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(M. S. Thesis)

December 1968

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December, 1968

ABSTRACT

The creep behavior of a 4w%Mo spheroidized steel from 875 to 1075°K, obeys the emperical relation:

$$\frac{\dot{\gamma}_s kT}{DGbe^{-Hc/RT}} = A\ (\tau/G)^{6.8}$$

where A is a constant independent of temperature, τ is the applied shear stress, G is the shear modulus, D is the self diffusivity of α-Fe, H_c is a constant independent of temperature and stress and is equal to 13 Kcal/mole, k is the Boltzmann's constant, R is the gas constant and T is the absolute temperature. Creep of this alloy was compared with that for α-Fe. A dislocation climb controlling mechanism is postulated.

I. INTRODUCTION

It is now recognized[1] that the high-temperature creep of most metals and some alpha solid solution alloys obey the relationship

$$\frac{\dot{\gamma}_s kT}{DGb} = A\left(\frac{\tau}{G}\right)^n \qquad (1)$$

where $\dot{\gamma}_s$ is the steady-state creep rate, kT the Boltzmann constant times the absolute temperature, D the self diffusivity, G the shear modulus of elasticity, b the Burgers vector, τ the applied shear stress; the constant A is usually about 25×10^7 and n varies from about 4.2 to 6.9 dependent on the stacking fault energy, purity and other as yet unidentified factors. Despite the greater engineering interest in the more creep resistant dispersion strengthened alloys, there have been relatively few systematic investigations[2] on the factors responsible for their behavior. Not only have the proposed theories for high-temperature creep of dispersion strengthened alloys proved to be inadequate but, more specifically, the limited experimental data that are analyzable for decisions on the mechanism that might prevail do not reveal consistent trends.

The creep of several dispersion strengthened alloys[3] appear to follow somewhat the general tenets of Eq. (1) with several significant deviations therefrom: (1) Whereas the apparent activation energies for creep of metals and some alpha solid solutions are in excellent agreement with that for self diffusion, those for dispersions are usually higher and often substantially so. For example, the activation energies for high-temperature creep and self diffusion[4] for Ni and Al are 65,000

and 34,000 cal/mole respectively, while those for creep of the oriated Ni[3] and SAP[5,6,7] are about 190,000 and 150,000 to 400,000 cal/mole respectively despite the fact that the deforming matrix in the dispersion strengthened alloys is about the same as in the metals themselves.
(2) Whereas n in metals[1] ranges from about 4.2 to 6.9, it is usually much higher for dispersion strengthened alloys; for the oriated Ni[3] it is about 40 and for SAP[7] approximately 10.

A major factor for deducing the dislocation mechanisms responsible for plastic behavior of crystalline materials is the activation energy of the process. It appears inevitable that the achievement of a steady-state creep rate must depend either directly or indirectly on the rate of climb of dislocations. In this event it is expected that diffusion must play some role in the creep process. At present, however, it is not known whether the apparent activation energies for creep of dispersion strengthened alloys are in any way associated with those for self diffusion in the matrix. Furthermore, it is difficult to derive an experiment that can reveal such possible association between the activation energy for creep of a dispersion strengthened alloy and that for self-diffusion in the matrix.

Recent investigations[8] have shown that the apparent activation energy for creep of alpha Fe shows a pronounced hump over the region of the magnetic curie transformation that is directly associated, quantitatively as well as qualitatively, with an identical hump in the apparent activation energy for self diffusion. If the activation energy for creep of a dispersion strengthened steel were not to exhibit this hump, it would reveal that self diffusion does not play a direct role in the creep mechanism. But if this hump appears in the higher apparent activation energy for creep of dispersion strengthened steel, the mechanism does involve self diffusion with modification resulting from complicated interaction of dislocations. The following investigation was initiated to resolve this important issue.

II. MATERIALS AND TECHNIQUE

An ideal steel for this investigation would be one in which the dispersed phase remains unaltered during the high-temperature creep tests. To approximate this idealization, a Mo-C steel was selected and so heat treated as to obtain a fairly stable dispersion of Mo_2C in the steel matrix. The analysis in weight percent of the steel used was as follows: Mo-4.00, C-0.19, Mn-0.50, Si-0.08, O-0.029. The as cast 2-3/8 in. diameter by 10 in. high ingot was quench cast in a Cu mold and homogenized under argon for 7 days at 1100°C. Following removal of the surface by turning, it was forged to 5/8 in. in diameter at 1100°C and swaged in four steps at about 1000°C to 0.34 in. in diameter. Between each swaging step the bars were surface cleaned.

The bars were austenitized under argon at 1200°C for two hours, quenched in ice brine and thereafter cooled in liquid nitrogen to provide fairly complete transformation of the austenite to martensite. Each bar was tempered and given a spheroidization anneal under argon at 800°C for 24 hours and then quenched in water. Samples from the various bars exhibited the same uniform grain size and dispersion of carbides. Honeycomb[9] has previously shown that in a steel of about the same composition and heat treatment the dispersed phase consists of Mo_2C particles which are quite stable. The creep testing temperatures were somewhat below the spheroidizing temperature and should not have introduced any major alteration in the microstructure. Typical examples of the microstructure after quenching and before and after creep testing are shown in Figs. 1a, b and c respectively. No changes in the microstructure during the course of creep at the highest test temperature could be detected.

Tensile creep tests could not be conducted due to the early introduction of necking. Consequently, double shear types of specimens, previously used with high success, were adopted for this investigation. Their design is shown in Fig. 2. This type of specimen exhibited uniform shear over the gage section and the same shear strain on each gage section. Duplicate tests gave almost identical results and the design and technique appeared to be very satisfactory in every respect.

All creep tests were conducted in an argon atmosphere. Furnace temperatures were held constant by a proportioning controller that was activated by two chromel-alumel thermocouples placed on the specimen adjacent to the two gage section. Specimen temperatures were held constant to better than ±1°C throughout each constant temperature test.

Loads were applied through a lever arm and the stresses were determined to an accuracy of ±0.145 psi. Shear displacements of the specimen were determined by means of a linear differential transformer from which strains accurate to 10^{-4} were calculated; gage section dimensions were measured to the nearest 0.0002 inches.

The apparent activation energies for creep were determined from the effect of small changes in temperature, 14° to 16°C, on the secondary creep rate. The fixturing and specimens had sufficiently low heat capacity to permit the temperature to equilibrate and the new creep rate to be obtained in about 3 minutes. The new creep rates were determined following the 3 minute transient period.

The effect of stress on the steady state creep rate was obtained in a few cases directly from creep curves at constant stress and temperature. Most of the data on the correlation between stress and the steady-state creep rate, however, were obtained from constant temperature tests in which the stress was changed periodically. It was observed that following a brief transient upon change in stress a new steady state creep rate appropriate to the new stress was established. The same steady-state creep rate was obtained regardless of the differences in these two approaches.

III. EXPERIMENTAL RESULTS

A. Effect of Stress on the Steady-State Creep Rate

A typical creep curve is shown in Fig. 3. It reveals initial creep strain upon loading, followed by primary (I), secondary (II) and tertiary (III) creep as are obtained for high-temperature creep of annealed metals. The fact that a brief primary stage is followed by an extensive steady-state condition of secondary creep reflects the fact that a rather stable microstructure had been obtained and that it remains substantially unaltered over the entire steady-state condition.

Typical examples of the steady-state creep rate obtained when the stress was periodically changed are illustrated in Fig. 4. A rather brief transient in the creep rate was observed upon an increase or a decrease in the stress level. As in the case of metals, this was followed by a steady-state creep rate that was independent of the previous stress history and depended only on the acting stress. The same steady-state creeprates were obtained from the constant and the periodically varied stress tests.

The effect of stress on the secondary creep rates for the series of temperatures that were investigated is shown in Fig. 5, whereas the open symbols refer to data obtained by the periodically varied stress tests and the blocked symbols refer to data obtained from constant stress tests. It is easily noted that the two sets of data agree well within the usual limits of experimental error. The effect of stress on the secondary creep rate is insensitive to the test temperature as shown in Fig. 5, and can be represented with reasonable accuracy by

$$\dot{\gamma}_s = K \{T\} \tau^{6.8} \qquad (2)$$

where K is a function of the temperature.

B. Effect of Temperature on the Secondary Creep Rate

Creep must necessarily occur as a result of a thermally activated mechanism. Consequently the major influence of temperature on the creep rate must arise from an exponential term involving minus a free energy of activation per mole over the gas constant R times the absolute temperature. Since the temperature can also enter the analysis in other less pronounced ways, it has been convenient to define an apparent activation energy for creep by

$$Q_c = \left\{ \frac{\Delta \ln \dot{\gamma}}{\Delta (- 1/RT)} \right\}_{\tau} = R \frac{\ln \dot{\gamma}_2/\dot{\gamma}_1}{\frac{1}{T_1} - \frac{1}{T_2}} \qquad (3)$$

where $\dot{\gamma}_2$ and $\dot{\gamma}_1$ are the creep rates following and preceding small changes in temperature from T_1 to T_2. Typical examples of cyclic temperature creep curves are shown in Fig. 6. Following a very short temperature transient they invariably give a limiting creep rate. Most of the data on the apparent activation energies for creep were obtained for the steady state. However, as in the case of metals, the apparent activation energy for creep of this dispersion hardened alloy was also found to be independent of the stage of creep and of the applied stress. The apparent activation energies for creep and their scatter bands are shown in Fig. 7 as a function of the remaining pertinent variable of temperature.

IV. DISCUSSION

The apparent activation energy for creep of the Mo_2C dispersion strengthened steel exhibits a hump over the range of the magnetic curie transformation that is reasonably analogous to that for the apparent activation energy for creep of α-Fe[8] and also that for self diffusion in α-Fe.

These correlations reveal that the creep of the dispersion strengthened steel under investigation here is indeed largely dependent on a diffusion-controlled mechanism. No alternate explanation for the hump in the apparent activation energy appears possible.

On the other hand, the apparent activation energy for creep of the dispersion strengthened steel is higher than that for α-Fe by about 13,000 cal/mole. In view of the observation by Borg[10] that the diffusivity of Fe in α-Fe is not materially altered by minor amounts of alloying element, it appears that the excess value of the apparent activation energy for creep of the dispersion strengthened alloy above that for α-Fe must arise from dislocation substructural features in the dispersion strengthened alloy. This concept is strengthened by the observation that the apparent activation energies for high-temperature creep of dispersion strengthened alloys are generally greater than those for self-diffusion in the matrix.

The apparent activation energy for creep of the dispersion strengthened steel revealed no consistent trend when considered as a function of stress alone. As shown in Fig. 7, it appears to depend on the temperature. This is further confirmed by the empirical validity of Eq. (2). These observations suggest that high-temperature creep of this dispersion strengthened steel is controlled by some modified dislocation-climb mechanism having a slightly higher apparent activation energy than that for self diffusion. On this basis it is reasonable to assume that, in complete analogy to Eq. (1),

$$\frac{\dot{\gamma}_s kT}{DGbe^{-(Hc/RT)}} = A\left(\frac{\tau}{G}\right)^n \qquad (4)$$

where n = 6.8 and Hc is an extra enthalpy of activation for creep.

The agreement between the dictates of Eq. (4) and the experimental data will now be investigated: The effect of the stress on the secondary creep rate, vide Fig. 5, is satisfied by Eq. (4) and the major remaining issue concerns agreement with the apparent activation energy for steady-state creep, namely

$$Q_c = \left(\frac{\partial \ln \dot{\gamma}_s}{\partial(-1/RT)}\right)_\tau = \frac{\partial \ln D}{\partial(-1/RT)} + Hc - RT - \frac{(n-1)RT^2}{G}\left(\frac{\partial G}{\partial T}\right) \qquad (5)$$

where the term

$$\frac{\partial \ln D}{d\,1/RT} = -H_D \qquad (6)$$

is the enthalpy for self diffusion. To make the comparison, Eq. (5) will be rewritten as

$$H_D + H_c = Q_c + RT + (n-1)\frac{RT^2}{G}\left(\frac{\partial G}{\partial T}\right) \qquad (7)$$

where $H_D + H_c$ is the total true activation energy for creep, H_T.

Lacking direct experimental evidence on the variation of the shear modulus of elasticity of the steel in question with temperature, this factor might be approximated in terms of the data reported by Axel Fuchs[11] and shown in Fig. 8 for an Fe-4 wt% Mo alloy. Then the last term on the right of the equality sign which always has a negative value is calculated taking (n-1) = 5.8 from the stress law. The sum of the three terms on the right of the equality sign is shown by the curve marked H_T in Fig. 9. Although the activation enthalpy for diffusion is not known for this alloy, it cannot differ much from that for self diffusion in α-Fe. Lai and Borg[10] have shown that the self-diffusivity in α-Fe is given to within ±6% by

$$\ln D = 3.115 - \frac{1.603 \times 10^{-4}}{T} - 0.163 \tanh 3\left(\frac{10^{-4}}{T} - 9.81\right) \qquad (8)$$

Introducing this value into Eq. (6) gives the curves marked H_D in Fig. 10. The difference $H_T - H_D = H_c$ is reasonably constant independent of temperature and amounts to about 13,000 cal/mole as shown in Fig. 11. Consequently the formulation given by Eq. (4) is in excellent agreement with all of the known experimental facts.

In summary, all of the experimental data are plotted in Fig. 12 in terms of the dimensionless parameters.

$$\frac{\dot{\gamma}_s kT}{DGbe^{(-Hc/RT)}}$$ and τ/G. These data might be compared with similar data for α-Fe[8] also shown in the same figure (12-b)

At $(\tau/G) = 4 \times 10^{-4}$ from Fig. 12

$$\frac{\dot{\gamma}_1 kT}{DG_1 b} \text{ for } \alpha\text{-Fe} \approx 5.47 \times 10^{-8},$$

$$\frac{\dot{\gamma}_2 kT}{DG_2 b e^{-13,000/RT}} \text{ for the Mo-steel} \approx 2.15 \times 10^{-8}$$

$$\frac{\dot{\gamma}_2 \text{ for the Mo steel}}{\dot{\gamma}_1 \text{ for } \alpha\text{-Fe}} = \frac{G_2}{G_1} \; \frac{2.15 \times 10^{-8}}{5.47 \times 10^{-8}} \; e^{-13,000/RT} \tag{9}$$

At 965.0°K (τ/G) for the Mo-steel $= 8.9 \times 10^{-4}$ and

At 963.0°K (τ/G) for α-Fe $= 2.4 \times 10^{-4}$,

the temperature T may therefore be taken approximately 964.0°K so from Fig. 8

G for the steel $= 5.32 \times 10^{11}$ dyne/cm²

G for the α-Fe $= 6.01 \times 10^{11}$ dyne/cm²

by substitution in Eq. (9)

$$\dot{\gamma}_2/\dot{\gamma}_1 \approx 3.9 \times 10^{-4};$$

therefore the Mo-spheroidized steel is more creep resistance than α-Fe, yielding a creep rate nearly four orders of magnitude lower than that for α-Fe under similar conditions. Most of this strengthening effect comes from the extra enthalpy of activation (13.Kcal/mole). Figure 12 proves clearly that Eq. (4) is applicable and that the factor A is temperature independent. In addition it gives a slope of 6.8, the value experimentally deduced.

V. CONCLUSIONS

1. The creep behavior of Fe - 4w% Mo, 0.2w%C, 0.50w%Mn spheroidized steel from 875° to 1075°K obeys the emperical relation:

$$\frac{\dot{\gamma}_s kT}{DGbe^{-Hc/RT}} = A\,(\tau/G)^{6.8}$$

where: $\dot{\gamma}_s$ is the secondary creep rate,

A a constant independent of temperature,

τ the applied shear stress,

G the shear modulus,

D the self diffusivity of α-Fe,

b the burgers vector

k Boltzmann's constant,

RT the gas constant times the absolute temperature

and H_c is the difference between the activation enthalpy for creep of the steel and that for self diffusion of α-Fe, which is temperature and stress independent.

2. The anomalous increase and then decrease in activation energy with increasing temperature over the range of magnetic transformation is in good agreement with the known decrease in the free energy of activation for diffusion of α-Fe.

3. Over the investigated temperature range, the creep behavior of the Mo-steel was found to be in agreement with climb mechanism, and the excess value of the apparent activation energy for creep above that for α-Fe might arise from dislocation substructural features in the dispersion strengthened steel.

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FIGURE CAPTIONS

Figure 1.	Microstructure of the alloy.
Figure 2.	Geometry of the test specimen.
Figure 3.	Typical creep strain vs time.
Figure 4.	Typical creep rate-extension curve under cyclic stress condition for use in the evaluation of stress dependence.
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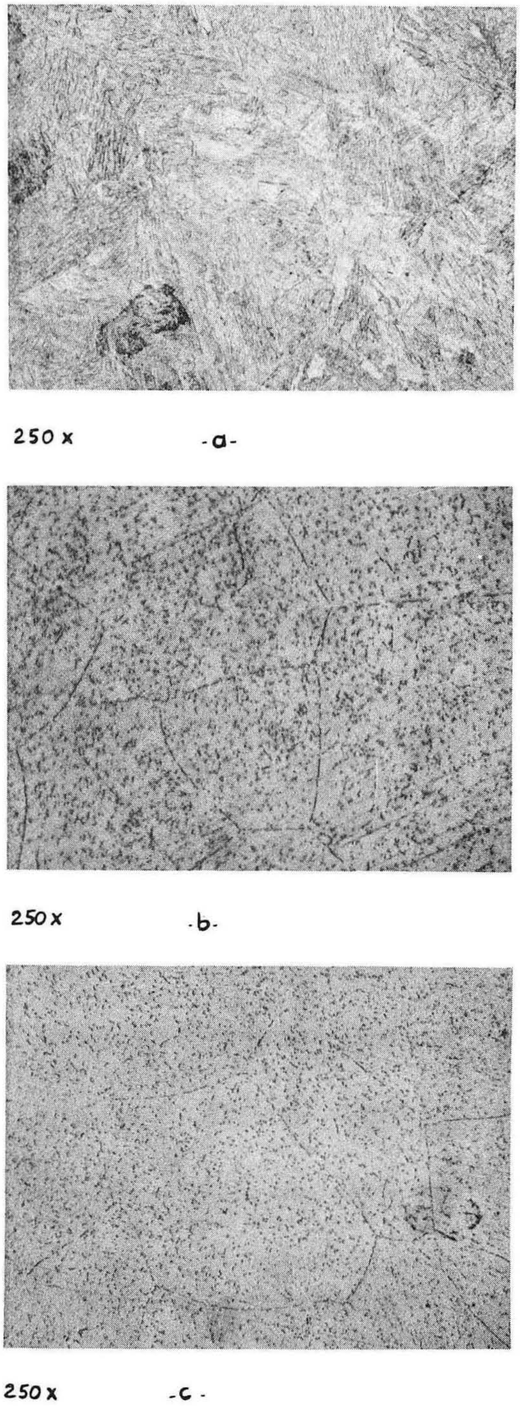
Figure 11.	Values of H_c.
Figure 12.	Effect of G,D,T and b on the secondary creep rate of the spheroidized steel and α-Fe.



a. after quenching
b. after spheroidization
c. after creep at 952°K

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Fig. 1 Microstructure of the alloy

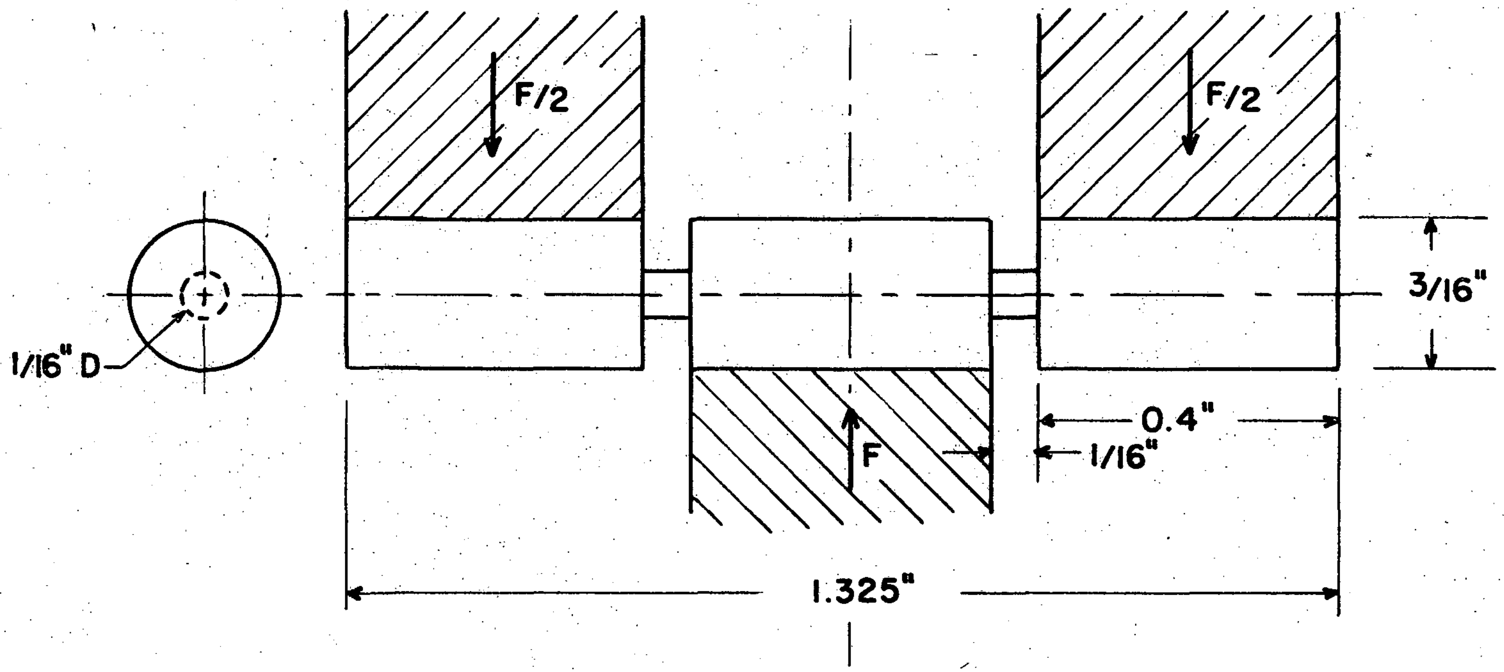

FIG. 2 Geometry of the test specimen.

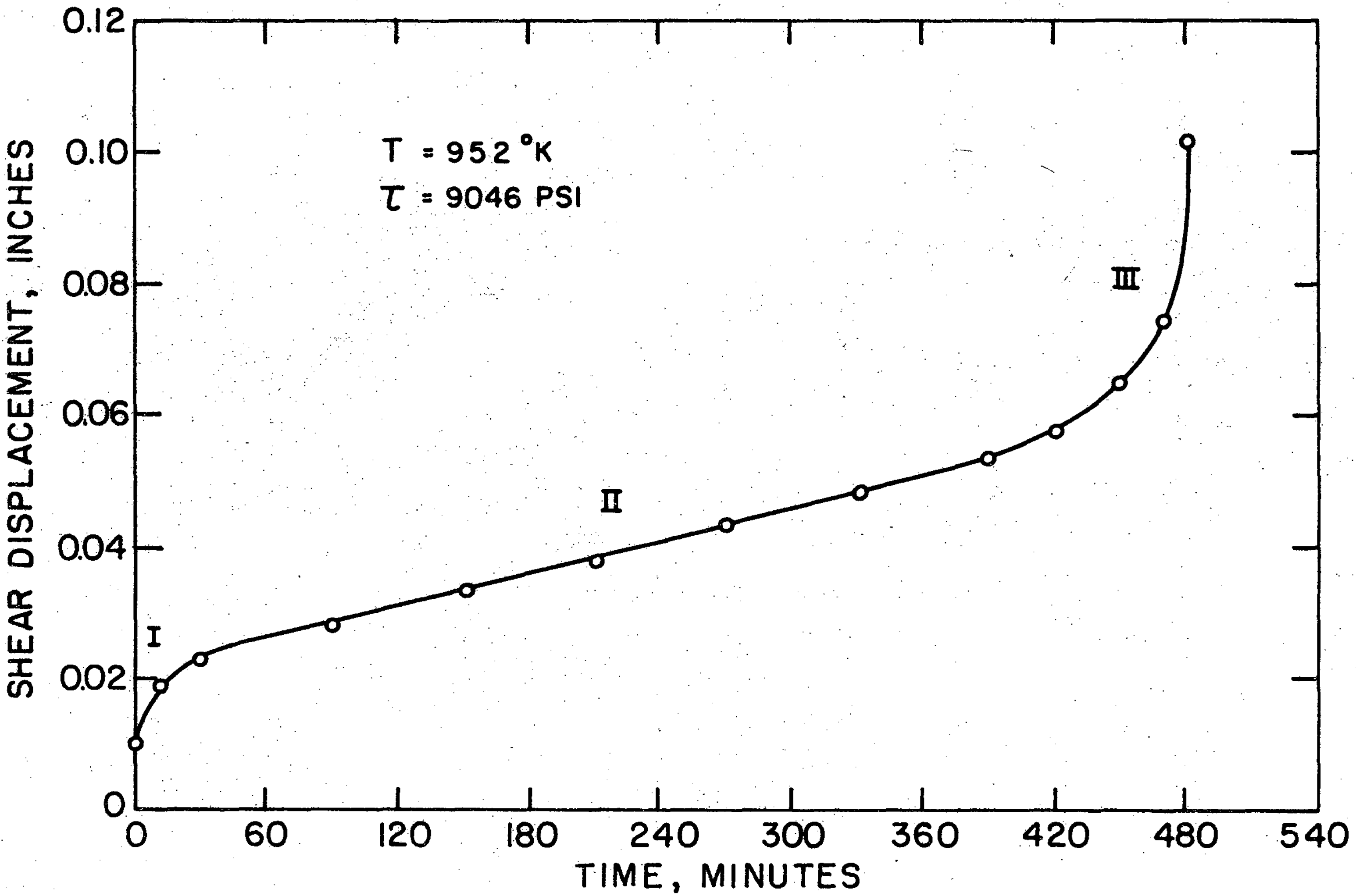

FIG. 3 Typical creep strain vs time.

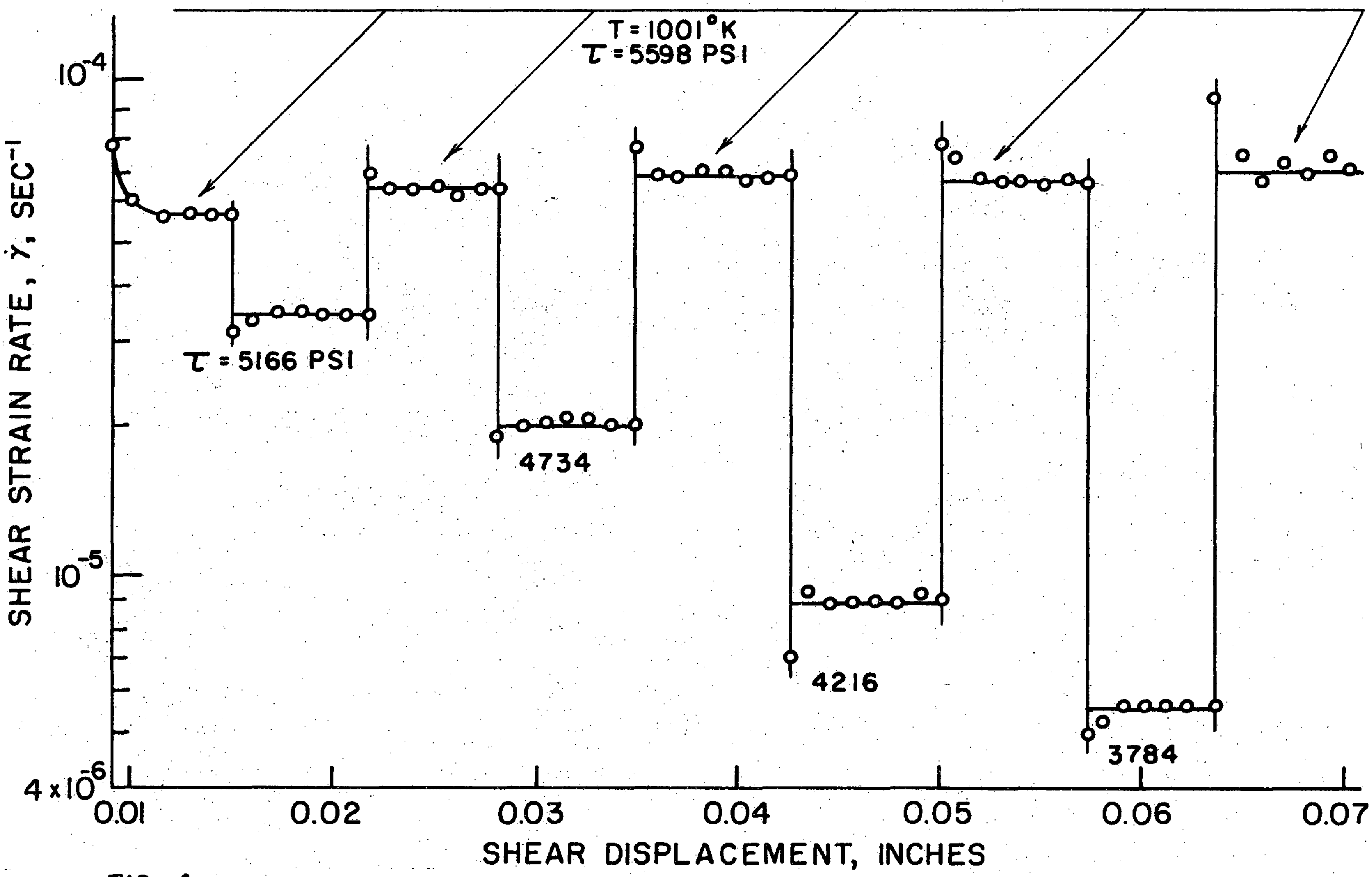

FIG. 4 Typical creep rate-extension curve under cyclic stress condition for use in the evaluation of stress dependence.

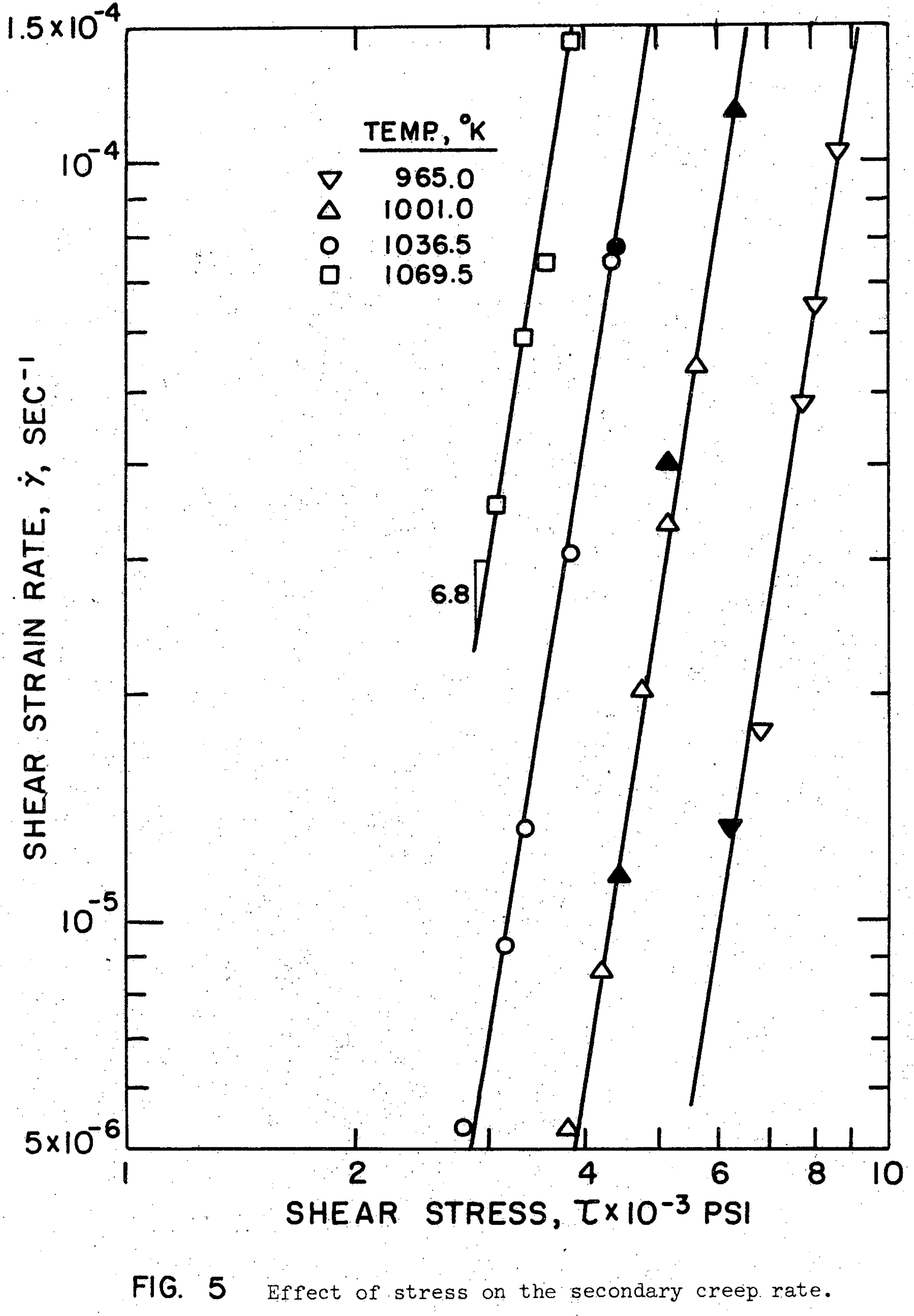

FIG. 5 Effect of stress on the secondary creep rate.

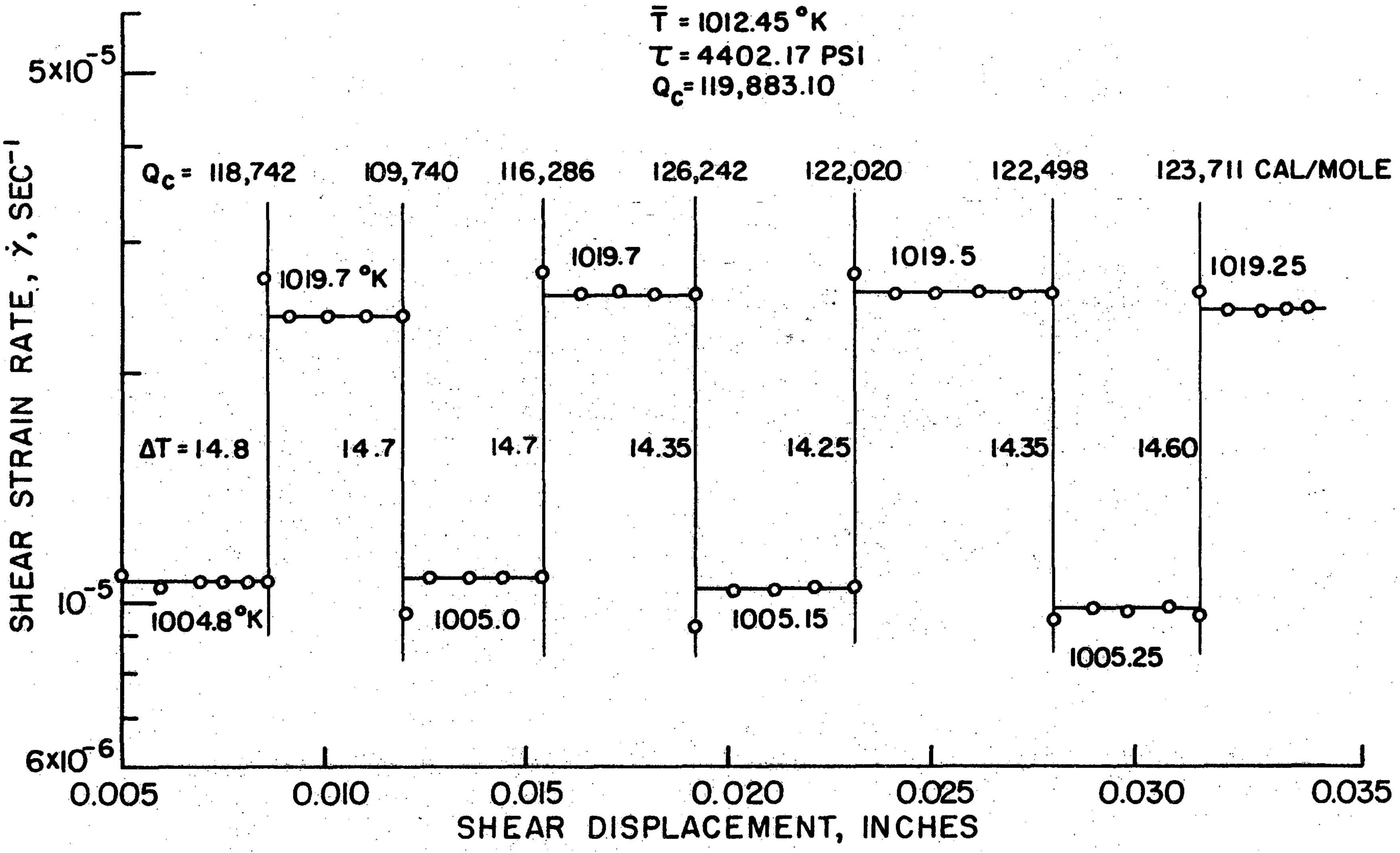

FIG. 6 Typical creep-rate-extension curve under cyclic temperature condition for use in the evaluation of Q_c.

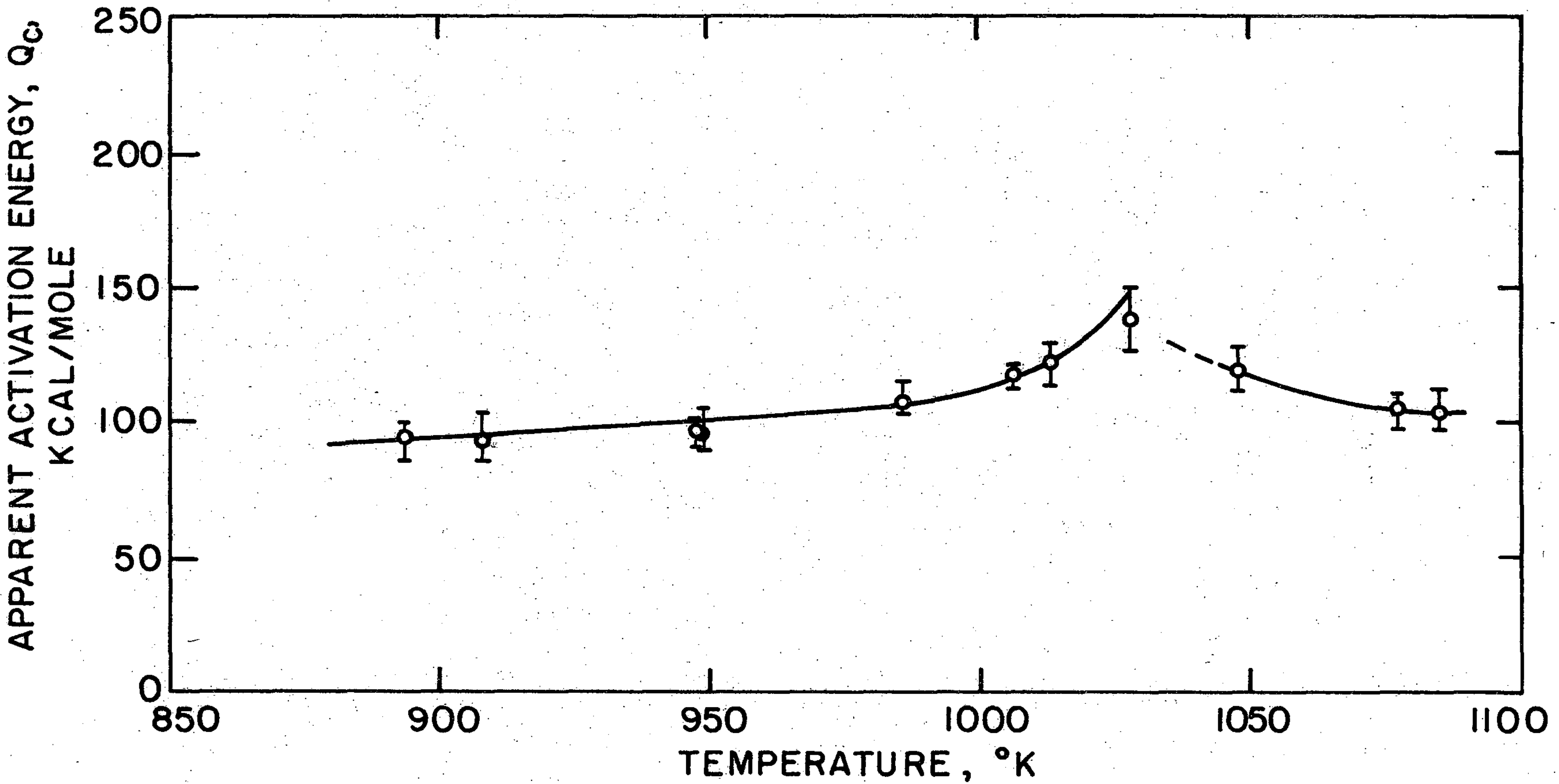

FIG. 7 Apparent activation energies for creep as a function of absolute temperature.

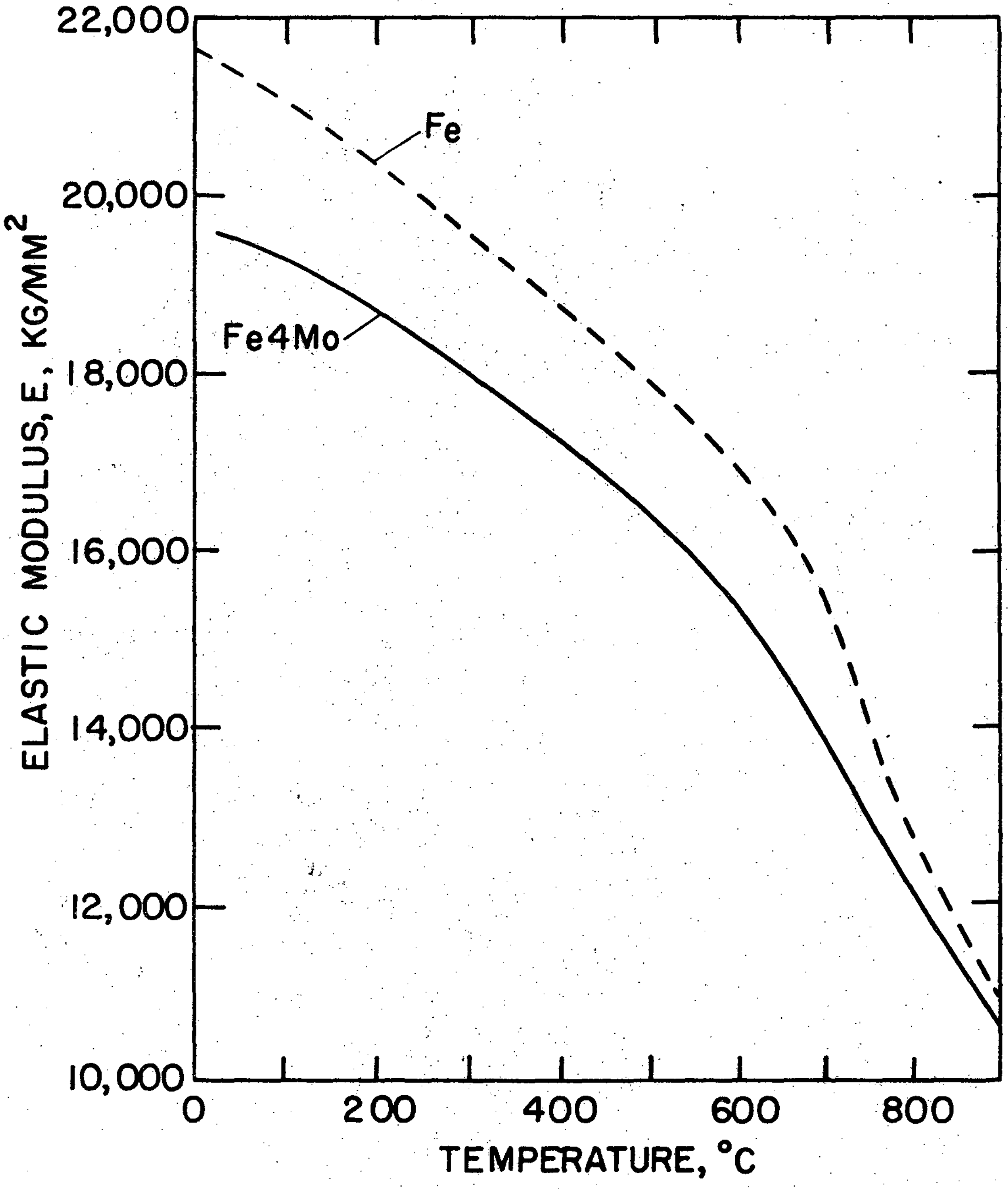

FIG. 8 Effect of temperature on the elastic modulus.

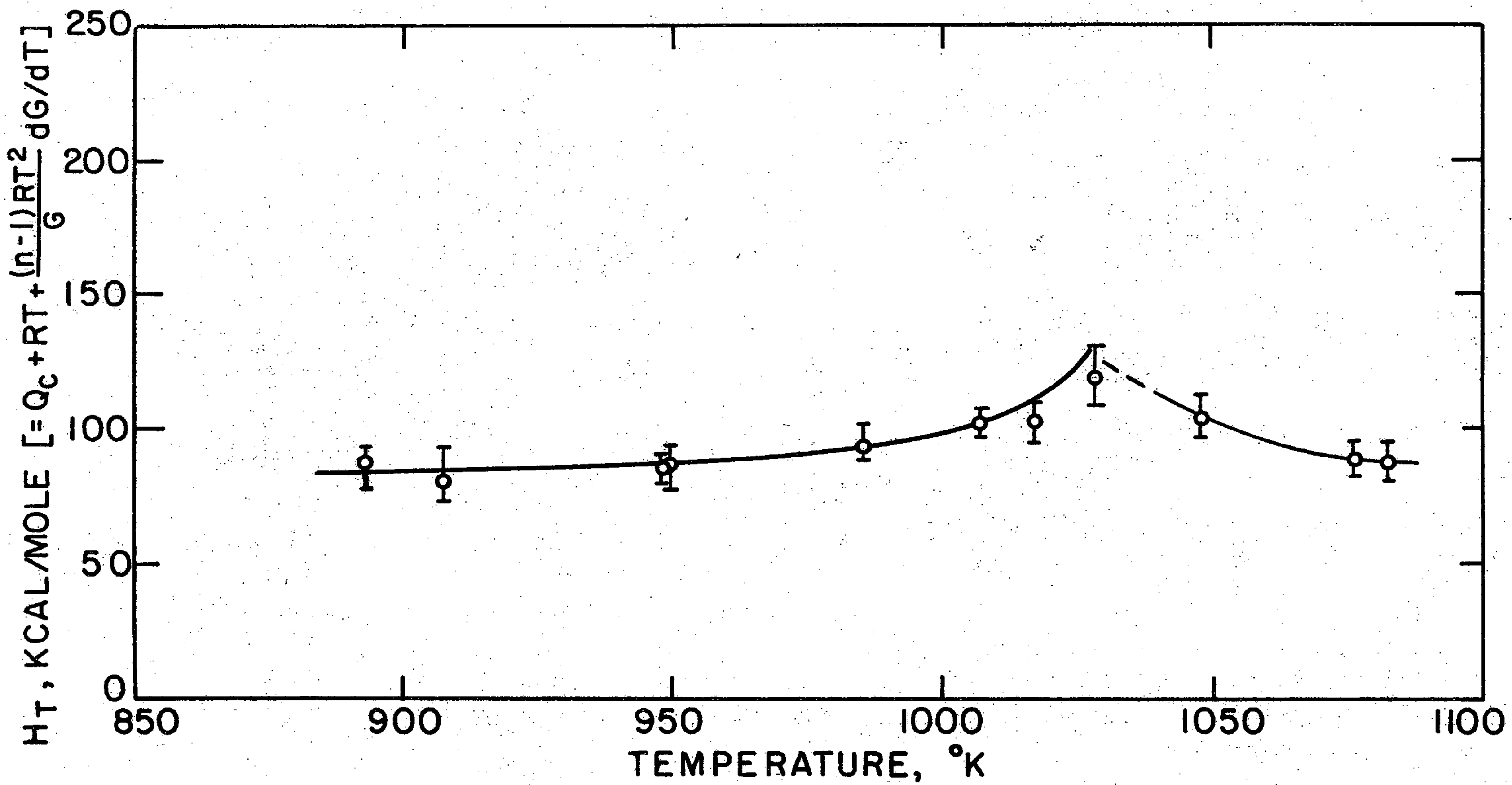

FIG. 9 Apparent activation energies corrected for changes of shear modulus as a function of temperature.

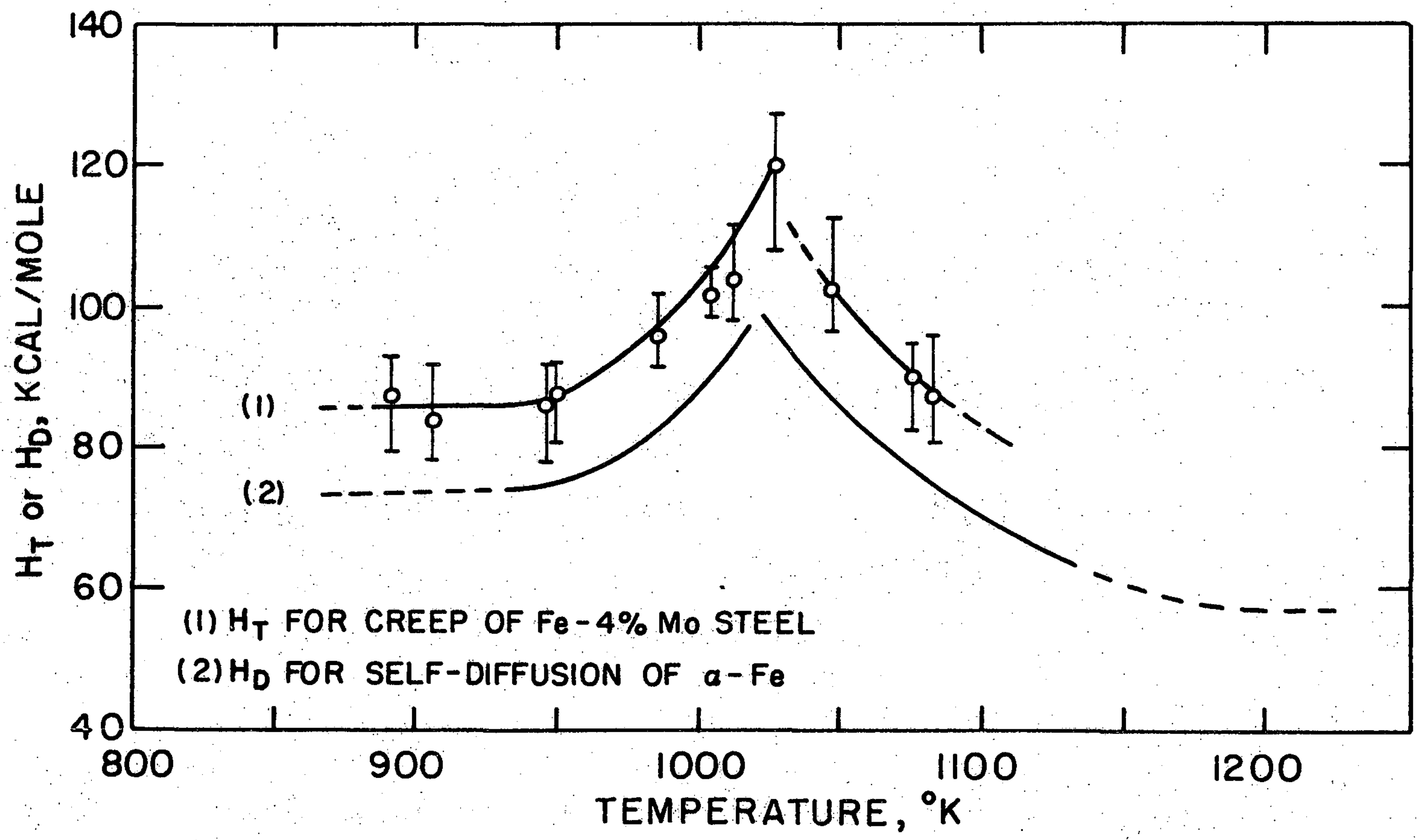

FIG. 10 Temperature dependence of activation enthalpy of creep for the spheroidized steel, and that for self diffusion of α-Fe.

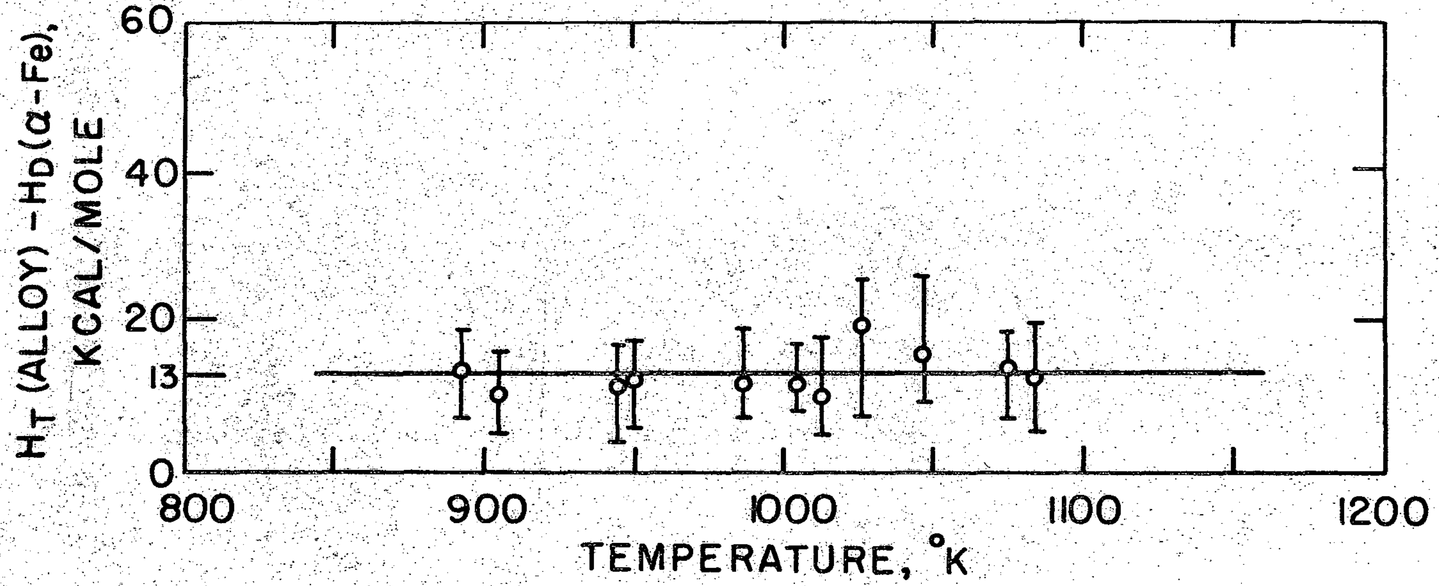

FIG. 11 Values of H_c.

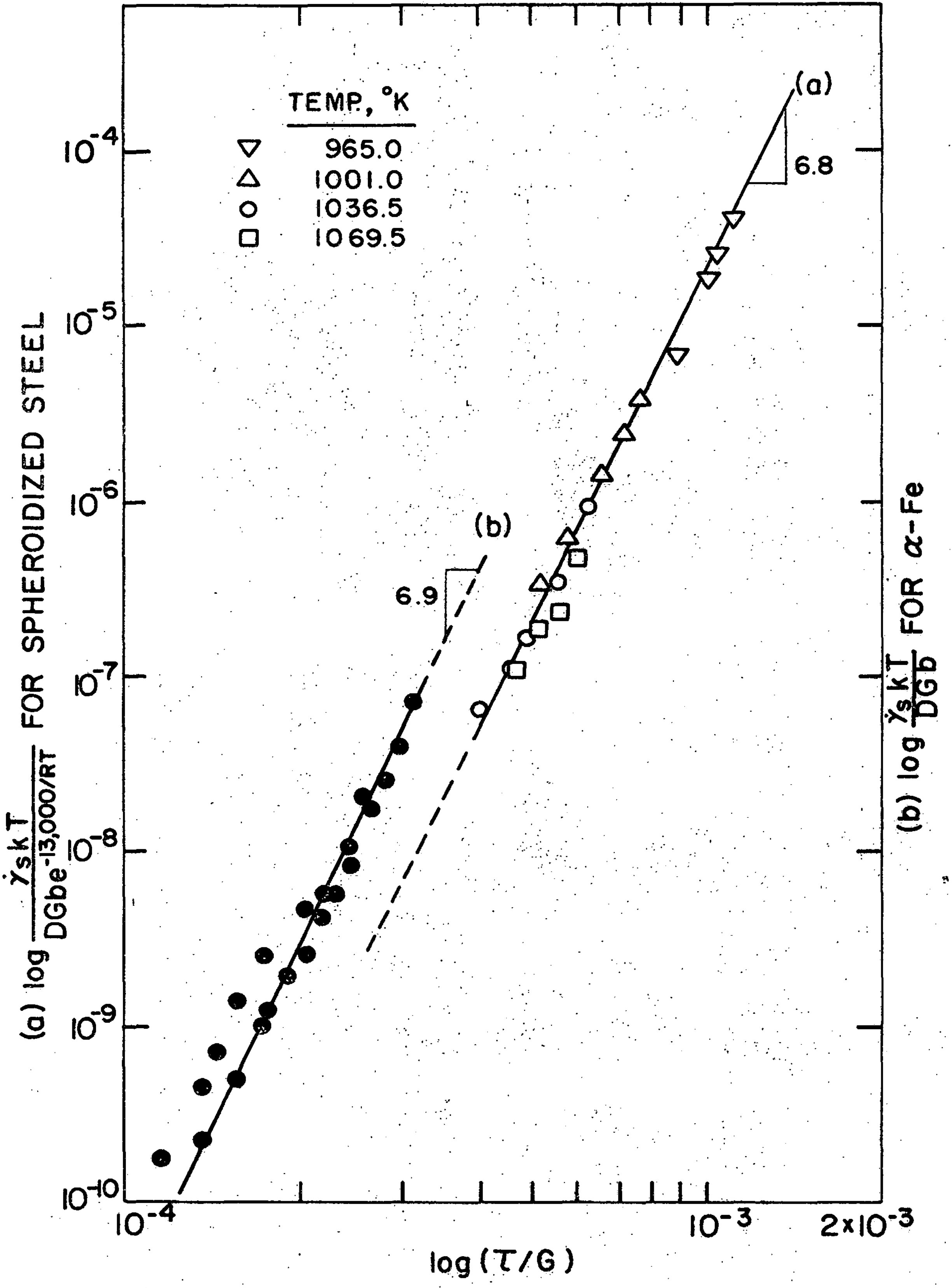

FIG. 12 Effect of G,D,T and b on the secondary creep rate of the spheroidized steel and α-Fe.

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