SANDIA REPORT SAND81-1952 • Unlimited Release • UC-38
Printed November 1981

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Prepared by
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Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789

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SF2900Q(8-81)

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Available from
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Printed copy: $6.00
Microfiche copy: A01

TEARING DURING PINCH-OFF OF ROLAMITE FILL TUBES*

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ABSTRACT

A failure mechanism is proposed to explain the bubble streaming and trichloroethylene infiltration which has been observed in failed Rolamite devices. An intergranular oxide network forms in the Kovar fill tube as a result of the glass-to-metal seal processing; it is suggested that tearing occurs in this oxide network during a subsequent pinching-off operation. It is demonstrated that bending over a mandrel causes this intergranular network to widen and deepen in a tearing mode. A modified preoxidation heat treatment or partial oxidation procedure prevents this problem.

Introduction

Rolamite devices sometimes fail a gross leak test in which, after fill tube pinch-off and trichloroethylene rinse, each device is visually inspected for bubble streaming. Failure rates ranging from 1/30 to 1/15 have been observed at this stage of product inspection (1,2). This failure mode had been attributed to elastic springback of the Kovar* fill tube during the pinch-off operation (3). This has prompted the inclusion of a silver wire inside the Kovar fill tube to improve the pinch-off weld. However, this has apparently not stopped the gross leak problem. In addition, trichloroethylene has been detected inside Rolamites which pass the gross leak test. This is thought to be due to the seeping in of trichloroethylene, during cleaning, and prior to final epoxy sealing of the fill tube. In this report an alternative failure mechanism to that of elastic springback which can lead to both of the above mentioned problems will be proposed. It will be shown that certain defects produced during Kovar fill tube oxidation processing can lead to gross leaks. The causes of the defects which result in this failure mechanism are determined and three solutions suggested.

*ASTM-F-15 29%Ni, 17% Co Balance Fe.

Results of Investigation

Rolamites which had failed the gross leak test were supplied by R. J. Martinez, 5811. These devices were broken and the end cap assemblies prepared for scanning electron microscope (SEM) evaluation. Figures 1-4 show the pinched-off fill tube of one of these devices at various magnifications and orientations. The most disturbing feature of the pinch-off is a large tear which is most obvious in Figures 2 and 3. It is claimed to be a tear, rather than a crack, because of the ductile rupture fracture surface morphology seen in Figure 4. This tearing behavior is not expected in a pinching process such as this, given that the Kovar is dead soft as it should be as a result of the heating cycles during glass to Kovar sealing.

These failed Rolamite devices were then mounted and sectioned for optical microscope examination of the pinched-off tube. Figure 5 shows a pinched-off fill tube (gray) with its silver filler wire (white). The region of the pinch shows significant porosity and the tears, mentioned above, can be seen in cross section at the edge of the tube. Figure 6 shows another pinched-off tube oriented perpendicular to that in Figure 5. In this view the silver wire has apparently served its function well. More important, however, are the dark features along the inner and outer surfaces of the fill tube. At higher magnification

(Figure 7) the features appear to be cracks or tears which are not necessarily associated with or caused by the pinch-off process However, the pinch-off process could probably lengthen these features to such an extent that a gross leak is possible.

The tubes shown in Figures 1-7 were obtained from Reeves-Hoffman (RH), a supplier of end cap assemblies, in the oxidized condition prior to glass sealing. The Kovar tubing in end cap assemblies obtained from Northeast Electronics Corporation (NEC) shows significantly fewer surface features but they still exist. For example, Figure 8 shows that in the etched condition the dark surface features are located at Kovar grain boundaries.

If the surface features were tears or cracks they could propagate into the bulk of the Kovar as the tube was bent. Figures 9-14 illustrate the results of bending RH oxidized Kovar tubes over cylindrical mandrels ranging in diameter from .500 inches to .180 inches. Bending over the .500 inch mandrel has little effect on the dark feature configuration. However, bending over the smaller diameters causes the features to widen and deepen, thus acting like cracks or tears. The results of an electron microprobe analysis of as received RH tubes are shown in Figures 15 and 16. Figure 15 is a SEM photomicrograph of the tube cross-section showing an oxide skin and the dark surface features mentioned above. Figure 16 is an oxygen X-ray photomicrograph which clearly shows that the dark features are oxide particles. After heat treating in dry hydrogen at 925°C for one hour all

signs of surface and grain boundary oxide are gone as shown in Figures 17 and 18. However, voids remain, thus the possibility of tearing during pinch-off remains.

Cold drawn Kovar tubing is often oxidized by Organization 1471 in preparation for in-house glass to metal seal processing. This oxidation treatment is performed in a Sargeant and Wilbur traveling belt furnace in a residual oxygen atmosphere obtained by flowing nitrogen at a rate of 10 cubic feet per minute. The temperature profile for this process is shown in Figure 19. Each specimen spends two to three minutes at the peak temperature of 900°C (4). This oxidation process yields a very different surface from the RH process as can be seen in Figures 20 and 21. The RH specimen has an oxide skin and penetration zone which are approximately 2.50μm and 25.0μm thick, respectively. The Sandia processed tube has an oxide skin which measures approximately 0.5μm in thickness while its oxide penetration zone is approximately 3.8μm thick. After six passes through the furnace the Sandia specimen has an oxide skin which resembles the RH specimen. However, the oxide penetration zone is not as deep as in the RH specimen. Furthermore, the grain size of the Sandia processed tube is much smaller than the RH tube.

Eight unoxidized tubes were given from one to eight passes through the belt furnace and prepared for metallographic investigation. The oxide layer was examined at a magnification of 1000 times and five thickness measurements were made. Each pass

through the furnace amounted to approximately 150 seconds at 900°C. The thickness measurements were plotted and are shown in Figure 22. The average, maximum and minimum of five measurements were plotted versus the square root of oxidation time. Although there is significant scatter a straight line fits the data quite well suggesting volume diffusion controlled oxide layer growth.

Discussion of Results

The intergranular oxide has been shown to be a cause of tearing during the Rolamite pinchoff operation. At best, gross leaks would result if these tears were large enough. At worst, the tear would not lead to a gross leak but, rather, to precarious Rolamite reliability. This oxide phase is a necessary consequence of typical glass-to-metal seal processing so a quick review of this technology would be beneficial.

There are many variables and parameters in the process of making a glass to metal sealed assembly. The assemblies for the Rolamites under investigation are fabricated by vendors under proprietary conditions beyond the control of the assembly user. As many as three separate heat treatments may be given to the Kovar parts to be sealed. The first is a degassing and decarburization to decrease bubble formation in the glass during sealing. The second heat treatment is an intentional oxidation step to

promote wetting of the Kovar by the glass and finally there is the sealing heat treatment in which the glass is made to wet and flow over the surface of the oxidized Kovar. Surface preparation, atmosphere, temperature and time all contribute to making this a very complex process. The manufacturing of reliable glass-to-metal seals is expected to be sensitive to process perturbations. When in addition, a Kovar pinch-off operation is performed process control appears even more important. The author was not able to find in the open literature on glass-to-metal seal technology any procedure for preparing Kovar for glass sealing and then subsequently pinching off.

During investigations on the oxidation and sealing of Kovar (ASTM-F-15) Abendroth (5), Zakraysek (6) and Trojanowski and Zakraysek (7) all observed the formation of an intergranular oxide similar in all respects to the oxide penetration discussed in the previous section. Abendroth (5) and Trojanowski and Zakraysek (7) observed parabolic growth kinetics of the surface oxide layer. The data of Abendroth (5) indicate a change in oxidation mechanism at 800°C. Some evidence exists (7,8) which implies that the ratio of intergranular oxide to surface oxide thickness is affected by oxidation processing. This suggests that to decrease the tearing tendency during pinch-off operations one should attempt to find those conditions necessary to keep the intergranular oxide thickness minimal. These conditions are, at least, approximately met by the Sandia preoxidation

treatment since after bending these tubes over the mandrels used to test the RH product no tears were observed in any of the samples. Alternatively, one might attempt a partial oxidation such that only one end of the Kovar tube is oxidized. This can be achieved by inserting the tubes into holes machined in a graphite block. A Kovar fill tube processed in this fashion is shown in Figure 23. It is conceivable that this tube could be sealed and pinched-off without extensive tearing. Finally it is suggested that an alternate fill tube alloy and sealing glass be considered. For example, ASTM-F-29 relies upon a borate coating to enhance wetting by glass (6).

Conclusions

1. Rolamite devices can fail during pinch-off due to tearing of the fill tube.
2. The tearing originates in an intergranular oxide network which lies just beneath the continuous oxide surface layer.
3. The degree of tearing depends upon the depth of the oxide network which is determined by the preoxidation and glass sealing heat treatments.
4. The tearing problem can be eliminated by heat treatment alteration or by partial oxidation of Kovar fill tubes.

Acknowledgements

The author would like to thank R. J. Martinez, 5811, K. E. Mead, 5811, D. O. Schuler, 2542, and P. C. Jones, Jr., 2542, for helpful conversation, C. R. Pennington, 1472, for helpful preoxidation experiments and Organization 5822 for extensive analytical support.

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1. Memo from K. E. Mead and R. J. Martinez, 5811, to L. A. Harrah, 5811, dated 2-19-81.
2. R. J. Martinez, 5811, private communication, 5-13-81.
3. Memo from L. A. Harrah to distribution, dated 7-9-81.
4. C. R. Pennington, private communication.
5. R. P. Abendroth, Materials Research and Standards, Sept. 1965, p. 459.
6. L. Zakraysek, IEEE Trans. on Parts, Hybrids, and Packaging, Vol. PHP-8, Dec. 1972, p. 45.
7. G. F. Trojanowski and L. Zakraysek, Final Technical Report 19, RADC-TR-79-98, Jan. 78 - 19 Feb. 79.
8. I. M. Kireeva, L. A. Plakhtii and S. I. Sachkov, Zashchita Metallor, Vol. 10, No. 3, May-June 1974, p. 342.

Table 1

Oxide Thickness and Oxidation Time at 900°C

Number of Furnace Passes	Time (sec) at 900°C	$\sqrt{\text{Time at 900°C}}$	Average Oxide Thickness (μm)
1	150	12.3	0.5
2	300	17.3	1.3
3	450	21.2	1.3
4	600	24.5	2.3
5	750	27.4	2.0
6	900	30.0	2.3
7	1050	32.4	2.5
8	1200	34.6	3.4

Figure 1. SEM photomicrograph of leaking Rolamite end cap assembly.

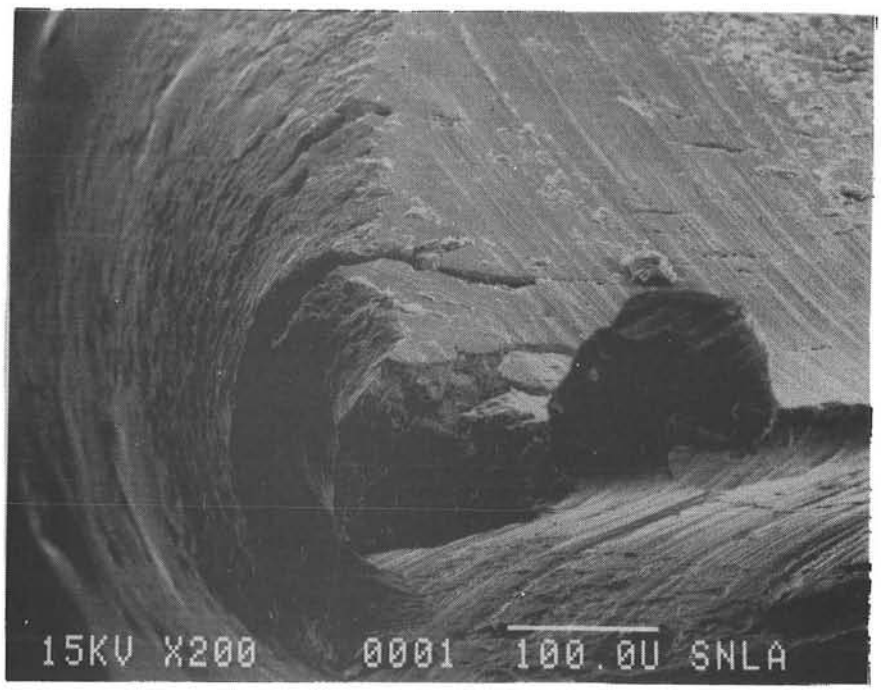

Figure 2. Large crack or tear near pinch-off of leaking Rolamite device.

Figure 3. Tear surface morphology showing indication of ductile failure.

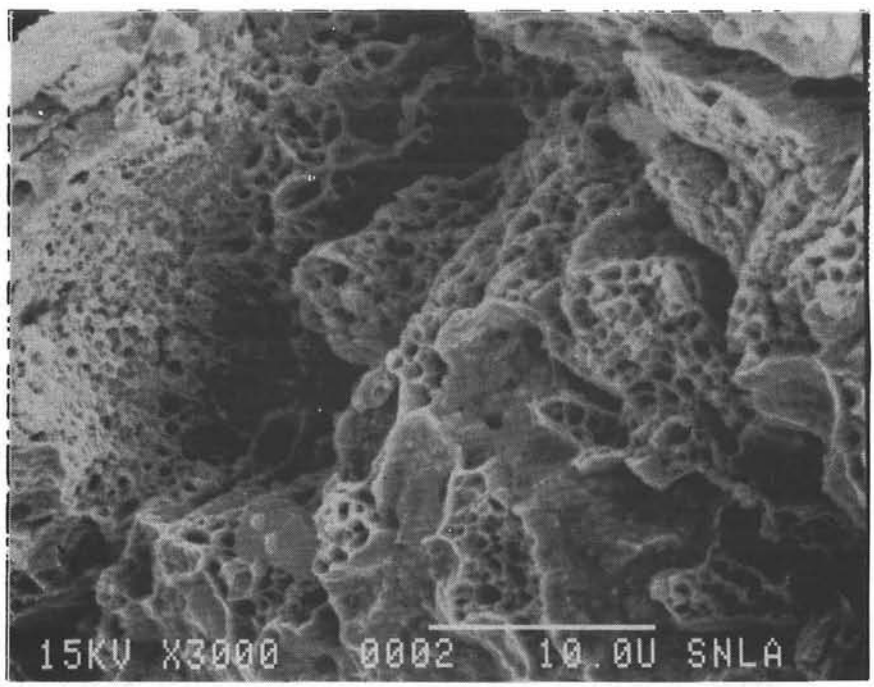

Figure 4. Ductile rupture failure mode on tear surface.

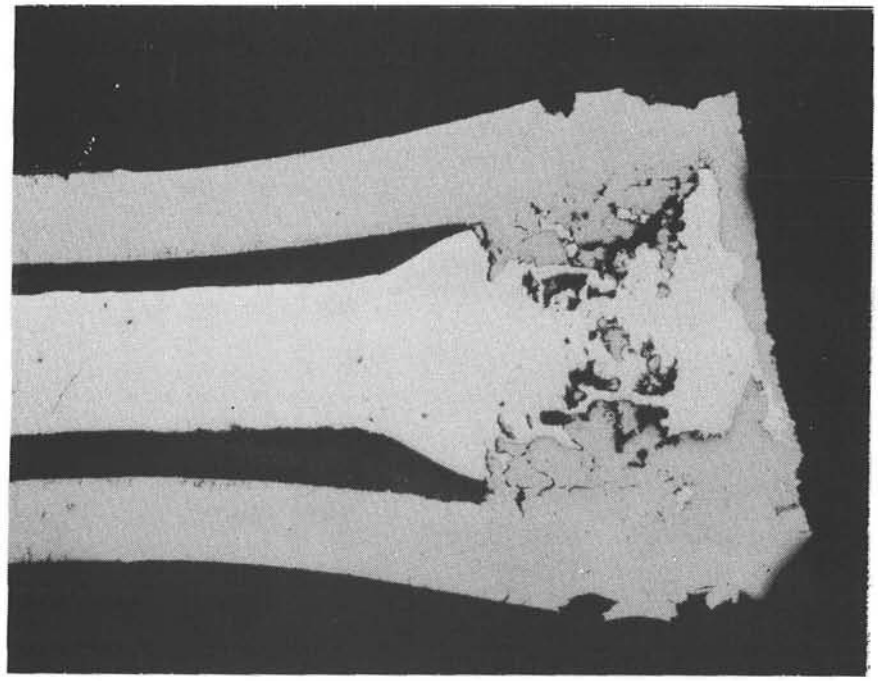

Figure 5. Cross section of pinch-off showing silver filler wire and significant porosity. Magnification 50X.

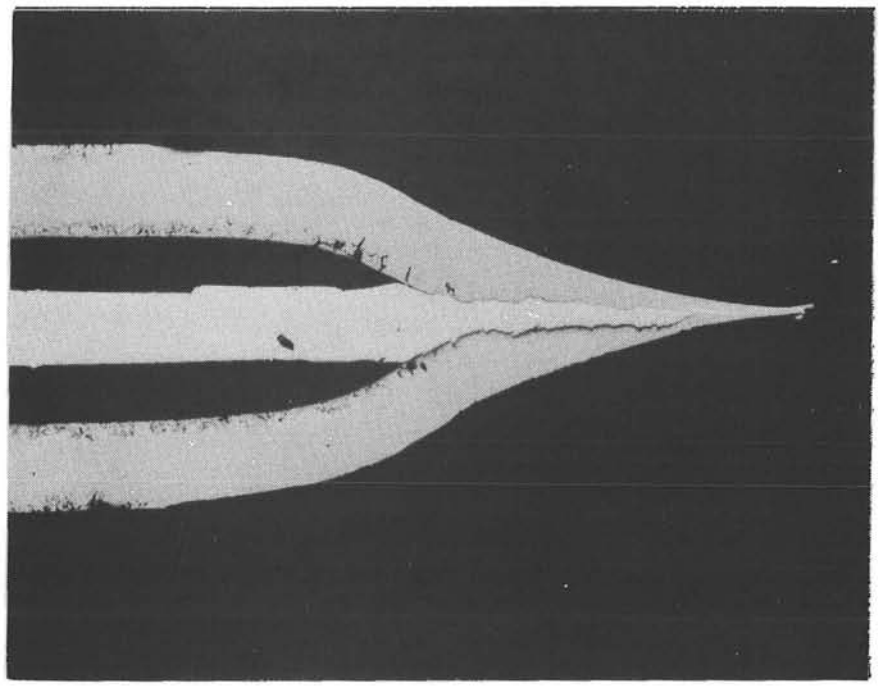

Figure 6. Pinched-off fill tube showing dark crack like features on inner and outer tube surfaces. Magnification 50X.

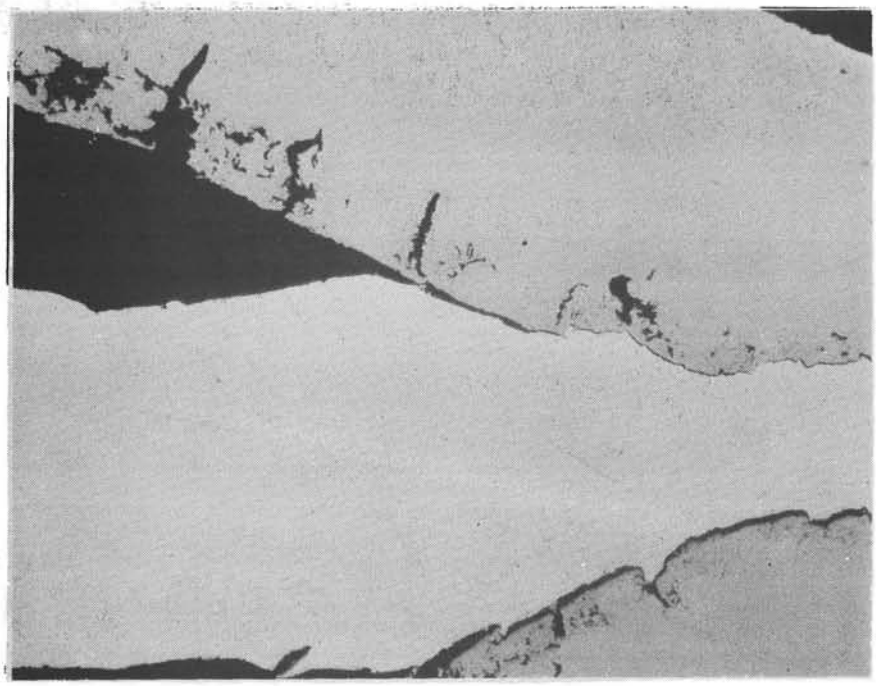

Figure 7. At higher magnification the dark features appear to be cracks or tears. Magnification 250X.

Figure 8. Etched NEC sample showing dark surface feature - grain boundary correlation. Magnification 250X.

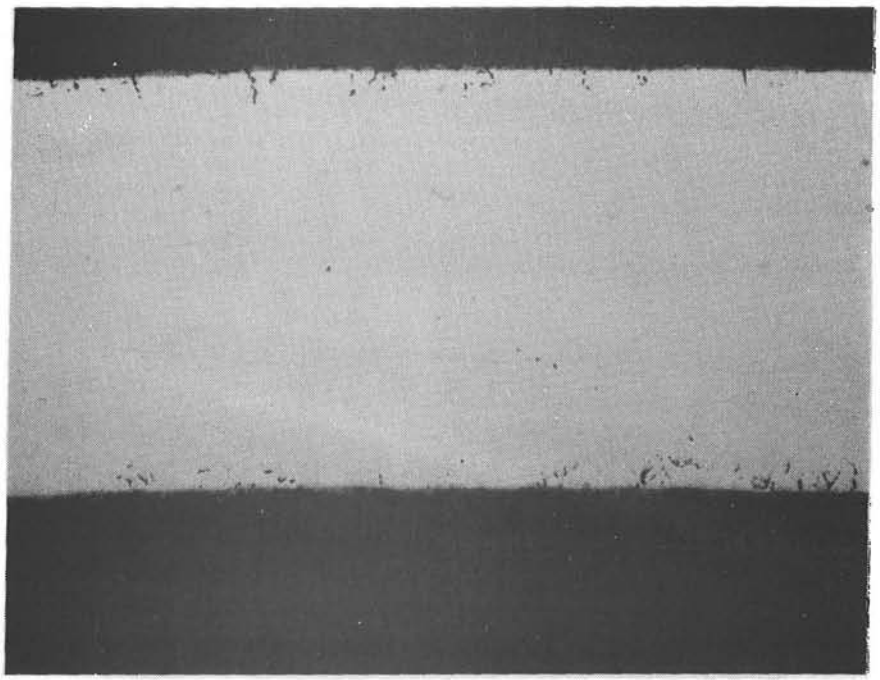

Figure 9. Bending over a .500 inch mandrel has little effect.
Magnification 250X.

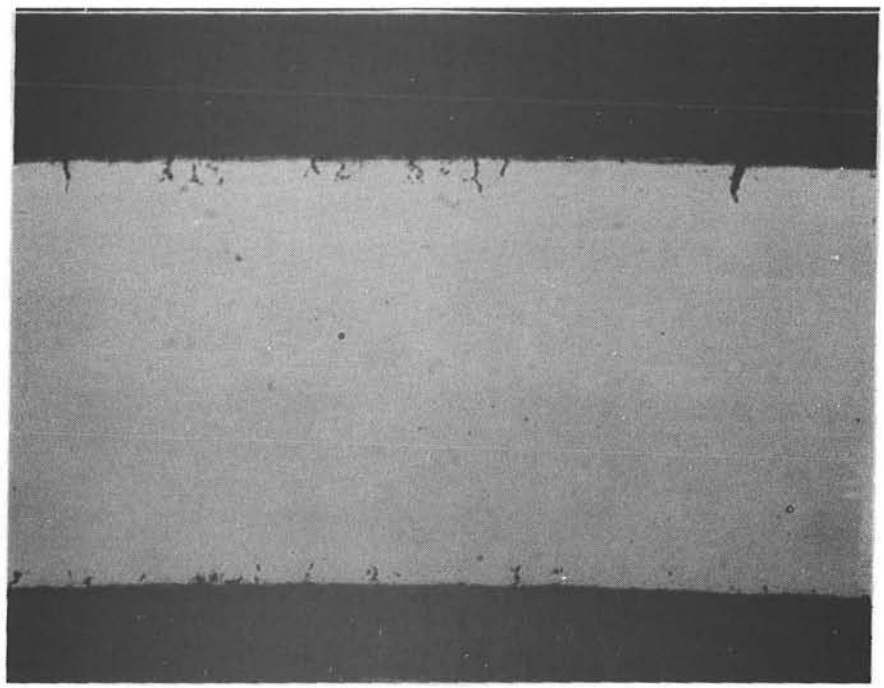

Figure 10. Bending over a .390 inch mandrel causes widening of dark features.
Magnification 250X.

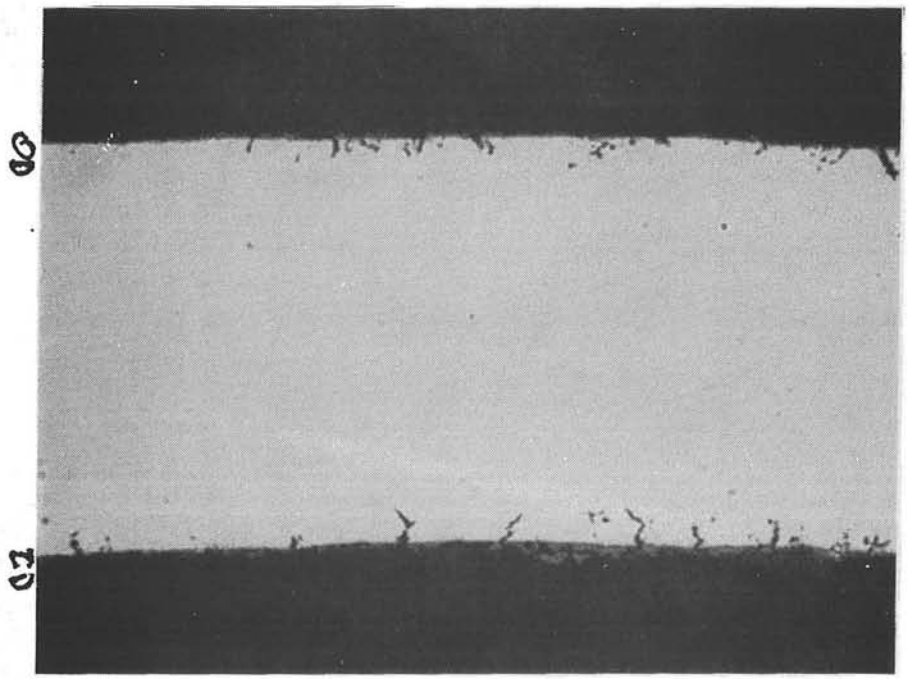

Figure 11. Bending over a .281 inch mandrel.
Magnification 250X.

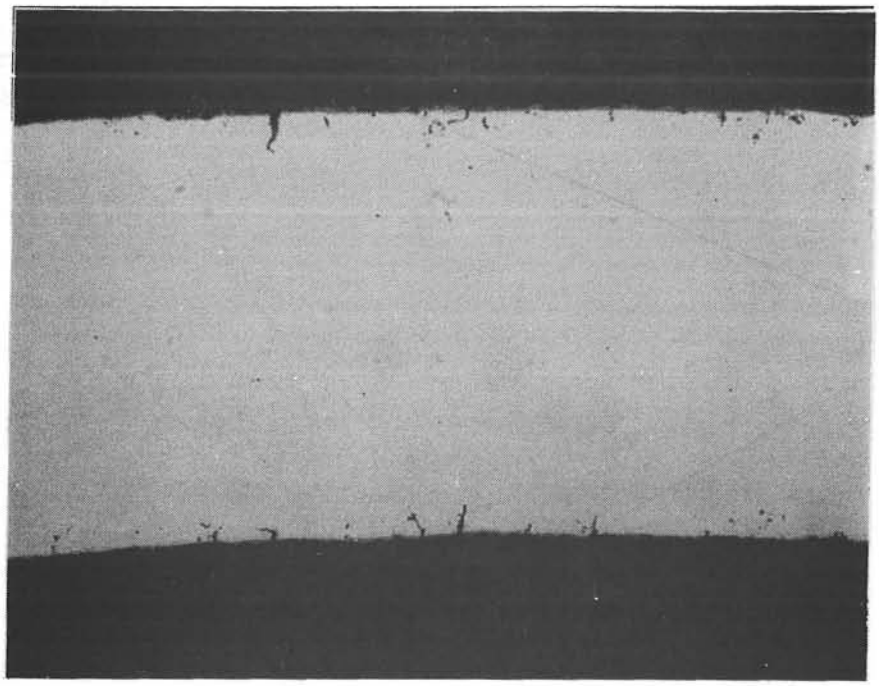

Figure 12. Bending over a .223 inch mandrel begins to deepen features.
Magnification 250X.

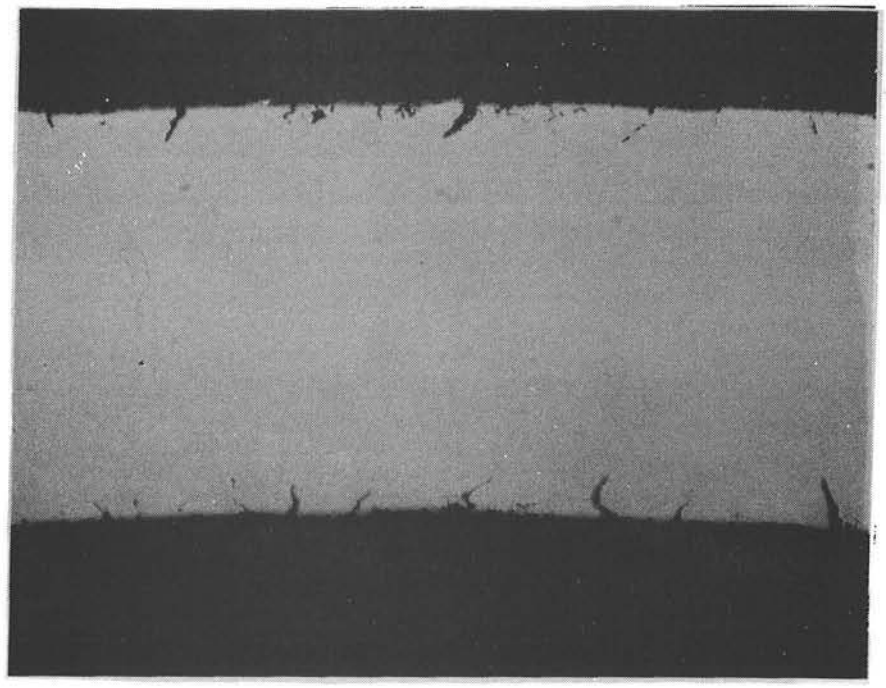

Figure 13. Severe widening of features after bending over .201 inch mandrel. Magnification 250X.

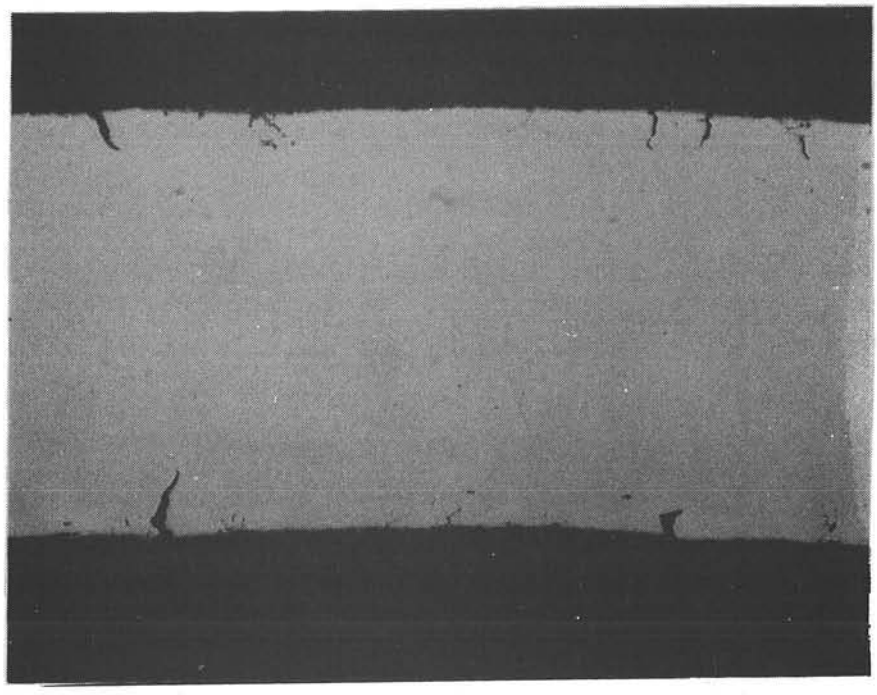

Figure 14. Severe widening and deepening of features after bending over .180 inch mandrel. Magnification 250X.

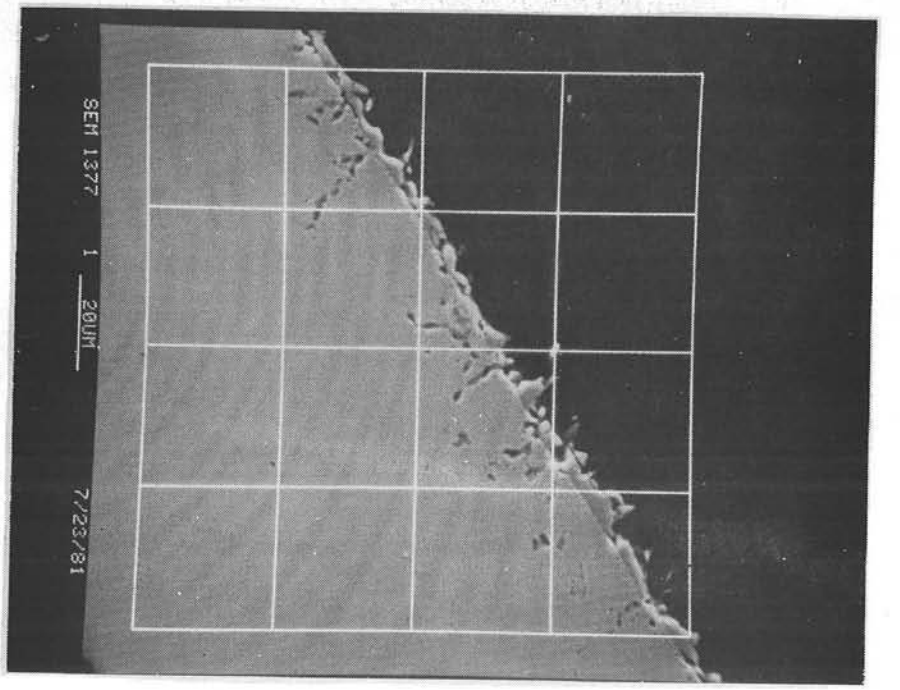

Figure 15. SEM photomicrograph of sectioned Kovar fill tube showing oxide skin and penetration.

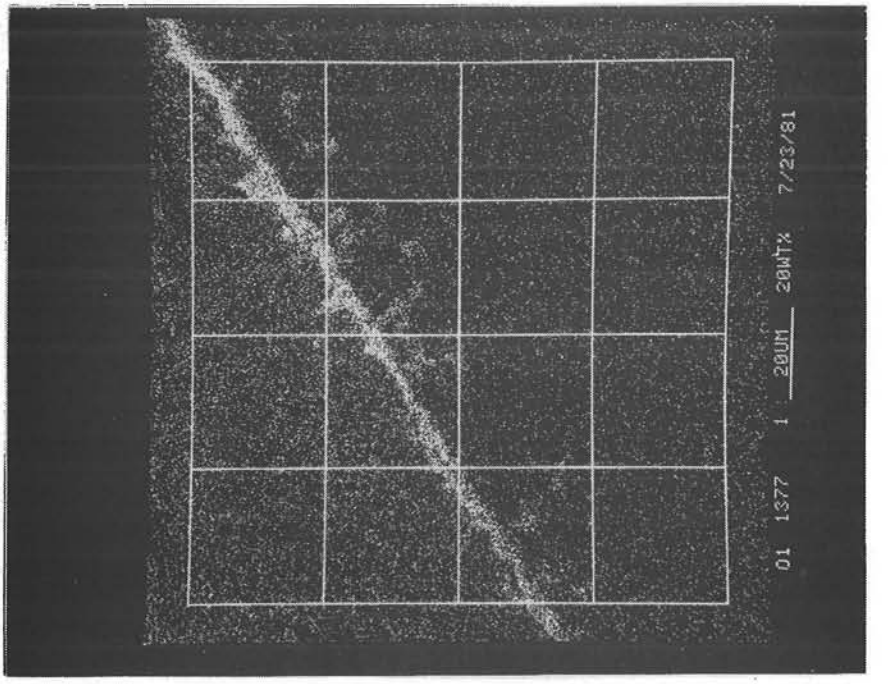

Figure 16. Oxygen X-ray photomicrograph of oxide skin and penetration.

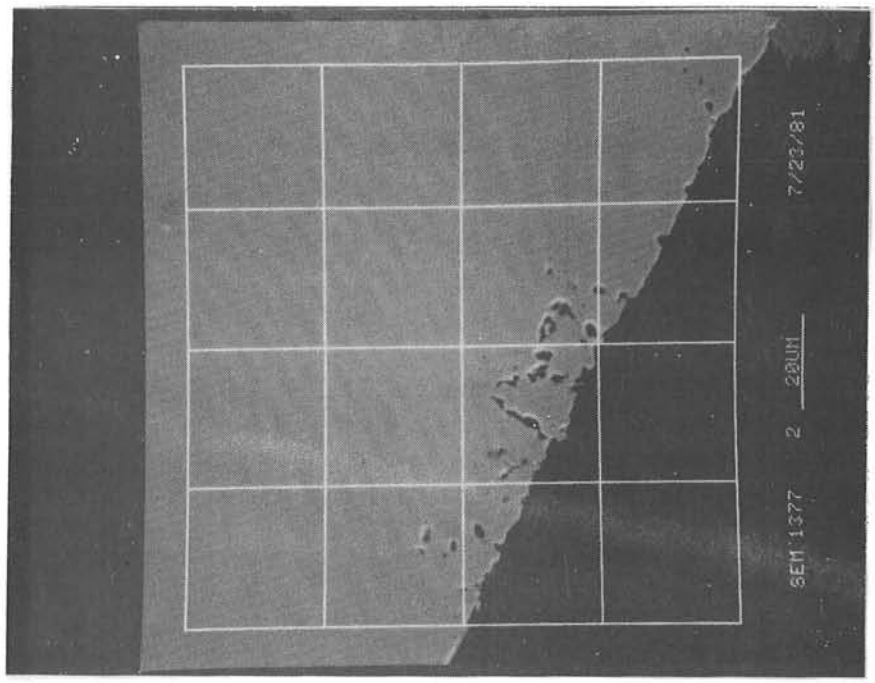

Figure 17. SEM photomicrograph of Kovar tube reduced in dry hydrogen.

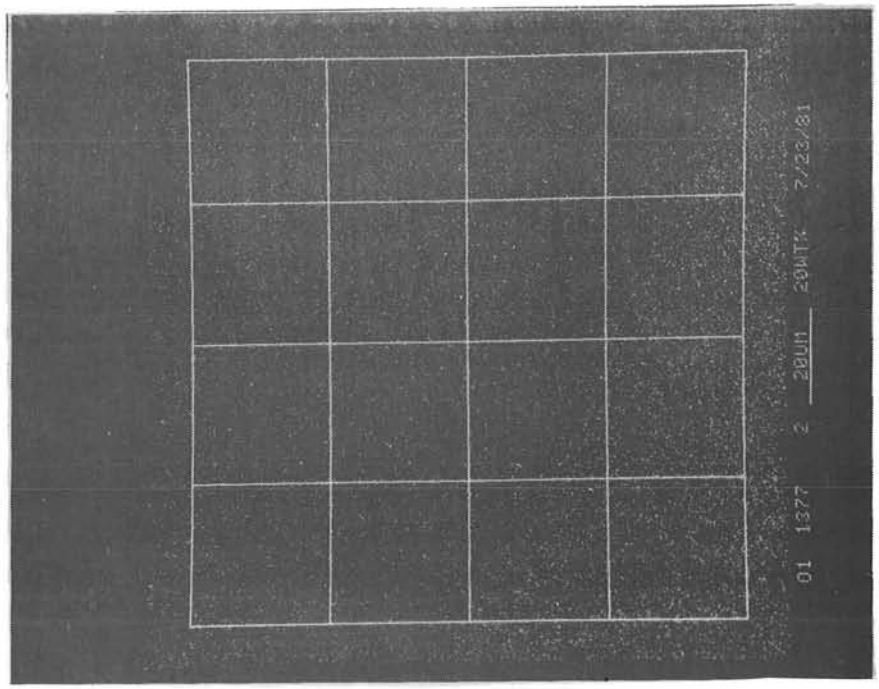

Figure 18. Oxygen photomicrograph of Kovar tube reduced in dry hydrogen.

TRAVELING BELT FURNACE

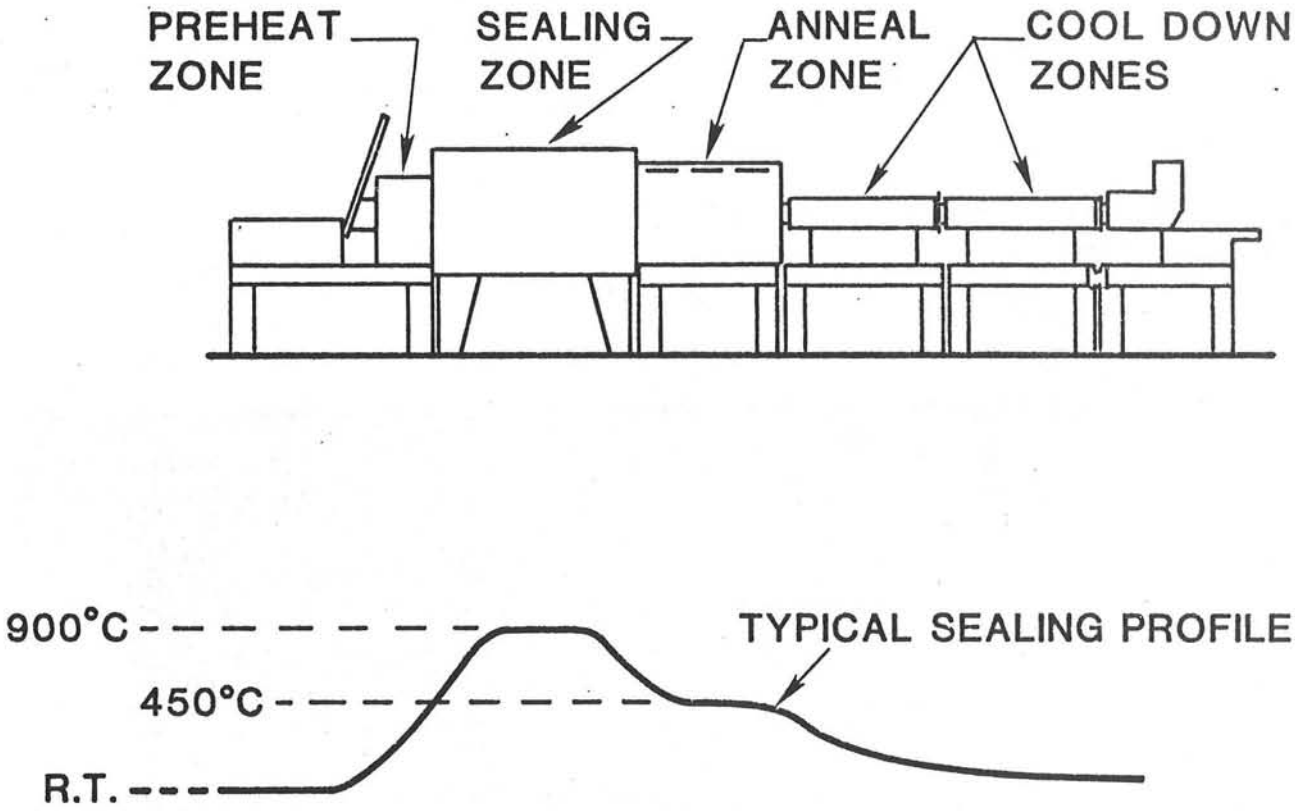

Figure 19. Configuration of traveling belt furnace and temperature profile.

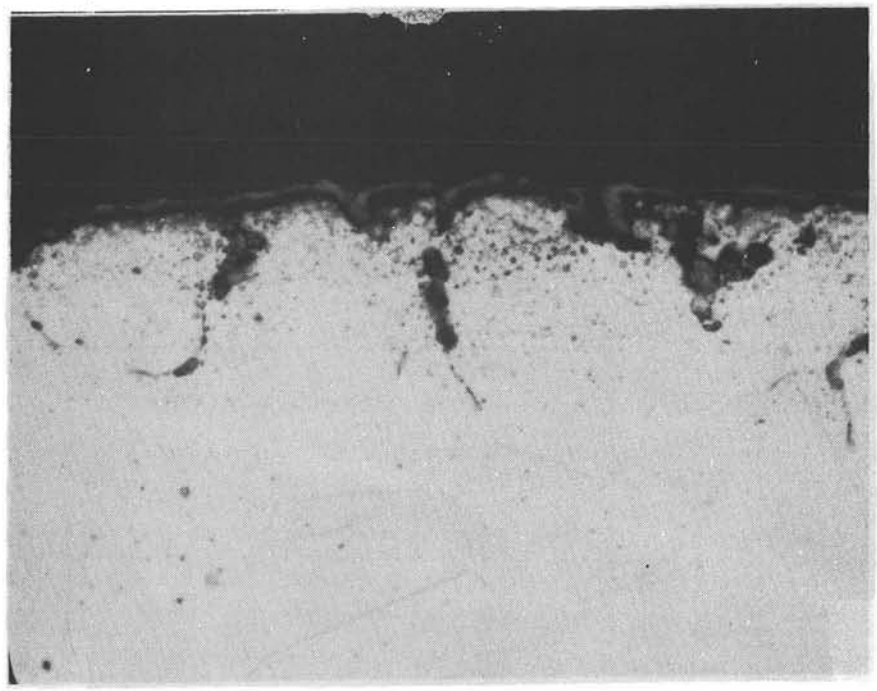

Figure 20. RH processed oxide layer and grain boundary penetration.
Magnification 1000X.

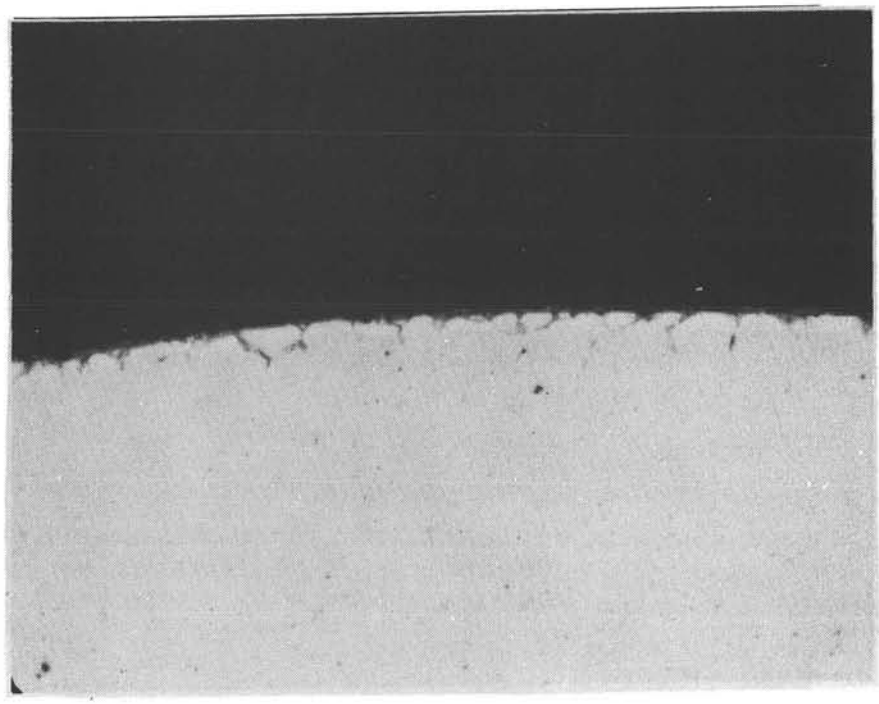

Figure 21. Sandia processed oxide layer and grain boundary penetration.
Magnification 1000X.

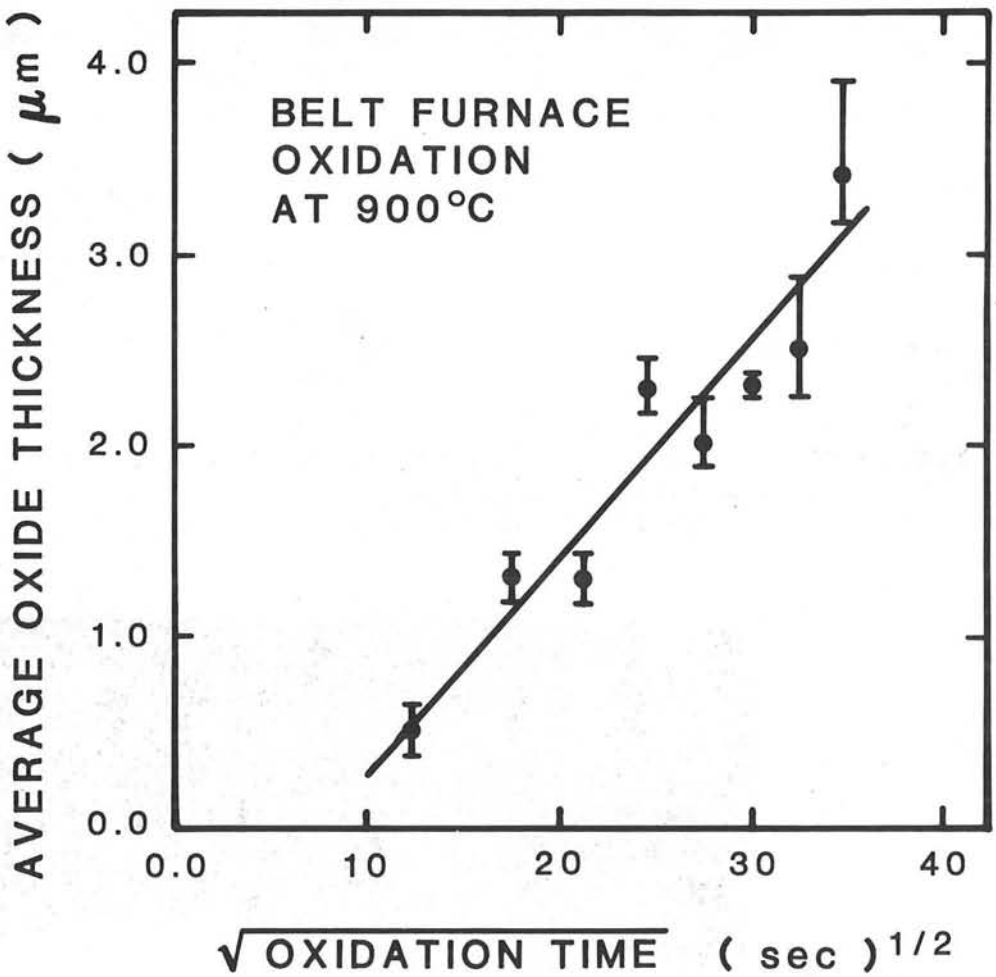

Figure 22. Oxidation kinetics of Kovar tubes in residual oxygen atmosphere of traveling belt furnace at 900°C.

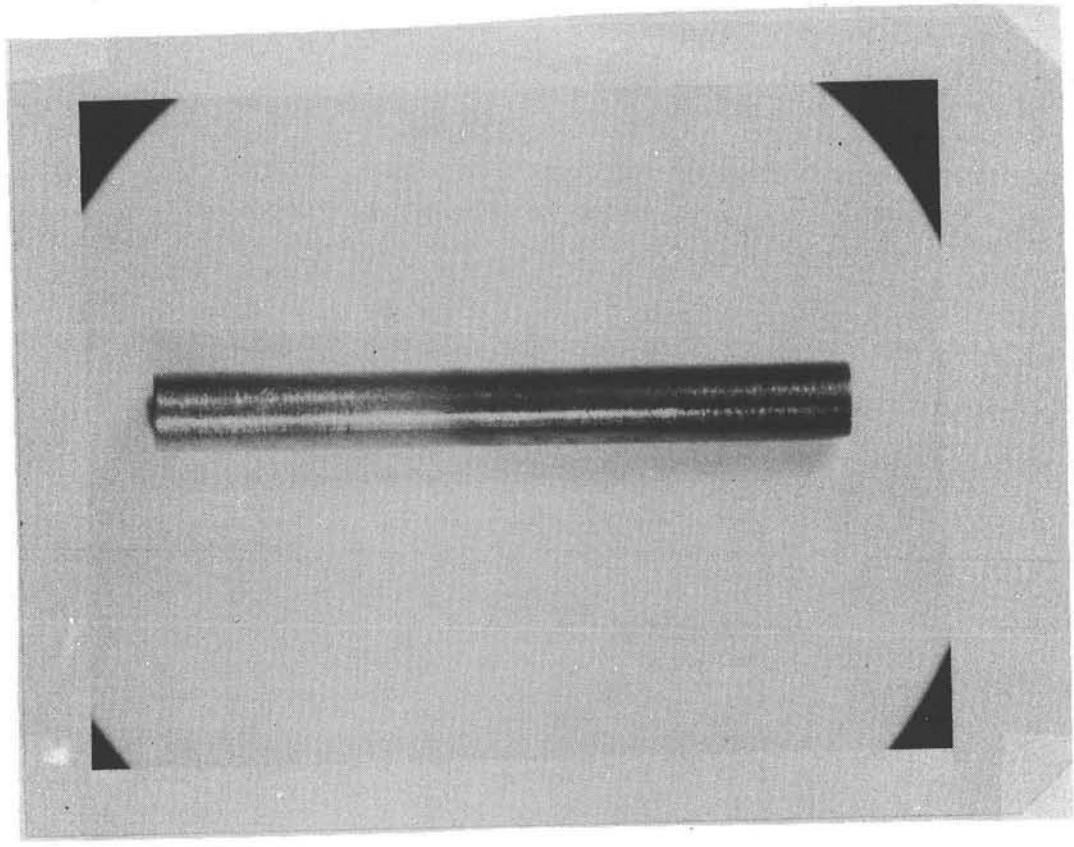

Figure 23. Partially oxidized Kovar fill tube processed at Sandia Labs. Magnification 10X.

Distribution:

1470	R. S. Wilson
1471	C. R. Pennington
1471	R. D. Snidow
2540	K. Gillespie
2542	R. S. Pinkham
2542	D. O. Schuler
2542	P. C. Jones
5810	R. G. Kepler
5811	L. A. Harrah
5811	R. J. Martinez
5811	K. E. Mead
5830	M. J. Davis
5832	R. W. Rohde
5832	F. G. Yost
3141	L. J. Erickson (5)
3151	W. L. Garner (3)
3154-3	C. Dalin (25) for DOE/TIC
8214	M. A. Pound