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GERMINATIVE GRAIN GROWTH CHARACTERISTICS OF ZIRCONIUM

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GERMINATIVE GRAIN GROWTH CHARACTERISTICS OF ZIRCONIUM

BY:

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TABLE OF CONTENTS

LIST OF FIGURES

ABSTRACT

Zirconium, because of its low neutron capture cross-section, is potentially an important structural material for use in nuclear reactors. At temperatures above 950° F, zirconium which has been strained a critical amount will experience germinative grain growth during recrystallization. This grain growth can result in a reduction in the fatigue life by a factor of 2 to a factor of 9 at both high and low temperatures. The critical strains for zirconium vary from 15 per cent at 900° F to about 2 per cent at 1125° F, while those for zircaloy III vary from 15 per cent at 1050° F to 5 per cent at 1200° F. A study was made of the variation of recrystallized grain size versus plastic strain and annealing temperature. This showed that in order to avoid germinative grain growth, a temperature limitation must be placed on inhomogeneously deformed zirconium and zircaloy III. The limitations are between 900° and 950° F for zirconium and 1050° F for zircaloy III. Zircaloy II experiences no germinative grain growth up to 1200° F.

I. INTRODUCTION

Nuclear reactor components are subjected to transient temperatures and in many cases have thermal gradients imposed across them. Service of this type imposes repeated flexural stresses and makes high temperature fatigue resistance an important property when evaluating material for use in reactor components. Recent work[1] on the fatigue properties of zirconium (Fig. 1 and 2) has shown that coarse grained zirconium has a much lower fatigue life than fine grained material. These fatigue data are for 1-inch cantilever specimens having a thickness of 0.030 inches + 0.001 - 0.000. Coarse grained structures are developed in zirconium which has been plastically strained a critical amount and annealed at 950° F or above for long periods (more than 100 hours). This grain coarsening is termed germinative grain growth during recrystallization or exaggerated grain growth.

When a metal is plastically deformed or, more specifically, work hardened, local microscopic areas of high peak stresses are formed. These regions of high energy are caused by slip, bending of atomic planes, twinning, and grain boundary movement during deformation. They are potential nuclei for recrystallization. The greater the strain, the more potential nuclei are formed and the higher the microscopic peak stresses. Annealing the metal in its recrystallization range results in the growth of these nuclei into new stress-free grains. The grain size obtained on recrystallization is determined by the rate of nucleation of new grains and the rate at which they grow. Low nucleation rates and high growth rates lead to coarse grained structures while high nucleation rates and low growth rates lead to fine grained structures. At a given temperature, both the nucleation rate and the growth rate increase with the amount of work hardening. Since nucleation and growth are diffusion dependent, the respective rates also increase with temperature.

When an inhomogeneously deformed metal specimen, i. e., one in which there exists a strain gradient, is annealed at a constant temperature in its recrystallization range, recrystallization will occur in regions strained sufficiently to have a finite nucleation rate. The critical strain is defined as that minimum strain necessary to promote nucleation in the time unit and temperature considered. The maximum grain size will occur at the region of critical strain since this

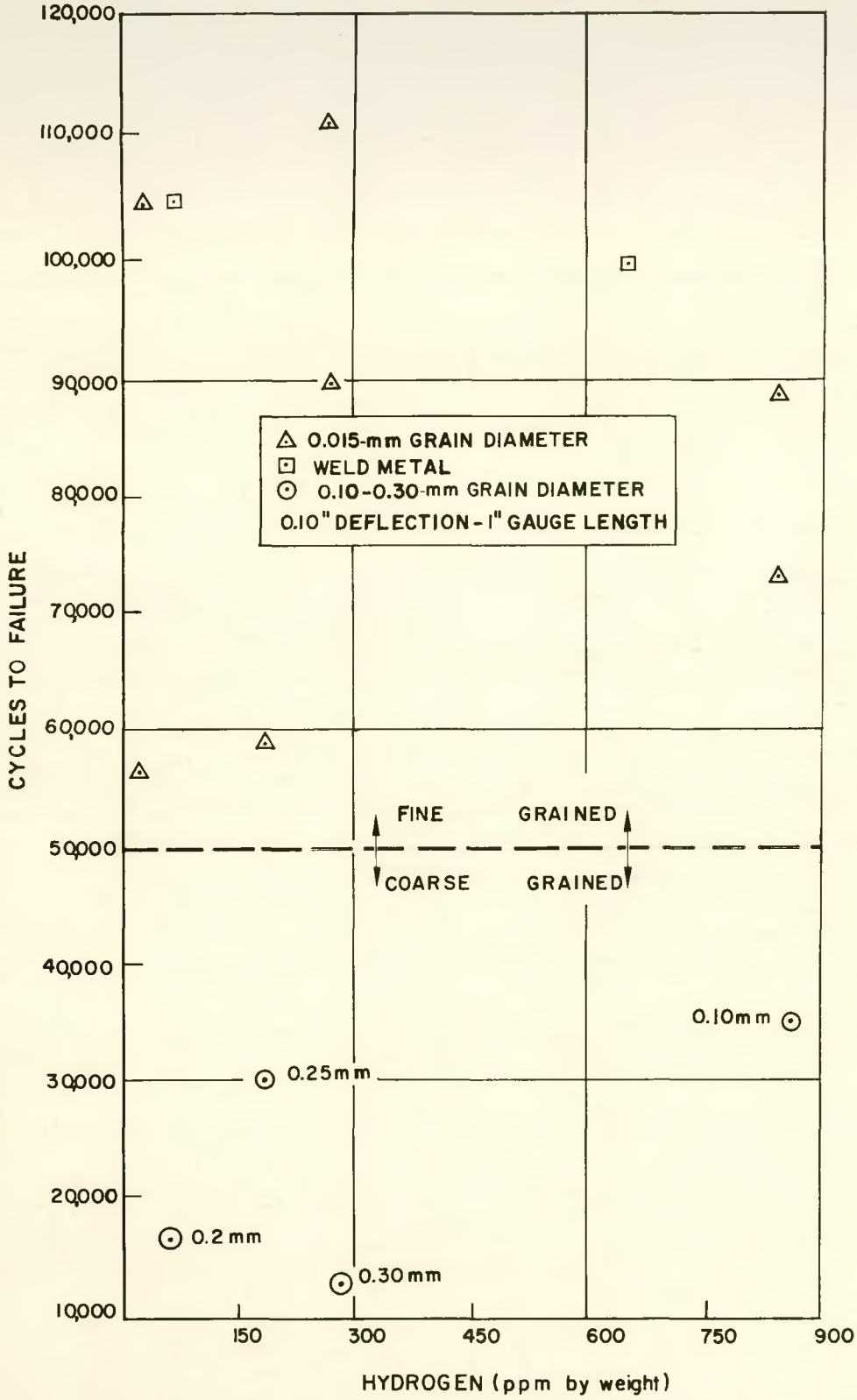

Fig. 1. Fatigue Cycles to Failure at 510° F

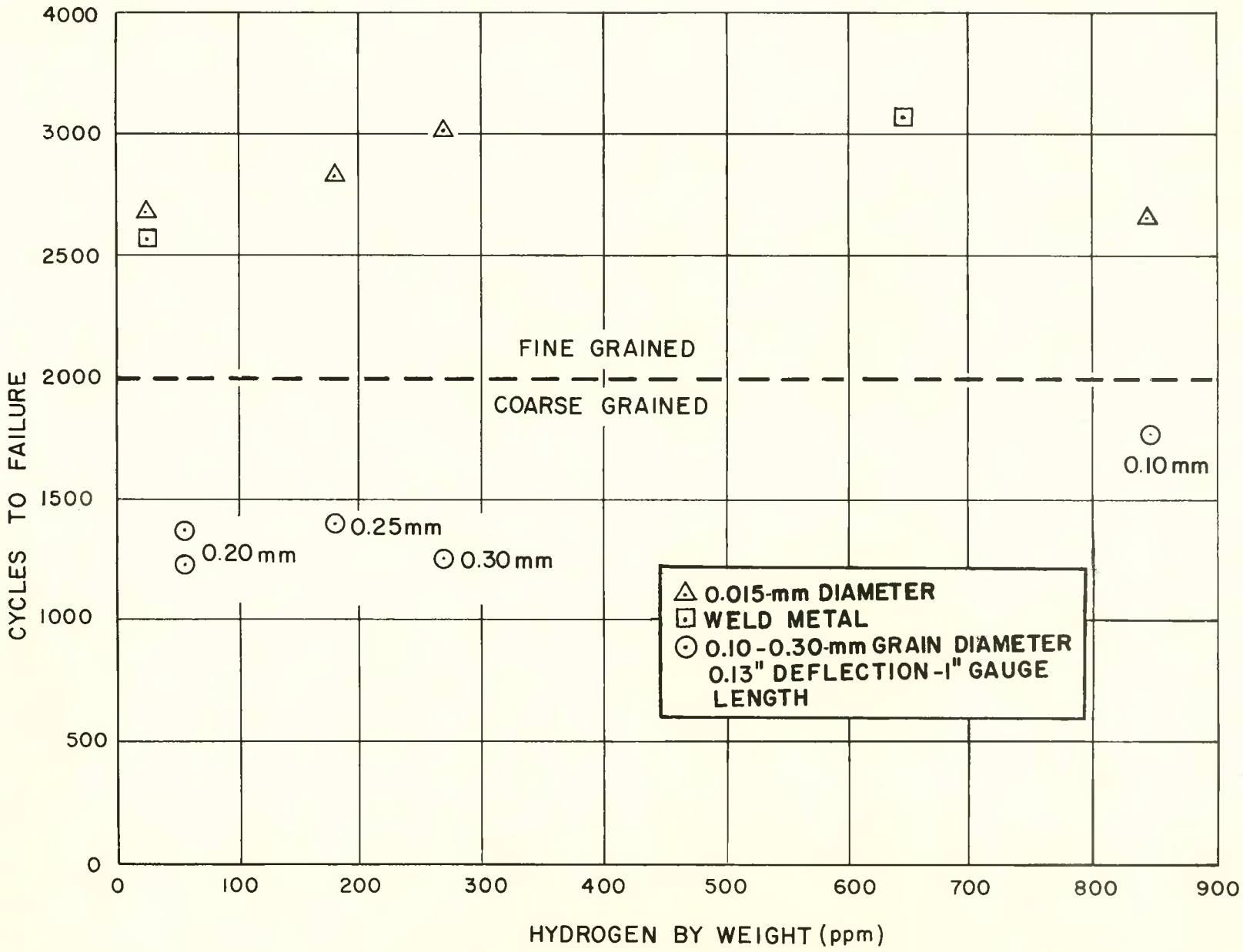

Fig. 2. Fatigue Cycles to Failure at 985° F vs Hydrogen Content

region has the fewest stable nuclei per unit volume which grow into new grains. Recrystallization is not evident below this strain since the nucleation rate is vanishingly low. Metal strained more than the critical amount has a higher nucleation rate per unit volume which results in a finer grained structure.

The maximum grain size which occurs at the critical strain is strongly temperature dependent. At high temperatures the rate of grain growth is high and the critical strain is low. This results in a small number of potential nuclei per unit volume and a large recrystallized grain size at the critical strain. At low temperatures the rate of grain growth is low and the critical strain is high, resulting in a higher number of potential nuclei per unit volume and a smaller recrystallized grain size at the critical strain.

Since the rate of strain hardening and the mechanism of deformation are temperature dependent, the nature and distribution of potential nuclei would be expected to change with the temperature at which the straining takes place. Hence, the critical strain will depend on the straining temperature.

The purpose of the investigation was to determine the critical strain for zirconium as a function of annealing temperature and temperature of strain, and to determine the resulting recrystallized grain size as a function of prior plastic strain. These data are compared with similar data obtained for two zirconium alloys.

II. MATERIALS

The zirconium used was hafnium-free double arc-melted sponge obtained from the Bureau of Mines. The ingots were forged and hot reduced to 0.08- to 0.10-inch sheet and susequently cold reduced to 0.035-inch sheet with intermediate and final anneals at 1200° F for fifteen minutes. The resulting sheets had the following typical composition.

Element	Weight (%)
Fe	0.040
Si	0.040
Cu	0.0002
Cr	0.050

Element	Weight (%)
O	0.100 to 0.120
N	0.0040 to 0.012
H	0.0025 to 0.0050

The zircaloy III used was 0.030-inch sheet in the annealed condition and had the following composition:

Element	Weight (%)
Sn	0.25
Ni	0.008
Fe	0.31
O	0.15
N	0.011
H	0.010

The zircaloy II was 0.035-inch sheet in the annealed condition and had the following composition:

Element	Weight (%)
Sn	1.60
Cr	0.07
Ni	0.041
Fe	0.20
O	0.11
N	0.007
H	0.025

III. EXPERIMENTAL

To determine the critical strain at a given temperature, tensile specimens having a 0.065-inch taper in a 2-inch gauge length were machined from the sheets parallel to the rolling direction (Fig. 3).

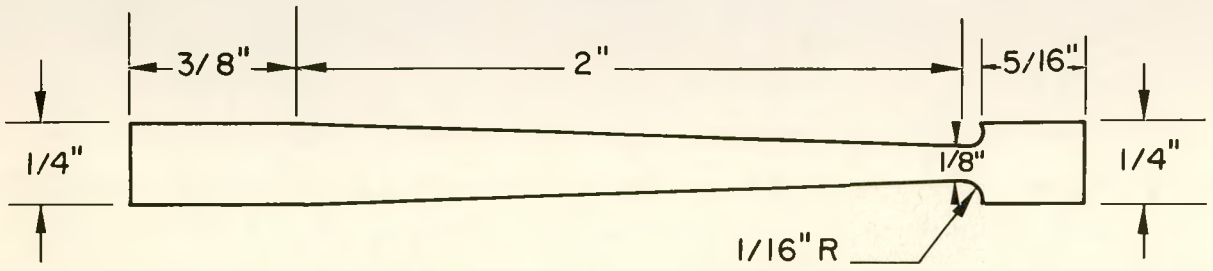

Fig. 3. Tapered Tensile Specimen

These were polished, etched, and examined metallographically to ensure that all specimens used were strain free initially. Tukon indentations were made every half millimeter along the gauge length of the specimen. These served as fiducial marks enabling the plastic strain to be measured with a microscope and micrometer stage. The specimens were pulled to failure at a rate of 0.002 in./min in an Instron tensile testing machine. Three temperatures were used for straining: room temperature, 500° F, and 900° F. The 500° and 900° F tests were run in an argon atmosphere. Since the rate of work hardening changes with temperature, a different critical strain was obtained for each temperature of strain.

Specimens prepared in the manner described were annealed in vacuum at various temperatures ranging from 900° to 1200° F for up to 1000 hours after which they were examined metallographically. The critical strain, at which exaggerated grain growth occurred, and the recrystallized grain size as a function of strain were determined for each specimen.

IV. RESULTS

Since the critical strain is dependent on the nucleation rate at the annealing temperature, the critical strain should change as the annealing time is varied. Increasing the time of anneal increases the probability of the nucleation of a new grain; as a result, the critical strain decreases with time of anneal. Previous

work[2] has shown that for some metals the nucleation rate for a given temperature and degree of work hardening increases rapidly to a maximum with time and then falls to a vanishingly low value. Under these conditions the critical strain should decrease with time at a decreasing rate and approach a constant value as the nucleation rate approaches zero. The data (Fig. 4 and 5) substantiate this view. For zirconium strained at 500° F the critical strains reach relatively constant values of 2, 5.0, 6.5, 9.5, and 15 per cent elongation at 1125°, 1050°, 1000°, 950°, and 900° F respectively. Zircaloy III strained at 500° F has critical strains of 5.2, 9.5, and 15 per cent elongation at 1200°, 1125°, and 1050° F respectively. For both zirconium and zircaloy III, annealing beyond 500 hours has little effect on the critical strain. Zircaloy II is not shown in these figures since it shows no evidence of exaggerated grain growth at any temperature up to 1200° F.

The variation of critical strain with temperature is shown in Fig. 6. For specimens strained at room temperature and 500° F, the logarithm of the critical strain varies linearly with the temperature, e.g.

$$\sigma_c = Ae^{-BT}$$

$$\ln\sigma_c = \ln A - BT$$

where σ_c is the critical strain at temperature T, and A and B are constants. Variation of straining temperature below the recovery and recrystallization range changes the y-intercept but does not change the slope. Also for the alloy, the y-intercept has changed but the slope remained the same as that of zirconium for specimens strained at 500° F.

The critical strains for specimens strained at 900° F in the recovery and recrystallization range when plotted in Fig. 6 fall on a straight line which has a different slope. This is undoubtedly due to a difference in the rate of work hardening and deformation mechanisms at this temperature. There is only a slight difference in the critical strain for specimens strained at 500° F and those at room temperature.

The variation of recrystallized grain size with strain for zirconium and zircaloy III is presented in Fig. 7 and 8. Recrystallization of zirconium strained less than 10 per cent at temperatures above 950° F results in a tremendous in-

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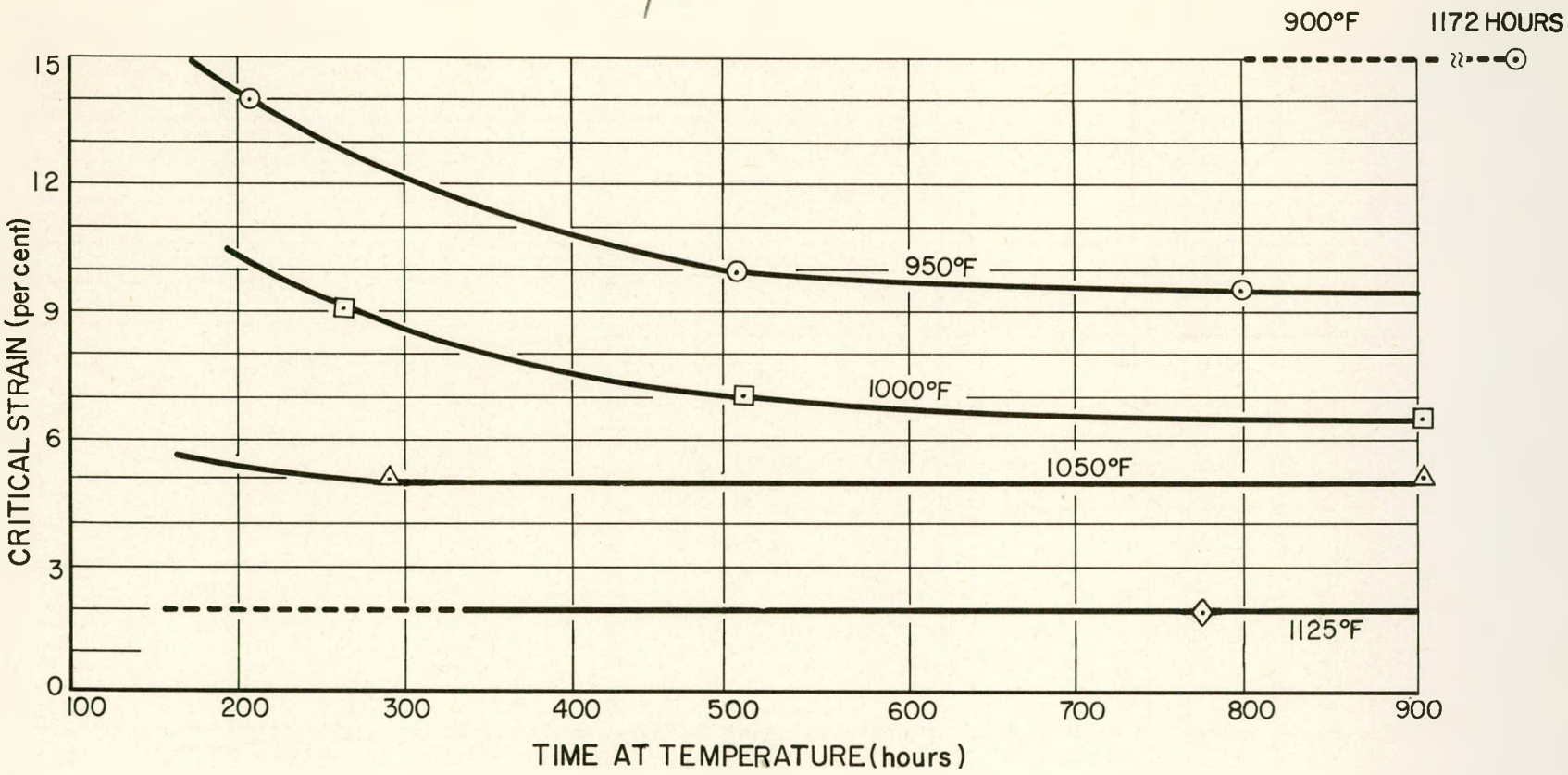

Fig. 4. Critical Strain vs Annealing Time for Zirconium Strained at 500° F

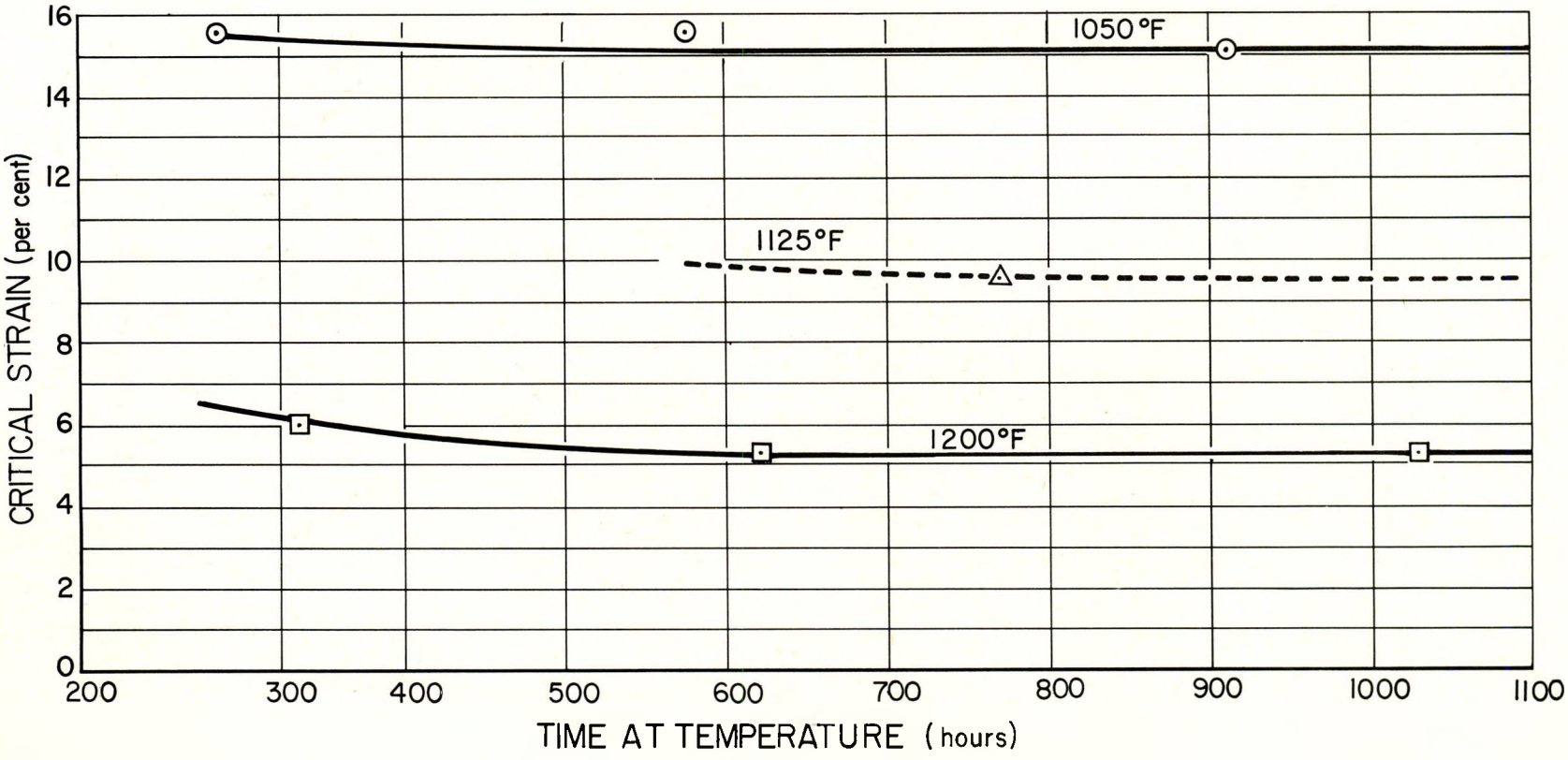

Fig. 5. Critical Strain vs Annealing Time for Zircaloy III Strained at 500° F

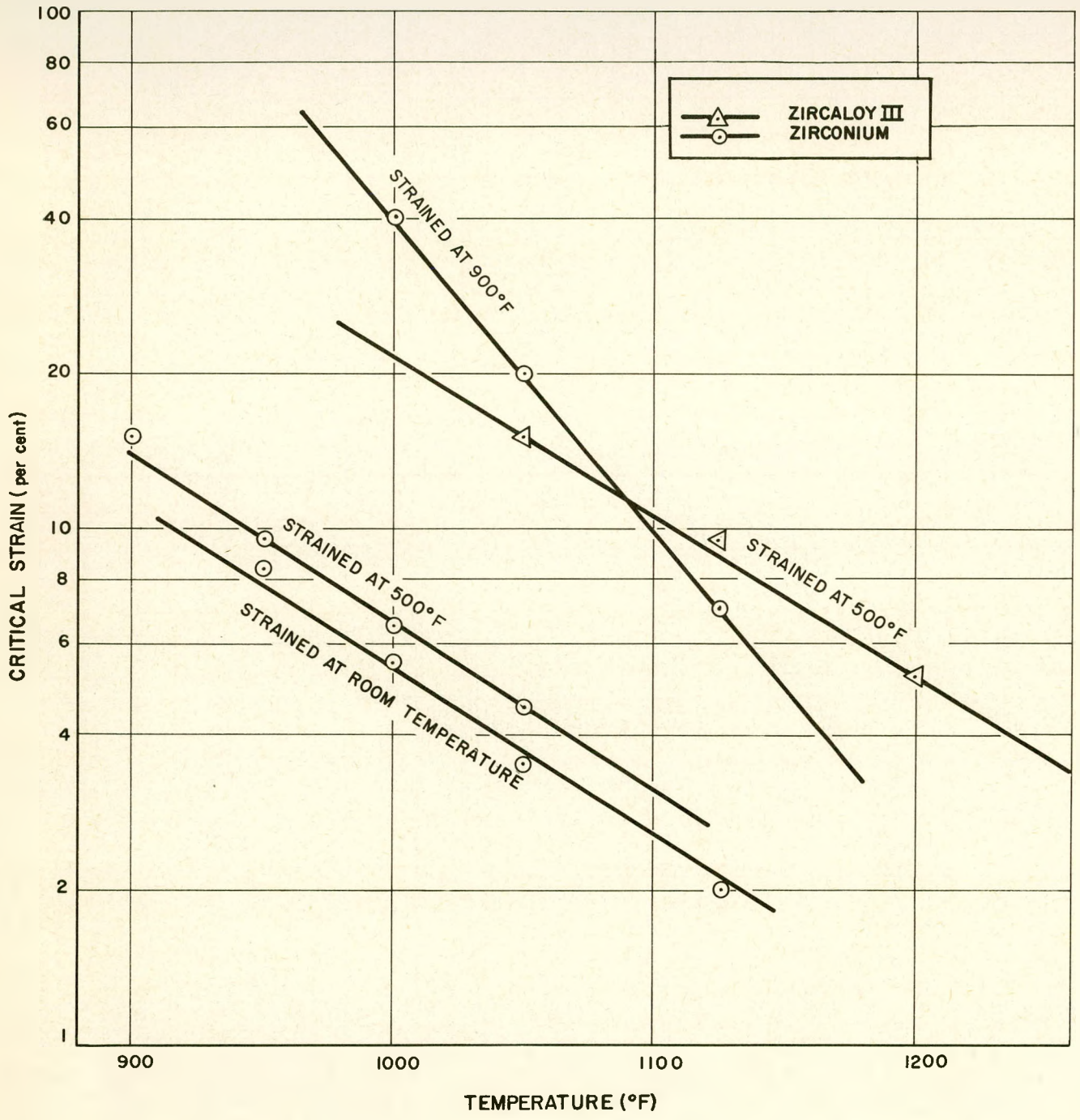

Fig. 6. Critical Strain vs Annealing Temperature for Zircaloy III and Zirconium

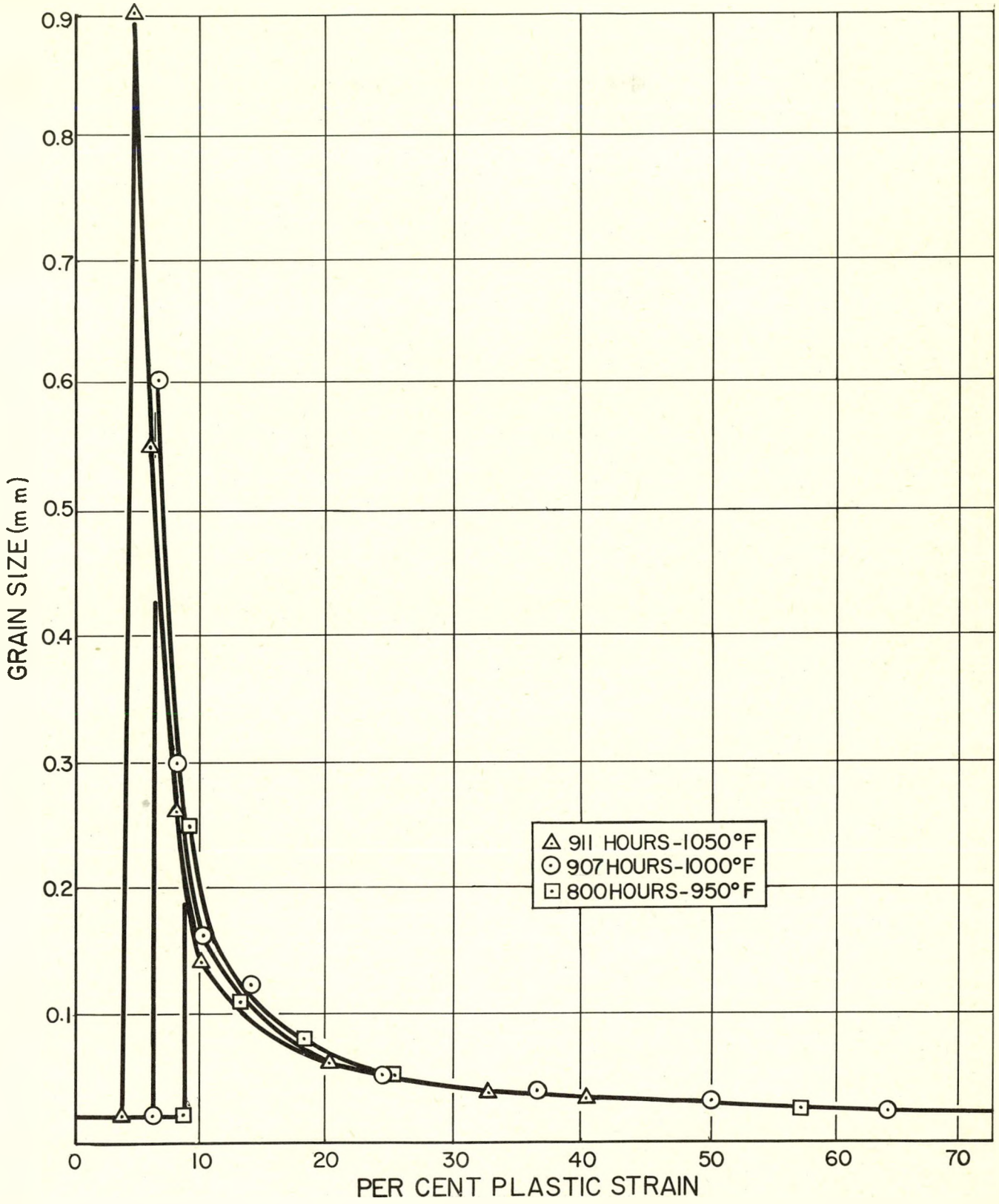

Fig. 7. Recrystallized Grain Size vs Plastic Deformation for Zircaloy III (Strained at 500° $\overline{F}$ and 0.002 in./min)

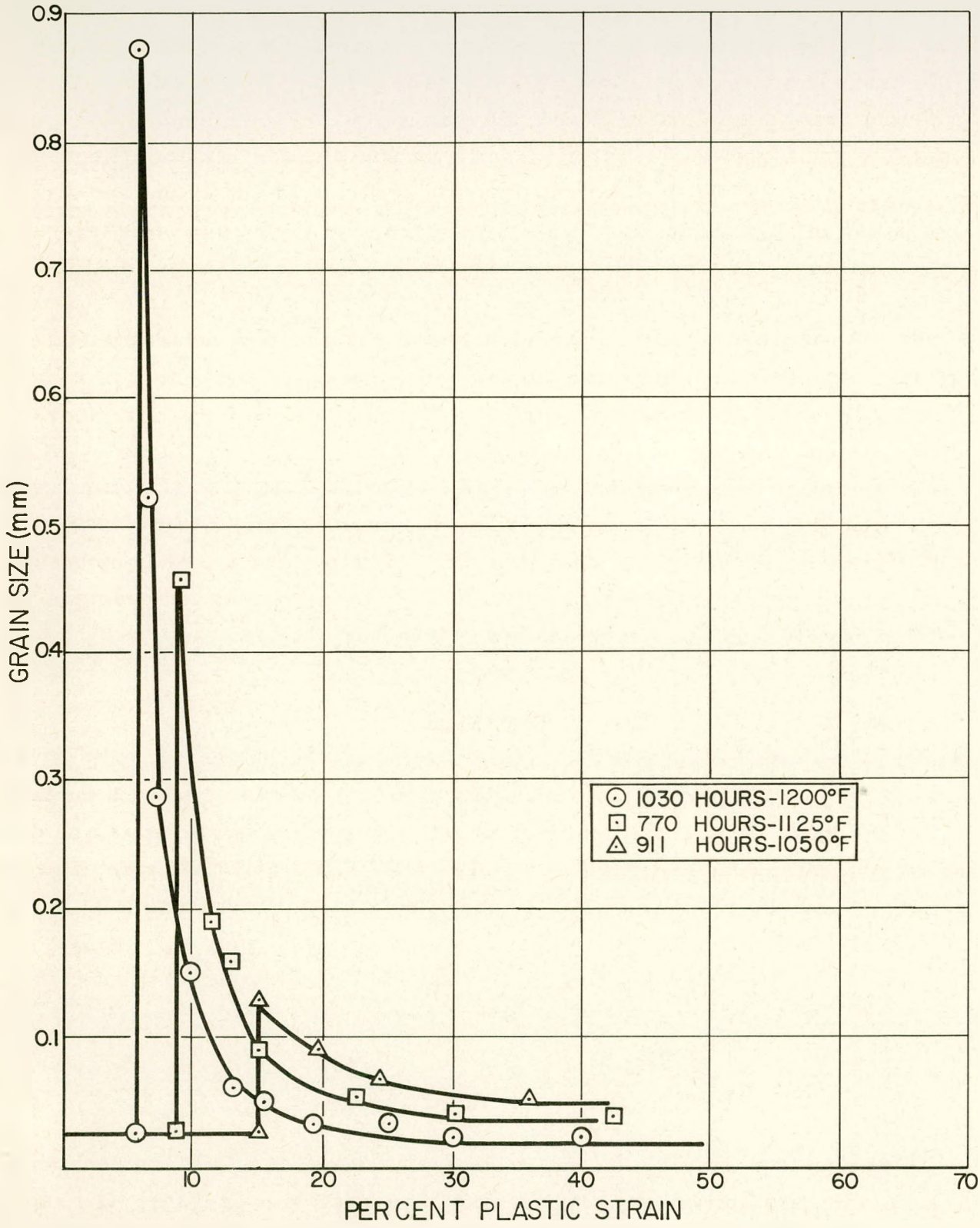

Fig. 8. Recrystallized Grain Size vs Plastic Deformation for Zircaloy III (Strained at 500° $\overline{F}$ and 0.002 in./min)

crease in grain size. Annealing for 800 hours at 950° F results in a 16-fold increase in grain diameter at the critical strain. A specimen annealed at 1125° F for 770 hours exhibited a maximum grain size of 1.7 mm or more than a 100-fold increase in grain diameter. Zircaloy III behaves in a similar manner except that comparable grain growth is shifted to higher temperatures. Photomicrographs comparing the exaggerated growth at the critical strain in zirconium and zircaloy III are shown in Fig. 9 and 10. A macrophotograph of the region of exaggerated grain growth in a zirconium specimen annealed at 1050° F is shown in Fig. 11. The maximum recrystallized grain size vs annealing temperature is presented in Fig. 12. The higher the annealing temperature, the coarser the recrystallized structure at the critical strain and the lower the critical strain. In this range, the zirconium recrystallized grain size is essentially independent of temperature (see Fig. 7) and depends only on the amount of work hardening. Zircaloy III behaves in a similar manner except that, at a given temperature, the critical strain is higher and the maximum grain size is much smaller. The grain size is not temperature independent in the alloy (see Fig. 8), e. g., for a given amount of strain, the recrystallized grain size decreases with increasing temperature while it remains nearly constant for zirconium.

V. DISCUSSION

The grain growth characteristics of zirconium can be explained with nucleation and growth theory. Recrystallization kinetics of work hardened metals are determined by the rate of nucleation of new stress free grains and their rate of growth. These rates have been shown [2, 3, 4] to obey the following relations:

$$G = Ae^{-Q_G/RT}$$

$$N = Be^{-Q_N/RT}$$

where T is absolute temperature, R is the gas constant, A and B are constants, and Q_G and Q_N are activation energies for the respective processes. Q_G represents the energy necessary for atoms in the distorted lattice to become attached

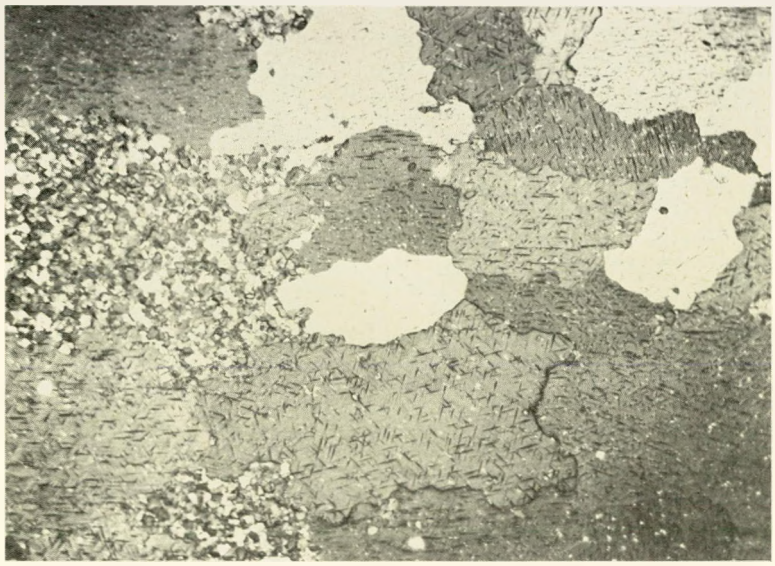

Fig. 9. Exaggerated Grain Growth Which Occurred at the Critical Strain in Zirconium Strained at 500° F and Annealed at 1050° F for 900 Hours. The critical strain is 5 per cent elongation. 50X

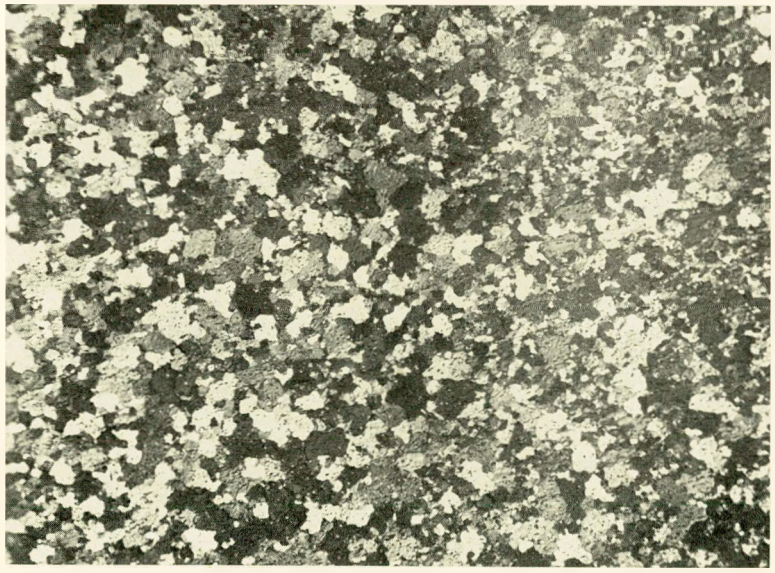

Fig. 10. Grain Growth Which Occurred at the Critical Strain in Zircaloy III Strained at 500° F and Annealed at 1050° F for 911 Hours. The critical strain is 15 per cent elongation. 50X

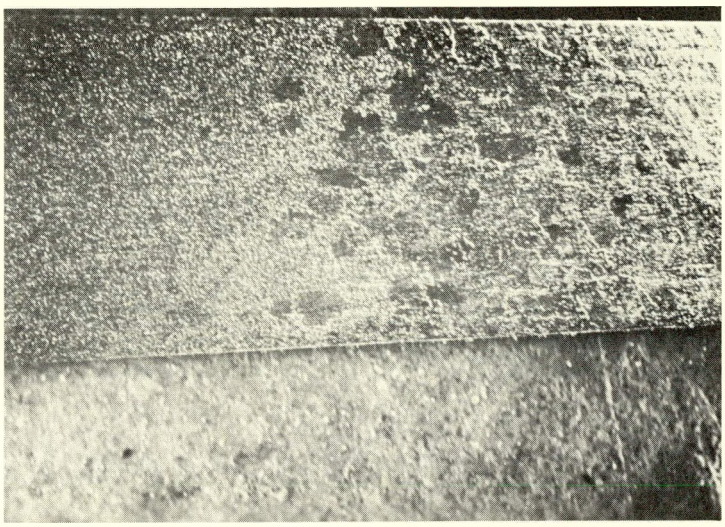

Fig. 11. The Region of Exaggerated Grain Growth in Zirconium Strained at 500° F and Annealed for 287 Hours at 1050° F. The critical strain for this specimen is 5 per cent elongation. 17X

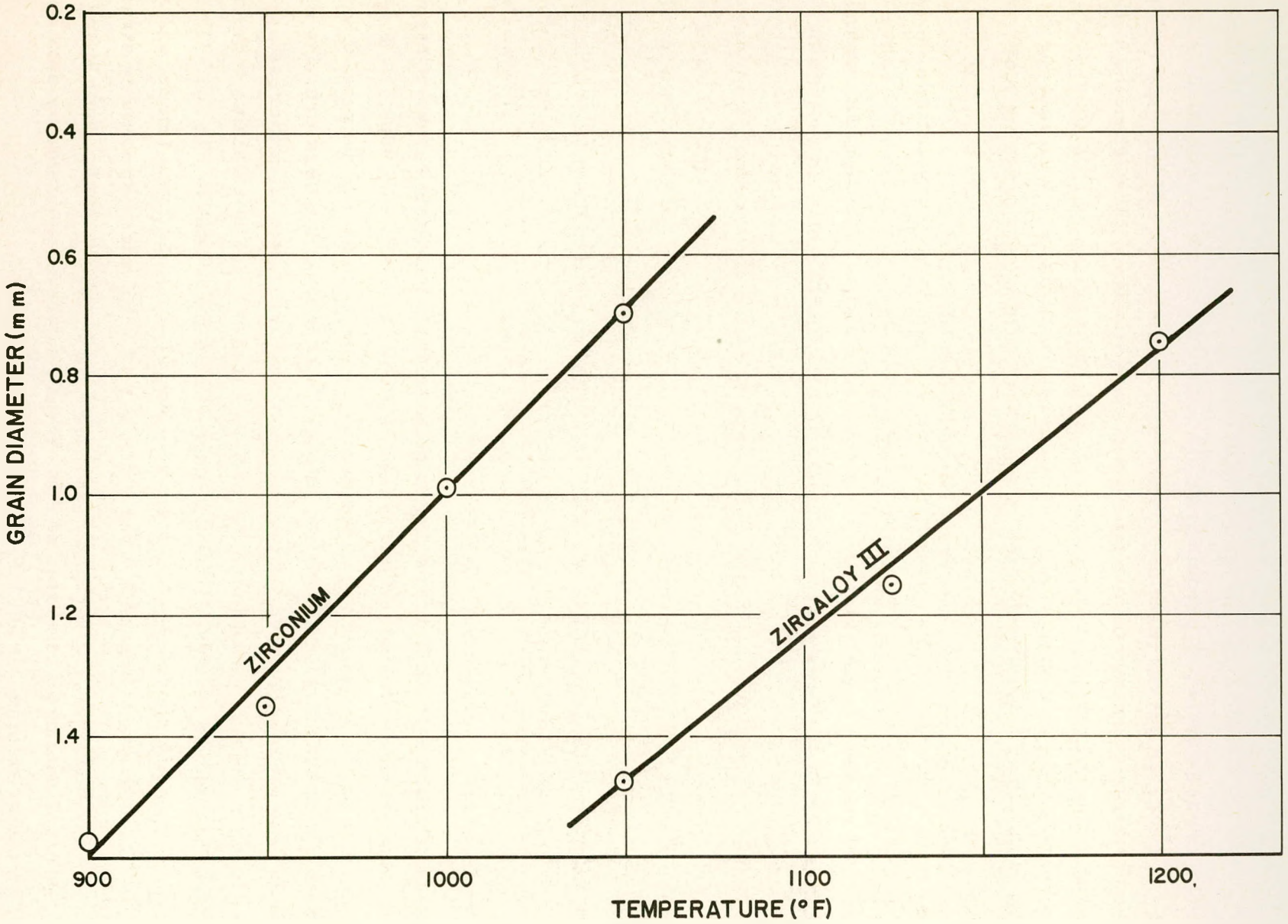

Fig. 12. Grain Size at the Critical Strain vs Annealing Temperature (Specimens Strained at 500° F and 0.002 in./min)

to the growing new lattice at the interface and Q_N is the energy necessary for atoms on the distorted lattice to form a nucleus for a new grain. In most cases N and G increase with work hardening at all annealing temperatures (that is the activation energies decrease) and increase with temperature at all deformations. The recrystallized grain size is a function of the ratio N/G; the higher the ratio the smaller the recrystallized grain size. With zirconium, as with most metals, the recrystallized grain size at a given temperature decreases with increasing degrees of work hardening. That is, N increases with work hardening more rapidly than G.

Annealing a metal having a strain gradient will result in recrystallization to a fine grain size at the regions of maximum deformation and recrystallization to coarser and coarser grain sizes as the deformation decreases (N/G decreases). For a given annealing temperature, the strain at which the nucleation rate becomes vanishingly low is the critical strain. The critical strain decreases with time of anneal at a decreasing rate and approaches a constant value, implying that the nucleation rate passes through a maximum with time for zirconium and zircaloy III. This type of behavior is shown in Fig. 4 and 5 for these two materrials.

The empirical relation between critical strain and temperature (Fig. 6) is interesting but probably of no basic significance. The relation would be of more value if the per cent elongation could be related to work hardening. This was not attempted in this investigation.

Since the amount of work hardening is dependent on the temperature of straining, specimens were strained at room temperature, 500° F, and 900° F. For a given amount of plastic elongation, the degree of work hardening decreases with increasing temperature. As a result, at a given annealing temperature, the critical strain when measured as a per cent elongation, increases with increasing temperature of strain. This increase becomes marked as the straining temperature approaches the recrystallization range. This is evident in Fig. 6. There is only a slight difference between the zirconium strained at room temperature and 500° F but a large increase in the critical strain for those specimens strained at 900° F. This means that, as far as grain growth is concerned, much more plastic elongation can be tolerated at 900° F than would be indicated by data obtained on metal strained at 500° F or room temperature.

For zirconium, the recrystallized grain size appears to be independent of annealing temperature and depends only on the amount of work hardening. This implies that the activation energies Q_N and Q_G are about equal, which results in a constant N/G with temperature. The critical strain decreases and the maximum grain size increases rapidly at the critical strain as the temperature of anneal is increased. This rapid increase in grain size is due to a more rapid decrease in N than G with decreasing work hardening.

The recrystallized grain size of zircaloy III at a given per cent elongation is not independent of annealing temperature as in zirconium but rather decreases with increasing annealing temperature. Mehl[2] shows that the number of grains, n, is proportional to N/G,

$$n \cong C\exp\left(\frac{Q_G - Q_N}{RT}\right)$$

and since the number of grains increases with temperature, the activation energy, Q_N, is greater than Q_G at a given degree of work hardening for zircaloy III. It should be emphasized that the recrystallized grain size need not necessarily increase with the temperature at which the recrystallization occurs. The variation of recrystallized grain size with temperature depends only on the temperature coefficients Q_N/R and Q_G/R. If Q_N is greater than Q_G for a given degree of work hardening, the recrystallized grain size will decrease with increasing temperature and vice versa. If the activation energies are equal, the recrystallized grain size will be independent of temperature and depend only on the amount of work hardening. In some cases, the true variation of recrystallized grain size is masked by uniform grain growth which occurs after recrystallization is complete. For zirconium and zircaloy III, this occurs at higher temperatures than were used for this study and the grain sizes reported are the true recrystallized grain sizes.

In many cases, the fatigue life of a structural material in nuclear reactors is important. These data place limitations on the service temperatures of zirconium and zircaloy III. For zirconium having small amounts of work hardening, reduction in fatigue life associated with the increase in grain size is avoided by holding operating temperatures below 950° F. This corresponds to a limitation of 1050° F for zircaloy III. No exaggerated grain growth occured in zircaloy II at 1200° F.

Evidently, this is due to the presence of a second phase in the grain boundaries which inhibits grain growth.

For temperatures in excess of those mentioned above, the coarse grained structures can be avoided by using material having enough work hardening to result in a fine recrystallized grain size at the temperature employed or by using stress free material. The second alternative seems to be quite impractical since the critical strain rapidly approaches very low values with increasing temperature.

VI. CONCLUSION

1) The critical strains have been determined at 900°, 950°, 1000°, 1050°, and 1125° F for zirconium. Also, the variation of critical strain with strain temperature has been determined. This variation is small at low temperatures (room temperature and 500° F) and becomes large in the recovery and recrystallization range (900° F).

2) The critical strains have been determined at 1050°, 1125°, and 1200° F for zircaloy III strained at 500° F.

3) The grain size as a function of prior plastic deformation has been determined at the above mentioned temperatures for zirconium and zircaloy III.

4) No exaggerated grain growth was observed in zircaloy II for temperatures up to 1200° F.

5) Temperature and strain limitation have been set for zirconium and zircaloy III to avoid exaggerated grain growth.

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