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"INVESTIGATION OF WELDING AND BRAZING OF MOLYBDENUM AND TZM ALLOY TUBES"

Final Report To:

NASA MARSHALL SPACE FLIGHT CENTER
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Purchase Order Number H-080640

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INTRODUCTION

This is the final report for work performed under purchase order number H-080640. This effort involved investigating the welding and brazing techniques of molybdenum tubes to be used as cartridges in the crystal growth cartridge.

DISCUSSION OF CURRENT PROBLEM

Figure 1 is a schematic of the crystal growth cartridge. A molybdenum tube, fabricated by rolling, is fitted with a spherical end cap (electron-beam welded) and a 304L stainless steel adjustment block (vacuum brazed). During the welding and brazing operations the molybdenum tube recrystallized and became extremely brittle. Hoop stresses generated by both the welding and brazing operations caused failures of the cartridge.

Figure 2 is a photomicrograph of a section of a NASA/MSFC supplied molybdenum cartridge. This cartridge has not been heat treated. As can be seen the molybdenum has an aligned grain structure due to the rolling process from which it was formed.

Figure 3 is a photomicrograph of a sample from the same cartridge but heat treated to 1950°F for one hour. This is the temperature and time at which the cartridge was brazed in a vacuum furnace. As can be seen the molybdenum has recrystallized. The original axial grain structure has been replaced by randomly orientated large grains. This type of grain structure yields a brittle material.

Figure 4 is a photomicrograph of a section of the adjustment block brazed to the molybdenum tube. Note the molybdenum has recrystallized. Also note that the molybdenum tube slightly crimped and pulled away from the braze and adjustment block. This crimping is due to the large circumferential stresses put on the tube by a thermal expansion mismatch between the stainless steel and the molybdenum. Figures 5 and 6 are the thermal expansion curves for 304L stainless steel and molybdenum, respectively. At 1400°F the expansion of the stainless steel is 14.0×10^{-3} in./in. The expansion of the molybdenum is about 4.4 x 10^{-3} in./in. at the same temperature. The large thermal expansion of the stainless steel causes a gap of about 0.0045 inches (at 1400°F) between the adjustment block and the tube. This gap then fills with braze. Upon cooling the braze solidifies and the stainless steel adjustment block contracts placing large hoop compressive and flexural stresses on the tube. Assuming equal compliance between the molybdenum and stainless steel adjustment block, the compressive elastic hoop stresses exceed the yield of both materials. This stress causes tube crimping or collapse. The flexural stress where the molybdenum exits the adjustment block is about 300,000 psi (again, elastic analysis). Thus one would also expect collapse of the molybdenum due to flexural stress.

Attempts were made by NASA/MSFC to place a 304L stainless steel mandrel in the tube to prevent collapse. But with the thermal expansion mismatch, the stainless steel mandrel expanded creating extensive stresses and failure in the molybdenum tube during heat up.

Figure 7 is a photomicrograph of the joint where the spherical end cap was electron beam welded. The large grain structure is easily visible at the heat affected zone.

In summary the problems associated with molybdenum cartridge are:

1] Recrystallization of the molybdenum tube during brazing.
2] Compressive hoop and axial stresses from the stainless steel adjustment block.
3] Tensile stresses from the stainless steel mandrel.
4] Recrystallization of the electron-beam welded joint at the spherical end cap.

EVALUATION OF POTENTIAL SOLUTIONS

The recrystallization temperature of molybdenum can be increased by alloying it with 0.5% titanium and 0.1% zirconium. The small amounts of titanium and zirconium inhibit grain growth. Recrystallization temperatures[1,2] for this alloy, known as TZM, become significant around 2500°F.

TZM alloy can be produced by two methods: Arc-cast and powder metallurgy. Historically, powder metallurgy techniques yielded TZM with a lower density than arc-cast. However, current technology produces powder metallurgy TZM (PM-TZM) with the same density and approximate mechanical properties as arc-cast TZM[1,2]. PM-TZM is much more readily available and less expensive than arc-cast TZM.

Figure 8 is a photomicrograph of a piece of arc-cast TZM alloy taken from a solid rod. The fine grain structure is evident.

Figure 9 is a photomicrograph of a piece of PM-TZM taken from a solid rod. Note that its grain structure is similar to that of arc-cast TZM. The small voids are created by the powder metallurgy process. The manufacturer claims that these voids have minimal affect on material properties.

Figure 10 is a photomicrograph of a piece of arc-cast TZM that has been heat treated to 2500°F for fifty hours. Slight changes in grain growth are evident but nowhere near as drastic as seen in pure molybdenum.

Figure 11 is a photomicrograph of a piece of PM-TZM that has been heat treated to 2500°F for 50 hours. Again, there is some slight recrystallization.

Figure 12 is a photomicrograph of a piece of virgin PM-TZM in the longitudinal direction of a solid bar. Figure 13 is a photomicrograph of a section of a PM-TZM cartridge run in the crystal growth furnace (CGF) for 90 hours at 2300°F. A comparison of these two figures shows no significant recrystallization.

A series of microhardness tests were run on samples of virgin and heat-soaked TZM. Figure 14 is a photomicrograph of a section of a virgin PM-TZM bar. The hardness indentations are visible. Tables 1 and 2 summarize the microhardness readings for PM-TZM and arc-cast TZM. The outside surface of the heat soaked materials apparently had a thin, hard coating. This is shown in Figure 15. The composition of the coating is not known. The data from Tables 1 and 2 indicate that continued exposure to high temperatures increases the hardness of the TZM. Microhardness was also run on the PM-TZM tube that was run in the CGF for 90 hours. Hardness reading were taken from an area at the braze joint and end cap. Table 3 summarizes this data. As expected, there is less change than seen in the 2500°F environment.

Figure 16 is a schematic of a test technique to qualitatively evaluate ring flexure of samples cut from CGF cartridges. A series of dead weight loads was employed to obtain deformations. Ring samples 0.50 inches wide were cut from an arc-cast molybdenum cartridge and a PM-TZM cartridge. Ring samples from both cartridges were heat treated to 2500°F for six hours. Figure 17 is the load-deflection curve for the arc-cast molybdenum rings. The effect of heat treating was to lower the strain to failure. Figure 18 is the load-deflection curve for the PM-TZM rings. Heat treating lowered the deflection response slightly. Failure could not be obtained with this geometry and facility (load limited).

The PM-TZM rings and the arc-cast molybdenum rings were of different diameters and wall thicknesses and the limitation of the facility/geometry prevented obtaining equivalent stress states. Further investigations into the properties of heat soaked TZM are needed for more substantial conclusions.

To check for ductility in the TZM scanning electron microscope was used to photograph the hardness indentations in the 80 hour heat soaked specimen. Figure 19 is a photomicrograph (3000x) of such an indentation. A brittle material would have cracks propagating from the corners of the indentation. A ductile material would have flow lines around the periphery. Neither of these effects was seen.

Based upon the recrystallization study and the simple ring flexure test PM-TZM may be an acceptable cartridge material. The electron-beam welding can be eliminated by machining the tubes with a closed spherical end from a solid bar of TZM.

The brazing of the stainless steel adjustment block to the cartridge tube (PM-TZM or molybdenum) will always pose a problem. A significant re-design of the adjustment block, which may include changing the material, will be required to eliminate the stresses built up by brazing. Lower temperature brazes as discussed below will reduce the stresses, but not eliminate them. Redesign of the adjustment block will be accomplished in a future effort.

Table 4 is a list of brazing alloys recommended[1,3] for molybdenum and TZM alloys. They are listed in decreasing order of braze temperature. Brazing pure molybdenum with any of the listed brazes will result in some recrystallization since the braze temperatures are in the molybdenum recrystallization temperature range. However, using these brazes on TZM should pose no problem. Quantities of each of these brazes (as indicated on Table 4) were obtained for experimental evaluation at MSFC and Southern Research.

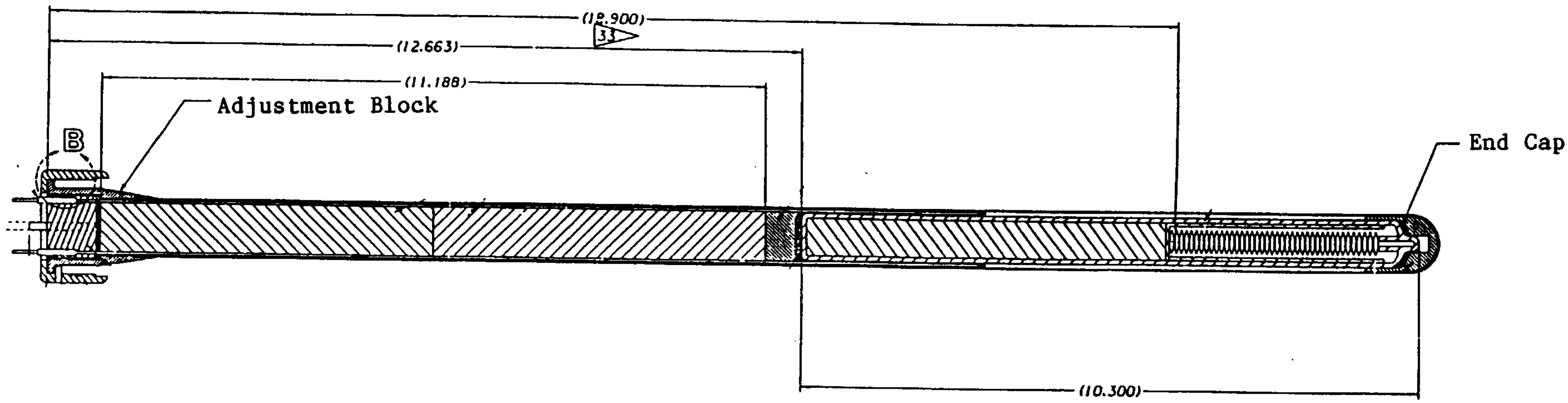

Figure 1. Cross-Section of Crystal Growth Cartridge Showing Placement of Adjustment Block and End Cap

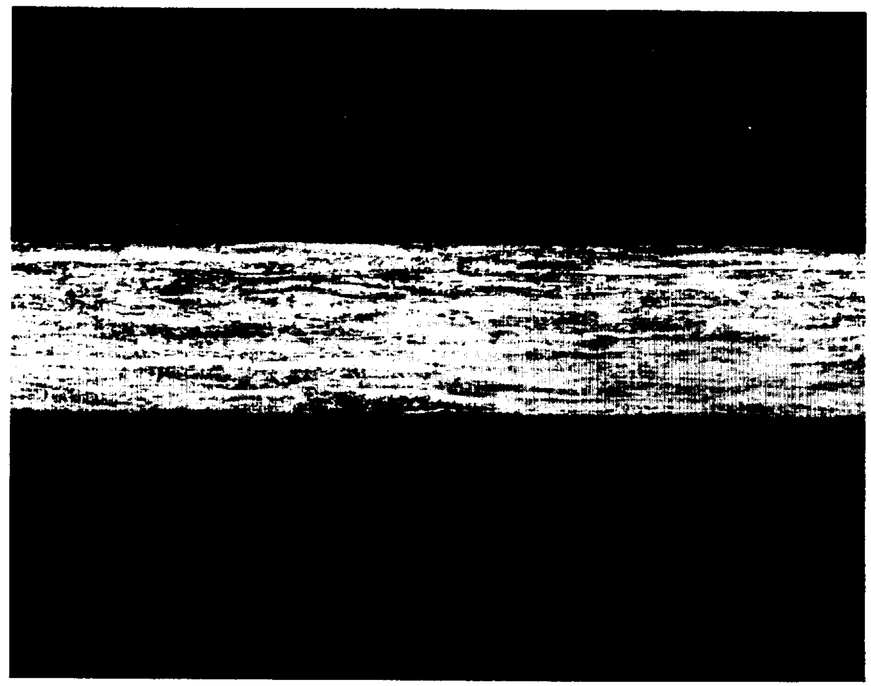

Figure 2. Photomicrograph (25x) of a Cross Section of Molybdenum Tube

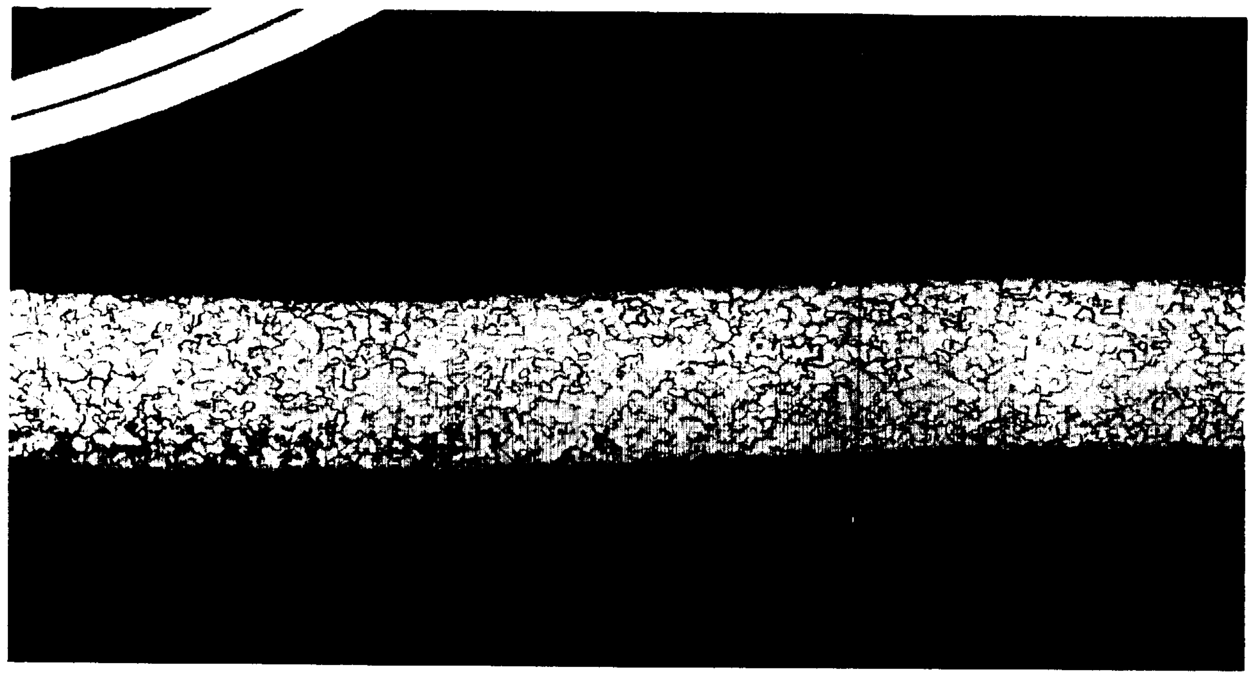

Figure 3. Photomicrograph (25x) of a Cross Section of Molybdenum Tube Heat Treated at 1950°F for One Hour

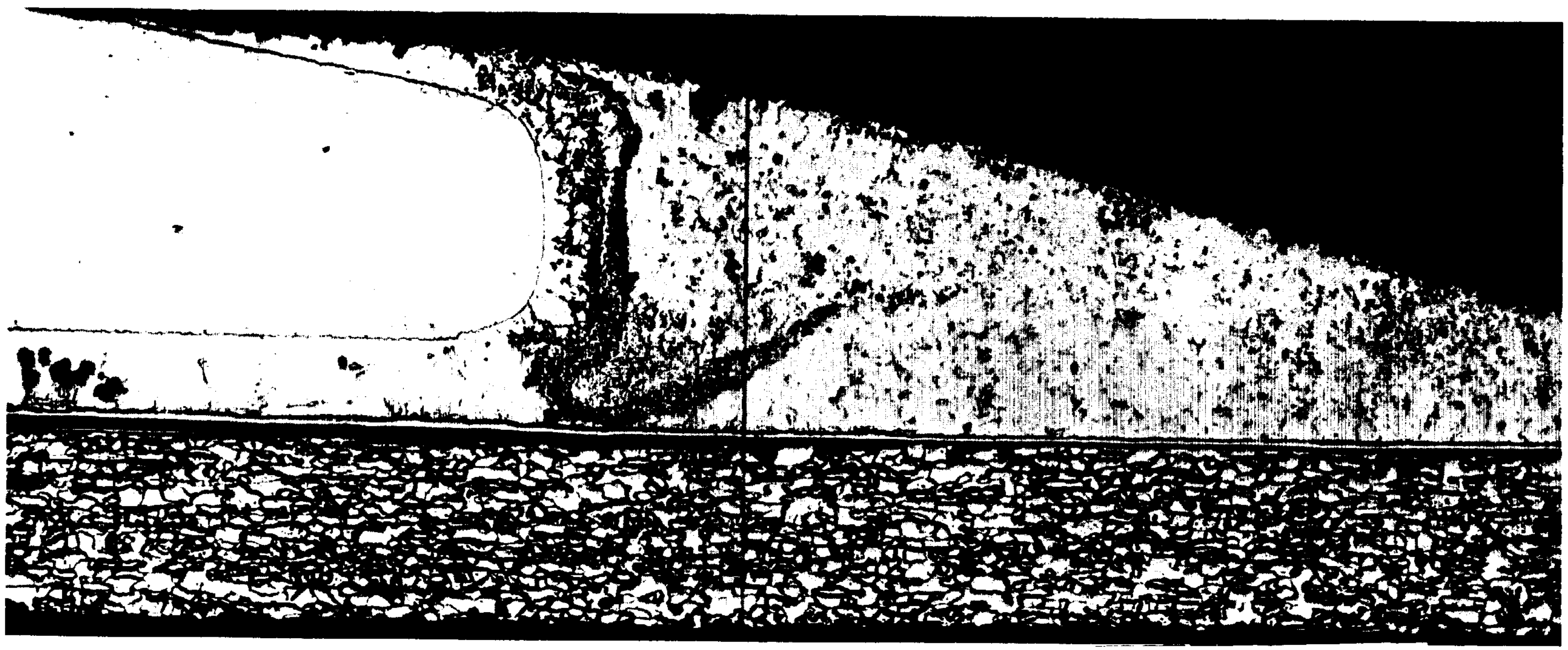

Figure 4. Photomicrograph (25x) of Adjustment Block Brazed to Molybdenum Tube

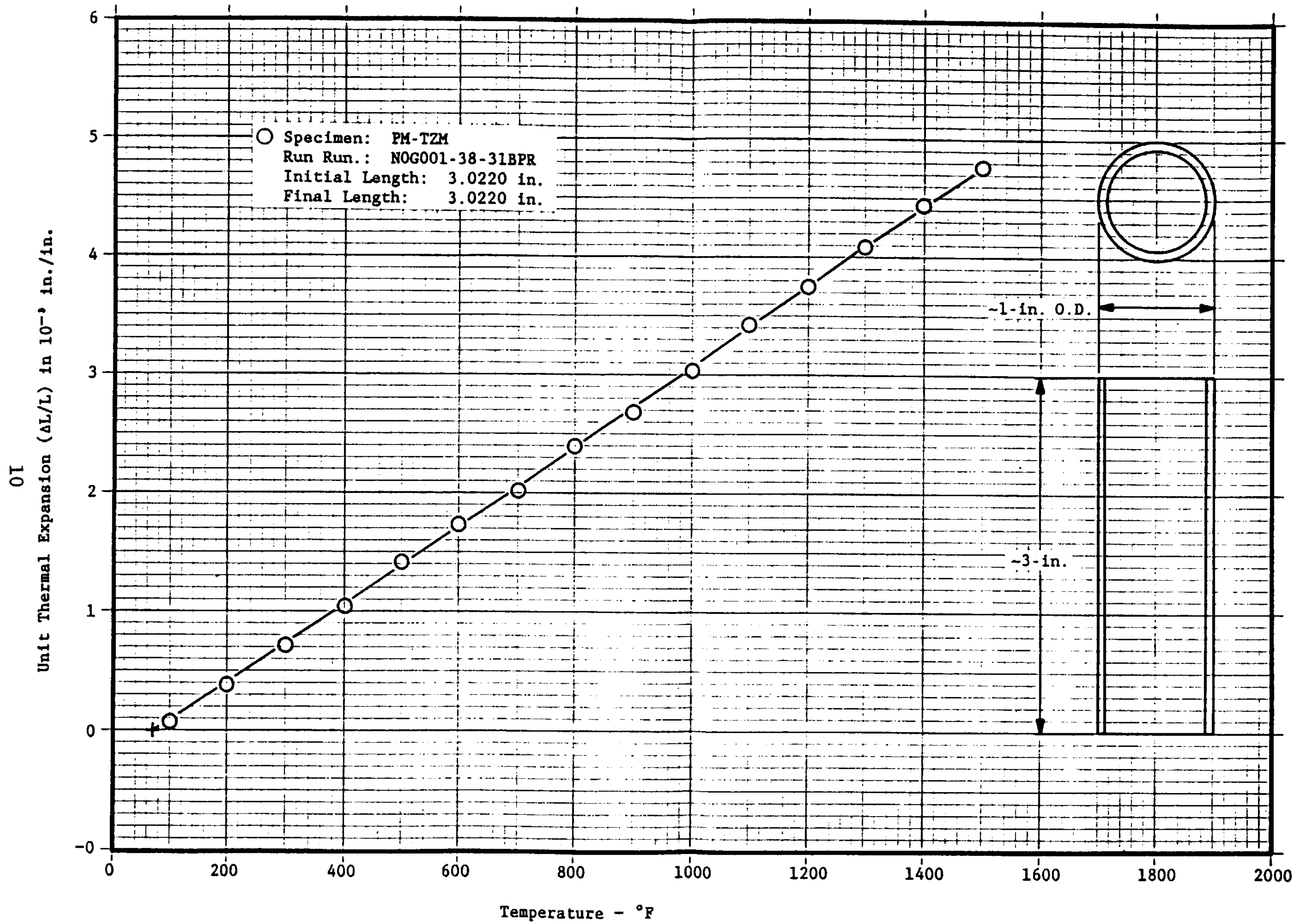

Figure 5. Thermal Expansion of PM-TZM (Same as Literature Values for Molybdenum)

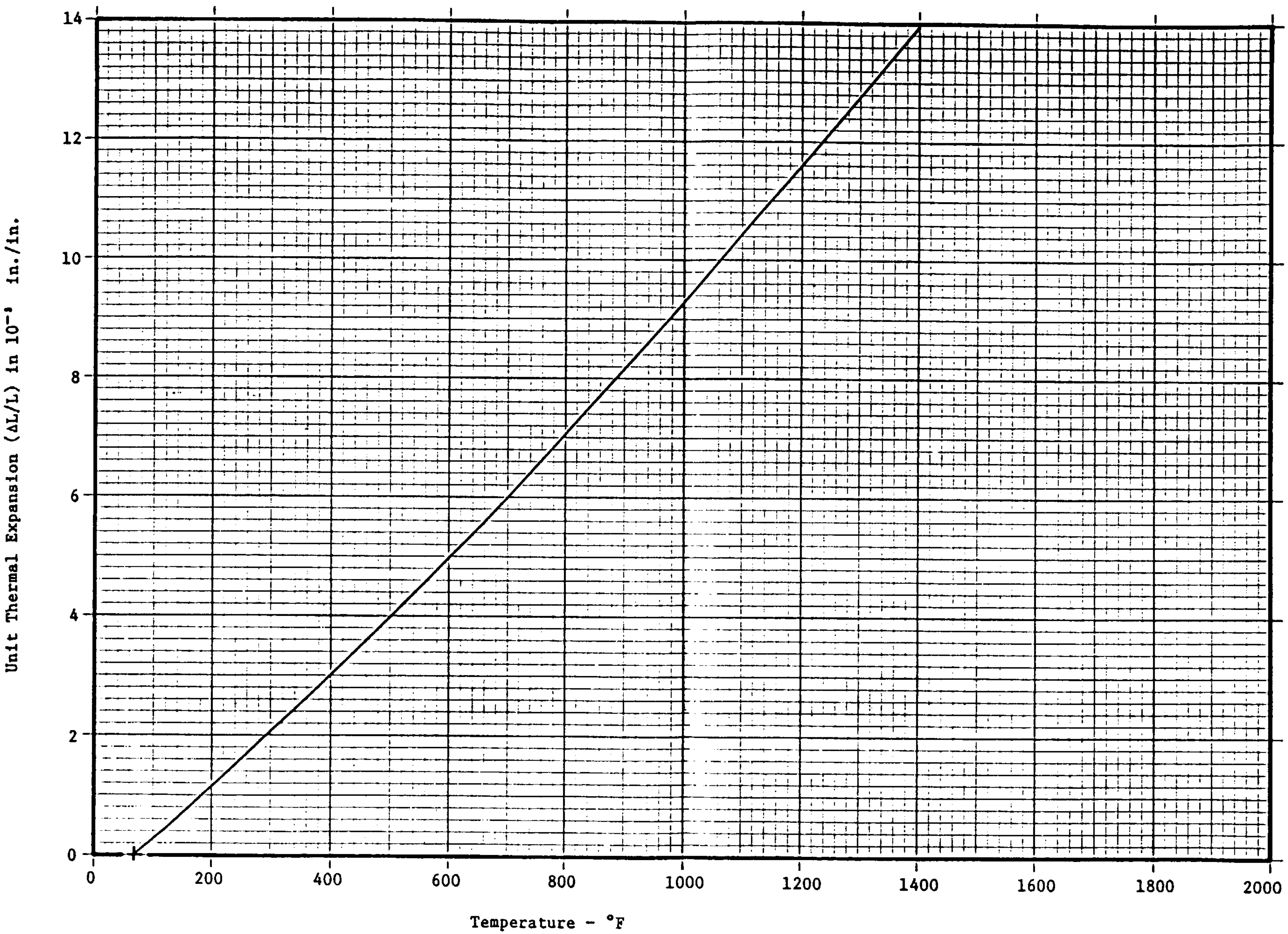

Figure 6. Thermal Expansion of 304L Stainless Steel (from TPRL Handbook)

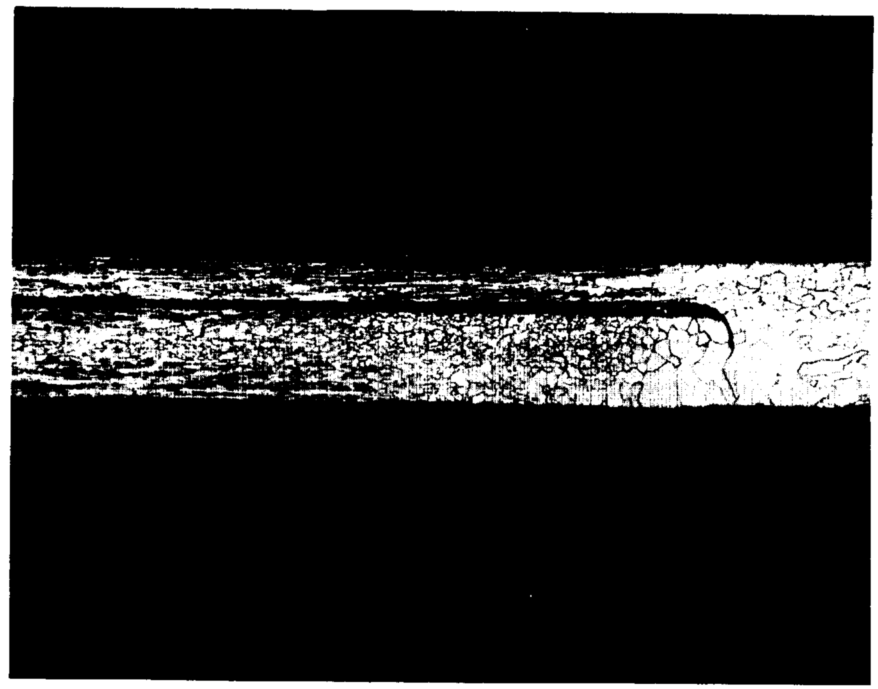

Figure 7. Photomicrograph (25x) of Electron Beam Weld Area of Molybdenum Tube

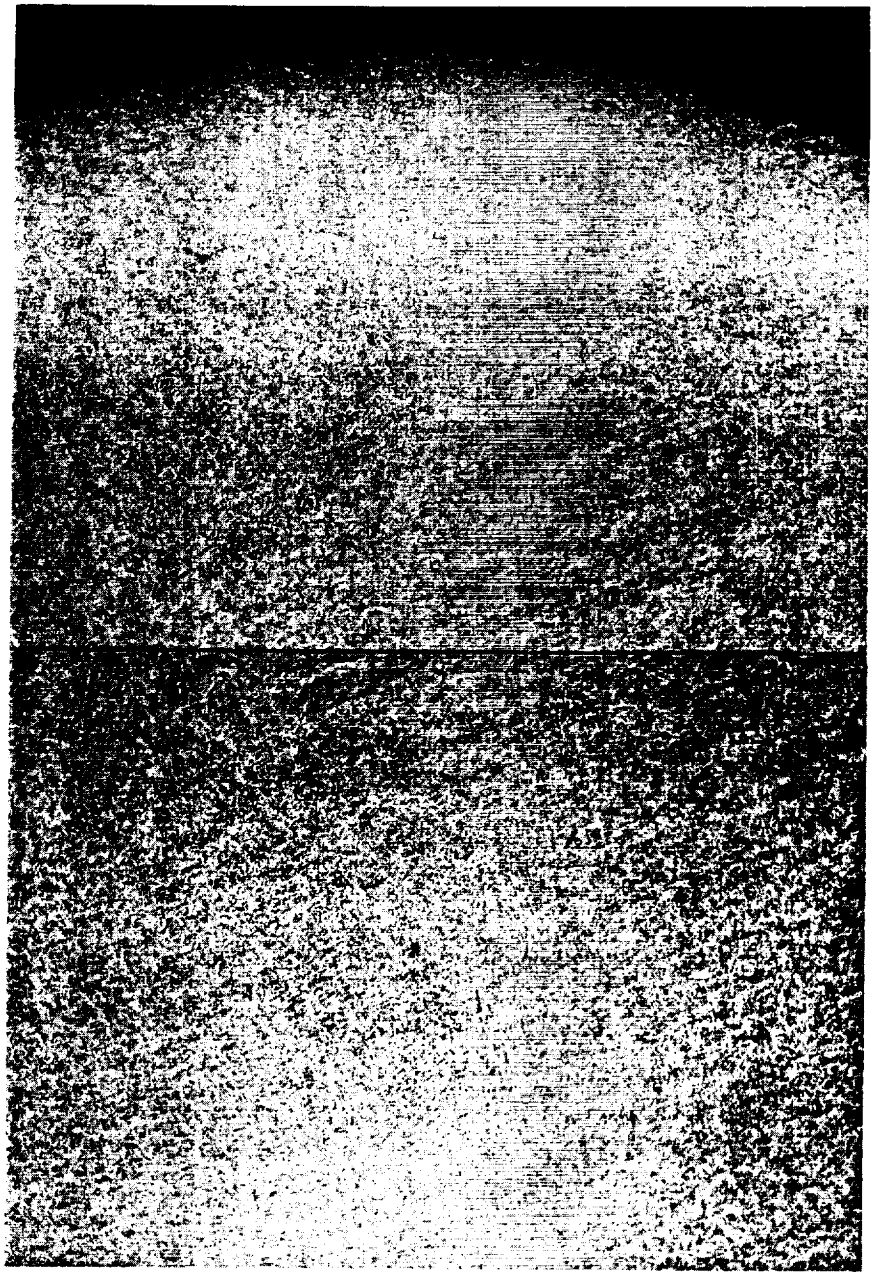

Figure 8. Photomicrograph (25x) of a Bar Section of Arc-Cast TZM Alloy

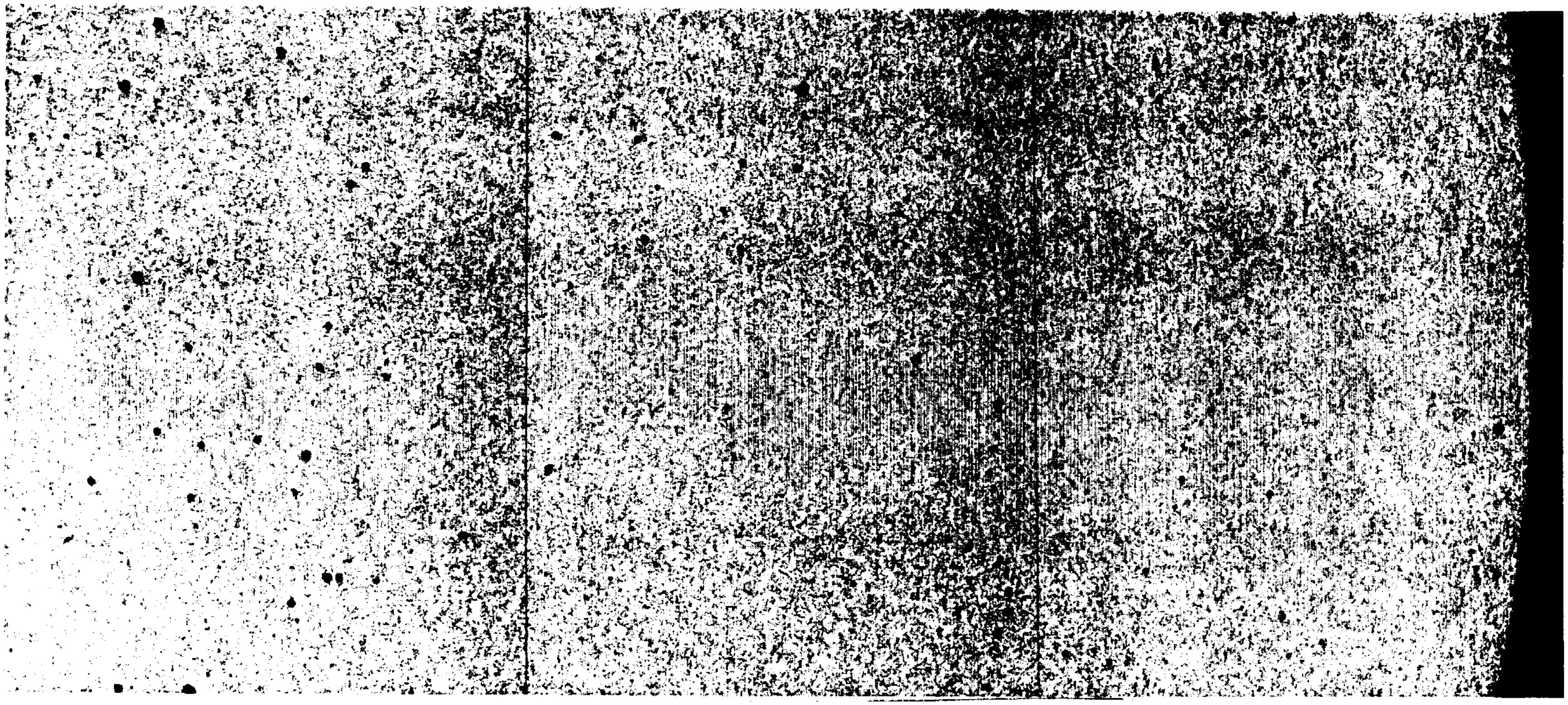

Figure 9. Photomicrograph (25x) of a Bar Section of PM-TZM

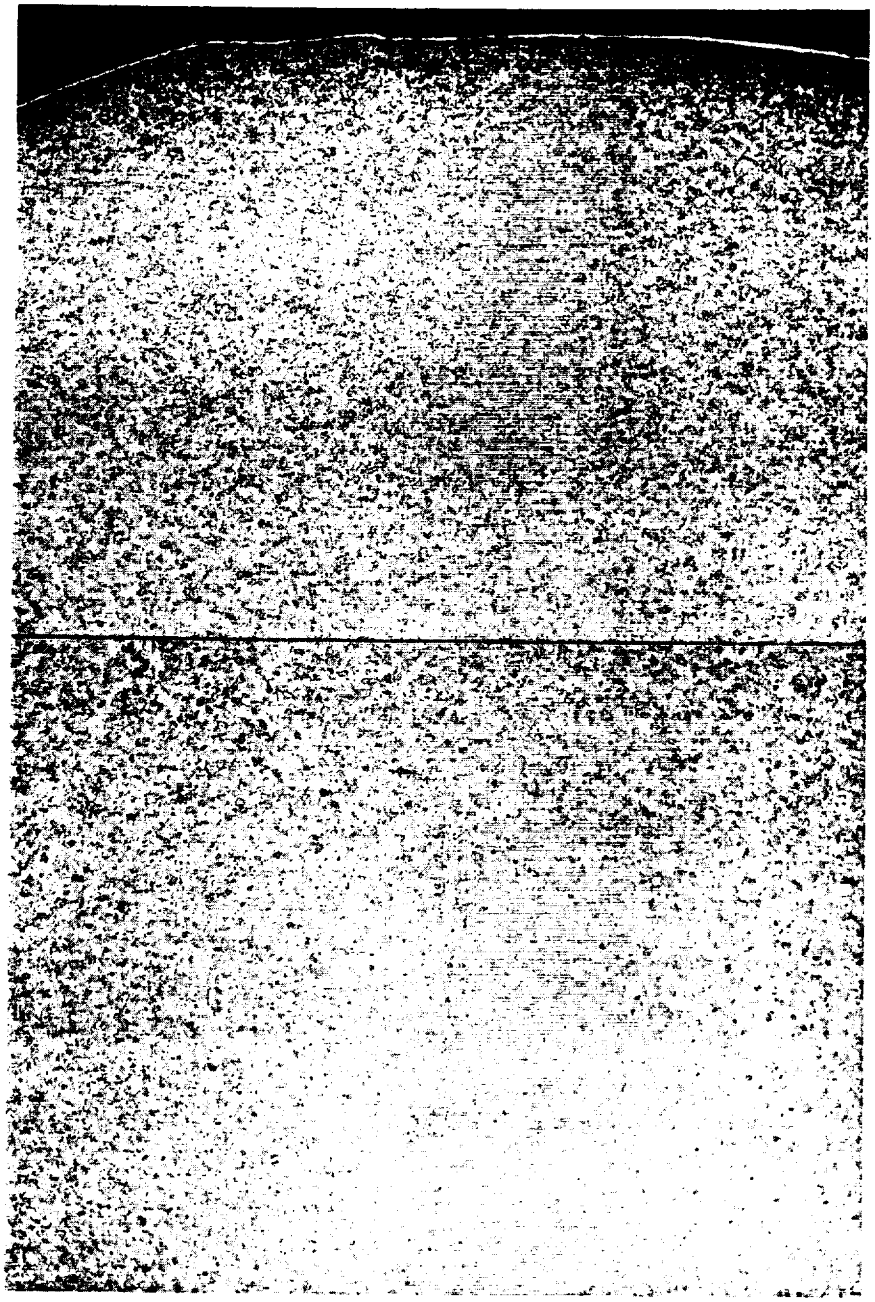

Figure 10. Photomicrograph (25x) of a Bar Section of Arc-Cast TZM Alloy Heat Soaked at 2500°F for 50 Hours

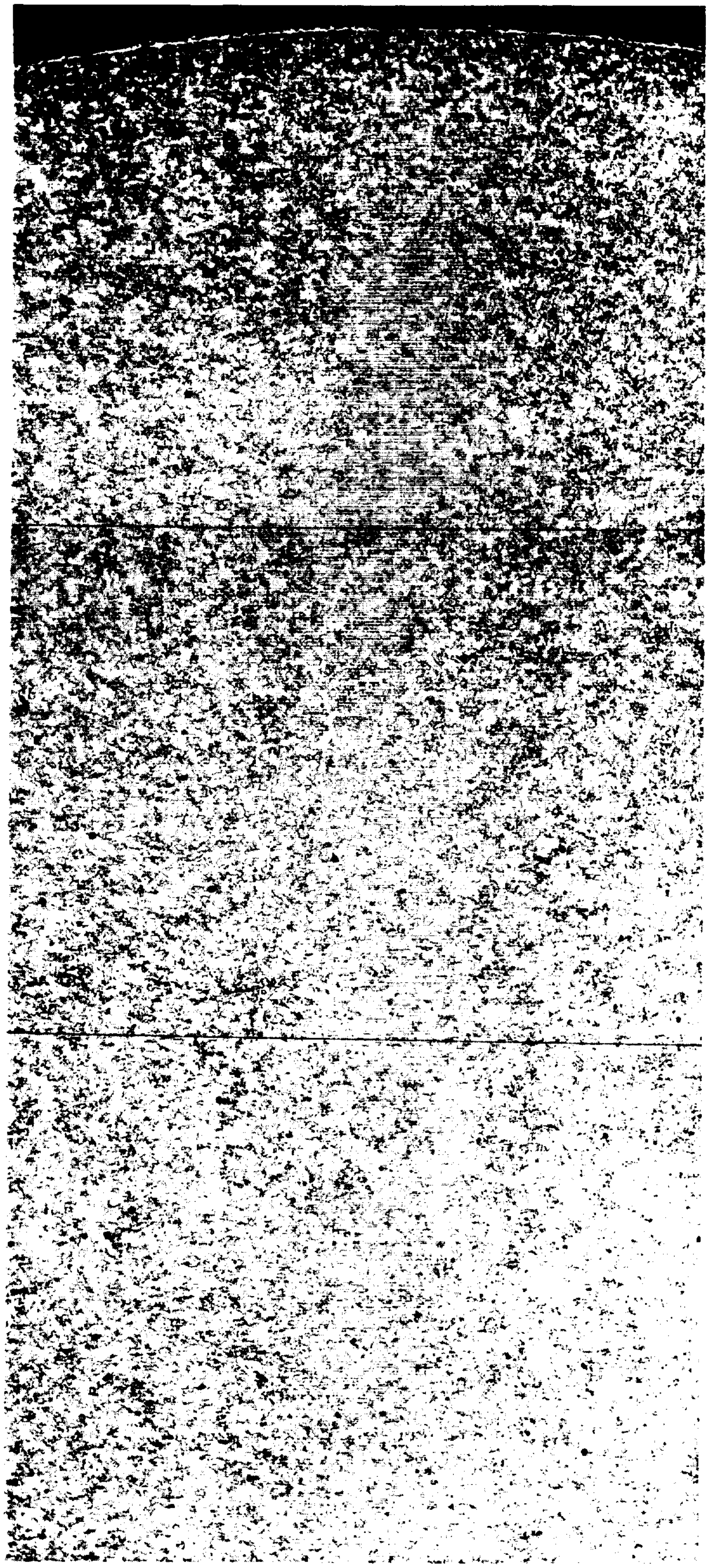

Figure 11. Photomicrograph (25x) of a Bar Section of PM-TZM Heat Treated at 2500°F for 50 Hours

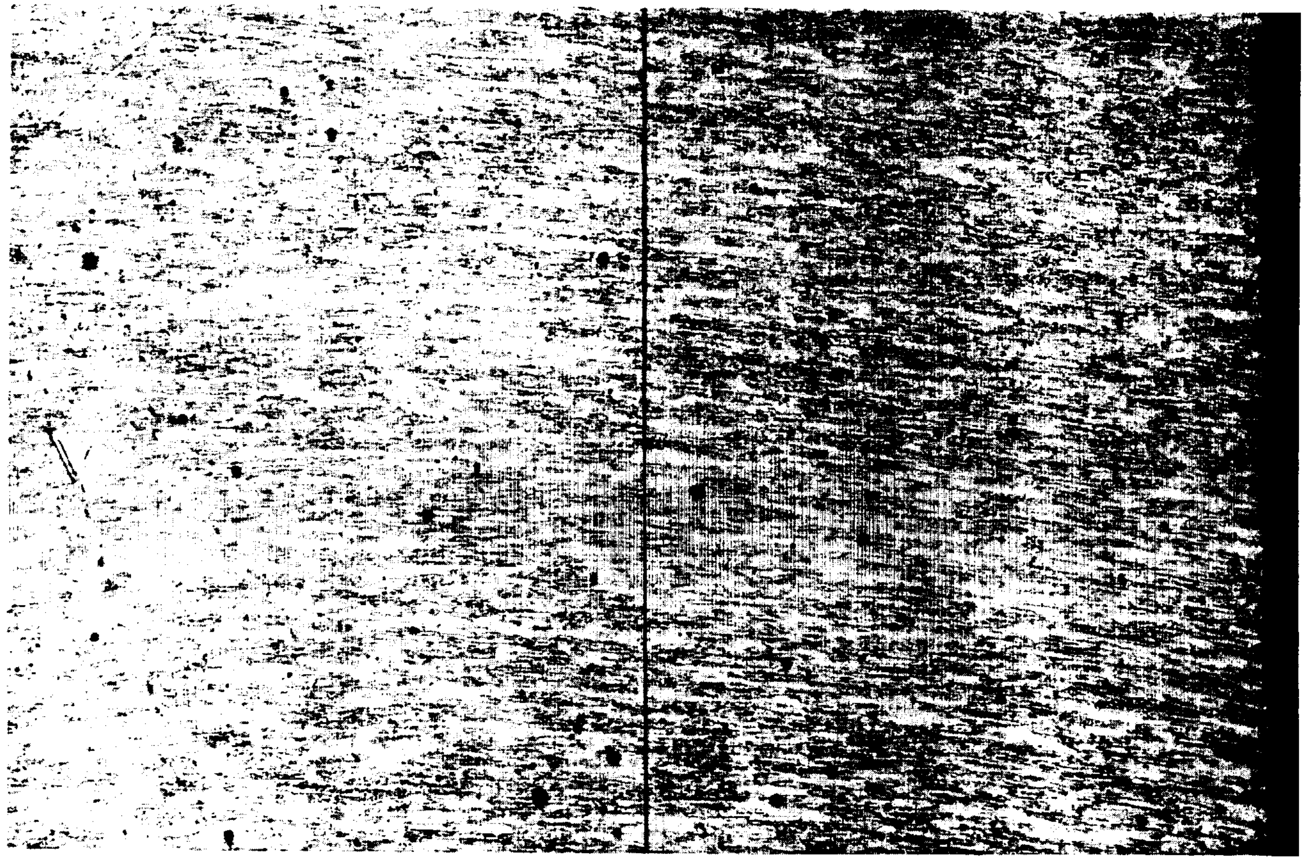

Figure 12. Photomicrograph (25x) of Virgin PM-TZM in Longitudinal Direction of Bar

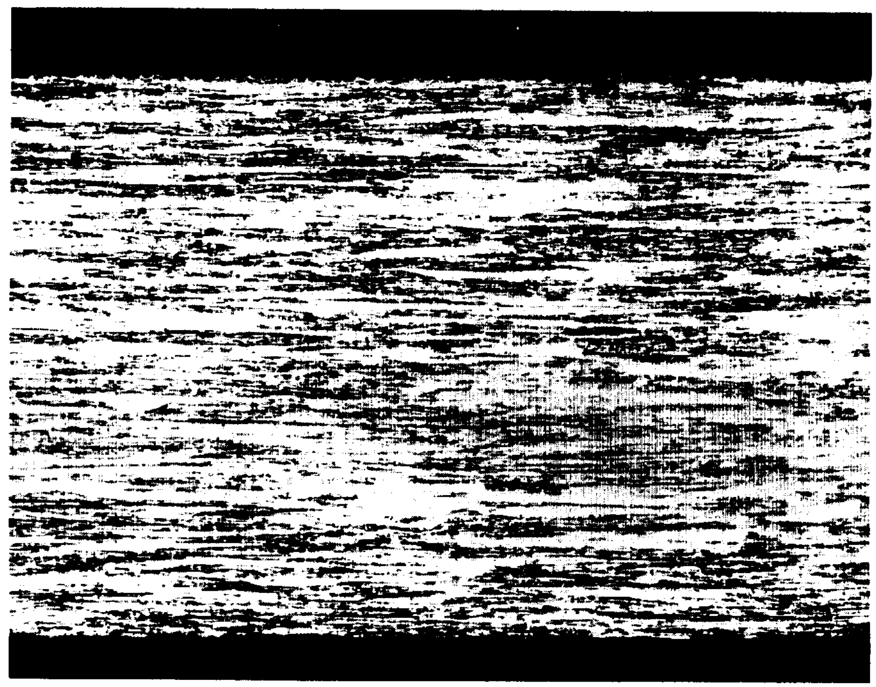

Figure 13. Photomicrograph (100x) of an Actual PM-TZM Cartridge Run in the CGF for 90 Hours at 2300 °F

Figure 14. Photomicrograph (100x) of Virgin PM-TZM Showing Microhardness Indentations

Figure 15. Photomicrograph (100x) of PM-TZM Bar Heat Treated at 2500 °F for One Hour Showing Hard Outside Coating

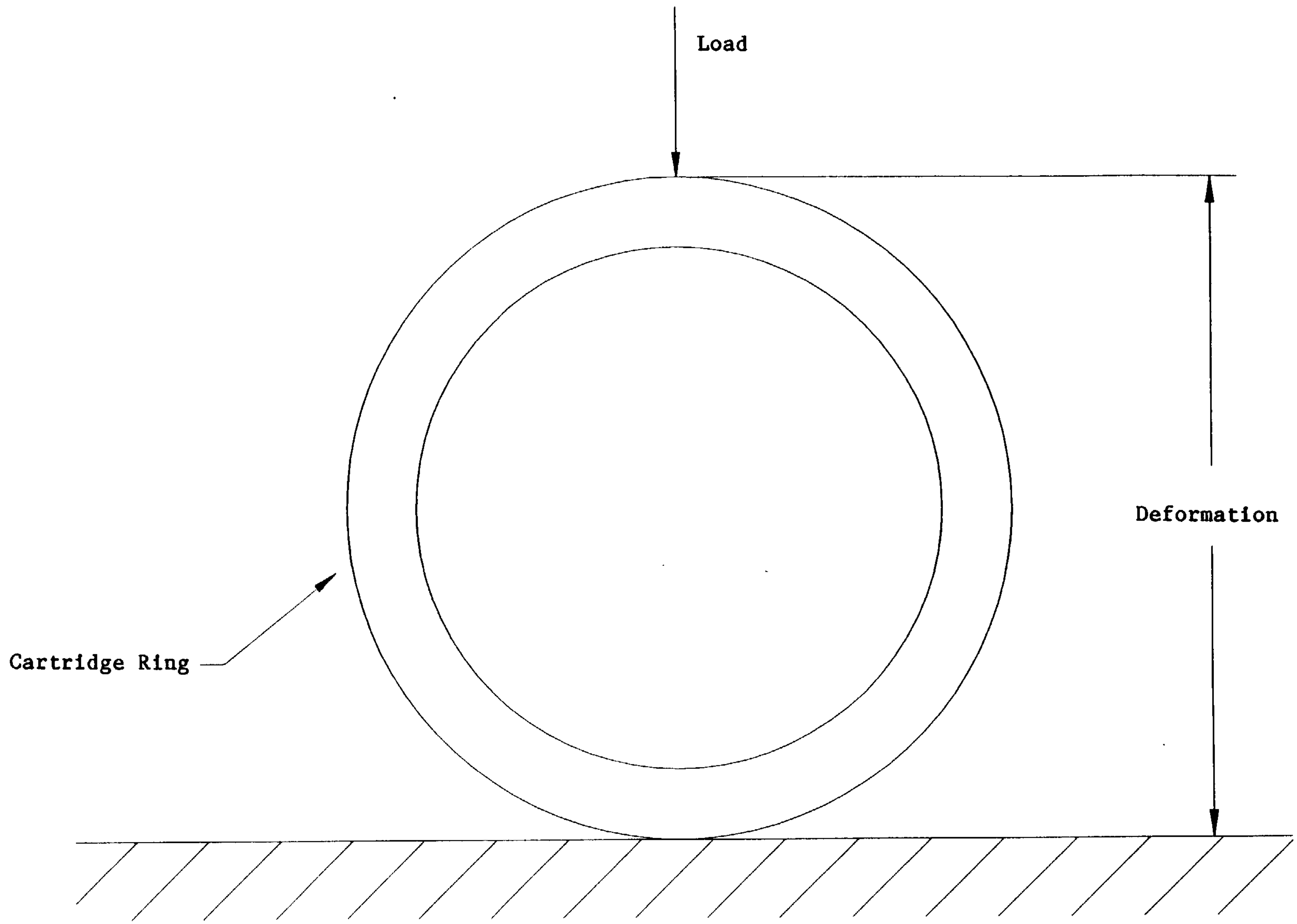

Figure 16. Schematic of Ring-Flex Test

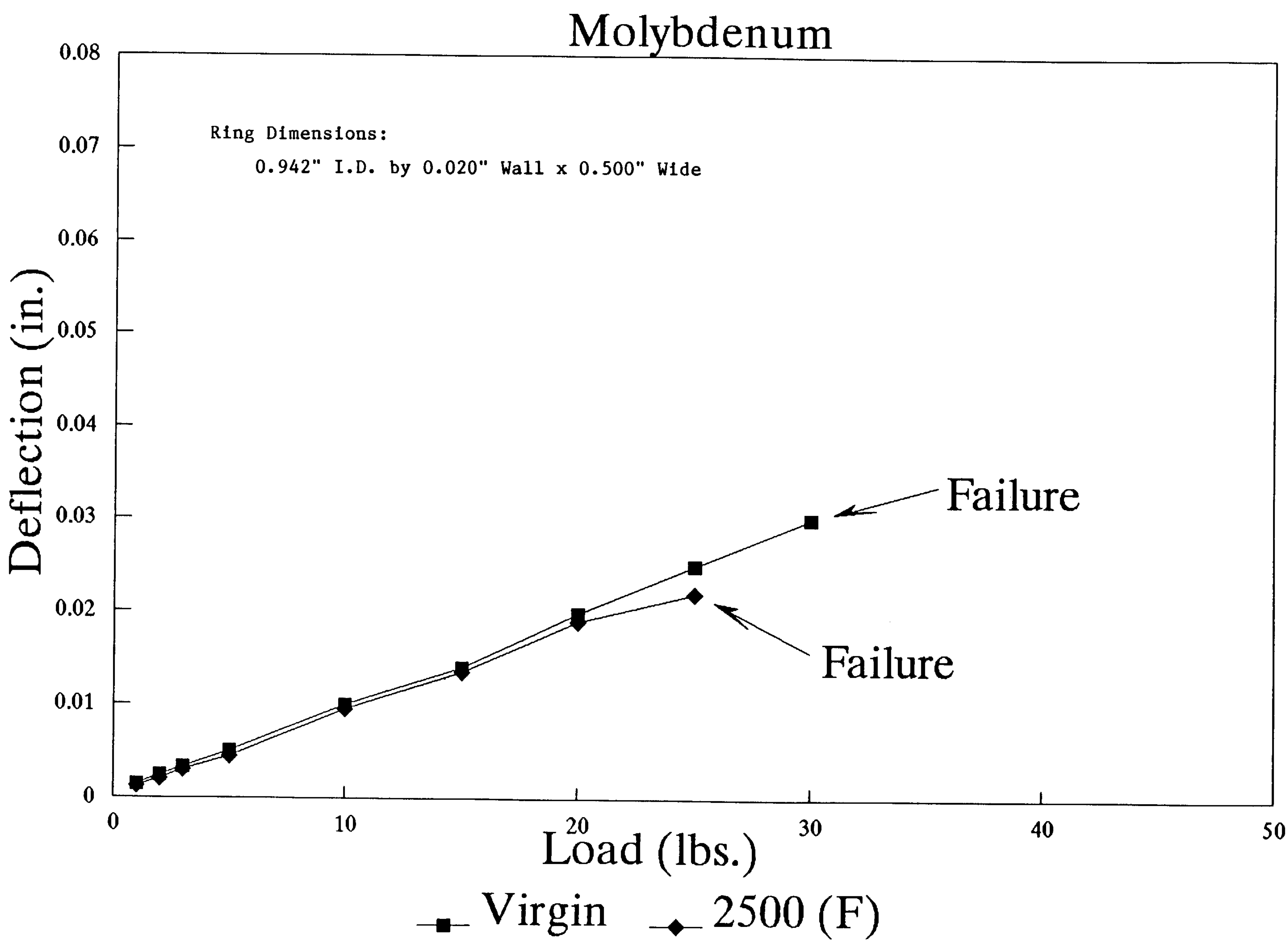

Figure 17. Load-Deflection of Arc-Cast Molybdenum Cartridge Rings

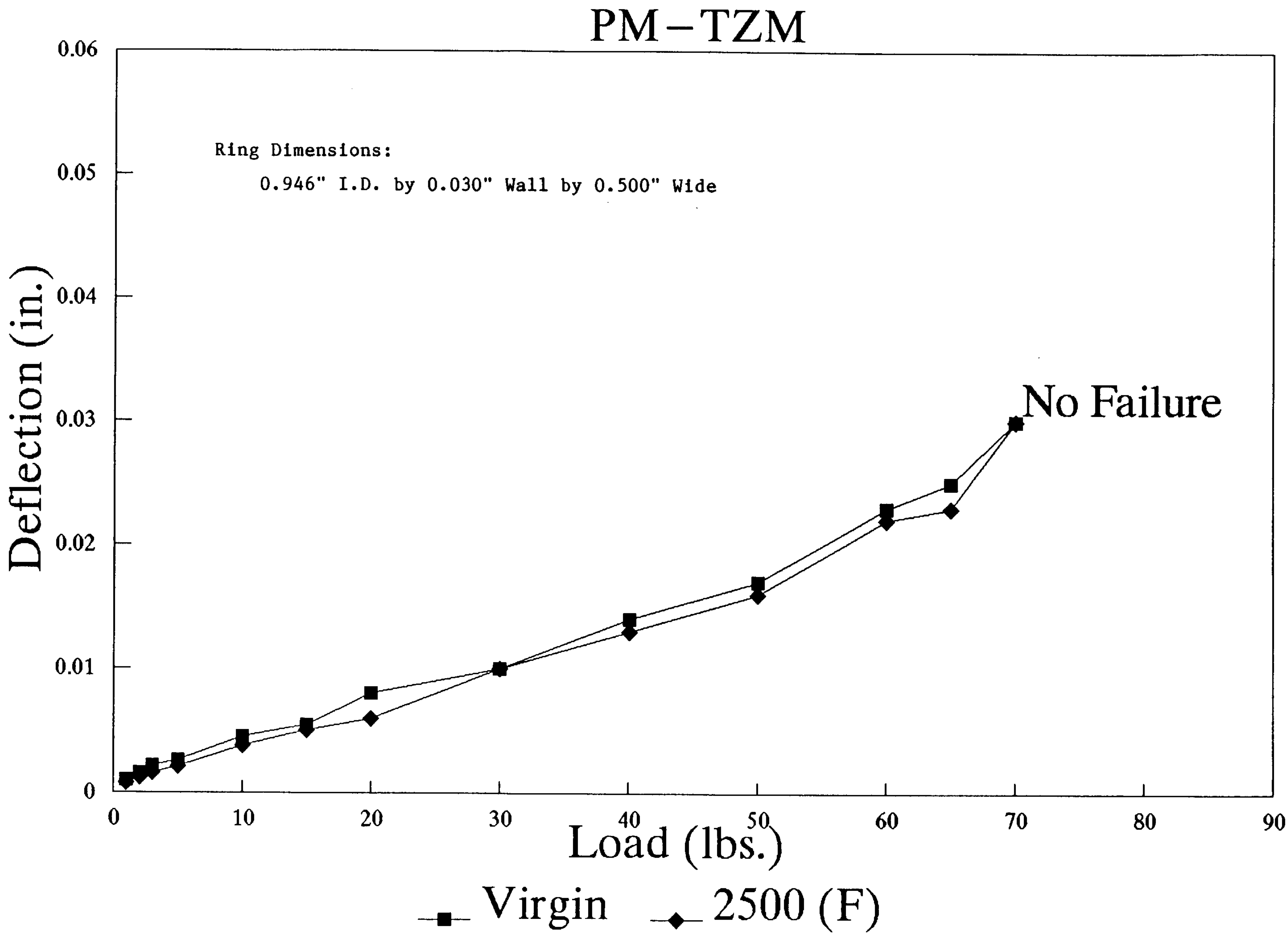

Figure 18. Load-Deflection of PM-TZM Cartridge Rings

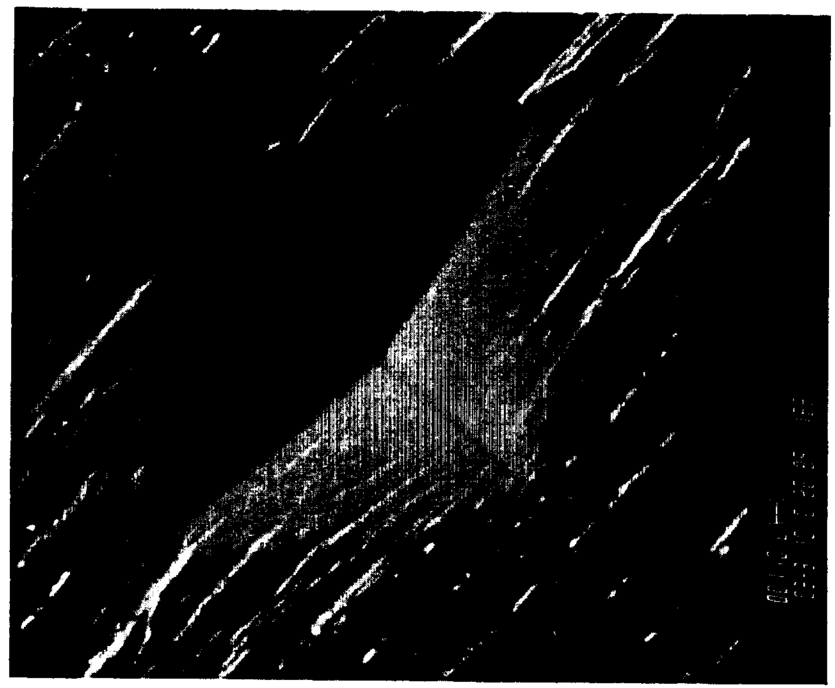

Figure 19. Photomicrograph (3000x) of Hardness Indentation in 80 Hour 2500°F Heat Soaked PM-TZM

Table 1. PM-TZM Micro-Hardness, 100 Gram Load

(Time at 2500 °F)

Position	Virgin	1 Hour	6 Hours	12 Hours	24 Hours	50 Hours	78 Hours
1	-	-	71	75	75	71	70
2	26	29	36	26	29	26	32
3	26	23	29	23	29	95	97
4	26	97	23	23	26	95	95
5	29	97	23	23	23	97	95
6	29	97	23	23	23	97	95
7	29	23	23	23	23	97	95
8	26	23	23	23	23	97	95

Rockwell Hardness

Table 2. Arc-Cast TZM Micro-Hardness, 100 Gram Load

(Time at 2500 °F)

Position	Virgin	1 Hour	6 Hours	12 Hours	24 Hours	50 Hours	78 Hours
1	-	-	-	-	74	72	75
2	29	-	-	-	26	29	32
3	29	-	-	-	97	23	26
4	29	-	-	-	95	97	26
5	32	-	-	-	95	97	26
6	26	-	-	-	95	97	26
7	29	-	-	-	95	97	26
8	29	-	-	-	95	97	23

Rockwell Hardness

Table 3. PM-TZM NASA CGF Cartridge Micro-Hardness (100 gm Load)

(90 Hours at 2300 °F)

Position	Braze Joint	End Cap
1	26	57
2	26	50
3	26	29
4	29	29
5	29	29
6	29	29
7	26	29
8	23	29

Rockwell Hardness

Table 4. Brazes for Molybdenum and TZM

Braze	Braze Temperature	Cost	Delivery	Purchased
Gold	1064°C	$1830./oz	Immediate	.5 oz.
Silver	960°C	$35./oz	Immediate	5 oz.
82 Au/18 Ni	949°C	$685./oz*	4 Weeks	2 oz.
80 Au/20 Cu	885°C	$690./oz*	4 Weeks	2 oz.
72 Ag/28 Cu	835°C	$485./oz*	4 Weeks	2 oz.
66 Ag/34 Cu-Ni-Ti	815°C	$84./oz	2 Weeks	2 oz.

*Add $800.00 initial set-up charge

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15. Supplementary Notes

16. Abstract

Studies were undertaken to determine the extent of recrystallization in molybdenum and TZM alloy when exposed to high temperatures (1260°C).

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