as oxidized. Oxygen decreased from 2100 to 1900 ppm. (c) Tested at 1000°C as oxidized. Oxygen decreased from 1200 to 290 ppm. (d) Higher oxygen sample tested at 1000°C as oxidized. Oxygen decreased from 1900 to 620 ppm. 100X. Reduced 44%.

Oxidized and Heat Treated. - Heat treatment at either 1300 or 1600°C made samples of alloy FS-85 that contained 1300 ppm O resistant to corrosion. However, a coupon that contained 1900 ppm O and that had been heat treated at 1300°C showed a slight amount of intergranular attack on one end, a significant depletion from 1900 to 930 ppm O, and a moderate weight loss of 0.05 mg/cm².

Several of the coupons tested at 1000°C suffered hydrogen pickup and subsequent cracking during lithium decontamination after test. However, no embrittlement due to hydrogen resulted in the case of tests at 500°C.

Alloy Cb-753 (Nb-5% V-1.25% Zr)

Test results for six coupons of alloy Cb-753 are given in Table 7. Our evaluation of oxidized specimens was restricted to only one oxygen level, about 2000 ppm.

Table 7. Corrosion Results of Alloy Cb-753 in Lithium

Condition Before Test	Oxygen		Nitrogen		Weight Change (mg/cm ²)	Metallographic Observations
	Concentration, ppm		Concentration, ppm			
	Before Test	After Test	Before Test	After Test		
<u>Exposed 100 hr at 500°C</u>						
As received ^a	170	160	76	81	0	No attack
Oxidized	2100	2200	110	88	0	No attack
Oxidized, heat treated at 1300°C	1900	2100	100	97	0	No attack
<u>Exposed 100 hr at 1000°C</u>						
As received ^a	170	87	76	81	0	No attack
Oxidized	2000	450	86	90	-0.5	0.005 to 0.010 in. of intergranular attack
Oxidized, heat treated at 1300°C	1600	1400	100	110	0	No attack

^aMaterial had been recrystallized at 1150°C by the vendor.

Exposed to Lithium at 500°C

No attack or change in interstitial chemistry occurred at any of three different specimen conditions: as received (recrystallized), oxidized, or oxidized and heat treated.

Exposed to Lithium at 1000°C

As Received (Recrystallized). - No attack occurred, although the oxygen content dropped from 170 to 87 ppm.

Oxidized. - Intergranular attack was found to a depth of 0.005 to 0.010 in., and oxygen was depleted from 2000 to 450 ppm.

Oxidized and Heat Treated. - After heat treatment for 2 hr at 1300°C, the oxidized coupon showed no attack or change in oxygen concentration.

Alloy T-111 (Ta-8% W-2% Hf)

The effect of oxygen additions on the behavior of T-111 in lithium is summarized in Table 8.

Exposed to Lithium at 500°C

Oxidized. - Attack in the form of transgranular Widmanstätten platelets occurred to a depth of 0.015 to 0.020 in. for samples that contained 1500 ppm O, as shown in Fig. 8(a). Similar attack to a depth of 0.030 in. was found at the 2500 ppm O level. Slight loss of oxygen and increase in lithium concentration were noted in all oxidized samples.

Oxidized and Heat Treated. - No attack was found for either 920 or 2100 ppm O in coupons heat treated at 1300°C [Fig. 8(b)].

Exposed to Lithium at 1000°C

As Received and Recrystallized. - No attack was found for coupons of T-111 tested in either the cold-worked or recrystallized condition. However, the 100 ppm O in these specimens before test was reduced to about 50 ppm after 100 hr.

Table 8. Corrosion Results of Alloy T-111 in Lithium

Condition Before Test	Oxygen Concentration, ppm		Lithium Concentration After Test (ppm)	Weight Change (mg/cm ²)	Metallographic Observations
	Before	After			
<u>Exposed 100 hr at 500°C</u>					
Oxidized	1500	1200	634	-0.013	0.015 to 0.020 in. of platelet attack ^a
Oxidized, heat treated at 1300°C	920	910	< 5	+0.007	No attack
Oxidized	2500	2400	798	-8.63	0.030 in. of platelet attack ^a
Oxidized, heat treated at 1300°C	2100	1800	< 5	+0.186	No attack
<u>Exposed 100 hr at 1000°C</u>					
Oxidized	1500	160	68	-0.833	0.030 in. of intergranular attack ^a
Oxidized, heat treated at 1300°C	920	1300	< 5	-2.146	0.005 to 0.010 in. of trans-granular cracks ^b
Oxidized	2500	300	27	c	0.030 in. of intergranular attack ^a
Oxidized, heat treated at 1300°C	1800	1400	< 5	+0.186	No attack
Oxidized, heat treated at 1600°C	1700	1300		+0.437	No attack
Cold worked	54	47	< 5	+0.015	No attack
Recrystallized at 1600°C	94	40	< 5	+0.059	No attack

^aComplete penetration for a 0.060-in.-thick sample = 0.030 in.

^bResult of hydrogen embrittlement during lithium decontamination after test.

^cGross corrosion reduced specimen to powdered remains.

Fig. 8. Effect of Oxygen on Compatibility of Alloy T-111 with Lithium. (a) Tested at 500°C, as oxidized. Oxygen decreased from 1500 to 1200 ppm. (b) Tested at 500°C, oxidized (920 ppm) and heat treated 2 hr at 1300°C. (c) Tested at 1000°C, as oxidized. Oxygen decreased from 1600 to 160 ppm. (d) Tested at 1000°C, oxidized (920 ppm) and heat treated 2 hr at 1300°C.

Oxidized. - Complete intergranular penetration to a depth of 0.030 in. occurred at oxygen concentrations of 1500 ppm [Fig. 8(c)] and 2500 ppm. After testing, the oxygen concentrations in these samples were 160 and 300 ppm, respectively.

Oxidized and Heat Treated. - No attack was observed in any of the contaminated coupons heat treated before exposure to lithium, nor was any significant change in oxygen concentration recorded. However, the specimens were found to be particularly susceptible to hydrogen embrittlement during lithium decontamination after test [Fig. 8(d)], as discussed below.

DISCUSSION OF RESULTS

In analyzing the present results, it is important to recognize that, while oxygen effects have been correlated in terms of bulk oxygen concentrations, a gradient in oxygen concentration existed between the surface and center of those specimens to which oxygen was added before test. (The oxidizing conditions and nature of the oxygen gradient are discussed in Appendix A.) Because the surface concentration exceeded the bulk concentration, we have tended to overestimate the effect of oxygen in these experiments. For example, from results for Nb-1% Zr given in Appendix A, we estimated that bulk samples that contain an average concentration of 2000 ppm O would have had a surface concentration of 3000 to 4000 ppm O. Thus, one can apply the results here to system design with considerable safety provided he uses the bulk oxygen concentrations in this study to establish maximum permissible concentrations at any one point in the system.

A summary of the results for the oxidized refractory alloys at 500 and 1000°C is given in Tables 9 and 10, respectively. Niobium-base alloys with concentrations of 1200 to 1800 ppm O were not attacked by lithium at 500°C. In contrast, the tantalum alloy exhibited platelet attack at 500°C at concentrations of 1500 ppm O and higher; however, the T-111 alloy was not attacked at 500°C at a concentration of 920 ppm O.

Table 9. Summary of Effect of Oxygen Added at 1000°C on Corrosion of Advanced Refractory Alloys in Lithium at 500°C^a

Alloy	Oxygen Concentration, ppm		Lithium Concentration After Test (ppm)	Depth of Corrosion Attack ^b (in.)
	Before Test	After Test		
				$\times 10^{-3}$
D-43	1200	1000	c	0
	1600	1300	c	3
B-66	1500	1200	< 10	0
	2700	2100	126	12
FS-85	1200	880	< 10	0
	2100	1900	64	5-10
Cb-752	1600	1300	< 10	0
	2100	2400	< 10	3
Cb-753	2100	2200	c	0
T-111	920	910	< 10	0
	1500	1200	634	15-20
	2500	2400	796	30

^a Summary of coupons exposed as oxidized to lithium 100 hr at 500°C.

^b Transgranular Widmanstätten platelet attack.

^c Not analyzed.

Table 10. Summary of Effect of Oxygen Added at 1000°C on Corrosion of Refractory Alloys in Lithium at 1000°C^a

Alloy	Oxygen Concentration, ppm		Lithium Concentration After Test (ppm)	Depth of Corrosion Attack ^b (in.) × 10 ⁻³
	Before Test	After Test		
D-43	990	380	c	4
	2000	780	c	12
B-66	1800	250	39	10
	2700	340	11	15-20
FS-85	1200	290	48	5-10
	1900	620	180	15
Cb-752	1400	300	35	3-5
	2500	730	< 10	3-5
Cb-753	2000	450	c	5-10
T-111	1500	160	68	30 ^d
	2500	300	27	30 ^d

^aSummary of coupons exposed as oxidized to lithium 100 hr at 1000°C.

^bPredominantly intergranular corrosion attack.

^cNot analyzed.

^dComplete penetration for 0.060-in.-thick specimen = 0.030 in.

At the higher concentrations of 1800 to 2700 ppm O, niobium alloys tested at 500°C showed varying amounts (0.003 to 0.012 in.) of transgranular platelet attack.

Chemical analyses of coupons that showed platelet attack at 500°C indicated a loss of oxygen and a significant increase in lithium. Some oxygen was lost from samples that were not attacked, but part of the difference in oxygen concentration before and after test could reflect initial differences in the opposite ends of the coupon from which samples were taken.

At 1000°C, all alloys that received oxygen additions without subsequent heat treatment were attacked, primarily intergranularly (Table 10). The depth of attack increased with increasing oxygen concentration in the alloy. As at 500°C, the effect of oxygen was greater for the tantalum alloy T-111 than for the niobium-base alloys. Oxygen-doped alloys tested at 1000°C lost a very large amount of oxygen and gained a small amount of lithium. Although more oxygen was lost at 1000°C than at 500°C, the increase in lithium that accompanied the intergranular attack at 1000°C was less than that associated with transgranular platelet attack at 500°C.

When niobium- or tantalum-base alloys are exposed to lithium, two processes occur: (1) oxygen diffuses out of the alloy and is gettered by the lithium, and (2) lithium penetrates into the alloy along preferential paths such as grain boundaries and certain crystallographic planes. The transition from a mixed intergranular and transgranular attack at 500°C to predominantly intergranular attack at 1000°C undoubtedly is related to these two processes. These results suggest that there is preferential segregation of oxygen on specific crystallographic planes at lower temperatures and at grain boundaries at higher temperatures.

Attack of oxygen-doped alloys at both 500 and 1000°C was eliminated by heat treating the alloys at 1300°C for 2 hr before they were exposed to lithium. As discussed above under "Previous Studies", this heat treatment precipitated dissolved oxygen from the alloy as either HfO_2 or ZrO_2 .

The absence of attack in heat-treated samples indicates that the initial concentration of oxygen at the surfaces of our oxygen-doped alloys, though greater than the oxygen concentration throughout the bulk of each sample, could not have exceeded the stoichiometric concentration needed to tie up all the available zirconium or hafnium.

The annealing temperature of 1300°C selected for this investigation was based on earlier corrosion studies of Nb-1% Zr in lithium.¹⁷ The latter studies had shown that Nb-1% Zr could be "immunized" against lithium attack by annealing at 1000 to 1600°C, although the lower temperature required annealing times of 8 hr or more. We did not evaluate annealing temperature as a variable in the present work, since the 1300°C temperature proved to be effective for all of the alloys studied. However, in the case of alloy FS-85, examination of a coupon contaminated to 1900 ppm O and heat treated 2 hr at 1300°C showed what appeared to be attack by lithium at 1000°C. We repeated this test and, at the same time, tested coupons of similar composition that had been annealed at 1600°C. We found no lithium attack after either of these annealing treatments.

If we compare the results for the one tantalum-base alloy (T-111) with those for the niobium-base alloys covered by this study, it is apparent that the corrosion resistance of the oxidized tantalum alloy is more adversely affected by oxygen than is that of any of the niobium alloys. This is in agreement with the observation¹⁸ that the threshold oxygen content required to initiate lithium attack is lower in unalloyed tantalum than in unalloyed niobium. This may be because the limit of solubility of oxygen in tantalum is lower, and hence any given weight percentage of oxygen is proportionately closer to the limit of solubility. Or it may be that the corrosion product formed between tantalum, lithium, and oxygen is more stable than its counterpart in niobium.

¹⁷J. R. DiStefano, Corrosion of Refractory Metals by Lithium, ORNL-3551 (March 1964). M.S. Thesis, the University of Tennessee.

¹⁸R. L. Klueh, Penetration of Refractory Metals by Alkali Metals, ORNL-TM-2836 (April 1970).

At 1000°C, the corrosion behavior of oxidized niobium alloys appears to parallel that of unalloyed niobium.¹⁷ All oxidized alloys were penetrated by lithium at the lowest oxygen level tested, 1200 ppm. At 500°C, however, lithium did not penetrate niobium alloys that contained 1200 to 1800 ppm O even when the alloys had received no heat treatment. Under the same temperature conditions, unalloyed niobium that contained 1000 ppm O was penetrated transgranularly by lithium.¹⁷ Thus there appears to be some interaction between zirconium and oxygen in these oxidized niobium alloys at 500°C. This interaction, however, is not as apparent at 1000°C. The existing model of lithium corrosion, based on the behavior of niobium and Nb-1% Zr, does not predict corrosion resistance for contaminated alloys at 500°C. This deficiency in the model reflects the fact that few data exist for oxygen levels of about 1000 ppm and for exposure to lithium at 500°C even for Nb-1% Zr. One must conclude on the basis of these present data on advanced refractory alloys that the interaction of zirconium and oxygen atoms (or hafnium and oxygen atoms) in the oxidized condition is strong enough to inhibit lithium attack at lower oxygen levels (about 1000 ppm) at 500°C but not at 1000°C.

In our examination of oxygen effects, we encountered some difficulty in discriminating between damage from lithium attack and that resulting from the dissolution of lithium residing on the specimen after test. The latter damage was in the form of transgranular and intergranular cracking and resulted from the uptake of hydrogen generated by the reaction of lithium with either water or alcohol. Our observations concerning the nature of this problem of hydrogen embrittlement and the conditions that caused it are discussed in Appendix B.

A considerable amount of work has been reported¹⁹⁻²⁶ concerning hydrogen embrittlement of refractory alloys. Experimenters at

¹⁹Robert J. Walter, The Columbium-Hydrogen System and Hydrogen Embrittlement of Columbium, Rocketdyne Research Report No. 64-6 (February 1964).

²⁰Robert J. Walter, Compatibility of Tantalum and Columbium with Hydrogen, Rocketdyne Research Report No. 65-3 (February 1965).

Rocketdyne¹⁹⁻²² (division of North American Aviation, Inc.) evaluated the compatibility of Ta-10% W and alloy B-66 with hydrogen over a wide temperature range. Unstressed Ta-10% W cracked in a hydrogen atmosphere whenever a freshly exposed metal surface was created. The investigators found that samples would fragment in hydrogen under the following conditions: (1) thermal cycling hydrogen-doped samples of Ta-10% W in helium, (2) introducing hydrogen over the sample at room temperature, and (3) scratching or filing the sample to expose a fresh surface to hydrogen. The authors explain^{21,22} that under certain conditions both B-66 and Ta-10% W could be made to absorb hydrogen at room temperature and that this absorption often resulted in general disintegration of the sample. If a completely clean or newly made surface was exposed to hydrogen at room temperature, the sample fragmented. The fragmentation created new surfaces for continued fragmenting. Whether or not actual formation of hydride at room temperature was responsible for the cracking was not stated.

The Rocketdyne observations concerning fragmentation and our observations concerning cracking during lithium decontamination after test may be related, since both indicate a susceptibility for propagation of

²¹R. J. Walter and J. A. Ytterhus, Compatibility of Columbium with Hydrogen Quart. Prog. Rept., Rocketdyne Report R-6345-2 (January 1966).

²²R. J. Walter and W. T. Chandler, "Compatibility of Tantalum and Columbium Alloys with Hydrogen," AIAA J. 4(2), 304-307 (February 1966).

²³B. Longson, The Hydrogen Embrittlement of Niobium, TRG-1035 (C) (1966).

²⁴W. M. Albrecht et al., J. Electrochem. Soc. 106(11), 981 (1959).

²⁵Albert G. Ingram et al., Notch Sensitivity of Refractory Metals, ASD-TR-61-474 (August 1961).

²⁶J. R. Stephens and R. G. Gorlick, Compatibility of Tantalum, Columbium, and Their Alloys with Hydrogen in Presence of Temperature Gradient, NASA-TN D3546 (August 1966).

cracks in tantalum and niobium when fresh, clean surfaces are exposed to a hydrogen atmosphere.

Longson²³ in studies of niobium found that the concentration of hydrogen that caused embrittlement obeyed an Arrhenius equation that gave an activation energy for hydrogen embrittlement of 3 kcal/mole. Interestingly, the activation energy for hydride formation in niobium was found to be 3.2 kcal/mole. Longson, however, concluded that it was unlikely that embrittlement resulted solely from hydride formation, since the hydrides were stable only over a narrow temperature range compared to that over which embrittlement occurred. Nevertheless, the similar activation energy for hydride formation and embrittlement does imply a common mechanism that is not due to hydrogen diffusion, which has an activation energy of 9.4 kcal/mole (ref. 24).

Several investigators^{20,23,25} have reported embrittlement of one type or another in either tantalum or niobium alloys before formation of a visible second phase. Thus, hydrogen in solution appears to be a sufficient condition to induce embrittlement.

As noted in Appendix B, we measured a small temperature increase (70°C or less) at the surface of specimens coated with lithium and then immersed in water at room temperature. The small thermal stresses associated with this temperature rise and the complete absence of external stresses suggest that cracking was induced by some form of internal stress. Possible sources include any volume changes as a result of hydrogen uptake or internal conversion of hydrogen to methane or water vapor. The latter possibility seems dubious in view of the zirconium or hafnium alloying additions which were available for reaction with oxygen and carbon, particularly in samples heat treated at 1300°C before test. However, the concentrations of interstitial impurities in solution in these alloys may affect the levels of hydrogen needed to induce embrittlement. This would explain why the specimens exposed to lithium at 1000°C were more sensitive to hydrogen embrittlement than those exposed at 500°C.

CONCLUSIONS

Oxygen and test temperature have the following effects on the resistance of advanced refractory alloys to corrosion:

1. Advanced niobium alloys with 1000 to 1800 ppm O had a resistance to lithium attack at 500°C that was not predicted by the current model for corrosion. We believe this resistance results from an interaction between oxygen and zirconium that changes as a function of test temperature.
2. At higher oxygen levels, corrosion at 500°C was both trans-crystalline and intergranular, while the attack at 1000°C was predominantly intergranular.
3. Heat treatment at 1300°C produced resistance to corrosion in all cases except one anomalous test of alloy FS-85 with 1900 ppm O.
4. Hydrogen pickup during decontamination can be a significant problem with advanced niobium- and tantalum-base alloys when rapid reactions that produce hydrogen are operative.

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APPENDIX A

Oxidation Procedure

The method used for adding oxygen to the coupons before test was patterned after that developed by DiStefano²⁷ for oxidizing specimens of niobium, tantalum, and Nb-1% Zr. Test coupons were placed inside a mullite tube furnace that was then evacuated to 9×10^{-7} torr and heated to 1000°C. Pure oxygen was bled into the furnace at a rate controlled to maintain a steady pressure of 9×10^{-5} torr. Coupons were exposed to this oxygen pressure for 2 to 4 hr depending on the desired oxygen level, and then the coupons were moved from the furnace zone of the mullite tube into a region near room temperature. Oxygen uptake by the coupons was estimated by weight measurements before and after the coupons were heated and was confirmed by chemical analysis.

While this oxidizing treatment produces a homogeneous distribution of oxygen in unalloyed niobium and tantalum, an oxygen gradient is produced in alloys that contain active elements such as zirconium and hafnium. Thus the oxidized coupons used in this investigation contained a higher oxygen concentration near the surface than the average oxygen concentration reported for each coupon.

Although we did not specifically determine the initial oxygen gradients in the present study, a previous evaluation of the oxygen distribution in Nb-1% Zr by DiStefano²⁸ is of value in assessing the present results. Table 11 gives the results of analyses made to determine the oxygen gradient on both a sheet and a tubing sample of Nb-1% Zr oxidized at 1000°C for 2 hr at an oxygen partial pressure of 9×10^{-5} torr. Incremental layers 0.005 in. thick were machined off the oxidized specimens and analyzed for oxygen by the vacuum fusion technique. The results indicated that oxygen was nonuniformly distributed.

²⁷J. R. DiStefano, Corrosion of Refractory Metal by Lithium, ORNL-3551 (March 1964).

²⁸J. R. DiStefano, personal communication, February 1964.

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Table 11. Oxygen Gradient in Nb-1% Zr^a

Depth of Machined Increment (in.)	Oxygen Concentration, ppm	
	After Oxidation	After 2 hr at 1300°C
$\times 10^{-3}$		
	<u>Sheet Specimens</u>	
0-5	2500	2400
5-10	2400	2300
10-15	1700	1800
15-20	1400	1200
20-25	1100	1100
25-30	990	1100
30-35	940	1100
35-40	1100	1100
40-45	1300	1300
45-50	1600	1700
50-55	2200	2400
55-65	<u>2500</u>	<u>3100</u>
	Average 1640	1717
	<u>Tube Specimens</u>	
0-5	4000	3000
5-10	3400	3100
10-15	2700	2800
15-20	2500	2600
20-25	2200	1700
25-30	1600	1100
30-35	1100	690
35-40	970	460
40-45	670	410
45-50	<u>490</u>	<u>390</u>
	Average 1960	1625

^aDuplicate samples oxidized at 1000°C under a partial pressure of 9×10^{-5} torr (turnings taken after oxidation on one sample and after postoxidation heat treatment of the other).

Furthermore, heat treating these same samples for 2 hr at 1300°C before machining the incremental layers did not reduce the oxygen gradient.

Based on the results for Nb-1% Zr, we can assume that an oxygen gradient existed in all oxidized samples at the start of the present tests, since every alloy contained either zirconium or hafnium. The major difficulty associated with this inhomogeneous oxygen distribution, of course, is in attempting to correlate the depth of attack with the average oxygen concentration in the alloy. However, such a gradient is representative of the condition that would exist in a refractory metal contaminated during welding or during annealing in the range 1000 to 1600°C. Also, the oxygen concentrations in this study were not so high that the surface concentrations exceeded what could be effectively tied up as ZrO_2 or HfO_2 . This latter conclusion is based on the fact that none of the oxidized alloys exhibited attack by lithium after vacuum heat treatment.

APPENDIX B

Hydrogen Embrittlement Caused By Removal of Lithium After Test

The advanced refractory alloys were found to be particularly susceptible to hydrogen pickup, which caused embrittlement during lithium decontamination after test. Although previous decontamination experience with unalloyed niobium and tantalum as well as with the alloy Nb-1% Zr had not indicated that hydrogen embrittlement would be a problem, we found that cracking resulted from the use of water or other fast-reacting solvents that produced hydrogen when they reacted with the lithium present after draining.

Preliminary observations indicated that the susceptibility of a given alloy to embrittlement was dependent on (1) the thermal history before decontamination, (2) the type of solvent used to dissolve lithium, and (3) the surface condition of the sample. Alloys with high initial oxygen concentrations cracked worse than those with lower oxygen contents. Alloys that were oxidized, heat treated, and exposed to lithium at 1000°C were much more susceptible to cracking than similar specimens exposed to lithium at 500°C. Cracking was always associated with an increase in the hydrogen content of the alloy; however, the cracks were not a result of hydride formation, for no hydride phase was observed in the microstructure. Bulk hydrogen increases of as little as 50 ppm to as high as 1200 ppm were recorded for samples that showed cracks.

In all cases cracks formed at the surface and propagated inward. In most cases they began as intergranular cracks and branched off to transgranular cracks in the interior, as shown for alloy Cb-752 in Fig. 9. Some, however, did originate as transgranular cracks at the surface as shown in Fig. 10 for alloy B-66. In no case did we observe transgranular cracks in specimens attacked by lithium. Figures 11 and 12 show the crack morphology in the refractory alloys T-111 and FS-85. In many cases, cracking was very localized, indicating that only when a sufficient quantity of residual lithium was present could enough hydrogen be generated to cause embrittlement.

Fig. 9. Cracks in Alloy Cb-752 After Test. Sample was recrystallized at 1600°C, oxidized to 2600 ppm O, heat treated for 2 hr at 1300°C, and exposed to static lithium for 100 hr at 1000°C. The residual lithium was dissolved in water at room temperature. Sample showed a bulk hydrogen increase of 70 ppm. 100x.

Fig. 10. Transgranular Surface Cracks in Alloy B-66 After Test. Sample was recrystallized at 1600°C and exposed to static lithium for 100 hr at 1000°C. The residual lithium was dissolved in water at room temperature. Hydrogen content was not determined. 100x. Reduced 22.5%.

Fig. 11. Cracks in Alloy T-111. Specimen was recrystallized at 1600°C and tested in lithium 100 hr at 1000°C with no oxygen added. The residual lithium was dissolved in water at room temperature. Sample showed a bulk hydrogen increase of 400 ppm. 200x. Reduced 19%.

Fig. 12. Cracks in Alloy FS-85. Specimen was tested in lithium 100 hr at 1000°C in the stress-relieved condition. Residual lithium was dissolved in water at room temperature. Sample showed a bulk hydrogen increase of 97 ppm. 500x. Reduced 13%.

Cracks apparently formed in these alloys near room temperature without any applied stress, and no hydrides were observed by optical microscopy even for bulk hydrogen increases as high as 1200 ppm. We considered the possibility that localized surface heating and subsequent thermal expansion of the sample might have resulted from exothermic reaction of lithium with water. Accordingly, a high-speed temperature recorder (Visicorder) was attached to a small test coupon with 0.020-in.-diam thermocouple lead wires. The sample with the thermocouple spot welded to the surface was coated with lithium and then reacted in water at room temperature to measure the surface temperature. Maximum surface temperatures of 30 and 70°C were measured during duplicate runs. Such a temperature increase appears insufficient to cause cracking even in a very brittle material.

The problem of hydrogen embrittlement during lithium decontamination can be overcome by several techniques, the most successful of which is the use of anhydrous liquid ammonia, which dissolves the lithium without generating hydrogen. However, if the solution of ammonia and lithium is allowed to stand for a period of hours or is heated above room temperature under pressure, lithium can react with ammonia to form lithium amide and generate hydrogen. This reaction is also catalyzed in the presence of certain metals. Our experience to date, however, has shown no evidence of hydrogen pickup by tantalum or niobium alloys when we have used ammonia to dissolve lithium residues.

Vacuum distillation of lithium at 700°C is also a feasible technique for removing residual lithium films, provided that the quantities of lithium to be distilled are not excessive. Organic solvents that react slowly and generate hydrogen very slowly, such as butyl cellosolve, are much less prone to produce hydrogen embrittlement than solvents that react fast, such as alcohol and water, but the use of these solvents is generally not as reliable as the use of ammonia or vacuum distillation.