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Ernest O. Lawrence Radiation Laboratory

MELTING, FABRICATION, AND CREEP TESTING OF A 1.39% Ti + 0.34% Zr + 0.30% C MOLYBDENUM ALLOY

Livermore, California

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INTRODUCTION

The three major methods of strengthening molybdenum alloys are solid-solution strengthening, dispersion hardening, and strain hardening. Much of the early work on the effects of alloying additions on the strength and recrystallization temperature of molybdenum alloys is attributable to Semchyshen et al.[1-3] at the Climax Molybdenum Company. It was Chang[4-6] at General Electric, however, who did the fundamental work and phase identification that led to an understanding of the importance of dispersion hardening in the higher strength alloys.

(TZC)

Out of this large amount of work, a Mo + 1.25% Ti + 0.32% Zr + 0.30% C was reported to have the highest rupture life at 2400° F of any other alloy tested.[1] The alloy was also reported to have a 1-hr recrystallization temperature of 3200° F. The significance of a high recrystallization temperature is that one can take advantage of molybdenum's high work hardening rate as a means of strengthening at higher temperatures. The usefulness of the dispersed carbide phase in this alloy is not only in its role in dispersion hardening but also in retarding recovery and raising the recrystallization temperature.[7]

This TZC (0.3% C) alloy seemed to offer great potential. However, no creep data were available for the alloy nor was it commercially available from the alloy producers. It was therefore necessary for us to have the composition melted, fabricated and tested on an experimental basis at various specialized facilities throughout the country.

SUMMARY AND CONCLUSIONS

The creep rupture strength values at 2400° F of TZC (0.3% C) were found to be about the same as those reported for commercial 0.15% carbon TZC alloy, rather than the much higher values previously reported for this high-carbon TZC composition. Creep properties at 2400° F and 2600° F were disappointing. Because of the limited number of specimens available, it was not possible to investigate the improvement in properties no doubt possible through precipitation hardening heat treatments. In light of the recent work leading to a better understanding of the phase equilibria involved in this type of alloy, optimization of fabrication temperatures and procedures would additionally improve properties.

→ p2

Depletion of carbon at the specimen surface was found to occur during testing in conventional diffusion pumped vacuum systems. Decarburization apparently occurs as a result of a reaction between residual oxygen in the vacuum system and carbon in the specimen forming CO. Testing in an ultra-high vacuum, utilizing a sputter-ion pump, prevents decarburization. End

PREPARATION OF THE Mo-TZC (0.3% C) ALLOY

Melting of Ingot

The alloy was vacuum-arc-melted on an experimental basis by the Climax Molybdenum Company of Michigan. The ingot was cast to a 4-in.-diameter by 30-3/4-in.-long size, weighing 132 lb.

The intended analysis was Mo + 1.25% Ti + 0.3% Zr + 0.30% C; the actual ingot analysis was Mo + 1.39% Ti + 0.34% Zr + 0.30% C.

Ultrasonic inspection confirmed that the ingot was sound; however, there was a trace of micro-porosity throughout the structure upon metallographic examination. The ingot was cleaned up to a 3-1/8-in.-diameter by 27-in.-long cylinder weighing 75 lb.

The fractograph and photomicrographs supplied by Climax[8] (Fig. 1) show that the alloy is oxide-free with a carbide network phase present. In addition to the semicontinuous carbide network in the grain boundaries, carbides are also present within the grains. These are evident in Figs. 1b and 1c as globules and stringers in sub-grain boundaries and also as a fine precipitate.

Extrusion

Two 3-in.-diameter by 6-in.-long extrusion blanks weighing 14 lb each were sent to Wright-Patterson Air Force Base for extrusion. The billets were extruded at 3100° F at a ratio of 4:1. A die coating of flame-sprayed alumina kept the die wash negligibly small. The two extrusions finished up to 1-1/2-in. diameter by 22 in. long. The extrusions had smooth surfaces but severe nose burst. Extrusion straightening was performed at 2400° F.

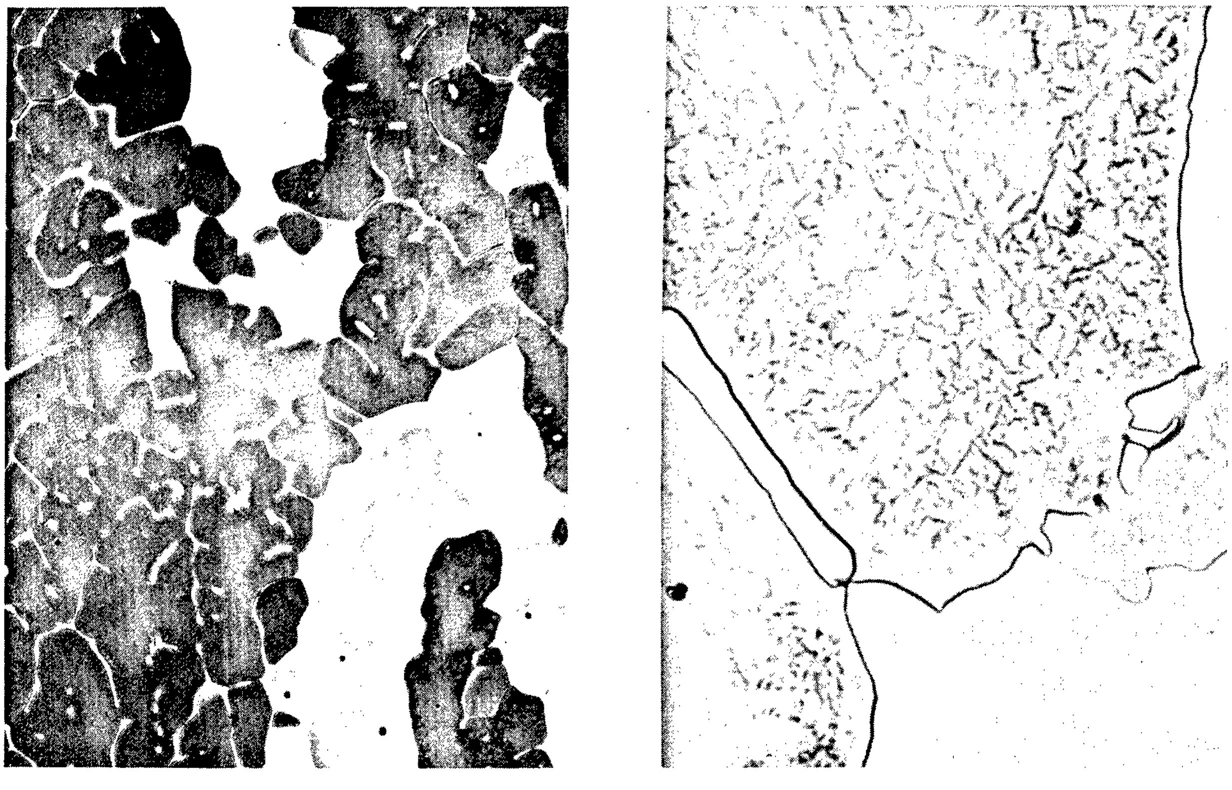
Figure 2 shows the structure transverse to the extrusion direction. It can be seen that the cast ingot structure has been broken up somewhat but that the carbide agglomerates and semicontinuous stringers persist. This suggests that a greater extrusion ratio would be beneficial.

Swaging to 1/2-in.-Diameter Bar

The extrusions were swaged down to 1/2-in. diameter at the Cleveland Tungsten Works of the General Electric Company. This was accomplished in six reductions starting at 3000° F and finishing at 2460° F. Two intermediate anneals were used. Details of this operation are summarized in Table 1.

The final structure of the swaged bar is shown in Fig. 3 in transverse section for comparison with the extruded structure of Fig. 2. This represents about 48% reduction

A) Fractograph ×2000

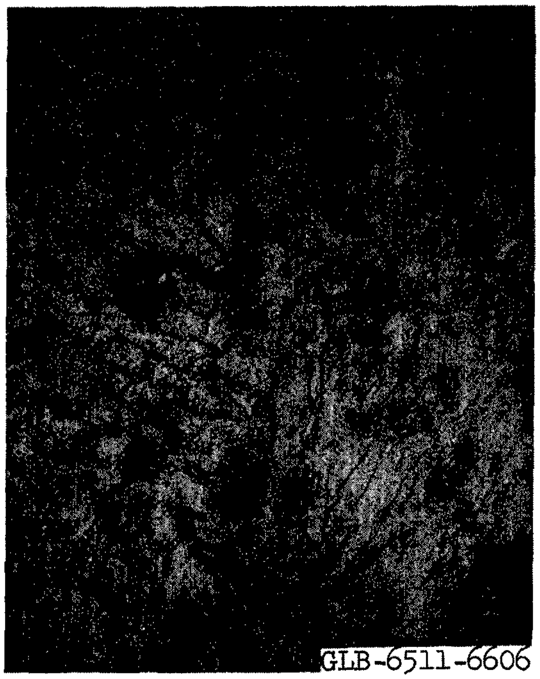


B) ×100 C) ×2000

Mechanically Polished + Light Electropolish and Etched in NaOH + $K_3Fe(CN)_6$

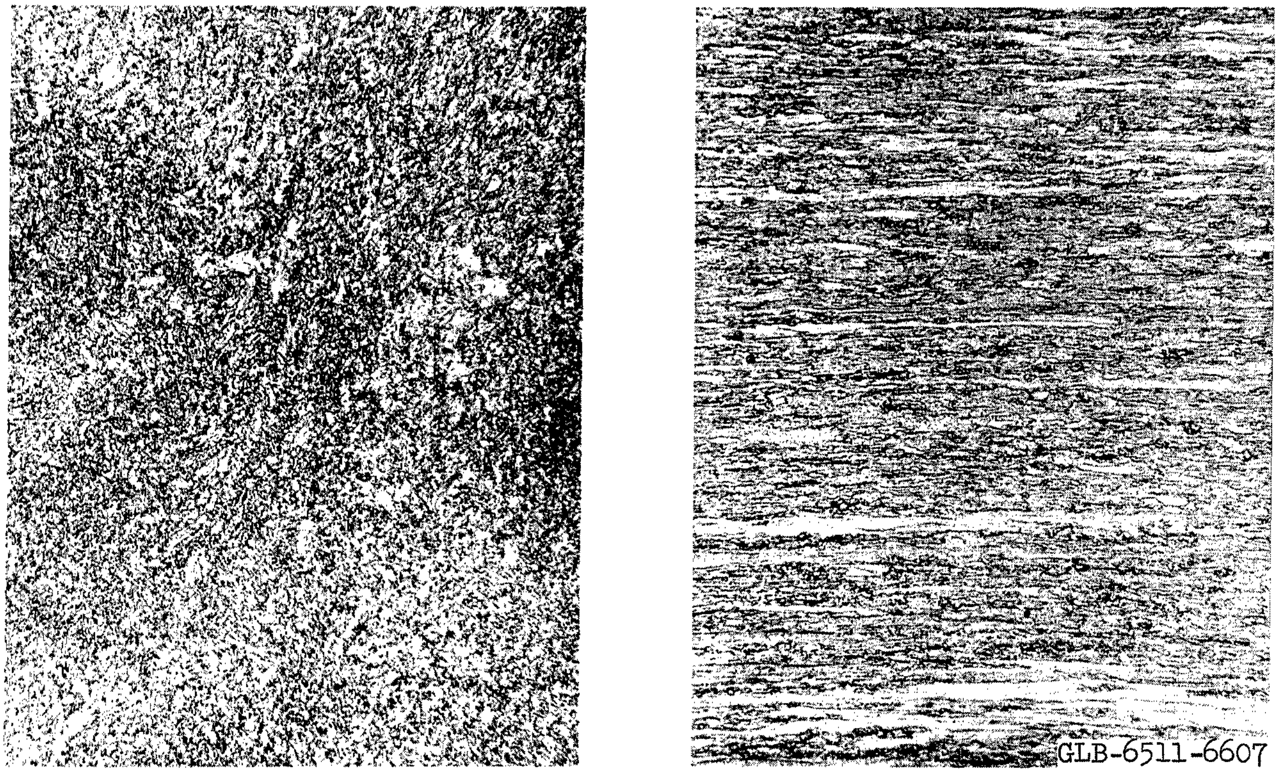
GLB-6511-6605

Fig. 1. Mo + 1.39% Ti + 0.34% Zr + 0.30% C, "As-Cast," Heat 3-3696.



TRANSVERSE SECTION

Fig. 2. After extrusion at 4:1 ratio to 1.5-in. diameter at 3000° F. 100X



TRANSVERSE

LONGITUDINAL

Fig. 3. After swaging to 0.5-in. diameter in six steps. 100X

Table 1. TZC (0.3% C) molybdenum alloy fabrication history.

1. Ingot melted by Climax Molybdenum Co.			
Analysis:	Mo-1.39% Ti-0.34% Zr-0.30% C		
Ingot:	4-in. diam × 30-3/4 in; 131.8 lb		
D. P. H.:	236 (10 kg load)		
Cropped ingot:	3-1/8-in. diam × 27 in., 75.4 lb		
2. Extruded at Wright Field			
Extrusion billets:	2.97-in. diam × 6 in. (2)		
Temperature:	3100° F		
Ratio:	4:1		
Load:	570-650 tons		
Extrusion:	1-1/2-in. diam × 22 in.		
3. Extrusions straightened			
Temperature:	2400° F		
Oxidation loss:	1/2 lb per extrusion		
4. Extrusions swaged by Cleveland Tungsten			
Process:	a.	Swage to 1.0 in.	3000° F 55% reduction
	b.	Recrystallize	
	c.	1 in. - 0.785	3000° F 38% reduction
	d.	0.785 - 0.710	2750° F 18% reduction
	e.	Recrystallize	
	f.	0.710 - 0.670	2550° F 11% reduction
	g.	0.670 - 0.560	2460° F 30% reduction
	h.	0.560 - 0.515	2460° F 15% reduction

from the last recrystallizing anneal. The longitudinal section shows the banded structure typical of cold worked molybdenum alloys. Note again that the large carbide agglomerates still persist.

CREEP RUPTURE TESTING

Equipment

Specimens obtained from the 1/2-in.-diameter swaged rod were creep-rupture tested by the Westinghouse Research and Development Center. Westinghouse[9] stated that the following testing conditions were maintained: The pressure during all the tests was well below 10^{-5} torr and the temperature control was well within ±10° F.

A load-corrected stainless steel bellows was used on the vacuum chamber to allow specimen elongation. The load was applied through a calibrated leaf spring whose load accuracy is better than 1%. Elongation measurements were made from the crosshead motion with a sensitivity of ±0.0002 in.

Creep Data

A complete set of isothermal constant-stress creep curves are given in Appendix A. Tabulated data abstracted from the creep curves are given in Tables 2 and 3. Specimen dimensions are also reported. It will be noted that two specimens are sub-sized. It is believed that this had no effect on test results.

Table 2. TZC (0.3% C) molybdenum alloy 2400° F creep rupture test data.

Stress (psi)	30,000	20,000	12,500	5,000
Rupture time (hr)	11.75	125	744	282+
Rupture strain (%)	20.7	35.9	38.9	1.14+
Reduction of area (%)	76.9	90.4	93.9	–
Minimum creep rate (% hr)	0.75	0.070	0.013	0.0015
Time to 1% strain (hr)	0.8	1.5	12	228
Time to 3% strain (hr)	3.4	27	155	–
Time to 5% strain (hr)	5.8	49.5	281	–
Transition time (hr)	5.5	45	245	–
Transition strain (%)	4.8	4.6	4.3	–
Diameter (in.)	0.1125	0.1781	0.1782	0.1125
Gage length (in.)	1.00	1.75	1.75	1.70
Original hardness, VHN (30 kg)	–	305	295	–
Final hardness, VHN (30 kg)	–	280	265	–

Table 3. TZC (0.3% C) molybdenum alloy 2600° F creep rupture data.

Stress (psi)	15,000	10,000	8,000	5,000
Rupture time (hr)	15.5	178.0	227	908.0
Rupture strain (%)	26.1	21.2	29.6	36.4
Reduction of area (%)	83.2	44.1	97.4	77.3
Minimum creep rate (%/hr)	0.66	0.053	0.038	0.0085
Time to 1.0% strain (hr)	0.8	2.5	5.0	3.0[a]
Time to 3.0% strain (hr)	3.4	42.0	57	165.0
Time to 5.0% strain (hr)	6.0	77.5	98	380.0
Transition time (hr)	8.0	79.0	100	430.0
Transition strain (%)	5.8	5.1	5.1	5.2
Original diameter (in.)	0.1780	0.1780	0.1785	0.1782
Original gage length (in.)	1.75	1.75	1.75	1.75
Original hardness, VHN (30 kg)	301	298	308	307
Final Hardness, VHN (30 kg)	268	266	227	211

[a] The initial portion of the creep curve from which this value was taken appears to be in error.

Hardness readings were determined on the unstressed ends of the specimens before and after testing. As expected, the hardness was reduced slightly by the thermal exposure.

Creep data are plotted in the conventional manner, giving log stress versus log time for rupture and time to 5, 3 and 1% strain in Figs. 4 and 5. The transition time to tertiary creep is very close to the time to 5% strain in all cases, but is not plotted for clarity's sake. The curvature of these plots would make extrapolation to longer times extremely tenuous.

From the shape of the curves, it appears that at extended times metallurgical instabilities such as carbide agglomeration or recrystallization or both are increasing creep rates.

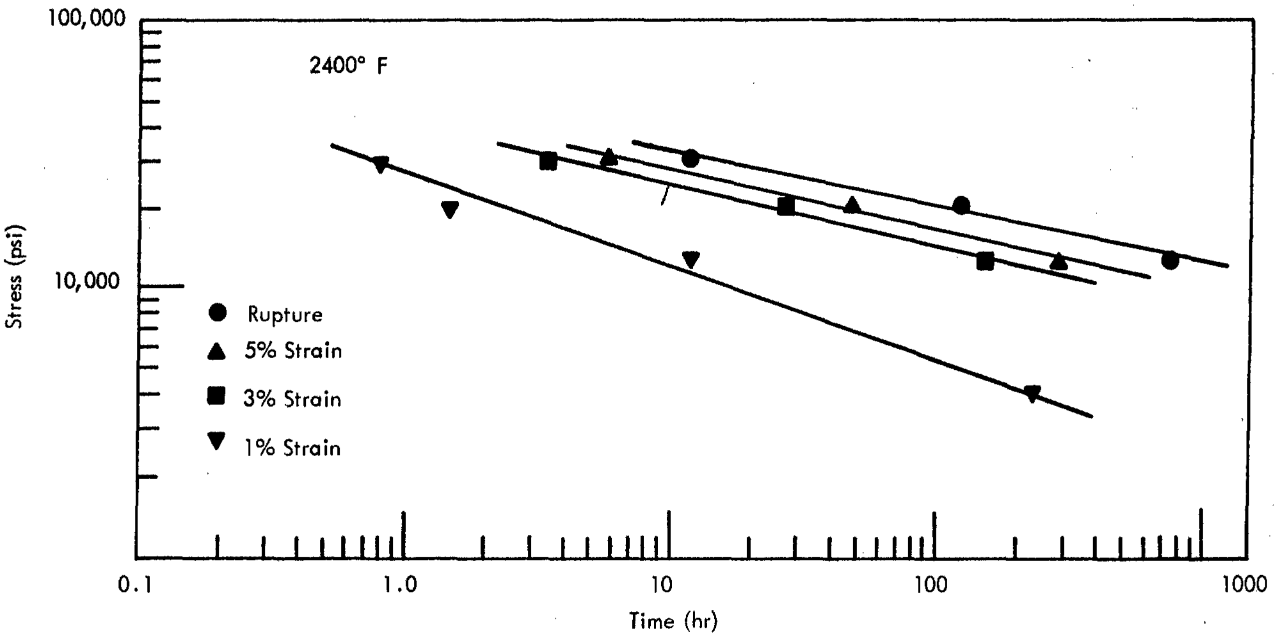
The minimum creep rate versus stress is shown in Fig. 6 for both temperatures. The creep properties of the Mo-TZC (0.3% C) alloy are somewhat disappointing. The stress rupture strengths are much lower than the 2400° F-55,000 psi-1 hr rupture life and the 33,000 psi-100 hr rupture life data reported earlier by Semchyshen[1] for an almost identical composition (Mo-1.27% Ti-0.29% Zr-0.30% C). The present data for the 0.3% C alloy agree more closely with the 2400° F stress rupture values reported by Climax Molybdenum Company[10] for their commercial 0.15% C TZC alloy.

Figure 7 shows the structure of the gage section of the specimen after testing at 2400° F and 20,000 psi. Rupture occurred in 125 hr. The progress of the recrystallization reaction can be seen when it is compared with Fig. 3, which typifies the initial structure.

Because of the limited number of specimens available, it was not possible to examine the effect of various precipitation hardening heat treatments upon the creep properties of the TZC (0.3% C) alloy. Chang[4-6] has shown that the titanium-zirconium-carbon alloys of molybdenum are amenable to age hardening. Using his work as a point of departure combined with further examination of the 0.3% C alloy, it would no doubt be possible to improve the properties of this composition through optimization of fabrication procedures and temperatures and through the application of precipitation hardening heat treatments.

In-Fab Experiment

A 3-1/8-in.-diameter by 8-in. section from the arc-cast ingot was sent to Universal-Cyclops for an attempt at forging in their inert-gas "In-Fab" facility. The ingot was impact forged starting at 4000° F and finishing at 3750° F. Severe longitudinal cracking took place. It appears that this hot-shortness is due to a low melting point grain boundary constituent derived from the high titanium and carbon content.



Mo
Fig. 4. Stress vs time for TZC (0.3% C) at 2400° F.

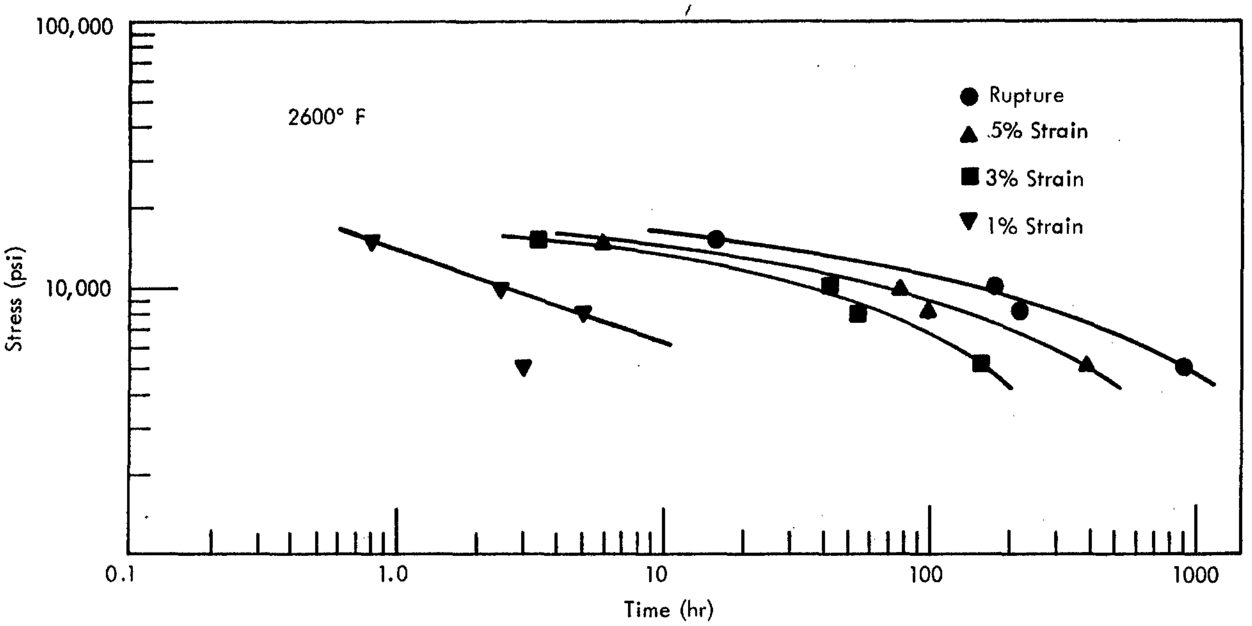


Fig. 5. Stress vs time for TZC (0.3% C) at 2600° F.

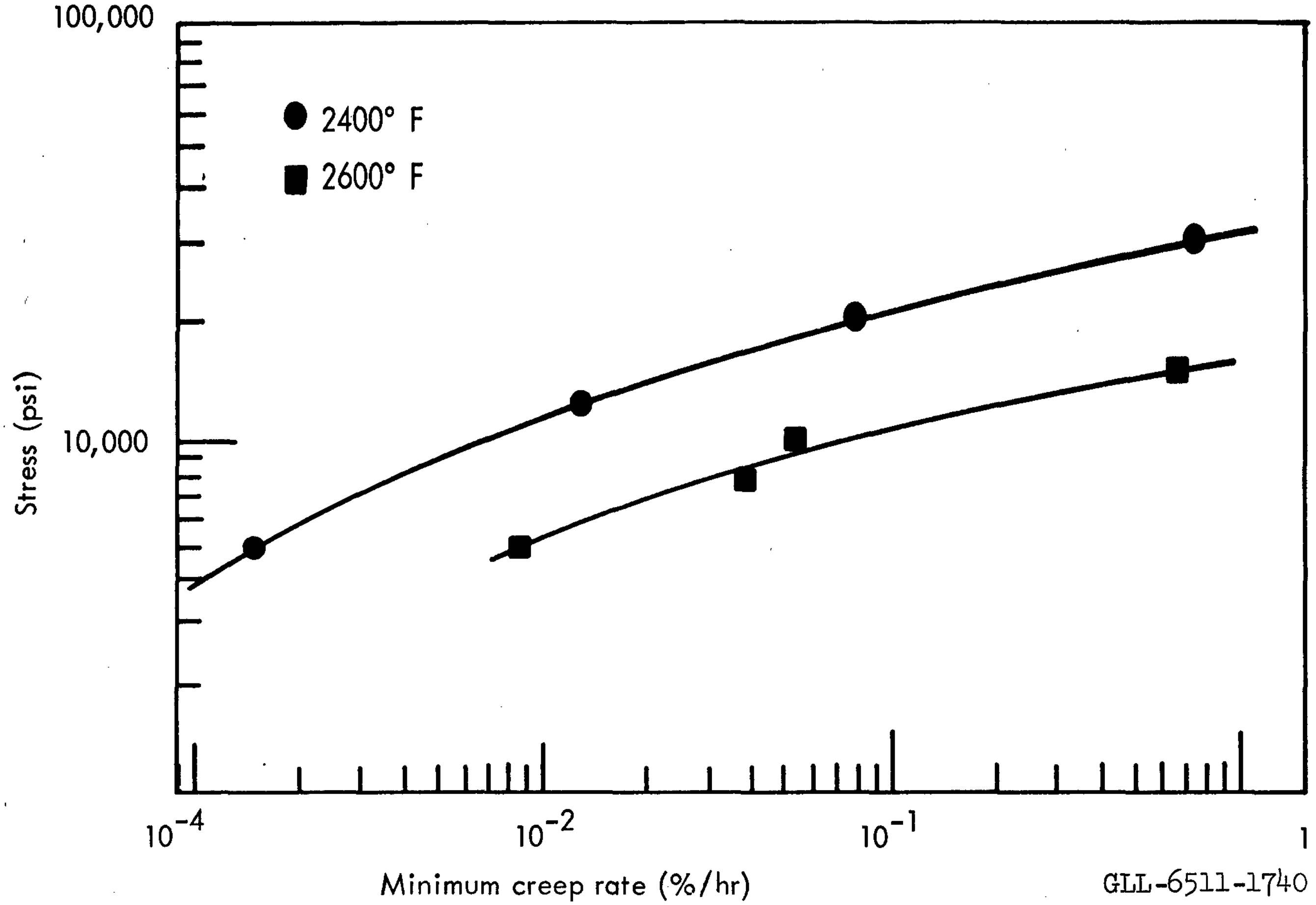
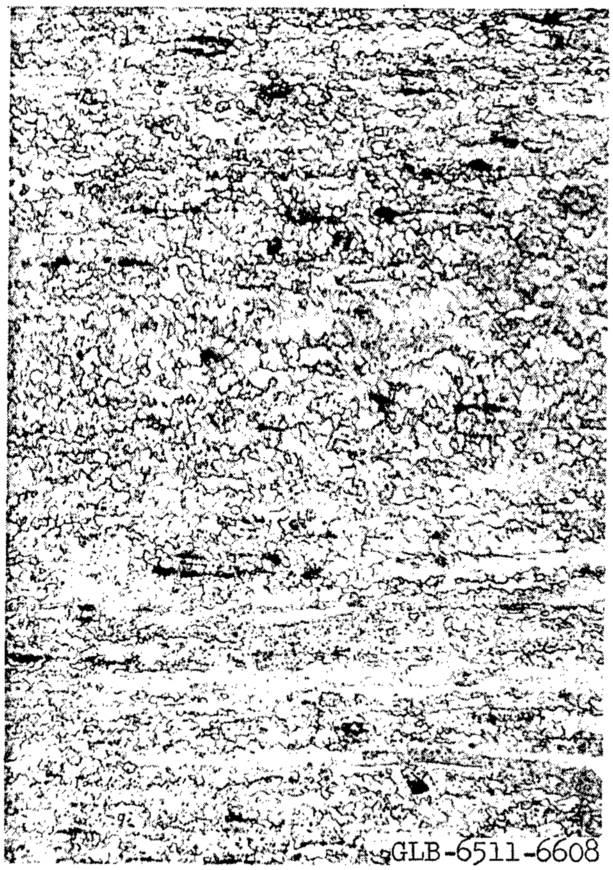


Fig. 6. Stress vs minimum creep rate at 2400 and 2600° F.



250×

Fig. 7. TZC (0.3% C) specimen tested at 2400° F and 20,000 psi. 125 hr to rupture. Etching has exaggerated agglomerated carbides as dark areas.

DECARBURIZATION AND RECRYSTALLIZATION

To add further difficulty to the interpretation of the creep test results, an effect due to the testing environment was encountered. Figure 8 illustrates the microstructure near the surface of the gage length of a specimen tested at 2600° F and 5000 psi for 908 hr to rupture. As the surface of the specimen is approached, an increase in the extent of recrystallization can be seen.

This can be explained in the following manner. At the specimen surface a reaction takes place between carbon in the specimen and residual oxygen in the testing atmosphere, forming a CO reaction product. As the decarburization progresses through the surface layers, the recrystallization temperature of the carbon depleted zone is lowered. The effect of surface decarburization and recrystallization is very troublesome, since the loss of carbon not only has a weakening effect but also it has been shown that recrystallization may also accelerate creep.[11]

We have shown that decarburization can be avoided by testing in an ultrahigh vacuum, pumped by a sputter-ion type pump. Samples of the TZC (0.3% C) alloy held at 3000° F for 50 hr in a Varian Associates Ultra High Vacuum Furnace showed no evidence of decarburization metallographically. The pressure maintained during these heat treatments was no greater than 5×10^{-8} torr. A quadrupole residual gas analyzer applied to the system at 3000° F indicates the partial pressure of oxygen to be less than 5×10^{-11} torr.

An ultrahigh vacuum system similar to ours has been described by Buckman and Hetherington.[12] They point out that conventional vacuum systems utilizing a diffusion pump are not adequate for heat treating refractory metals even though pressures indicated are in the range of 10^{-5} to 10^{-7} torr. TZC (0.3% C) samples heat treated by us in such a conventional vacuum system have shown decarburization in 100 hr at 2600° F and 1 hr at 2800° F. We conclude that all creep tests reported herein were affected by decarburization.

The problem of decarburization in molybdenum alloys has received attention in the literature recently. For example, Chang[13] reports that the decarburization rate appears to be sensitive to the particular specie of carbide present in the alloy. Begeley[14] has reported experiences with oxygen contamination similar to our own and points out the need for further work in this area.

Figure 9 shows the recrystallization behavior of TZC (0.3% C) at 3000° F. The heat treatments were conducted in an ultrahigh vacuum furnace of the type previously described. After 50 hours recrystallization is well advanced but grain growth has not yet begun. It is estimated that the 1-hr recrystallization temperature is 3200°F for bar stock having approximately 50% cold work.

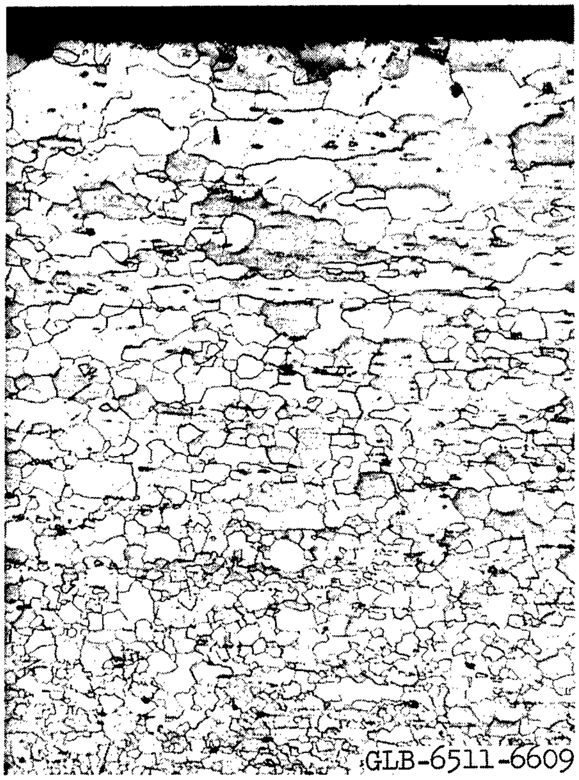
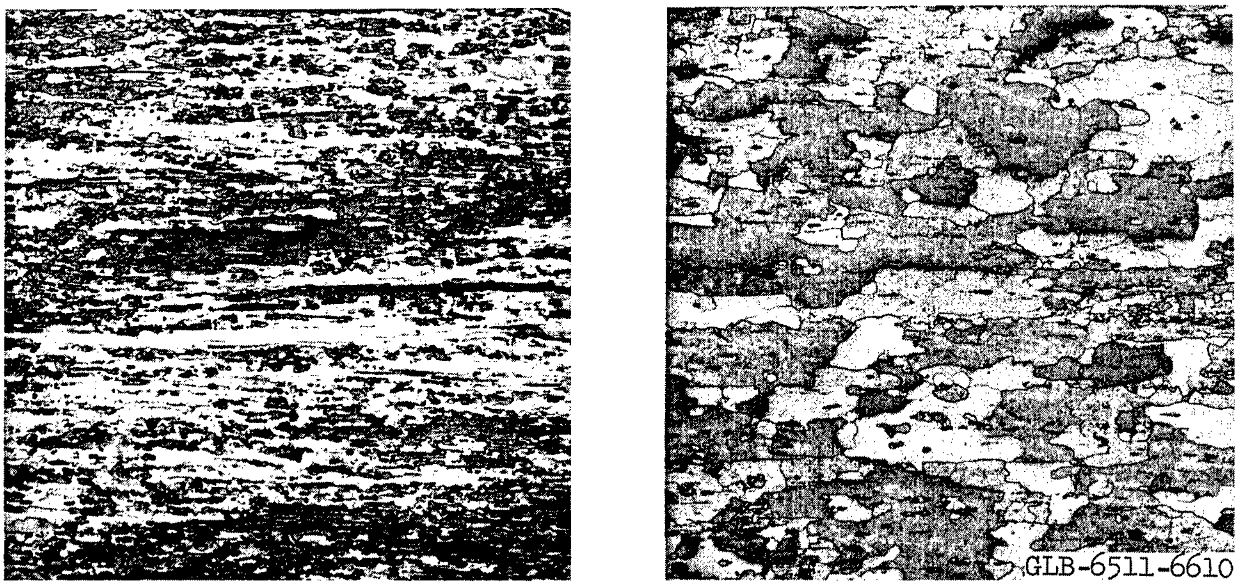


Fig. 8. Gage section of creep specimen tested at 2600° F and 5000 psi. 908 hours to rupture. Note effects of surface decarburization. 250X



10 hr

50 hr

Fig. 9. Recrystallization behavior at 3000° F. 100X

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APPENDIX A

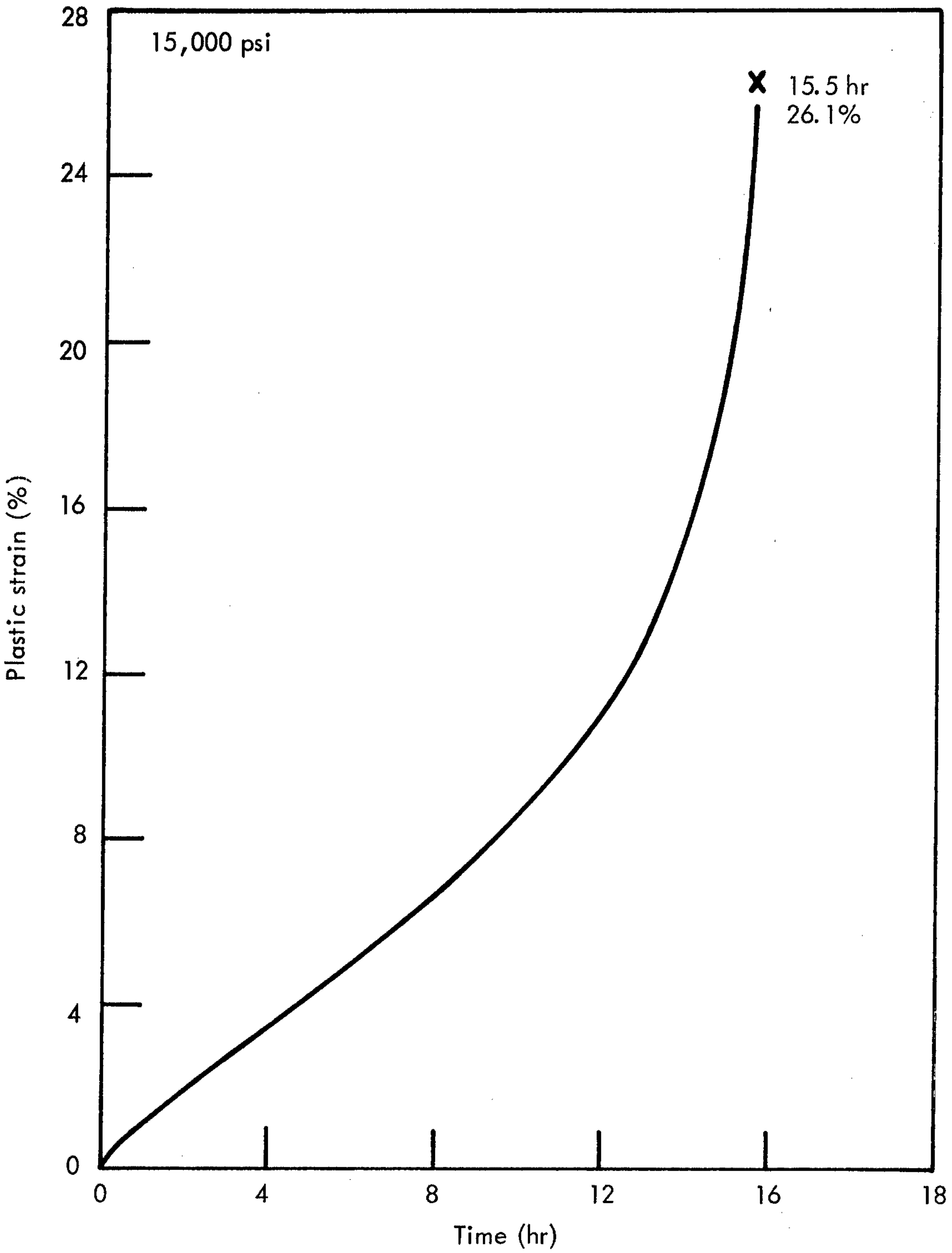

Fig. A.1. Creep curve, 2600° F, 15,000 psi.

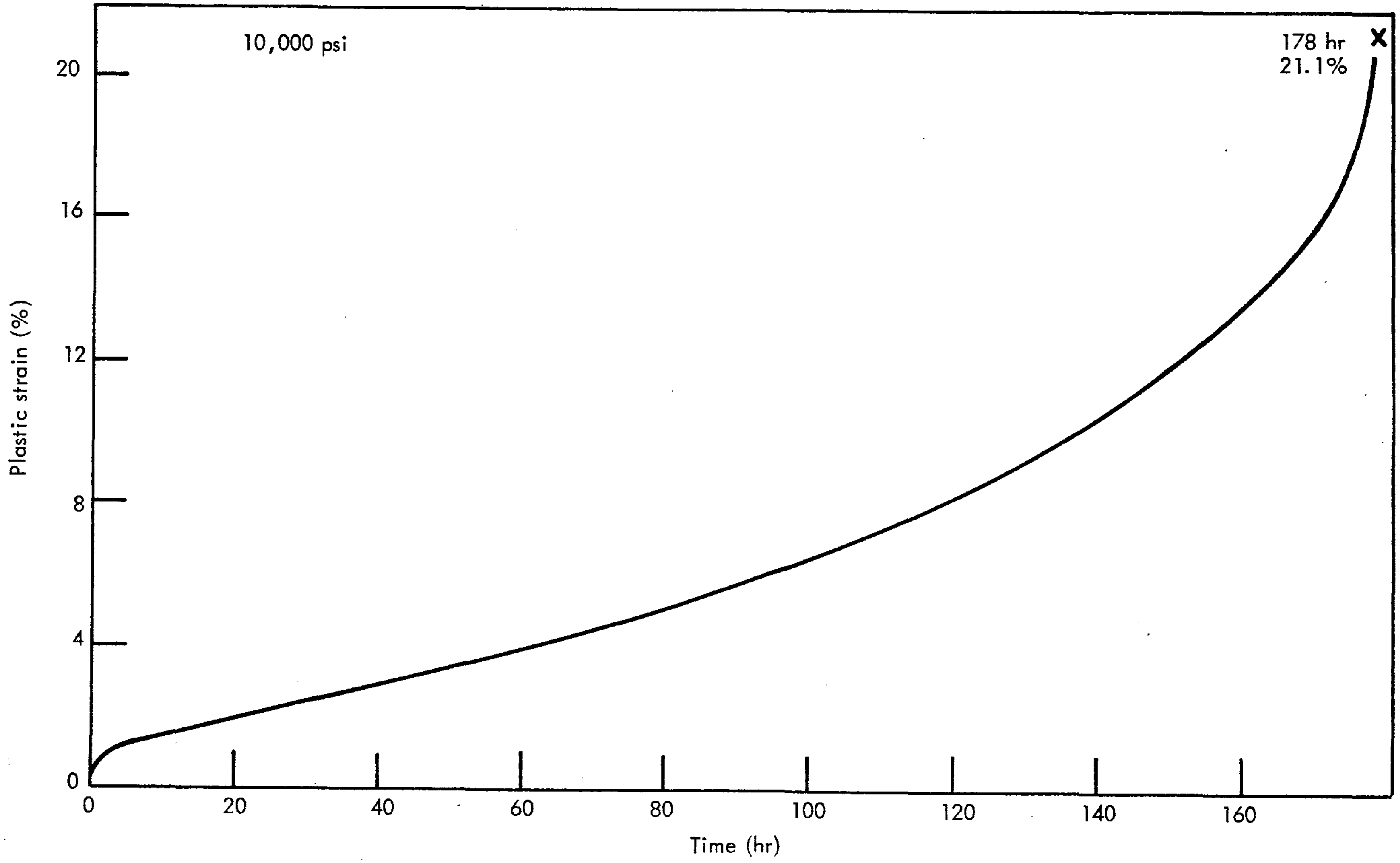

Fig. A.2. Creep curve, 2600° F, 10,000 psi.

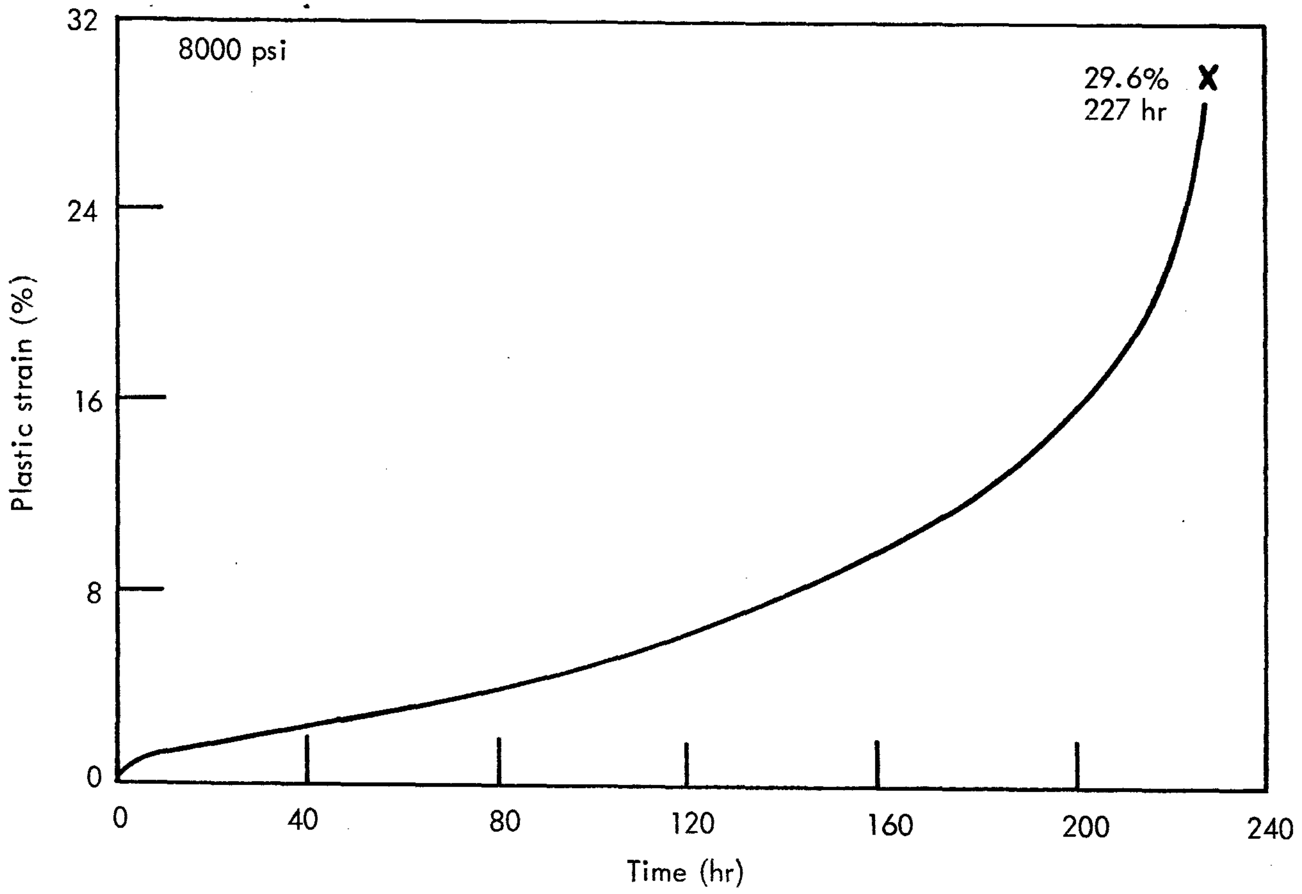

Fig. A.3. Creep curve, 2600° F, 8000 psi.

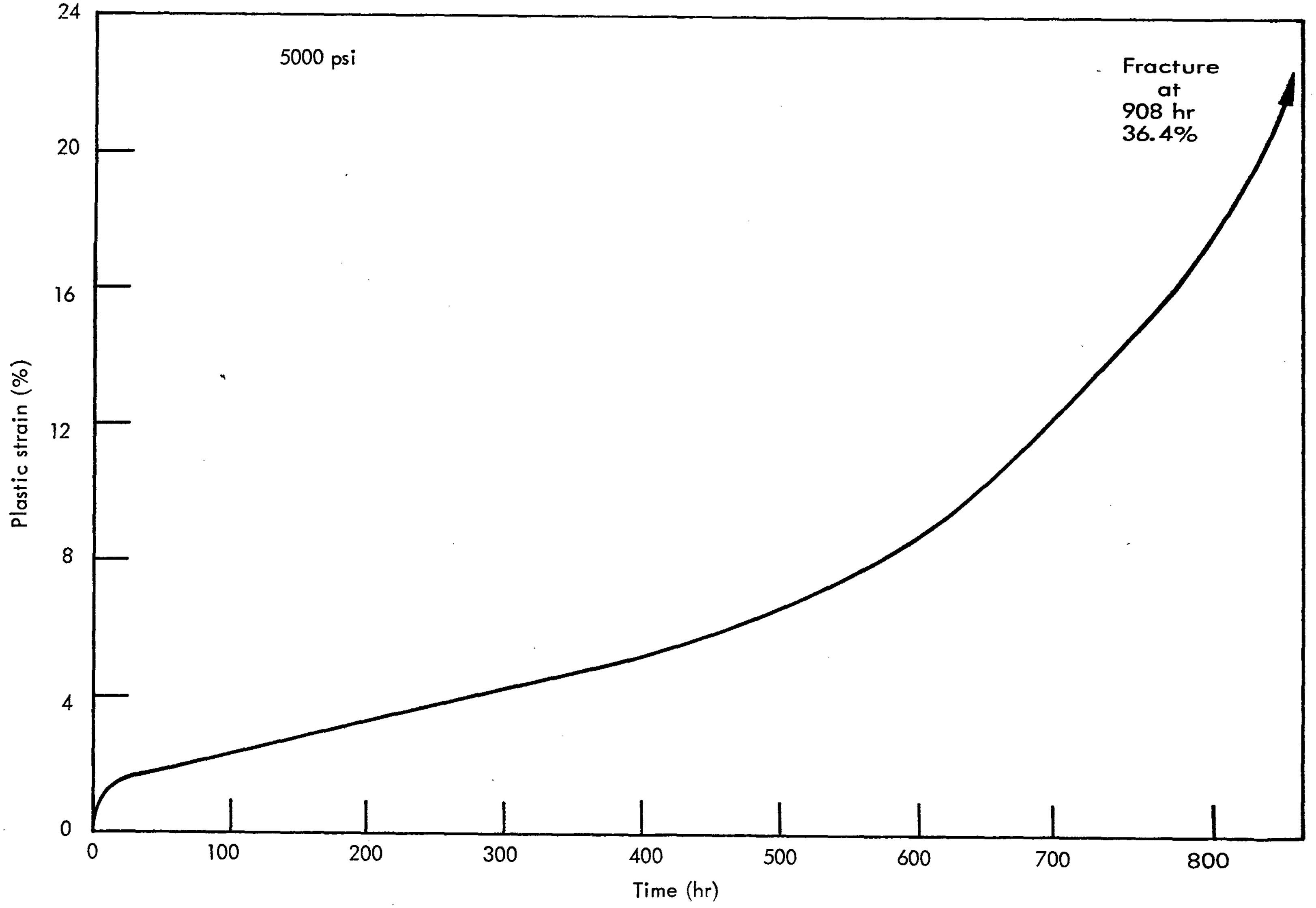

Fig. A.4. Creep curve, 2600° F, 5000 psi.

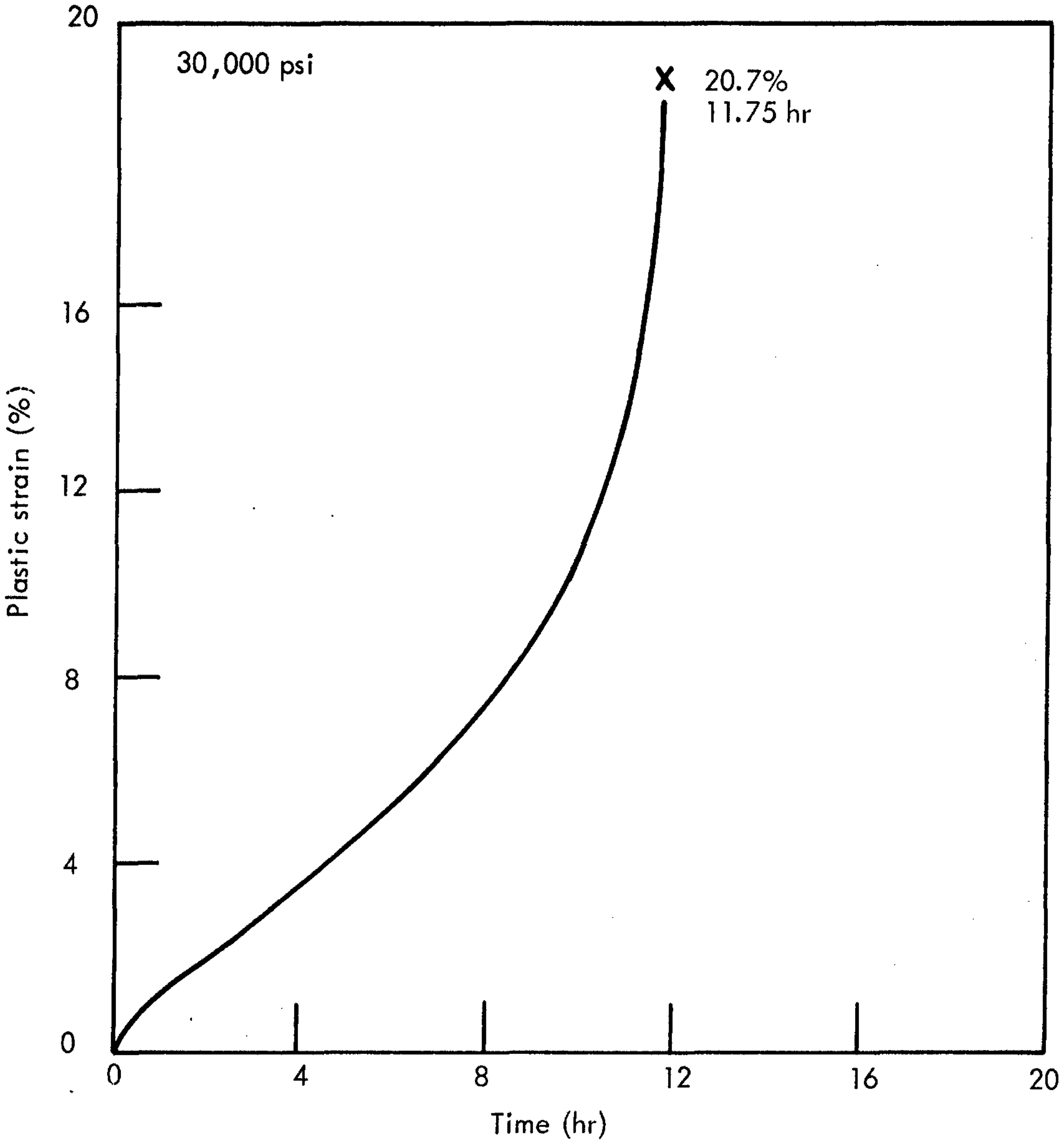

Fig. A.5. Creep curve, 2400° F, 30,000 psi.

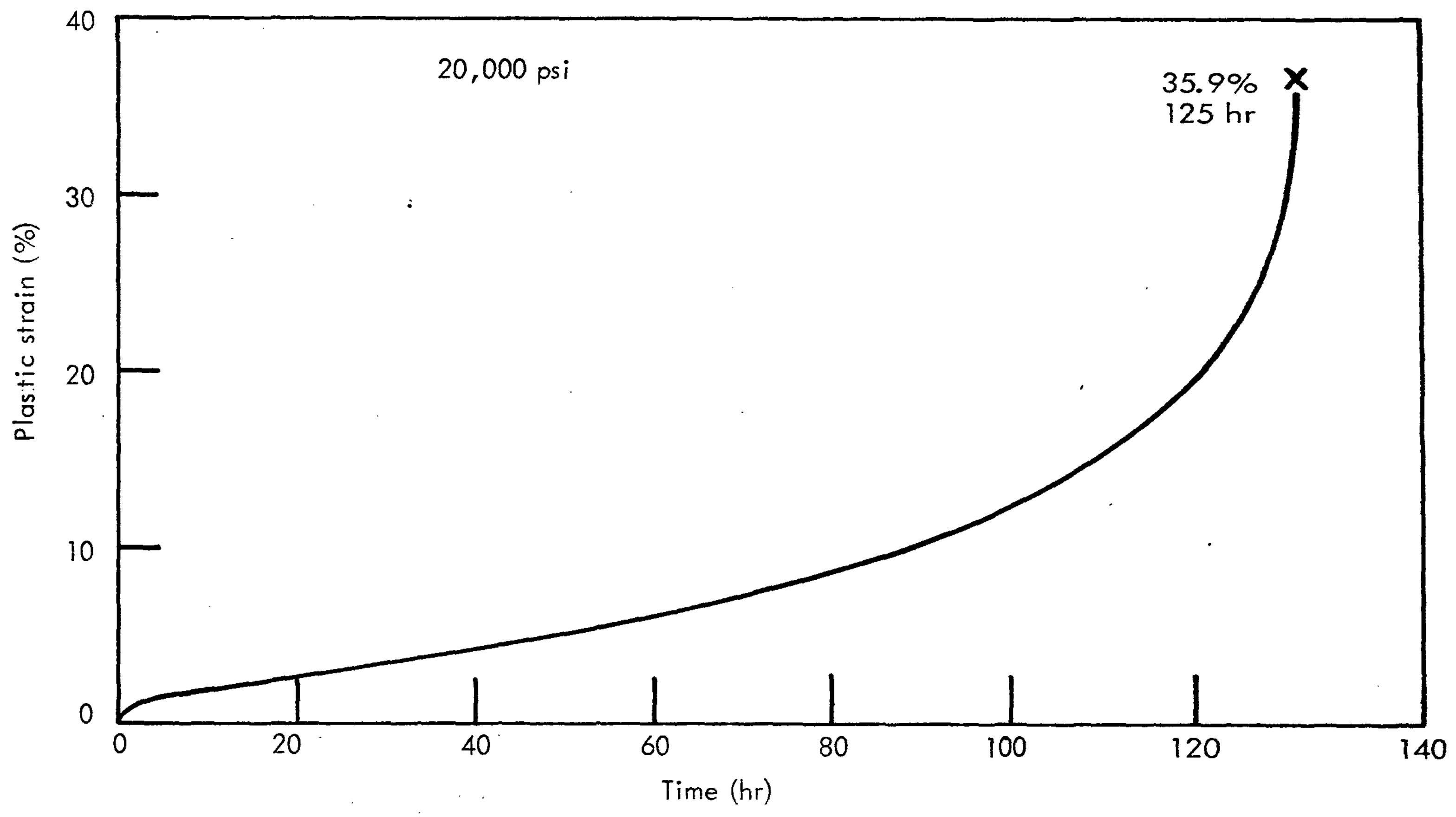

Fig. A.6. Creep curve, 2400° F, 20,000 psi.

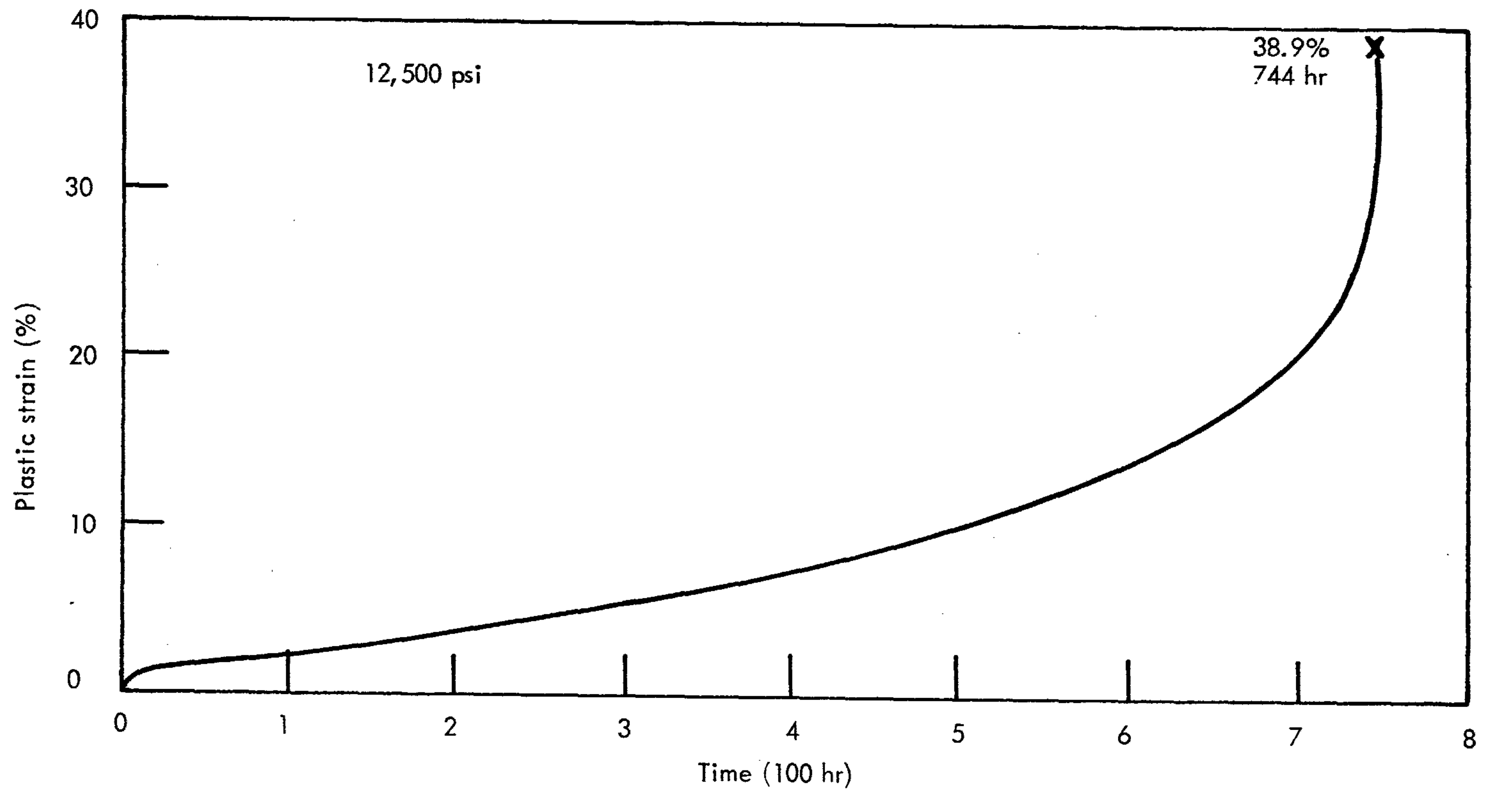

Fig. A.7. Creep curve, 2400° F, 12,500 psi.

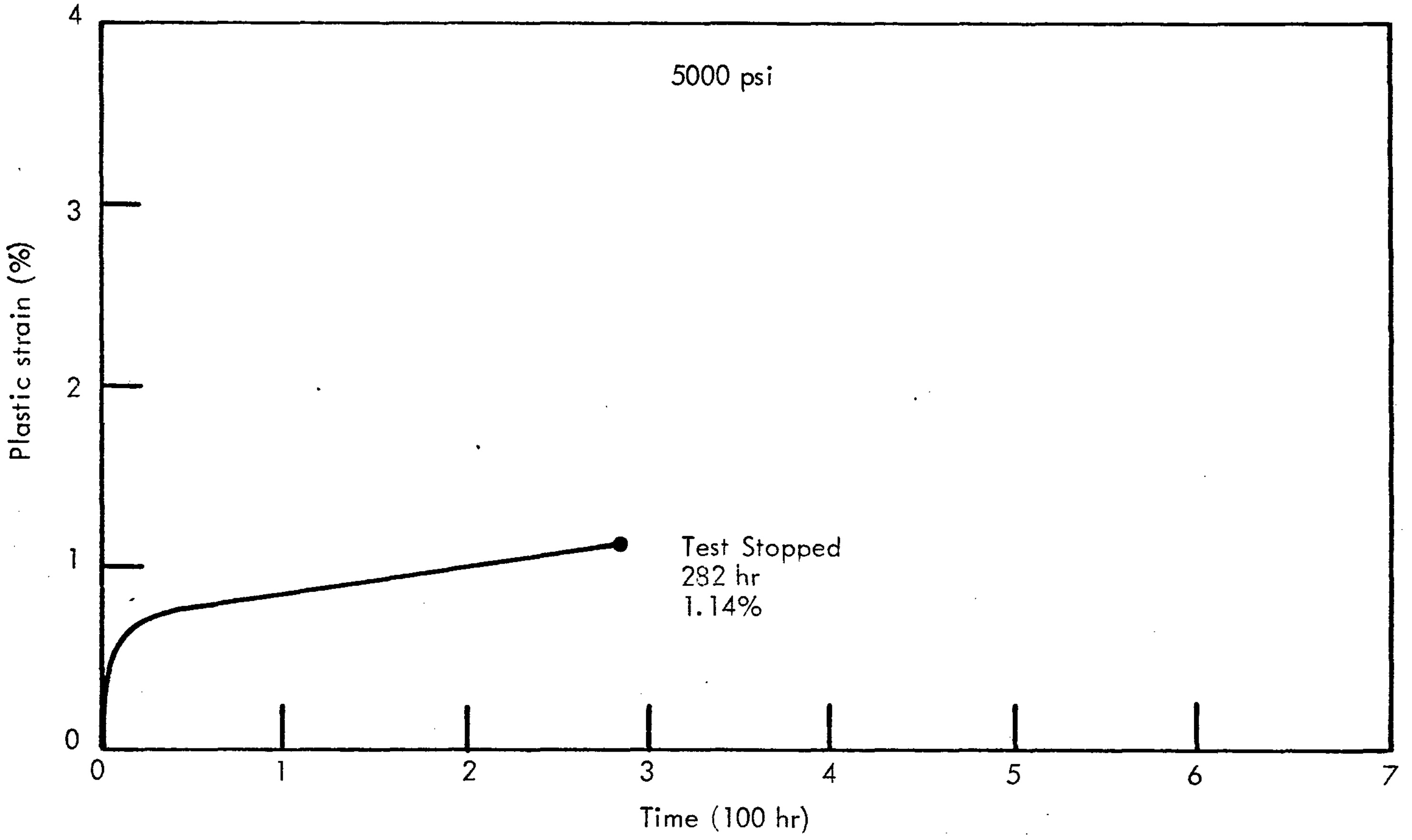

Fig. A.8. Creep curve, 2400° F, 5000 psi.

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