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THE EFFECTS OF OXYGEN AND NITROGEN ON THE CORROSION RESISTANCE OF COLUMBIUM TO LITHIUM AT ELEVATED TEMPERATURES

E. E. Hoffman

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E. E. Hoffman

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This report is a portion of a Thesis, ORNL-2674, Corrosion of Materials by Lithium at Elevated Temperatures, which is to be issued in the near future.

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THE EFFECTS OF OXYGEN AND NITROGEN ON THE CORROSION RESISTANCE OF COLUMBIUM TO LITHIUM AT ELEVATED TEMPERATURES

E. E. Hoffman

ABSTRACT

Columbium was observed to undergo a type of intergranular corrosion attack when tested in molten lithium at elevated temperatures both in static systems at constant temperature and in flowing, non-isothermal systems. This type of attack was found to be particularly severe in and near weld zones. A systematic investigation of the role of atmospheric contaminants revealed that the attack was due primarily to contamination of the metal by oxygen. The results indicated that grain-boundary columbium oxide was reduced by lithium, forming a two-phase grain-boundary corrosion product of lithium oxide and columbium, and that columbium nitride was not attacked. These observations were found to be consistent with the relative thermodynamic stabilities of columbium oxide and columbium nitride in molten lithium.

INTRODUCTION

Early screening-type static corrosion tests indicated columbium to be a promising container material for molten lithium. Subsequent tests of this material under flowing, non-isothermal conditions in thermal convection loops, however, revealed a type of intergranular corrosion attack, particularly in and near weld zones, which had not been detected in the more cursory preliminary evaluations in static systems. Because columbium rates high as a potential high-temperature nuclear reactor structural material, an intensive study was undertaken to determine the cause of the observed intergranular attack.

Additional static tests as well as a more thorough examination of the weld zones of the early static test systems established that columbium is attacked intergranularly by lithium in the absence of flow and of temperature gradients. The research which followed, therefore, was carried out using static test systems since, relative to thermal convection loops, static systems not only are easier to fabricate but also lend themselves to more stringent control of important test variables.

[redacted]

In this report, the lithium corrosion studies on columbium are presented chronologically, beginning with the initial observations in thermal convection loops and terminating with systematic studies in static systems. On the basis of the latter an hypothesis is developed to explain the intergranular attack of columbium by lithium.

INITIAL OBSERVATIONS

In the first columbium-lithium thermal convection loop test severe cracking was observed in the saddle-weld area at the top of the hot leg as shown in Figure 1. In this test the loop was operated for 500 hours at a hot-leg temperature of 1500°F (816°C). The columbium was protected from oxidation by cladding it with type 310 stainless steel. The saddle-weld area was protected by a type 310 stainless steel shroud which was welded to the cladding as shown in Figure 1.

Subsequent loop tests were performed in a stainless steel vacuum chamber at pressures from 1 to 5 microns of mercury to eliminate the effect of stresses due to the difference in thermal expansion of stainless steel and columbium in the clad-and-shroud test design. In all cases the vacuum-chamber tests on non-clad loops were terminated as the result of actual penetration of the columbium tube walls by lithium, especially at weld zones. Typical grain-boundary penetrations in a weld zone and in base material not affected by welding are shown in Figure 2 and Figure 3, respectively. The photomicrographs in each of these figures show a given penetrated region in three different stages of metallographic preparation: a) as polished, b) polished and allowed to "stain" in air for two weeks, and c) polished and etched.[1] The extent of penetration is detected most readily in the "stained" specimens, as shown by the areas enclosed by dashed circles. The staining effect was attributed to the formation of lithium hydroxide by the reaction of lithium, or lithium compounds, with water vapor in the atmosphere.

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[1]The columbium specimens shown in the etched condition in this report were etched by immersion in H_2O-HF-H_2SO_4-HNO_3, 55-25-10-10 volume per cent.

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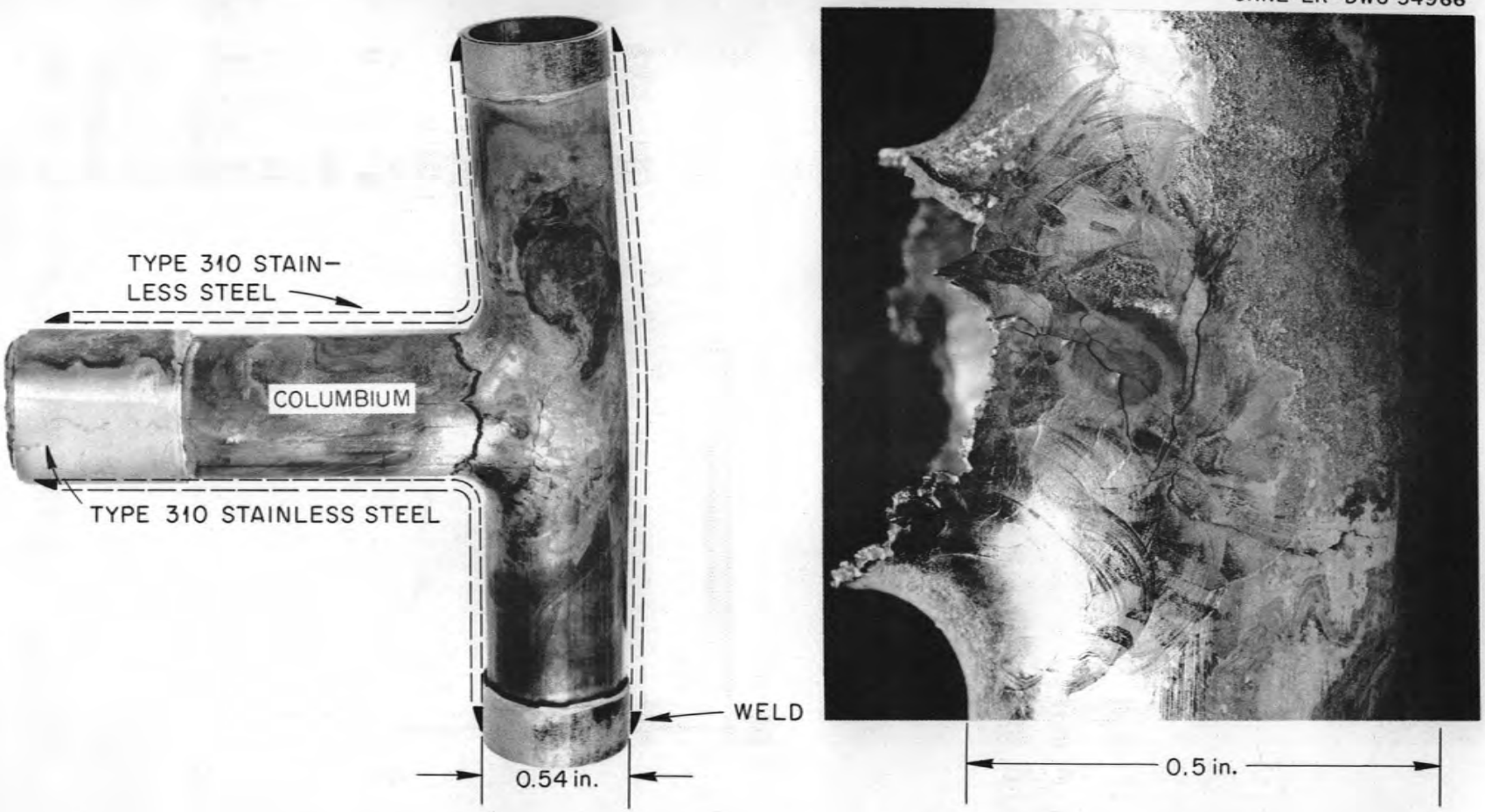

Fig. 1. Saddle-Weld Area at Top of Hot Leg of Columbium Loop. Dotted Line Shows the Location of Protective Stainless Steel Shroud which was Removed Following Test to Reveal Cracks in the Columbium. Photograph on Right Shows the Weld Area of the Columbium at Higher Magnification.

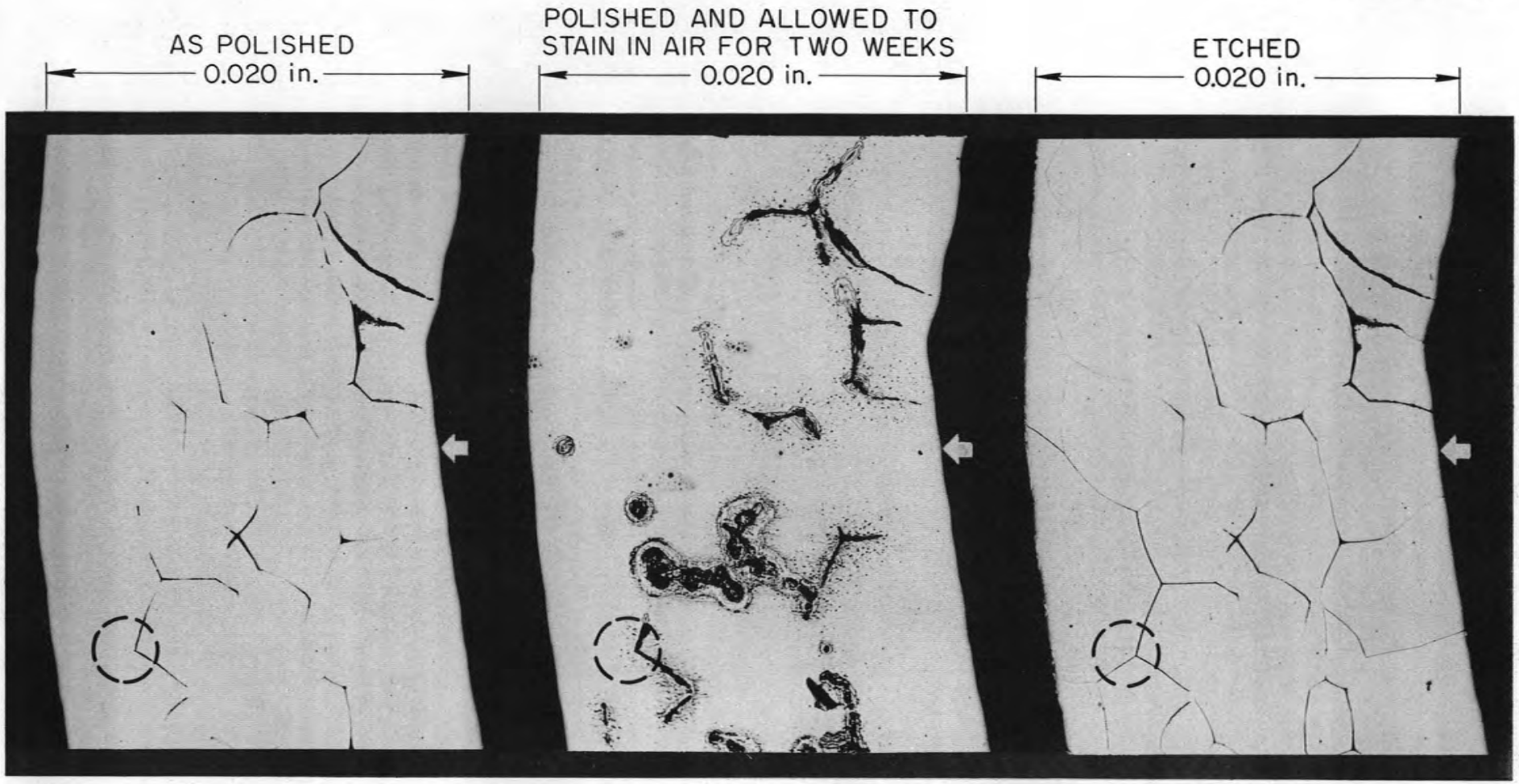

Fig. 2. Weld Zone of Columbium Tube Wall from Hot Leg of Thermal Convection Loop.

LOOP NO. 54 TEST CONDITIONS: 1600°F (871°C) FOR 23 hr ARROW INDICATES SURFACE EXPOSED TO LITHIUM

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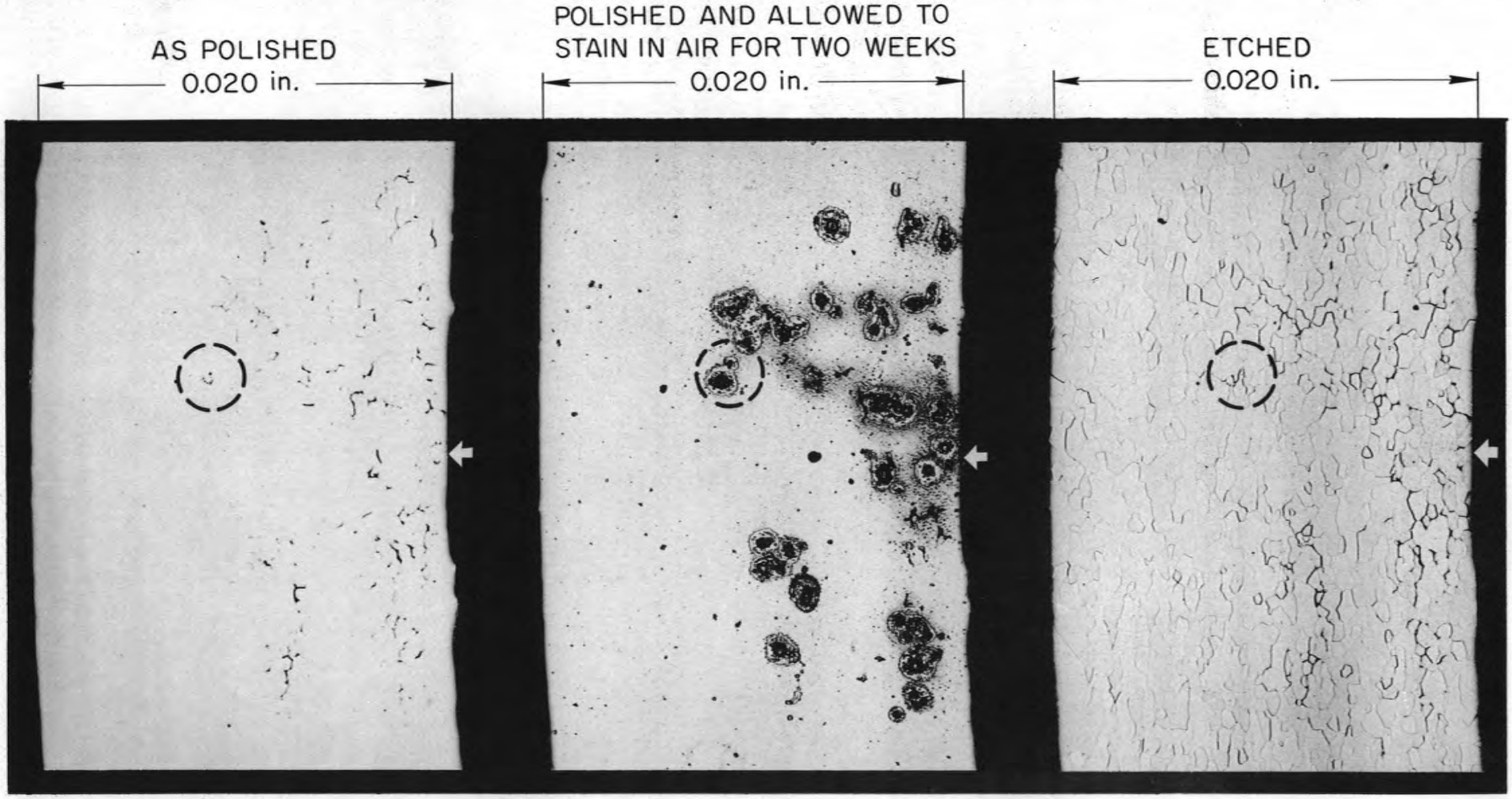

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Fig. 3. Columbium Tube Wall from Hot Leg of Thermal Convection Loop.

LOOP NO. 54 TEST CONDITIONS: 1600°F (871°C) FOR 23 hr. ARROW INDICATES SURFACE EXPOSED TO LITHIUM

The presence of lithium in penetrated grain boundaries was confirmed by chemical analysis of successive five-mil turnings machined from both hot and cold legs of several loops. The excellent correlation between lithium content, as a function of distance from the outside surface of the tube wall, and the extent of intergranular attack observed metallographically is shown in Table I.

The corrosion test results described thus far were on sintered[2] columbium tubing formed by powder metallurgy techniques. For comparison of these results with those for denser and perhaps purer arc-cast material, a two-inch section of arc-cast tubing was inserted by braze-welding as part of the hot leg of a sintered columbium loop. A vacuum-chamber corrosion test using this loop was terminated after 36 hours by heater failure due to lithium contamination, the penetration having occurred in a longitudinal seam weld in the sintered tubing. Metallographic examination of this loop after the test showed that severe attack had occurred in both types of tubing and that a non-metallic gray phase was present in the attacked regions. These results are shown in Figure 4. The absence of a micro-hardness gradient across the tube walls indicated that evacuation to pressures of 1 to 5 microns of mercury in the vacuum-chamber test apparatus was adequate to prevent contamination of the columbium by interstitial oxygen and nitrogen.

Additional static tests, conducted on sintered columbium tubes, showed that the type of corrosion attack observed in the thermal-convection loop tests was not related to flow of lithium or to temperature gradients in the system. An examination of weld zones of components used in the earlier screening-type static tests confirmed this conclusion. Figure 5 shows a typical static-test result. Grain-boundary phases, both metallic and non-metallic in appearance, were observed, as indicated by arrows in Figure 5. The attack was found to be heaviest in weld zones and heat-affected zones adjacent to welds.

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[2]The terms "sintered" and "arc-cast" as applied to columbium tubing in this report refers to the method of preparing the starting material which is used in the subsequent fabrication of tubing.

TABLE I

LITHIUM CONCENTRATION AS A FUNCTION OF DISTANCE FROM OUTSIDE OF TUBE WALL IN COLUMBIUM-LITHIUM THERMAL CONVECTION LOOP TESTS[a]

LOOP NO.	CUTS[b] MACHINED FROM O.D. OF TUBE WALL (MILS)	LITHIUM CONCENTRATION (ppm)		METALLOGRAPHIC RESULTS	
		HOT LEG	COLD LEG	HOT LEG	COLD LEG
52 Test Conditions: Hot Leg: 1600°F Cold Leg: 1300°F Time: 155 hr	0–5 5–10 10–15 15–20	<1 <1 <1 25	<1 <1 2 4	Up to 10 mils attack in longitudinal weld and heat affected zone. No attack on base material.	No attack
54 Test Conditions: Hot Leg: 1600°F Cold Leg: 1300°F Time: 23 hr	0–4 4–8 8–12 12–16 16–20	135 230 450 450 470	<1 <1 <1 <2 11	Complete penetration (20 mils) of longitudinal weld. Up to 10 mils attack on base material.	No attack
55 Test Conditions: Hot Leg: 1600°F Cold Leg: 1400°F Time: 55 hr	0–5 5–10 10–15 15–20	1 7 42 70	1 1 25 65	Complete penetration (20 mils) of longitudinal weld, heat affected zone and base material.	3 mils penetration in heat-affected region of weld. No attack in base material.

[a]LOOP TESTS PERFORMED IN VACUUM BOX.

[b]0 MILS = OUTSIDE SURFACE.
20 MILS = INSIDE SURFACE.

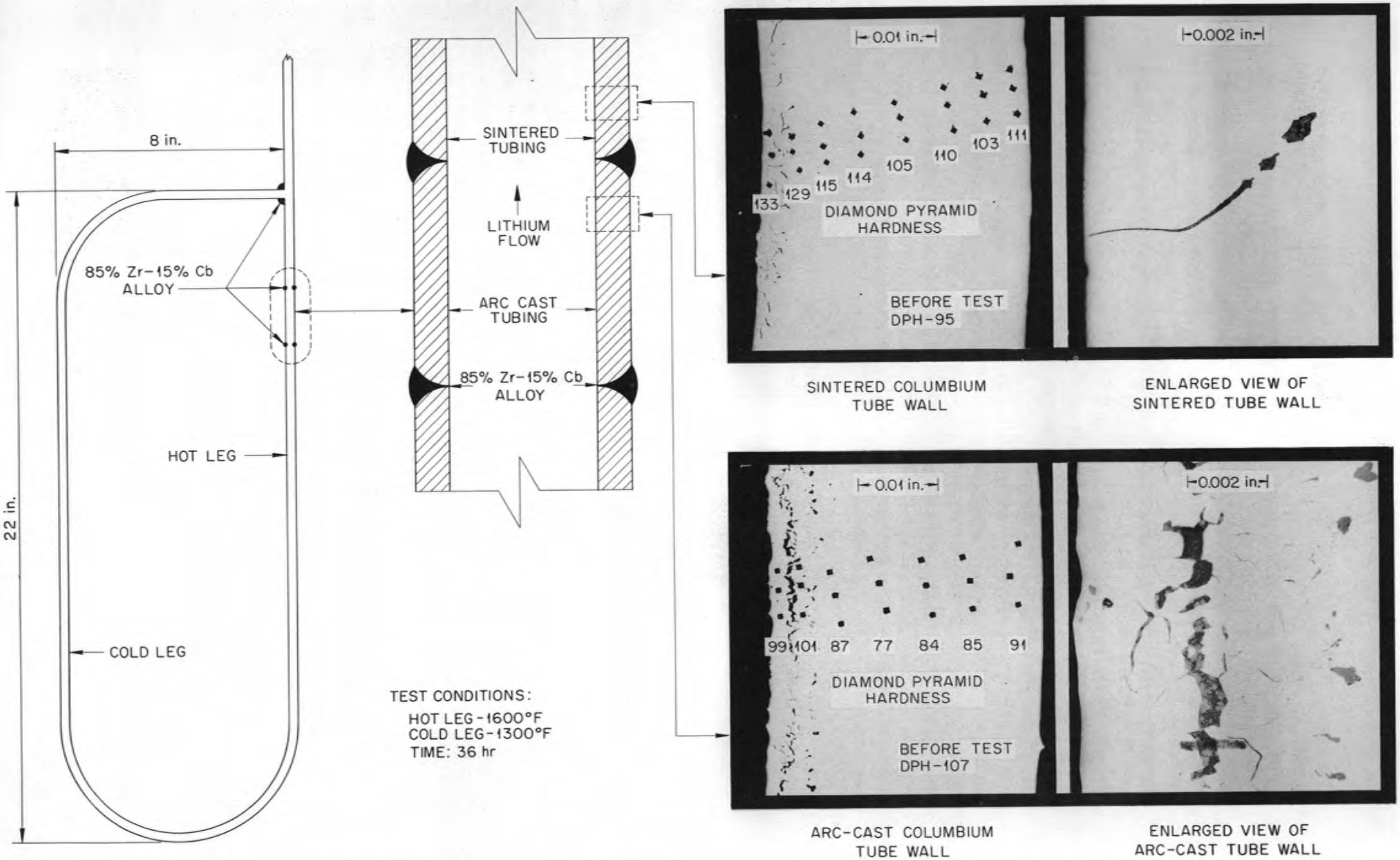

Fig. 4. Results of Dynamic Lithium Corrosion Test on Sintered Columbium Loop Containing a Two-Inch Arc-Cast Columbium Insert.

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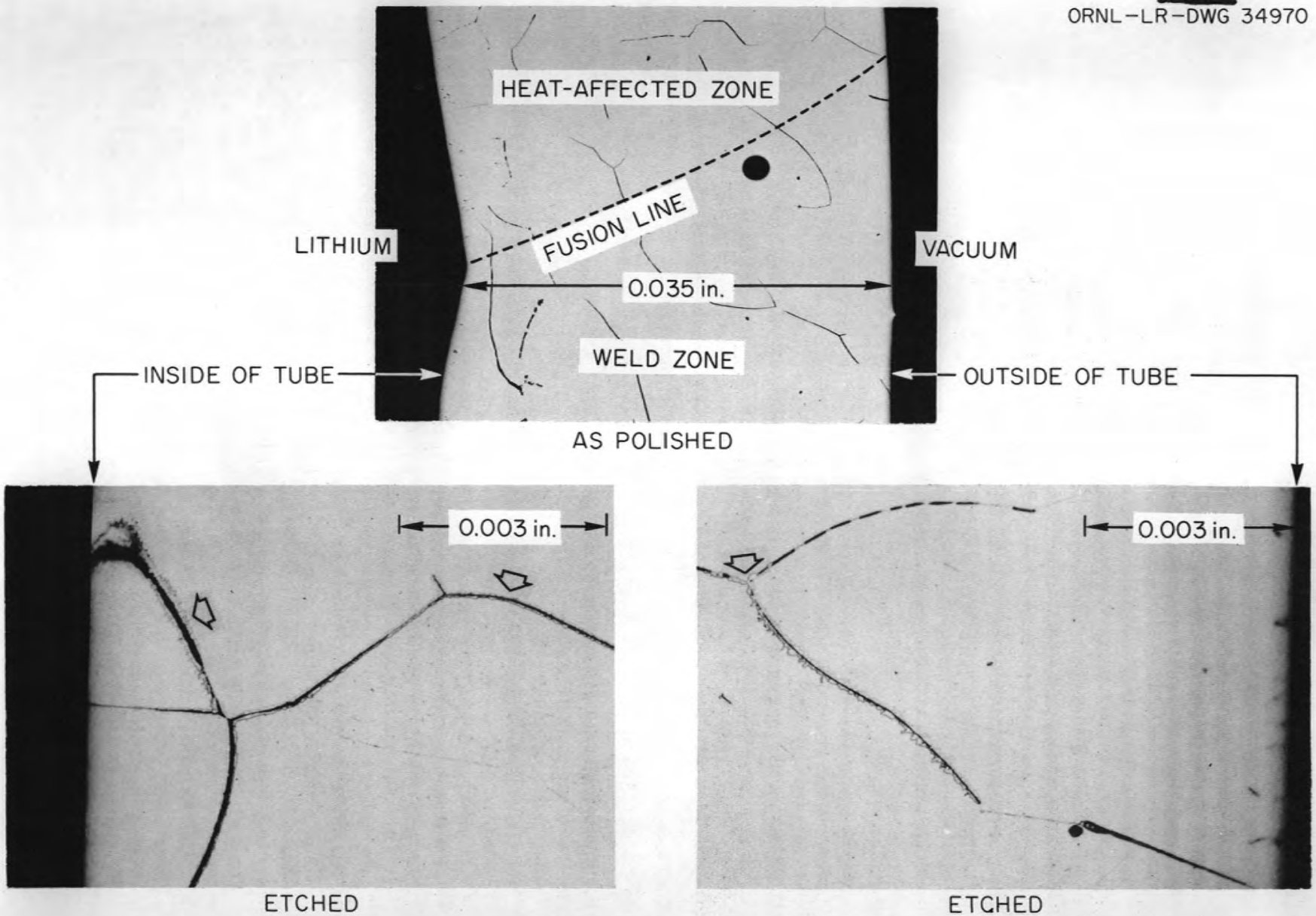

Fig. 5. Weld Zone of Columbium Tube Wall after Exposure to Lithium. Arrows Indicate Corrosion Product Phases in Attacked Grain Boundaries. Test Conditions: Static, 1500°F (816°C), 100 hours.

EFFECT OF WELDING ENVIRONMENT

The predominance of intergranular penetrations at and near weld zones in both static and dynamic test components suggested the possibility that the corrosion of columbium by lithium was associated with contamination of the metal by either oxygen or nitrogen, or both, during conventional shielded-arc or inert-gas-chamber welding. This consideration led to the second phase of the study in which the corrosion resistance of specimens welded in inert-gas environments containing varying amounts of oxygen and nitrogen was investigated.

In this study, both the fusion-welding and braze-welding techniques were used in preparing the specimens. The joining processes were carried out in three different environments: 1) argon plus air, 2) argon containing 1600 ppm nitrogen and 400 ppm oxygen, and 3) argon containing 67 ppm nitrogen and 3 ppm oxygen. The "argon plus air" designation is used to describe that environment associated with welding in air using conventional inert-gas coverage. The controlled environment welding was carried out in an inert-atmosphere chamber. Gas compositions were determined by the mass spectrograph technique and the values reported represent the average of results on duplicate samples taken prior to welding. Evaluation of the effects under consideration was based primarily on metallographic examination and on hardness determinations, the latter being a sensitive measure of the extent of contamination of columbium by the interstitial solutes, oxygen and nitrogen.[3,4]

The results of hardness determinations on fusion-welded specimens both before and after exposure to lithium are tabulated in Figure 6. Significant effects shown in this tabulation are: 1) the marked sensitivity of fusion-zone hardness to welding environment purity, and 2) the decrease in hardness following exposure to lithium of all specimen regions, including the non-heat-affected base metal of the specimen welded in the purest atmosphere.

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[3] Begley, R., "Development of Niobium-Base Alloys," Wright Air Development Center Technical Report 57-344, p. 93 (May, 1958).

[4] Tottle, C., "The Physical and Mechanical Properties of Niobium," J. Inst. Metals, 85, 377 (April, 1957).

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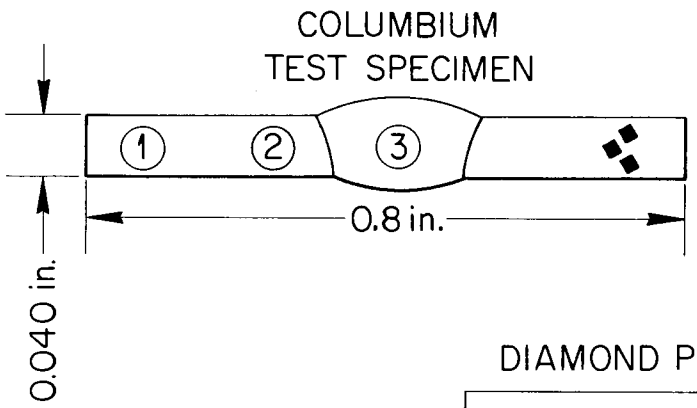

1 BASE MATERIAL
2 HEAT-AFFECTED ZONE
3 WELD ZONE

DIAMOND PYRAMID HARDNESS* (500 g LOAD)

FUSION-WELDING ENVIRONMENT	AS WELDED			FOLLOWING TEST IN LITHIUM		
	1	2	3	1	2	3
ARGON + AIR	127	127	356	97	90	128
ARGON + 1600 ppm N_2 + 400 ppm O_2	128	116	155	107	93	105
ARGON + 67 ppm N_2 + 3 ppm O_2	127	118	131	93	92	95

*AS-RECEIVED ARC CAST Cb: O_2-0.038 %, N_2-0.002 %, C-0.014 %; D.P.H.-137. EACH HARDNESS VALUE IS AVERAGE OF THREE DETERMINATIONS TAKEN AS SHOWN SCHEMATICALLY IN SKETCH.

Fig. 6. The Effect of Welding Gas Purity on the Microhardness of Fusion-Welded Columbium Specimens Before and After Exposure to Lithium. Test Conditions: Static, 1500°F (816°C), 100 hours.

The results of metallographic studies on specimens containing fusion welds are shown in Figures 7, 8, and 9. The photomicrographs in Figure 7 demonstrate that welds representative of all three environments were corroded intergranularly by lithium, but that the severity of attack decreased with increasing purity of welding environment. The intergranular penetrations in the weld made in the purest environment may be related to grain-boundary segregation of existing base metal impurities during solidification of the weld.

Catastrophic intergranular failure of the "argon plus air" weld is apparent in all three figures. The surface of this weld contained numerous macroscopic cracks which were easily visible upon removal of the specimen from the lithium bath. The apparent soundness of this weld prior to corrosion testing is demonstrated in Figure 8.

The thin but continuous white surface layer present on the specimens after corrosion testing was identified by x-ray diffraction analysis as columbium nitride. This nitride layer is formed by reaction of columbium with nitrogen in the lithium. The white-etching feathery constituent adjacent to attacked grain boundaries and the rod-like white phase in unattacked grain boundaries shown in Figure 9 were presumed to be columbium nitride also, since when viewed at a magnification of 1500X these phases were found to be continuous with the white surface layer.

Surface contamination during "argon plus air" welding resulted in the precipitation of either oxides or nitrides to a depth of approximately 0.001 inches as shown in the as-welded microstructure in Figure 8. It is to be noted that this region was so severely attacked by the etchant following the corrosion test that it appears almost totally black at a magnification of 100X. Some white-etching constituents, similar in appearance to the white nitride layer, are visible in this region at the higher magnification shown in Figure 9.

The presence of the dense but more or less shallow Widmanstätten-type precipitates in the microstructures of all specimens after corrosion testing is not clearly understood. This microstructural feature was discernible in the unetched specimens, as shown, for example, in Figure 8, but was most pronounced after metallographic etching. The microconstituents responsible

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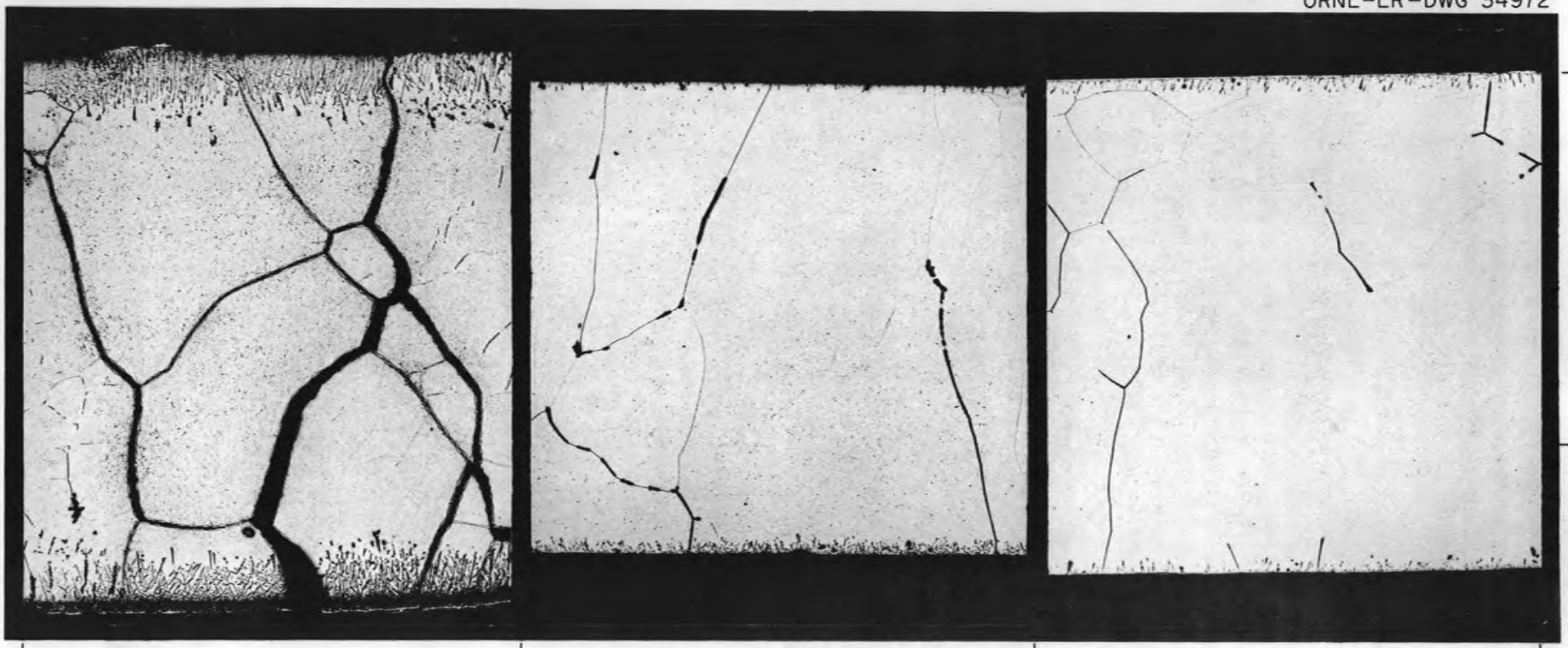
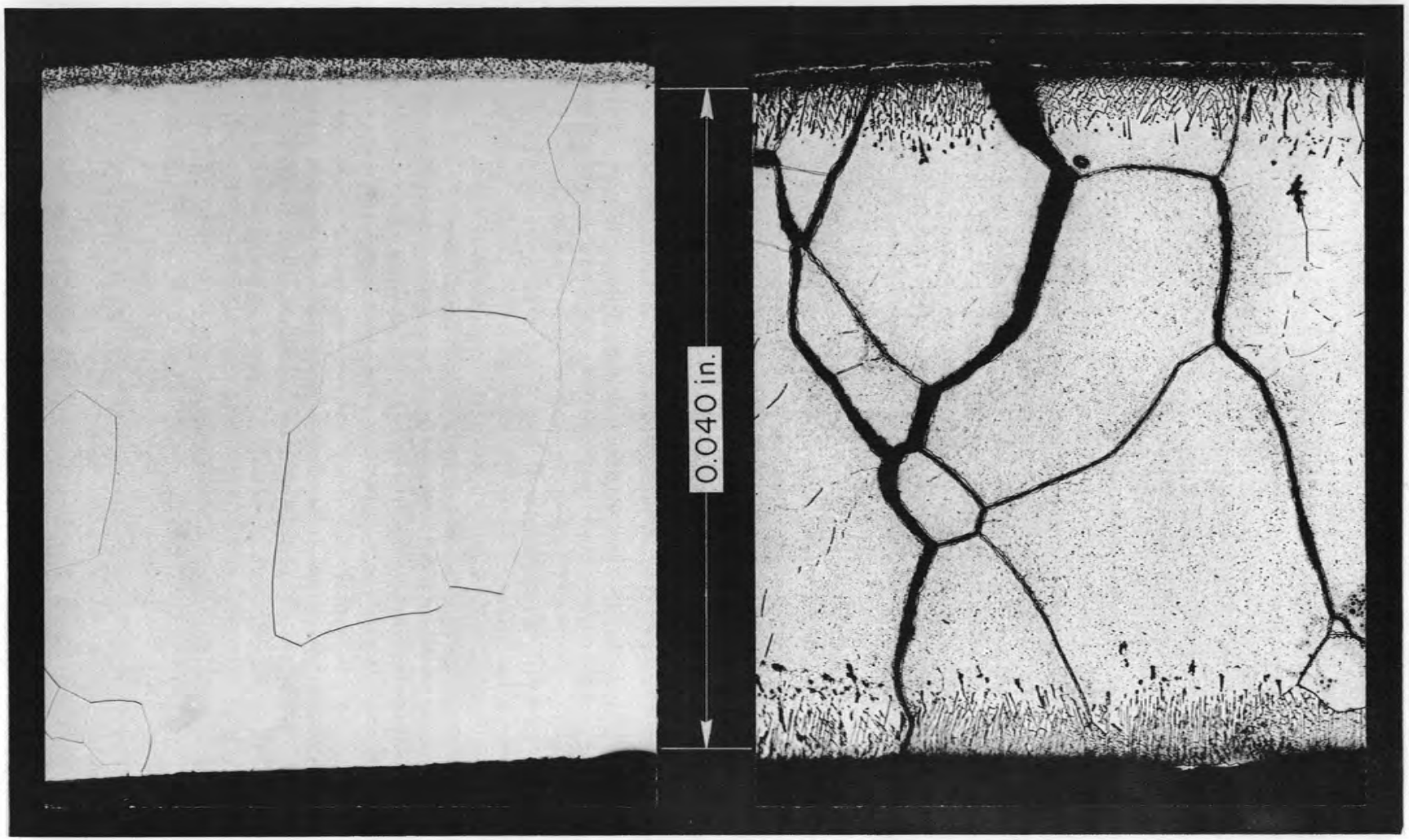


WELDED IN: ARGON + AIR	ARGON + 1600 ppm N_2 + 400 ppm O_2	ARGON + 67 ppm N_2 + 3 ppm O_2
DIAMOND PYRAMID HARDNESS:		
UNWELDED SHEET – 137	137	137
WELDED – 356	155	131
WELDED AND TESTED – 128	105	93

ALL SPECIMENS IN ETCHED CONDITION

Fig. 7. Effect of Welding Environment on the Hardness and Lithium Corrosion Resistance of the Fusion-Weld Zone of Columbium Specimens. Test Conditions: Static, 1500°F (816°C), 100 hours.



BEFORE (ETCHED, 100X) AFTER (ETCHED, 100X)

Fig. 8. Fusion-Weld Zone of Columbium Specimen Welded in Argon + Air Before and After Exposure to Lithium. Test Conditions: Static, 1500°F (816°C), 100 hours.

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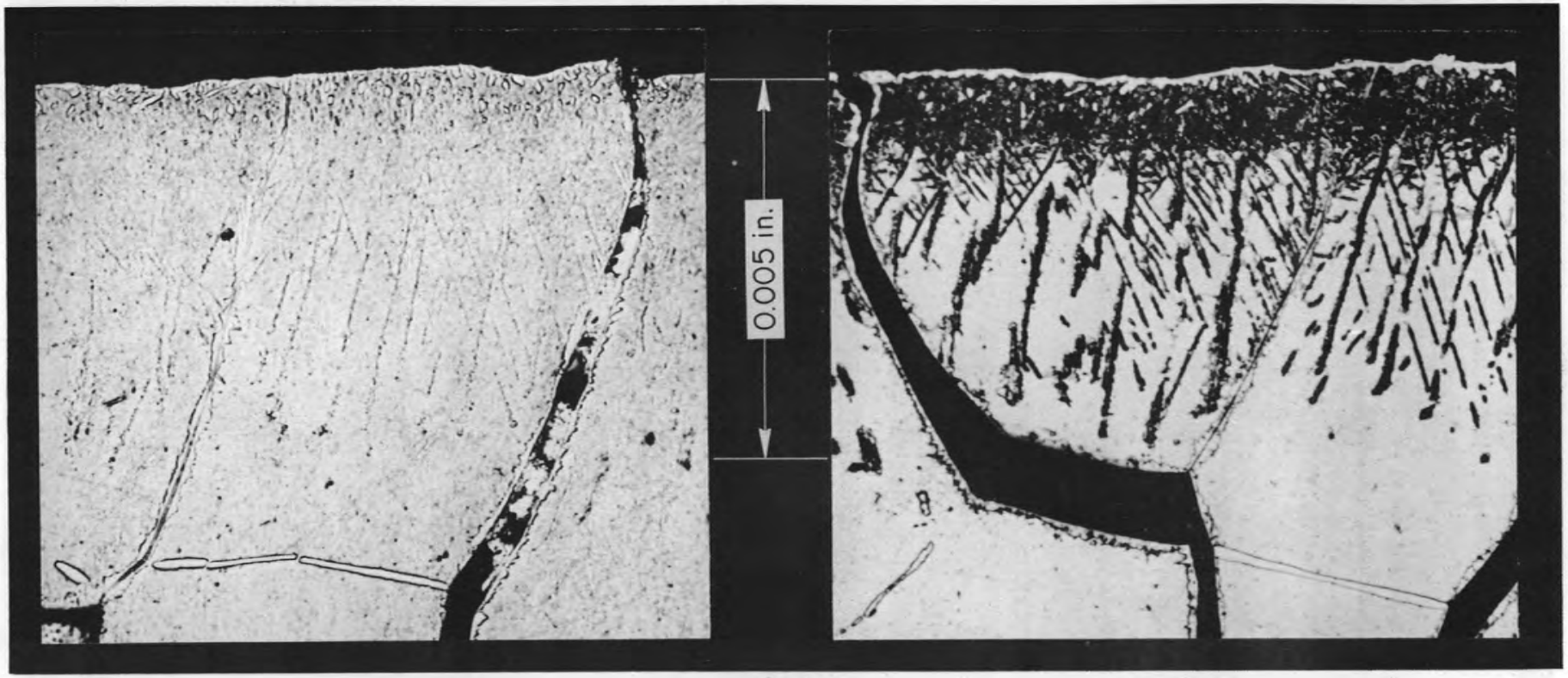

UNETCHED 500X ETCHED 500X

Fig. 9. Fusion-Weld Zone of Columbium Specimen Welded in Argon + Air and Exposed to Lithium. Test Conditions: Static, 1500°F (816°C), 100 hours.

for this effect are believed to be oxides or nitrides of columbium formed as the result of the 100-hour heat treatment at 1500°F (816°C) during corrosion testing. The presence of the continuous, unattacked surface layer of columbium nitride and the general behavior of this region during metallographic preparation suggest that exposure to lithium, per se, was not a factor in the development of the Widmanstätten-type microstructure.

An 85Zr-15Cb weight per cent filler-wire alloy[5] was used in the braze-welding studies. This alloy, which melts at a temperature about 1400 Fahrenheit degrees less than the melting point of columbium, was used in an effort to reduce both contamination and grain growth during welding. The effect of braze-welding environment on the hardness of various zones of the specimens before and after exposure to lithium is given in Figure 10. Of particular significance is the marked reduction in hardness of the heat-affected zones after corrosion testing. The hardness in all zones was uniform to within ± 10 DPH units across the wall thickness except for the heat-affected zone of the "argon plus air" specimen shown in Figure 11. It is important to note that the hardness gradient in the heat-affected zone of this specimen was reversed as a result of exposure to lithium. This effect was attributed to gettering by lithium of oxygen which with nitrogen was responsible for the high as-braze-welded hardness in this zone. The gettering characteristics of lithium were demonstrated in an independent experiment in which the oxygen content of one-eighth-inch cube-shaped columbium specimens were reduced from 4000 to 1500 ppm by exposure to lithium for 100 hours at 1500°F (816°C) while the nitrogen content remained essentially unchanged.

The effect of braze-welding environment on the extent of corrosion attack on columbium is illustrated in Figure 12. The specimen joined in the purest environment showed no attack while the specimen joined in the most contaminated environment was heavily attacked. A Widmanstätten-type precipitate similar to that observed in the fusion-welded specimens is visible in the as-polished microstructures of the "argon plus air" specimen after corrosion testing shown in Figures 11 and 12. In brief summary, the

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[5] Heestand, R. L. and Hoffman, E. E., Welding of Columbium, Part I. Joining Techniques for Systems to Contain Lithium, ORNL-2423 (to be published).

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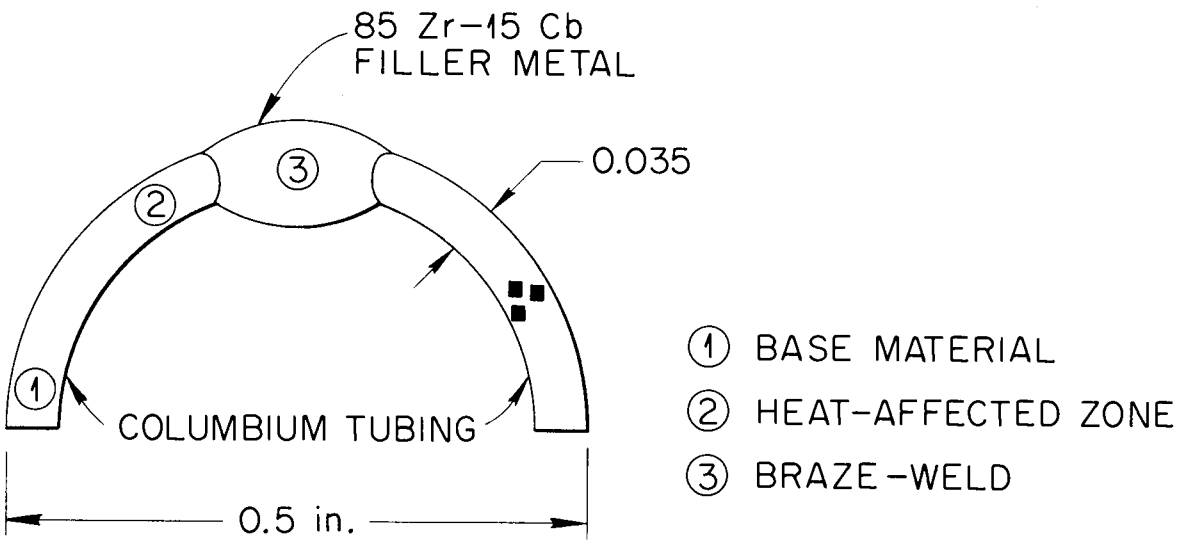
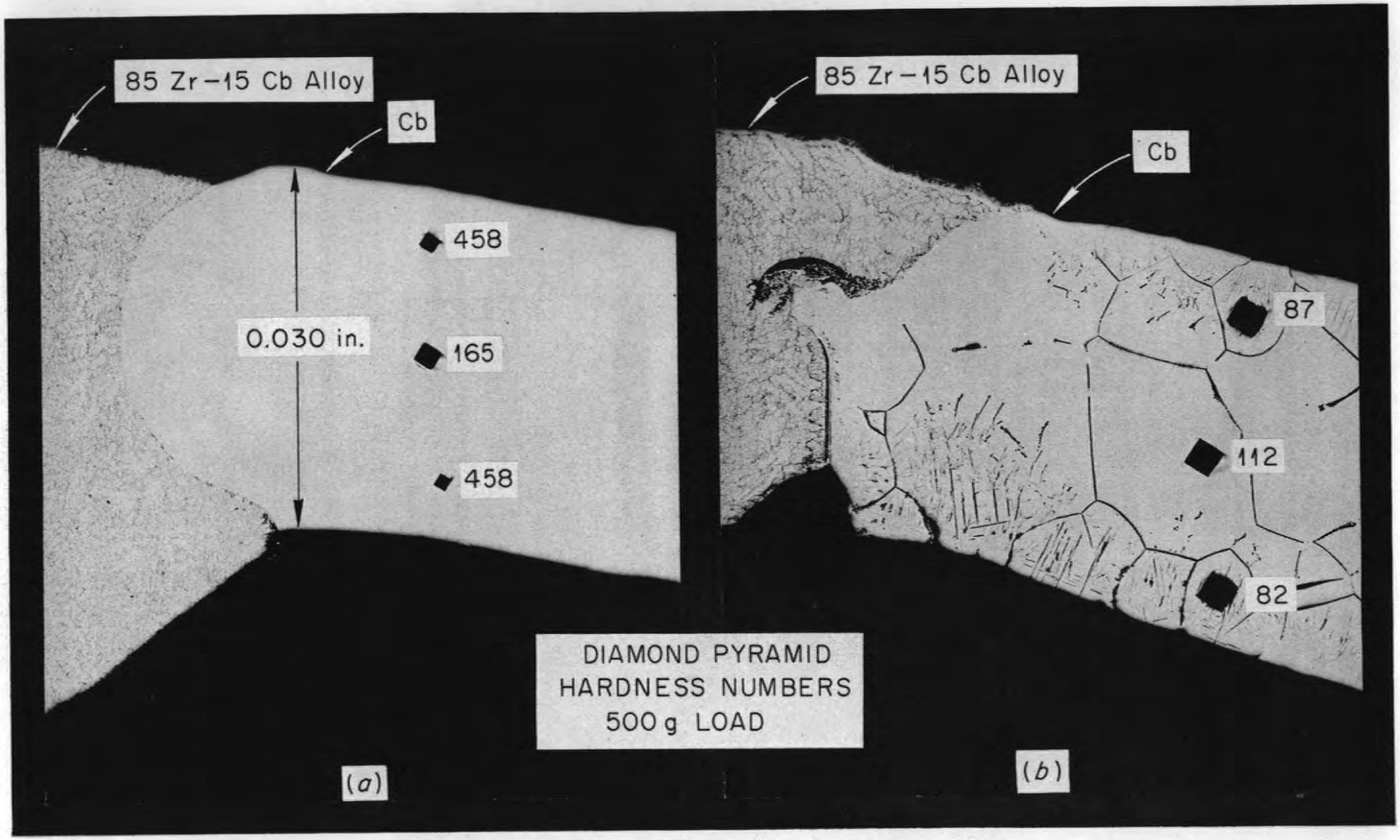


BRAZE-WELDING ENVIRONMENT	DIAMOND PYRAMID HARDNESS* (500g LOAD)					
	AS BRAZE-WELDED			FOLLOWING TEST IN LITHIUM		
	①	②	③	①	②	③
ARGON + AIR	129	360	361	112	94	343
ARGON + 1600 ppm N_2 + 400 ppm O_2	120	114	285	104	98	246
ARGON + 67 ppm N_2 + 3 ppm O_2	113	122	289	105	98	242

*AS-RECEIVED ARC CAST Cb: O_2-0.038%, N_2-0.002%, C-0.014%; D.P.H.-137. EACH HARDNESS VALUE IS AVERAGE OF THREE DETERMINATIONS TAKEN AS SHOWN SCHEMATICALLY IN SKETCH.

Fig. 10. The Effect of Welding Gas Purity on the Microhardness of Braze-Welded Columbium Specimens Before and After Exposure to Lithium. Test conditions: static, 1500°F (816°C), 100 hours.



SPECIMENS IN THE AS POLISHED CONDITION
(*a*) AFTER BRAZE-WELDING
(*b*) AFTER BRAZE-WELDING AND EXPOSURE TO LITHIUM

Fig. 11. Columbium Braze-Welded in Argon + Air. Test Conditions: Static, 1500°F (816°C), 100 hours.

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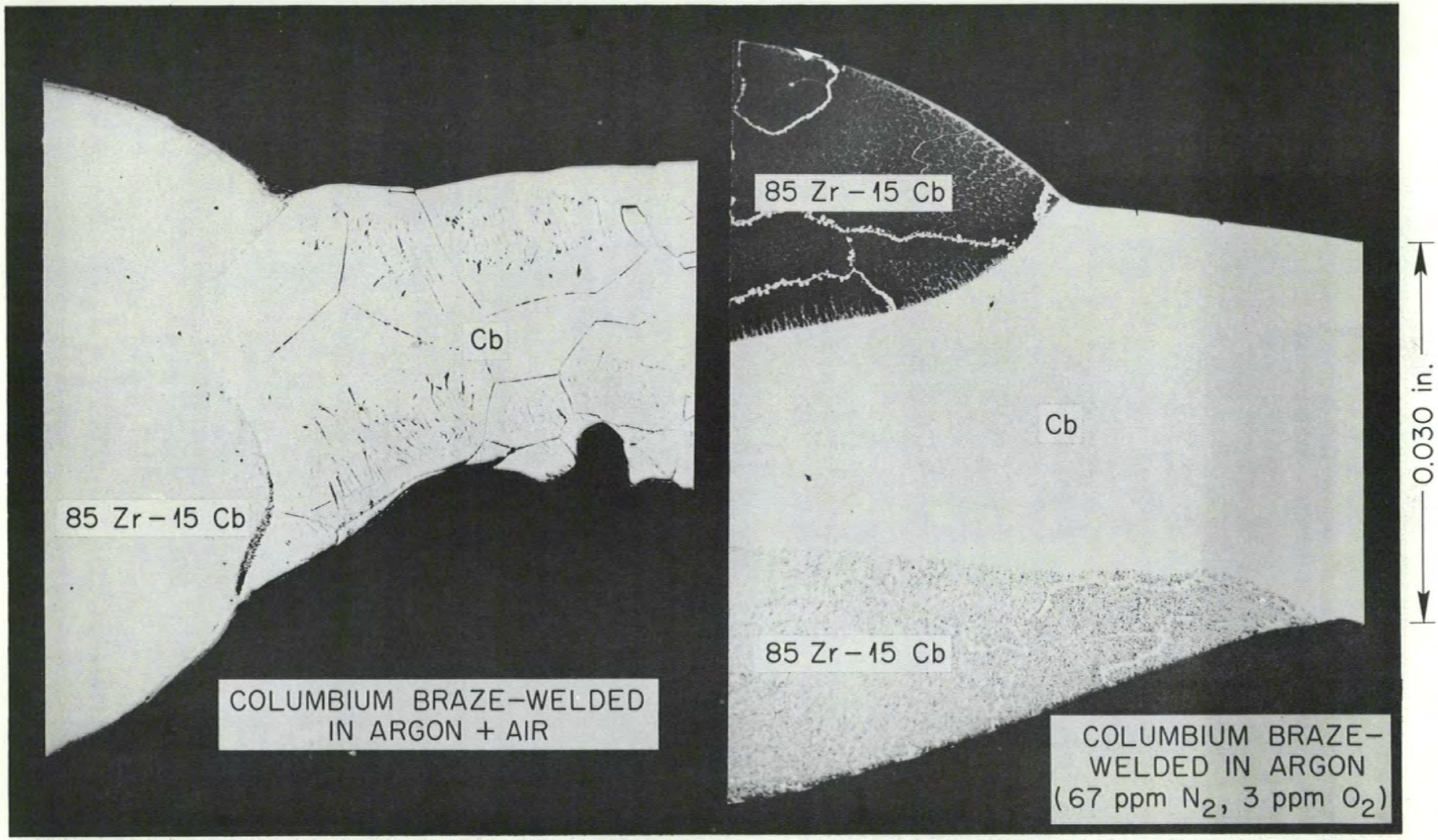

AS POLISHED — 75X

AS POLISHED — 75X

Fig. 12. Effect of Braze-Welding Environment on the Corrosion Resistance of Columbium to Lithium. Test Conditions: Static, 1500°F (816°C), 100 hours.

welding environment studies showed clearly that contamination by oxygen and nitrogen renders columbium susceptible to corrosion attack by lithium and indicated that an investigation of the effect of each of these contaminants considered individually was in order.

THE EFFECTS OF OXYGEN AND OF NITROGEN

The separate effects of oxygen and nitrogen were investigated using specimens to which controlled amounts of these gases had been added in a modified Sieverts' gas-absorption apparatus. The concentration levels studied are given in Table II. According to the portions of phase diagrams[6,7] shown in Figures 13 and 14, concentrations in excess of the limit of solid solubility at the corrosion test temperature of 1500°F (816°C) were represented in both the oxygen series and the nitrogen series.

The specimens were tested in static lithium for 100 hours in three heat-treated conditions: 1) homogenized at 1832°F (1000°C) for 2.5 hours; 2) homogenized and aged at 1000°F (538°C) for 336 hours; and 3) homogenized and "welded" by subjection to a single fusion pass in relatively pure argon containing 20 ppm oxygen and 75 ppm nitrogen. All specimens were tested in a single columbium capsule to eliminate lithium purity as a test variable. The lithium used contained 245 ppm oxygen and 69 ppm nitrogen.

Evaluation of the test results was based on metallography and on weight and hardness changes. Since the heat treatments performed were found to have no effect on the corrosion resistance, the results of metallographic and hardness studies on specimens representing only one condition of heat treatment were selected for presentation in this report. In view of the data presented in the previous sections, the "welded" specimens were chosen for this purpose.

Weight changes after exposure to lithium are given in Table II. It is to be noted that regardless of heat treatment the high-oxygen specimens showed substantial weight losses while the specimens charged with nitrogen were affected only slightly. The surfaces of the most heavily contaminated

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[6] Seybolt, A. U., "Solid Solubility of Oxygen in Niobium," J. Metals, 6, 774 – 776 (June, 1954).

[7] Ang, C. Y. and Wert, C., "Some Properties of Columbium Containing Nitrogen," J. Metals, 5, 1032 – 1036 (August, 1953).

[redacted]

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TABLE II

EFFECT OF OXYGEN AND NITROGEN ADDITIONS ON WEIGHT CHANGE OF COLUMBIUM SPECIMENS EXPOSED TO STATIC LITHIUM AT 1500°F (816°C) FOR 100 HOURS

ADDITIONS[a]		WEIGHT CHANGE (mg/in.^{2}) AFTER TEST		
OXYGEN, Wt %	NITROGEN, Wt %	HOMOGENIZED[b]	HOMOGENIZED AND AGED[c]	HOMOGENIZED AND "WELDED"[d]
0	0	+0.3	+0.5	+0.8
0.056	0	0	0	+0.3
0.111	0	0	0	+0.5
0.237	0	−1.2	−0.9	−1.2
0.371	0	−3.3	−4.2	−3.9
0.527	0	−7.2	−7.7	−5.5
0	0.061	−0.5	+0.3	0
0	0.134	−0.3	0	−1.7[e]

[a]AS-RECEIVED ANALYSIS IN WEIGHT PER CENT: O_2 – 0.0061; N_2 – 0.0046; C – 0.0007; H_2 – 0.0005; Zr – 0.074.

[b]HOMOGENIZED AT 1832°F (1000°C) FOR 2.5 HOURS.

[c]AGED AT 1000°F (538°C) FOR 336 HOURS.

[d]FUSION PASS MADE IN CENTER OF 0.5-INCH × 0.5-INCH × 0.040-INCH SPECIMEN IN ARGON ATMOSPHERE CONTAINING 20 ppm O_2 AND 75 ppm N_2.

[e]PART OF WEIGHT LOSS DUE TO CHIPPING OF SPECIMEN EDGE FOLLOWING TEST.

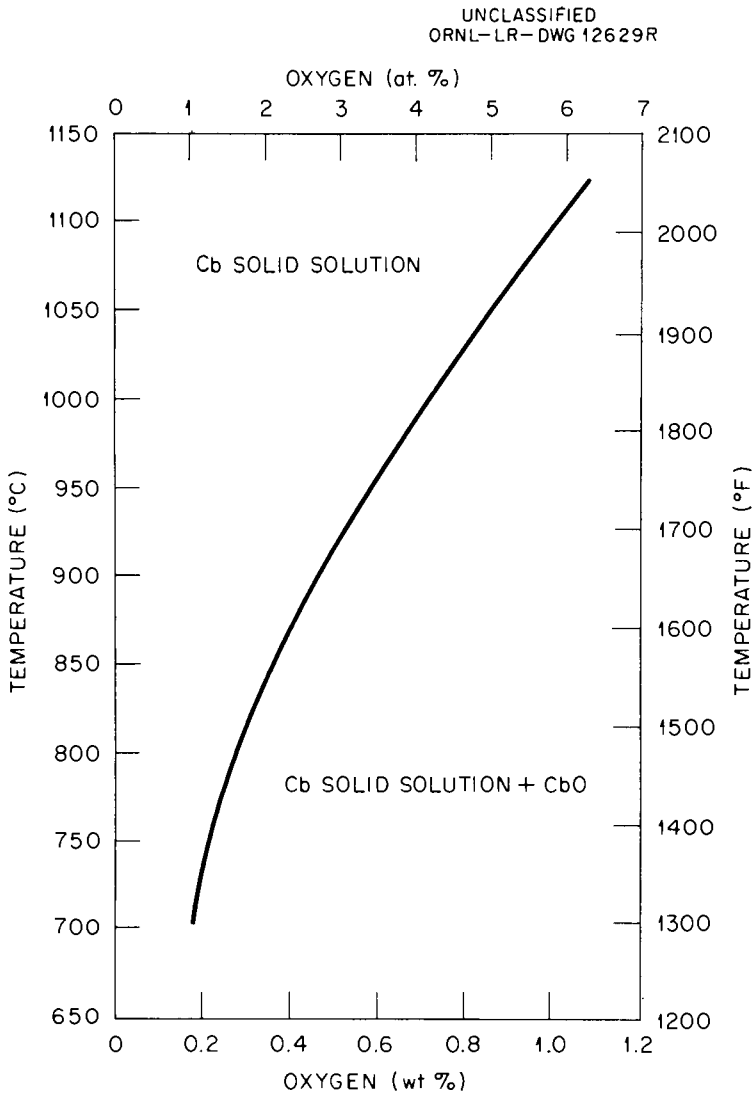

Fig. 13. Solubility of Oxygen in Solid Columbium.

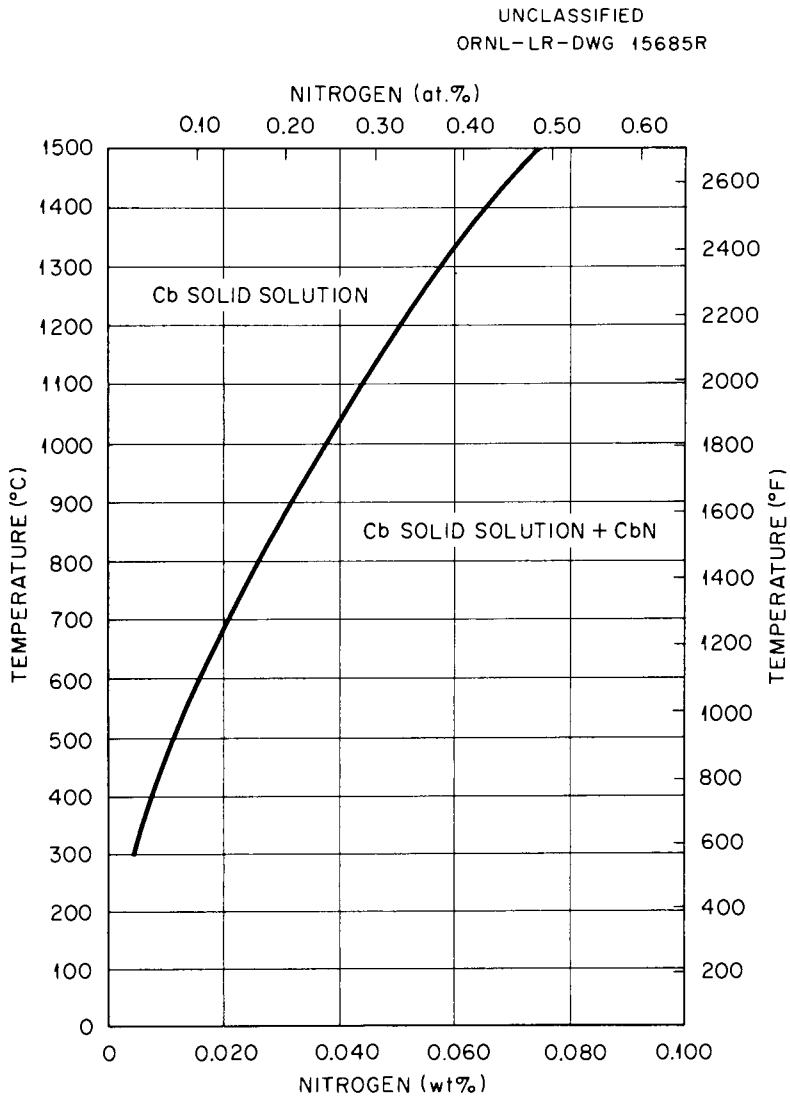

Fig. 14. Solid Solubility of Nitrogen in Columbium.

specimens after corrosion testing are compared in the photomacrographs of Figure 15. The mottled appearance of the high-oxygen specimen is indicative of surface grain removal. Severe cracking can be seen in the weld and heat-affected zones of this specimen.

The results of hardness studies are given in Table III. The drastic reduction in hardness of the high-oxygen specimen after corrosion testing is attributed to the removal of interstitial oxygen by the gettering action of lithium, as discussed in the previous section. The relatively moderate softening which occurred in the high-nitrogen specimens after exposure to lithium appears to have been due to the effects of heat treatment alone. The specimens to which no contaminants had been added showed essentially no change in hardness. Metallographic examination revealed that these specimens had undergone no attack and no change in microstructure after corrosion testing.

As-polished microstructures of the most heavily contaminated specimens in both series are shown in Figures 16 through 20. Figures 16 and 18 show that the high-nitrogen specimen was not attacked and that the grain-boundary phase, which at the higher magnification in Figure 18 is seen to extend to the surface of this specimen, was not affected by lithium during the test. This phase has been identified metallographically as columbium nitride.

The marked effect of oxygen is illustrated in Figures 17 through 20. In Figure 17, it is evident that in the high-oxygen specimen every grain boundary suffered attack. In spite of the extreme care exercised in metallographic preparation, several grains in the interior of this specimen became dislodged during polishing. The nickel plate shown on the specimen in Figure 18 was deposited for purposes of edge preservation during polishing.

The increase in attack by lithium as a function of the oxygen content of the columbium is illustrated in Figure 19. It is to be observed in this series of photomicrographs that the extent of grain-boundary attack was appreciable even at oxygen levels considerably less than the reported oxygen solubility limit of about 0.3% at 1500°F (816°C).

Examination of the weld zone of the high-oxygen specimen in Figure 20 at a magnification of 750X reveals two corrosion products in the grain boundaries. One of these phases is metallic in appearance and is present in the form of long stringers and small particles. The darker and more

[redacted]

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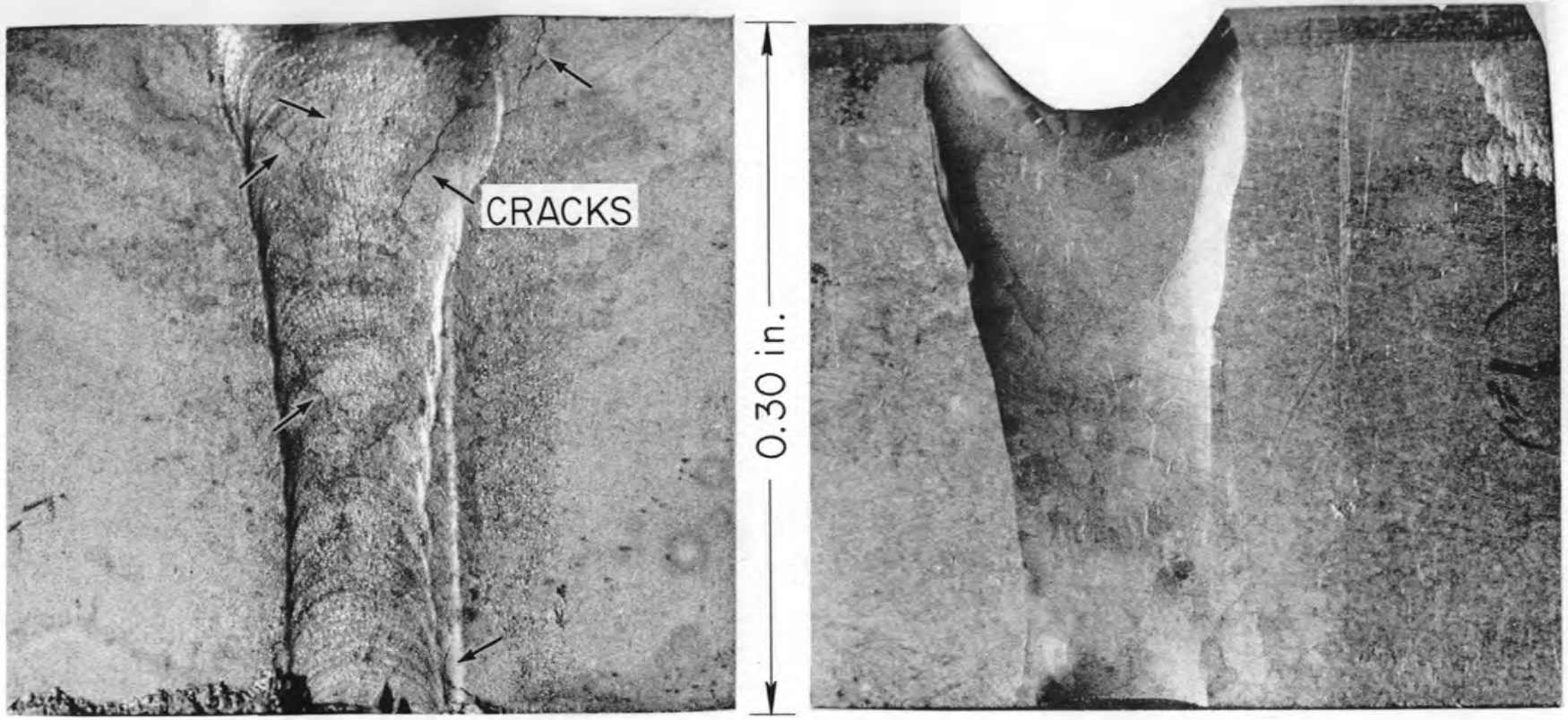

WEIGHT CHANGE IN Li = −5.5 mg/in.^{2}

(*a*) 0.527% O_2 ADDED TO Cb PRIOR TO WELDING

WEIGHT CHANGE IN Li = −1.7 mg/in.^{2}

(*b*) 0.134% N_2 ADDED TO Cb PRIOR TO WELDING

Fig. 15. Columbium Weld Specimens Following Exposure to Lithium for 100 hr At 1500°F (816°C). Specimens Welded in Argon Containing 20 ppm O_2 and 75 ppm N_2.

TABLE III

EFFECT OF HEAT TREATMENT AND EXPOSURE TO LITHIUM ON THE HARDNESS OF CONTAMINATED COLUMBIUM WELD SPECIMENS

Specimen Treatment	Diamond Pyramid Hardness[a] (500 gram Load)	
	Base Material	Weld Zone
1. As-Received Columbium Sheet[b]		
(a) following welding[c]	80	96
(b) a) plus 100 hr-1500°F in Argon	91	101
(c) a) plus 100 hr-1500°F in Lithium	87	84
2. Oxygen Added (0.527 weight per cent)		
(a) following welding	330	366
(b) a) plus 100 hr-1500°F in Argon	242	241
(c) a) plus 100 hr-1500°F in Lithium	71	85
3. Nitrogen Added (0.134 weight per cent)		
(a) following welding	220	231
(b) a) plus 100 hr-1500°F in Argon	151	155
(c) a) plus 100 hr-1500°F in Lithium	122	137

[a]Each hardness value is an average of three determinations.

[b]As-received analysis in weight per cent: O_2 - 0.0061; N_2 - 0.0046; C - 0.0007.

[c]All specimens homogenized at 1832°F (1000°C) for 2-1/2 hours prior to welding.

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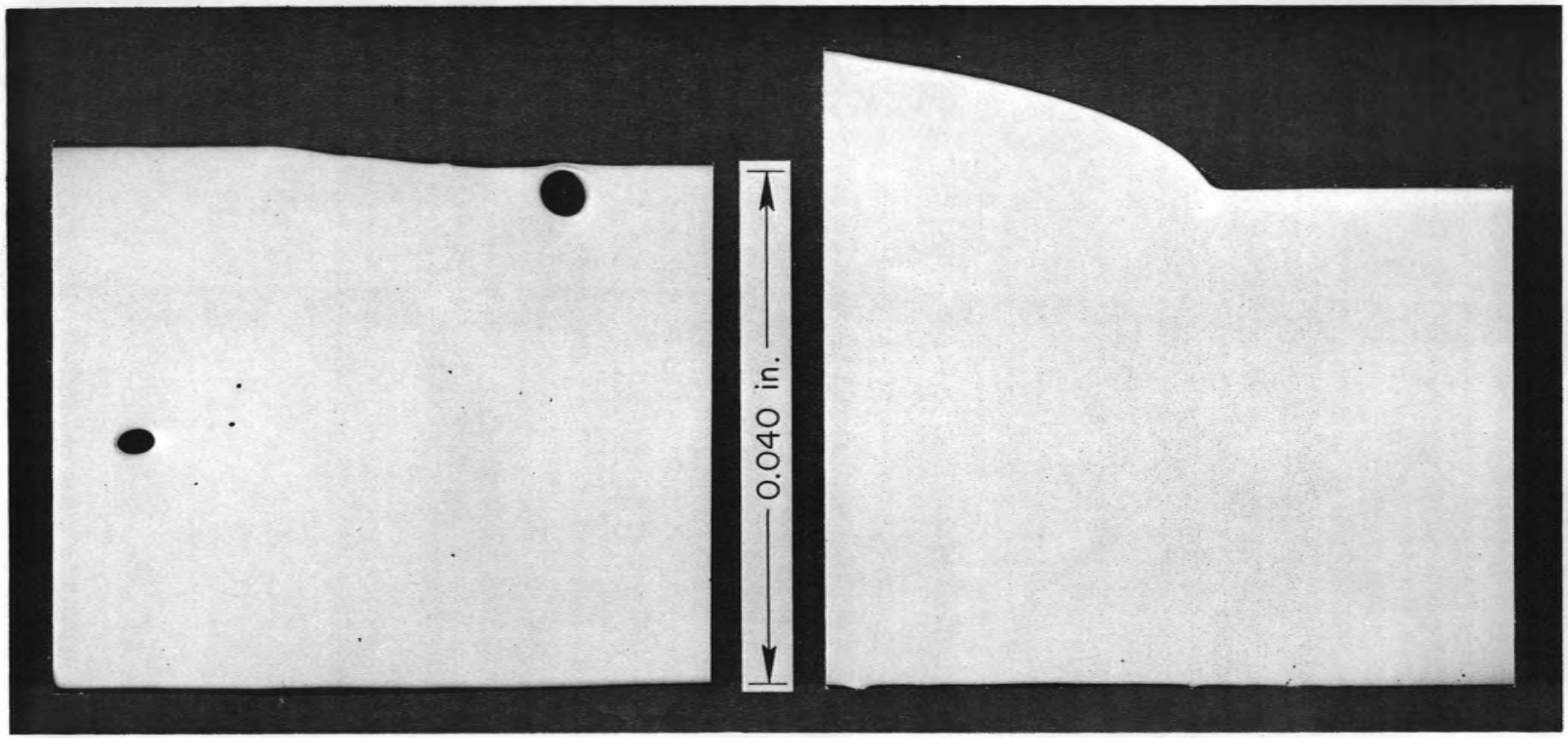

(AS POLISHED-75X)

(*a*) BEFORE EXPOSURE TO LITHIUM

(AS POLISHED-75X)

(*b*) AFTER EXPOSURE TO LITHIUM

[redacted]

Fig. 16. Weld Zones of Columbium Specimens to Which 0.134% N_2 was Added Prior to Welding. Test Conditions: Static, 1500°F (816°C), 100 hours.

[redacted]

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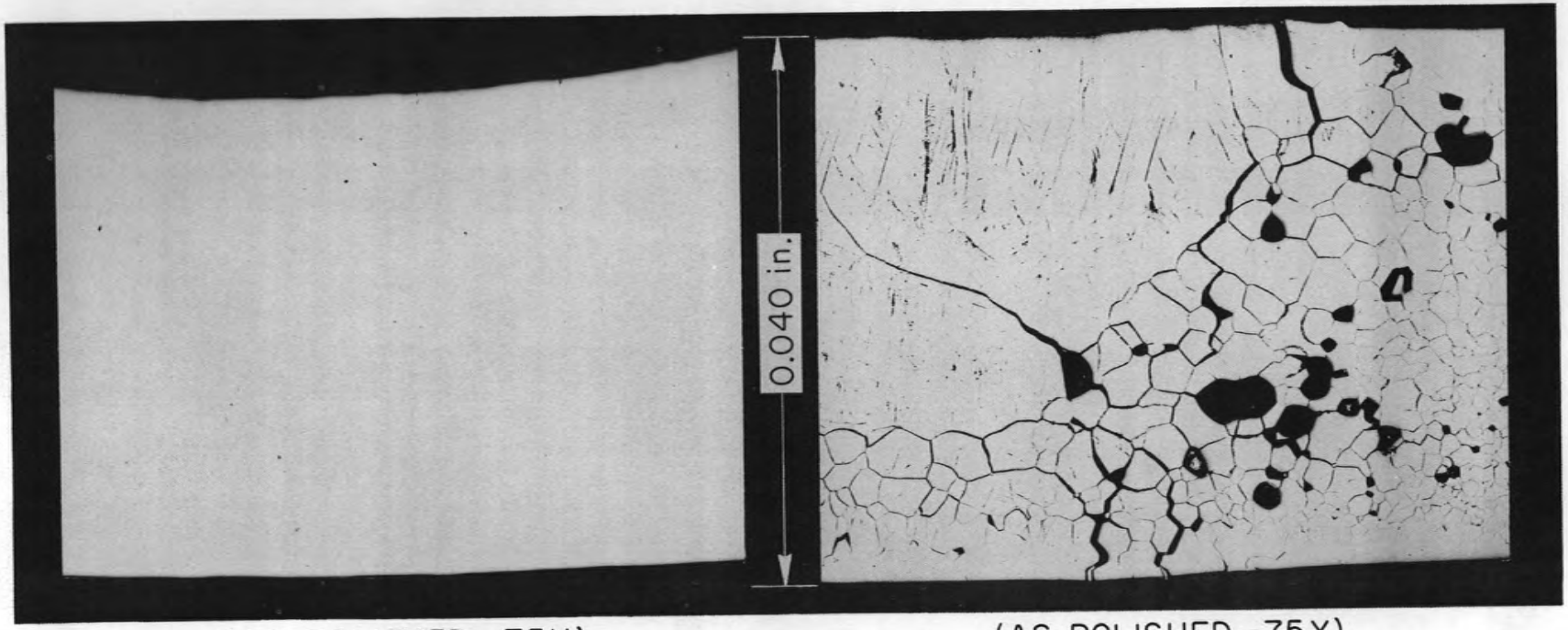

(AS POLISHED-75X) (AS POLISHED-75X)

(*a*) BEFORE EXPOSURE TO LITHIUM (*b*) AFTER EXPOSURE TO LITHIUM

Fig. 17. Weld Zones of Columbium Specimens to which 0.527% O_2 was Added prior to Welding. Test Conditions: Static, 1500°F (816°C), 100 hours.

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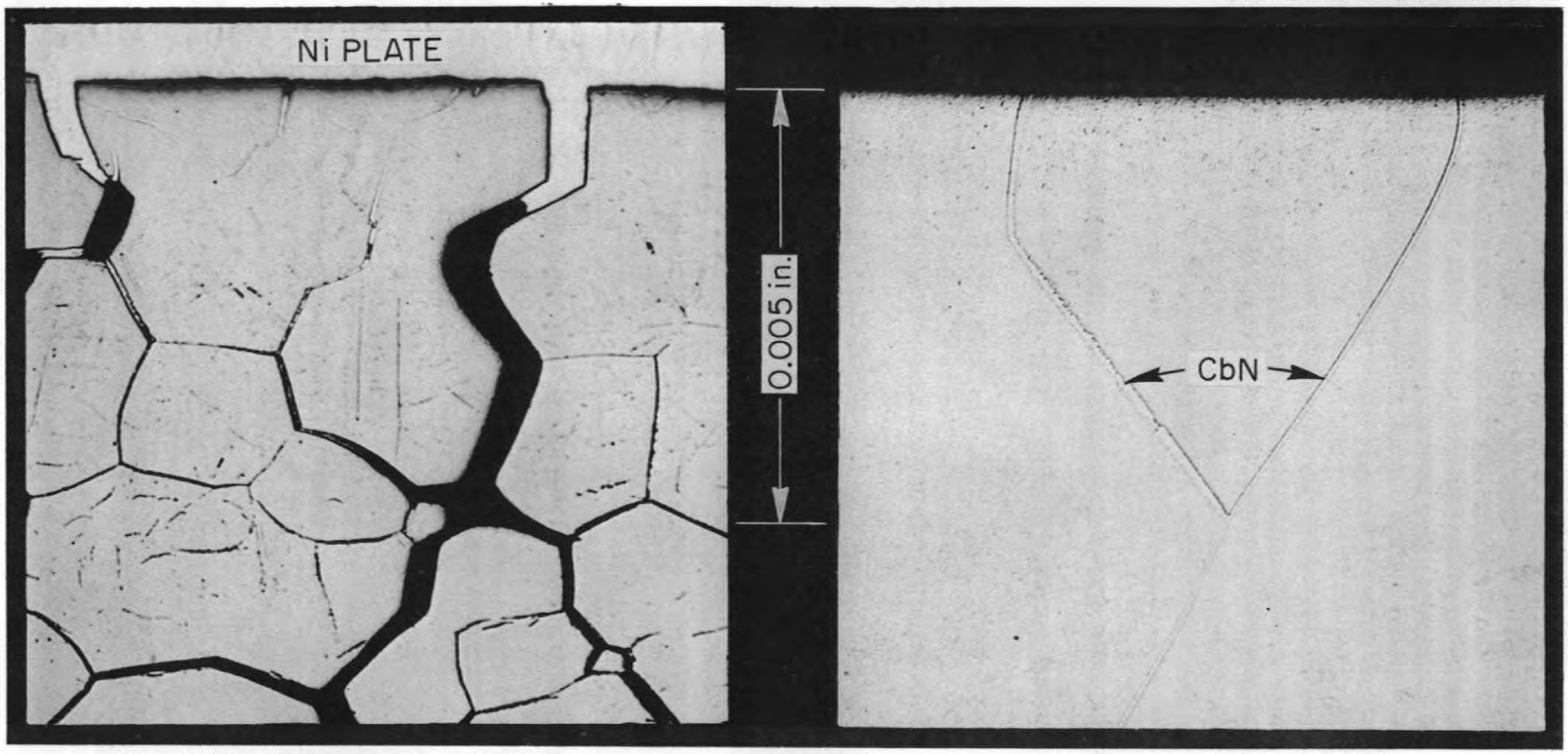

(AS POLISHED-500X)

(*a*) 0.527 % O_2 ADDED PRIOR TO WELDING

(AS POLISHED-500X)

(*b*) 0.134 % N_2 ADDED PRIOR TO WELDING

Fig. 18. Weld Zones of Columbium Specimens Following Exposure to Lithium. Test Conditions: Static, 1500°F (816°C), 100 hours.

[redacted]

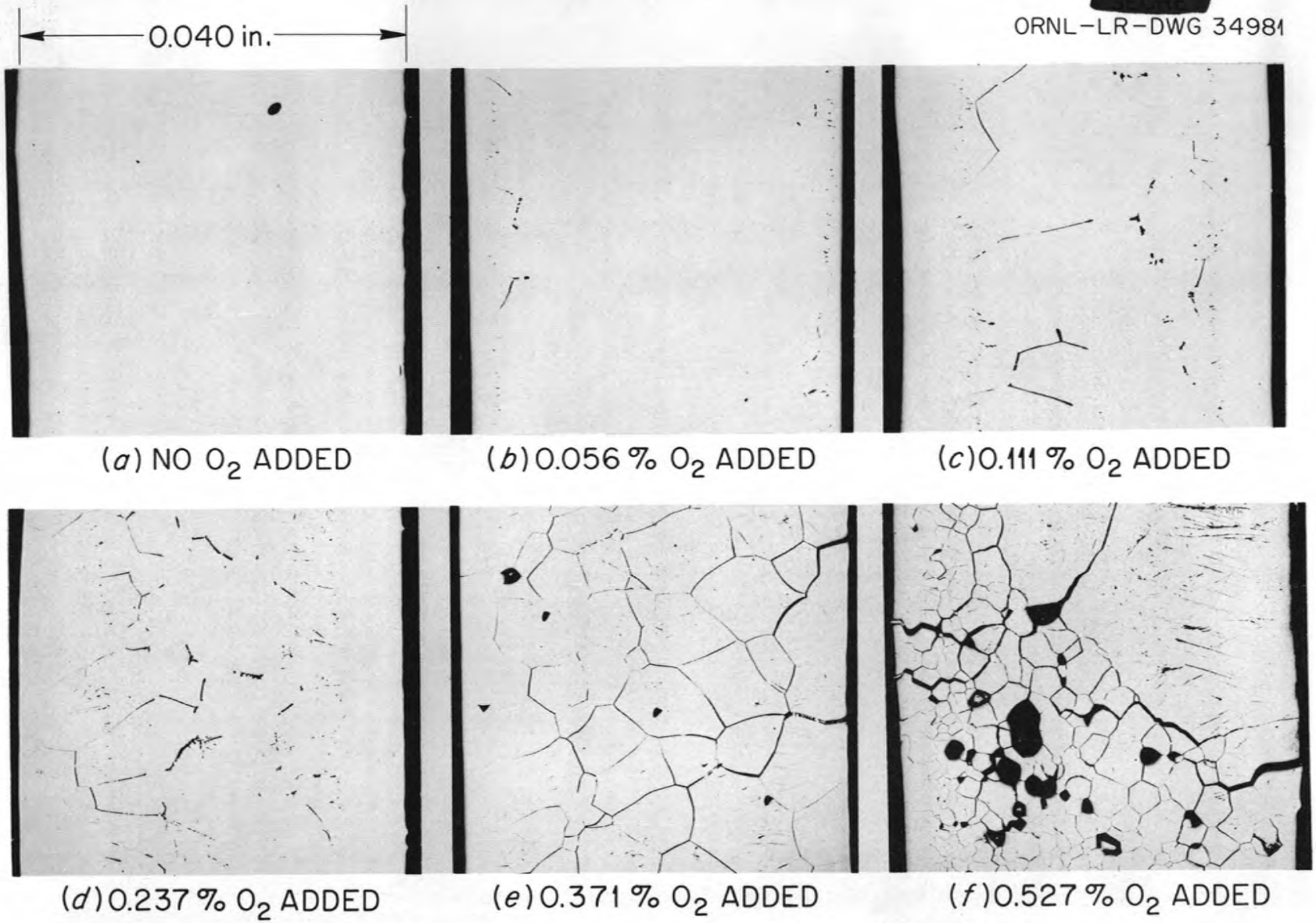

Fig. 19. Fusion-Weld Zones of Columbium Specimens to which Varying Amounts [redacted] were Added Prior to Welding. Specimens Shown in As-Polished Condition after Exposure to Lithium. Test Conditions: Static, 1500°F (816°C), 100 hours.

[redacted]

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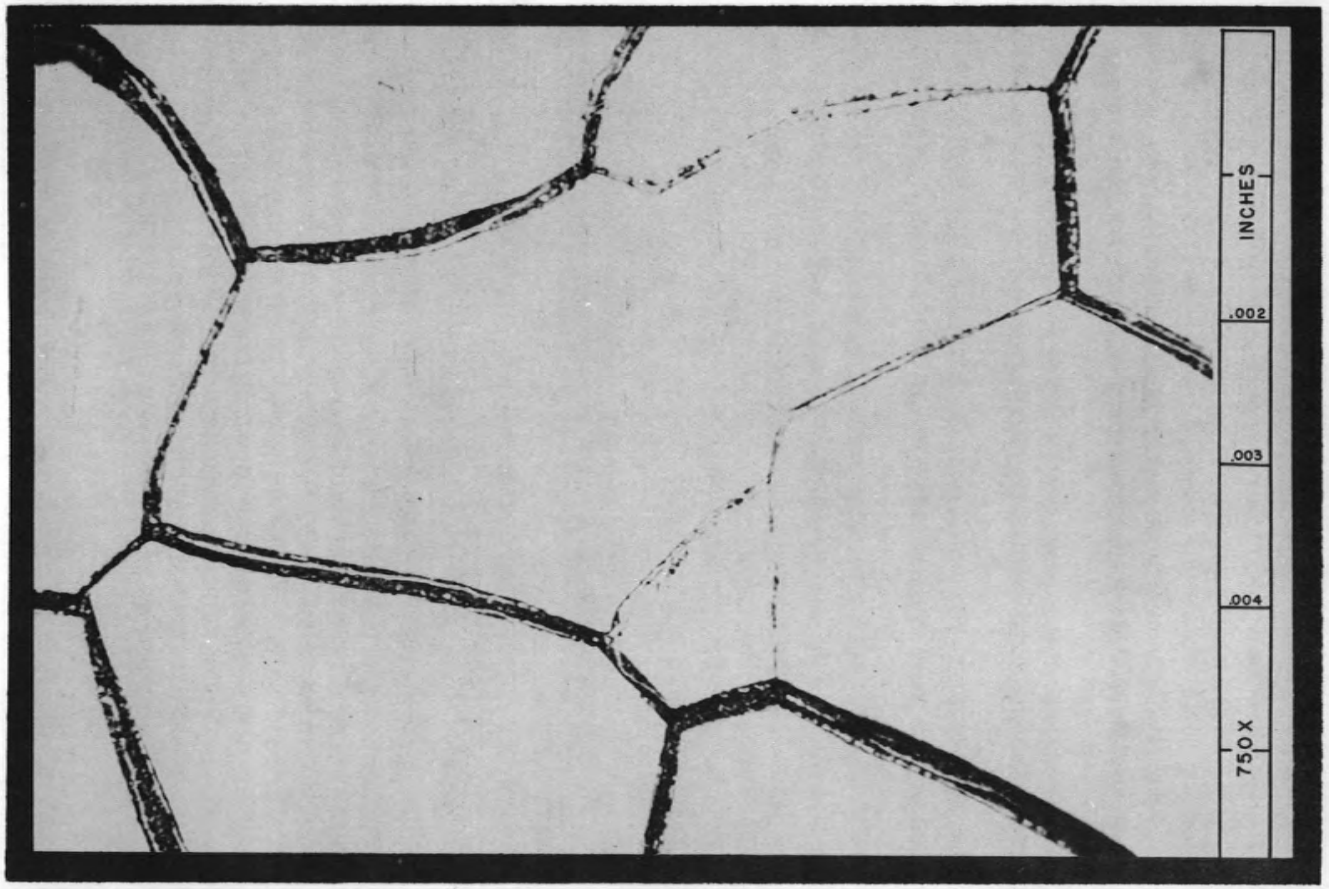


Fig. 20. Grain-Boundary Corrosion Products in Weld Zone of Columbium Specimen to which 0.527 % Oxygen was Added Prior to Welding. Specimen was Exposed to Lithium for 100 hours at 1500°F (816°C). As Polished, 750X.

continuous grain-boundary phase has a ceramic-like appearance and was extremely difficult to retain during metallographic polishing.

The evidence cited thus far clearly indicates that oxygen is by far more effective than nitrogen in promoting the susceptibility of columbium to grain-boundary attack by lithium. Moreover, it is evident that oxygen is particularly detrimental when present in amounts greater than its reported solubility limit in columbium and that nitrogen has no effect at comparable concentration levels. That these observations are consistent with the relative thermodynamic stabilities of columbium nitride and columbium oxides in molten lithium is shown by the calculated standard free energy of reaction values[8,9] listed in Table IV. In view of this correlation, it is proposed that the metallic phase in the duplex grain-boundary corrosion product shown in Figure 20 is columbium metal and the ceramic-like phase is lithium oxide.[10] The staining phenomenon mentioned earlier is accordingly attributed to the formation of lithium hydroxide by the reaction of lithium oxide in the grain boundaries with moisture in the atmosphere. The cracks observed on the surface of the high-oxygen specimens are attributed to the volume expansion which would occur as a result of the grain-boundary corrosion reaction. Based on room-temperature densities,[11,12] the formation of the proposed reaction products would be accompanied by a 47 per cent increase in volume.

---

[8] Glassner, A., The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, U. S. Government Printing Office, Washington 25, D.C.

[9] Brewer, L. et al., Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, p. 42, ed. by L. L. Quill, Mc-Graw Hill, New York (1950).

[10] In this connection a comment is in order concerning in-progress experiments in which the effects of additions of oxygen and nitrogen to lithium are being studied. Approximately 5000 ppm of each of these contaminants were added in separate experiments in the form of lithium oxide and lithium nitride, respectively. After 100-hour exposures at 1500°F (816°C), no attack was observed in any of the specimens in this study in spite of the impurity additions to the lithium. The only effect noted was the formation of a thin columbium-nitride surface layer on the specimens exposed to lithium to which nitrogen was added.

[11] Darnell, J. R. and Yntema, L. F., Technology of Columbium (Niobium), pp. 2 and 4, ed. by B. W. Gonser and E. M. Sherwood, John Wiley and Sons, Inc., New York (1958).

[12] Hodgman, C. D. et al., Handbook of Chemistry and Physics, p. 540, Chemical Rubber Publishing Co., Cleveland, Ohio (1953).

TABLE IV

RELATIVE THERMODYNAMIC STABILITIES OF COLUMBIUM OXIDES AND COLUMBIUM NITRIDE IN LITHIUM

Reaction	$\Delta F^\circ_{816^\circ C}$ (K cal)
$2\ Li + CbO = Li_2O + Cb$	- 31.7
$2\ Li + 1/2\ CbO_2 = Li_2O + 1/2\ Cb$	- 34.2
$2\ Li + 1/5\ Cb_2O_5 = Li_2O + 2/5\ Cb$	- 37.7
$3\ Li + CbN = Li_3N + Cb$	+ 24.9

Additional corrosion tests were performed on eight different lots of columbium tubing at 1500°F (816°C) and at 1800°F (982°C). At each temperature the specimens were contained in a single columbium capsule to eliminate lithium purity as a test variable. The results of these tests are presented in Table V in the form of metallographic observations. It is to be noted that the attack on most of the tube specimens was quite erratic. The inside surfaces of some specimens were attacked while the outside surfaces were not; in other cases the reverse was true. An example of this type of inconsistent behavior is shown in Figure 21. These metallographic results suggest that the tubing was contaminated with oxygen during manufacture and that careful control of processing techniques will be required to produce columbium tubing which is totally corrosion-resistant to lithium. It is of interest to note that according to the data in Table V the specimen with the highest oxygen content sustained the heaviest and most consistent attack and that no attack was observed on the specimen of lowest oxygen content. These specimens are designated in the table as St-1 and F-8, respectively.

CONCLUSIONS

1. Columbium contaminated with oxygen is attacked intergranularly when exposed to lithium at elevated temperatures in both static systems at constant temperature and in thermal-convection loops.

2. Nitrogen contamination does not appear to affect the corrosion resistance of columbium in lithium.

3. A two-phase grain-boundary corrosion product observed in high-oxygen specimens is believed to consist of lithium oxide and columbium metal formed as a result of the reduction by lithium of grain-boundary columbium oxide. This hypothesis is consistent with the relative thermodynamic stabilities of columbium nitride and columbium oxides in molten lithium.

4. Careful control of processing techniques will be required during fabrication of unalloyed columbium to prevent oxygen contamination to concentration levels which render the metal susceptible to intergranular attack by lithium.

5. It would appear that the development of corrosion-resistant columbium systems for the containment of lithium will depend ultimately

TABLE V

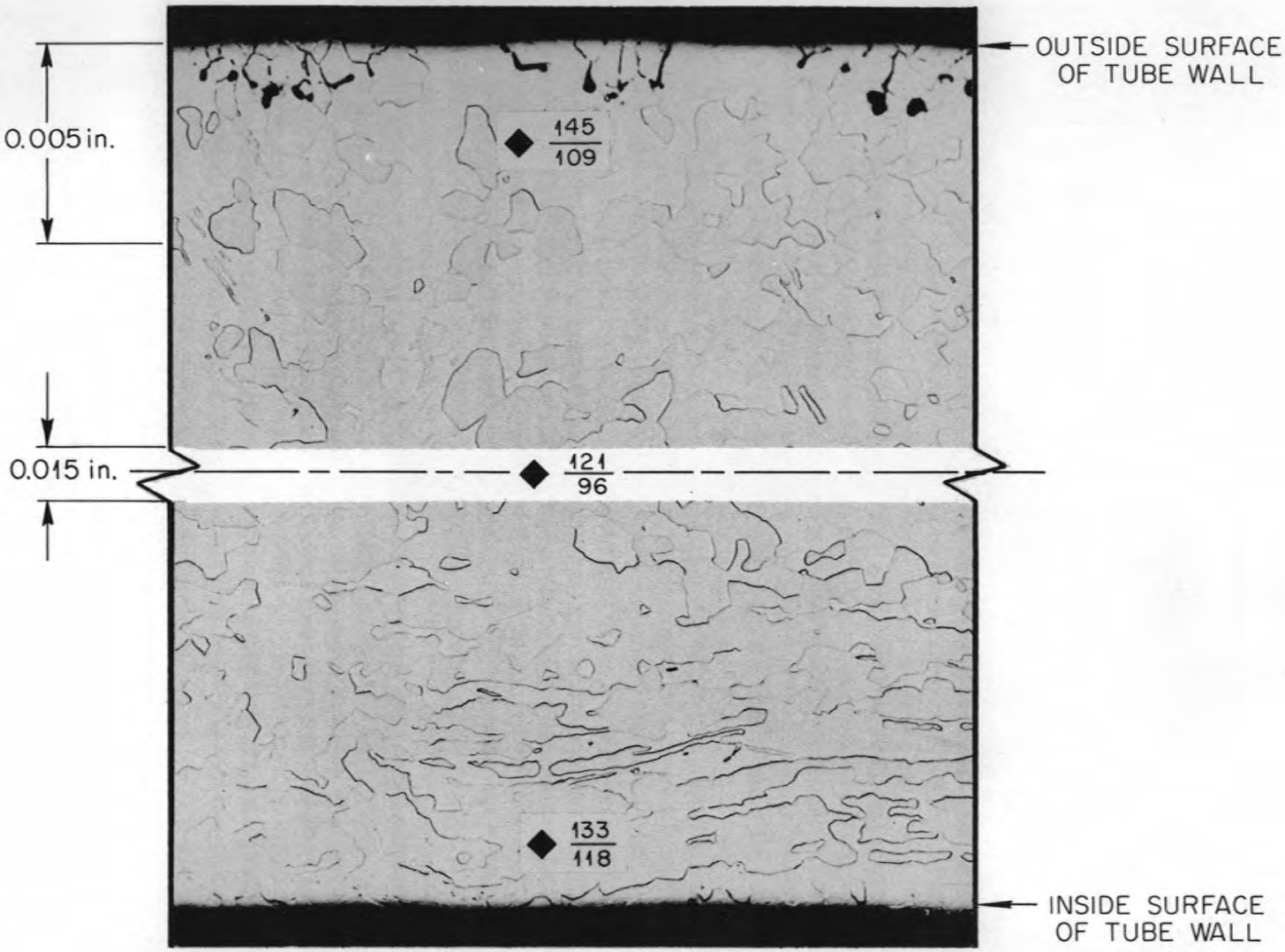
RESULTS OF LITHIUM CORROSION TESTS ON EIGHT LOTS OF COLUMBIUM TUBING[a]

TEST CONDITIONS: STATIC, 100 HOURS

TUBING CODE	COMPOSITION (Wt %)				RESULTS			
					1500°F (816°C)		1800°F (982°C)	
	O_2	N_2	H_2	C	INSIDE	OUTSIDE	INSIDE	OUTSIDE
WC-1	0.033	0.042	0.0053	0.030	No attack	No attack	No attack	No attack
WC-2	0.050	0.018	0.0026	0.0077	Subsurface phase to *1.5 mils*	No attack	No attack	No attack
ST-2	0.061	0.022	0.0009	0.017	No attack	Subsurface phase to *1 mil*	No attack	Subsurface phase to *1 mil*
F-8	0.013	0.0088	0.0008	0.0041	No attack	No attack	No attack	No attack
WC-3[b]	0.051	0.050	0.0004	0.0031	No attack	Subsurface phase to *2 mils*	No attack	Subsurface phase to *1 mil*
WC-4[b]	0.045	0.037	0.0001	0.0018	No attack	Subsurface phase *2–4 mils*	No attack	Subsurface phase to *2.5 mils*
WC-5[b]	0.026	0.0066	0.0002	0.0045	No attack	Subsurface phase to *1.5 mils*	No attack	No attack
ST-1[b]	0.080	0.032	0.0005	0.016	Subsurface phase to *1.5 mils*	Subsurface phase to *2 mils*	Subsurface phase to *1.5 mils*	Subsurface phase to *2.5 mils*

[a]0.5 IN. O.D. × 0.030 IN. WALL.

[b]TYPE 446 STAINLESS STEEL CLADDING MECHANICALLY STRIPPED FROM COLUMBIUM TUBING PRIOR TO CORROSION TESTS.



DIAMOND PYRAMID HARDNESS (500g LOAD) BEFORE TEST / AFTER TEST

Fig. 21. Outside and Inside of Tube Wall of Columbium Specimen Following Exposure to Lithium (Both Sides Exposed to Lithium). Test Conditions: Static, 1500°F (816°C), 100 hours. Etched.

on the addition to the base metal of an alloying element, whose oxide either is stable in both lithium and columbium at elevated temperatures or at least stable in columbium and can be prevented from forming at the grain boundaries by suitable heat treatment.

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The author wishes to acknowledge the contribution of Dr. W. O. Harms of the University of Tennessee, his thesis adviser, who labored at length in editing and reviewing the material presented in this report.

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