

Stress Versus Temperature Dependent Activation Energies in Creep

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Abstract

The activation energy for creep at low stresses and elevated temperatures is lattice diffusion, where the rate controlling mechanism for deformation is dislocation climb. At higher stresses and intermediate temperatures, the rate controlling mechanism changes from that of dislocation climb to one of obstacle-controlled dislocation glide. Along with this change, there occurs a change in the activation energy. It is shown that a temperature-dependent Gibbs free energy does a good job of correlating steady-state creep data, while a stress-dependent Gibbs free energy does a less desirable job of correlating the same data. Applications are made to copper and a LiF-22mol.%CaF₂ hypereutectic salt.

1 Introduction

Choosing the free energy for activation (or Gibbs free energy), ΔG , as the thermodynamic state function implies that stress, σ , and absolute temperature, T , are the independent state variables, *i.e.* $\Delta G = \Delta G(\sigma, T)$. This state function is related to the activation enthalpy, ΔH , through the isothermal relation-

ship

$$\Delta G = \Delta H - T \Delta S$$

where the activation entropy, ΔS , can be expressed as

$$\Delta S = - \left. \frac{\partial \Delta G}{\partial T} \right|_{\sigma}$$

Combining these two relationships results in the expression [1]

$$Q \equiv \Delta H = \left. \frac{\partial (\Delta G/T)}{\partial (1/T)} \right|_{\sigma} \quad (1)$$

where Q is the activation energy. This is a useful relationship because it provides a means whereby functional forms for the free energy can be determined from experimental data.

The probability, P , for the occurrence of an equilibrium fluctuation in energy greater than ΔG at a given absolute temperature is provided by Boltzmann's expression

$$P = \exp \left(\frac{-\Delta G}{RT} \right)$$

where R is the universal gas constant, *i.e.* $R = 8.314 \text{ J/mol.K}$. The creep rate

$$\dot{\epsilon} = \dot{\epsilon}_0 P = \dot{\epsilon}_0 \exp \left(\frac{-\Delta G}{RT} \right) \quad (2)$$

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is taken to be that fraction of the maximum attainable creep rate, $\dot{\epsilon}_0$, which is allocated by this probability of fluctuation [1].

The objective of this paper is to determine, at least for polycrystalline Cu and LiF-22%CaF₂, what functional forms for the Gibbs free energy best correlate experimental creep data, especially in the domain of power-law breakdown.

2 Thermal Activation

Three formulations for activation energy are considered, from which three different equations for free energy are derived. All three are utilized in the literature to correlate creep data. The ability of Eqn. 2 to correlate experimental creep data using these three free energies is further investigated in this paper.

2.1 $Q = \text{Constant}$

Considering the activation energy to be constant valued, *i.e.*

$$Q = Q_l$$

where Q_l is the activation energy for lattice or self diffusion, then from Eqn. 1 one quickly obtains

$$\Delta G = Q_l \quad (3)$$

as the expression for the free energy.

A constant-valued activation energy for creep, Q_c , roughly equivalent to that of lattice diffusion, *i.e.* $Q_c \approx Q_l$, is universally observed in the high-temperature creep of crystalline solids, where dislocation climb is the rate controlling mechanism [2]. This is a prominent mechanism when temperatures exceed about $0.5T_m$, where T_m is the absolute melting temperature.

2.2 $Q = Q(\sigma)$

At higher stresses and lower temperatures, one may consider the activation energy to be a function of stress; in particular, let this stress dependence be linear such that

$$Q = \Delta F \left(1 - \frac{\sigma}{\hat{\tau}}\right)$$

where ΔF is the enthalpy of activation in the absence of stress, and $\hat{\tau}$ is the maximum attainable stress state. From Eqn. 1, one readily obtains

$$\Delta G = \Delta F \left(1 - \frac{\sigma}{\hat{\tau}}\right) \quad (4)$$

as the expression for the free energy.

A free energy of this form is characteristic of obstacle-controlled dislocation glide, where a uniform distribution of 'rectangular' obstacles is assumed [1]. Figure 1 demonstrates the viability of such an activation energy. Here the activation energy observed during creep is normalized by the activation energy for lattice diffusion. Each experimental value for Q represents the slope of a line in a plot of $\ln(\dot{\epsilon})$ vs. T^{-1} for a set of creep tests conducted at the same stress level but at various temperatures. The solid lines in Fig. 1 represent this stress-dependent activation energy using the constants given in Tables 1 and 2 for Cu and LiF-22%CaF₂. Even though there is scatter amongst the data, this relationship does a reasonably good job of correlating these data.

2.3 $Q = Q(T)$

Finally, let the activation energy be a function of temperature; in particular, consider a linear temperature dependence such that

$$Q = \frac{T}{T_i} Q_c \quad \text{where } 0 < T \leq T_i$$

and T_i is a transition temperature above which the activation energy is taken to be Q_c . When

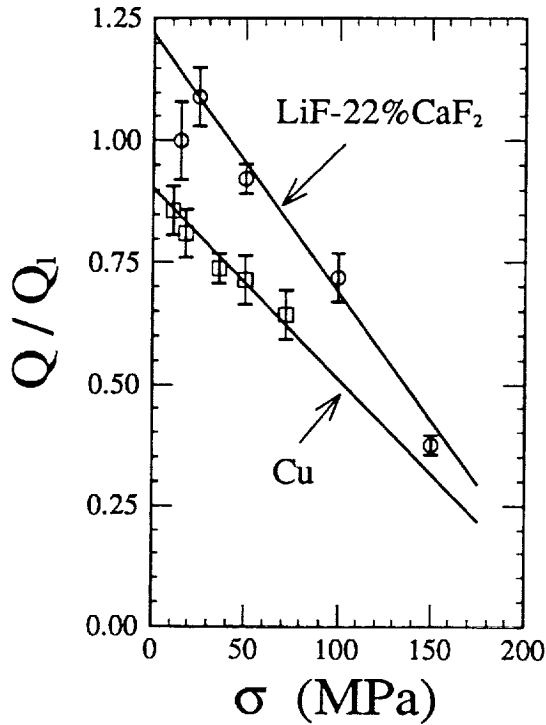


Figure 1: Stress dependence of the activation energy for creep. Data for LiF-22%CaF₂ are from RAJ & WHITTENBERGER [3] (○). Data for copper are from RAJ & LANGDON [4] (□).

Constant	Units	Value
A	s^{-1}	1×10^9
A_c	—	1×10^7
A_g	s^{-1}	5×10^8
b	m	2.56×10^{-10} [5]
C	MPa	55
D_0	m^2/s	6.1×10^{-5} [4]
ΔF	J/mol.	190,000
n	—	5
Q_c	J/mol.	200,000
Q_t	J/mol.	210,000 [4]
T_m	K	1356 [5]
T_i	K	610
μ	MPa	$47,500 - 17 T$ [4]
$\hat{\tau}$	MPa	230

Table 1: Constants for copper.

Constant	Units	Value
A	s^{-1}	5×10^{15}
A_c	—	1×10^{14}
A_g	s^{-1}	1×10^{17}
b	m	$3.86 \times 10^{-10} \dagger$
C	MPa	27
D_0	m^2/s	$1.3 \times 10^{-2} \dagger$
ΔF	J/mol.	390,000
n	—	5
Q_c	J/mol.	320,000 [3]
Q_t	J/mol.	360,000 †
T_m	K	1042 [3]
T_i	K	850
μ	MPa	$52,000 - 29 T$ [6]
$\hat{\tau}$	MPa	230

Table 2: Constants for LiF-22%CaF₂. †) Value for CaF₂ [3]. ‡) Diffusion of Ca⁺² in CaF₂ [7].

this relationship is substituted into Eqn. 1 and integrated, one obtains [8]

$$\Delta G = \frac{Q_c T}{T_i} \left[\ln \left(\frac{T_i}{T} \right) + 1 \right] \quad ; \quad 0 < T \leq T_i \quad (5)$$

as the expression for the free energy. The constant of integration in this result was determined from the boundary condition: $Q = Q_c$ at $T = T_i$.

There appears to be no theoretical motivation for a linear, temperature-dependent, activation energy; rather, its motivation is phenomenological [8]. The capability of such an expression to correlate experimental data is demonstrated in Fig. 2 for copper. Similar data for the LiF-22%CaF₂ hypereutectic salt are not available. As in Fig. 1, the activation energy observed during creep is normalized by the activation energy for lattice diffusion. However, here each experimental value for Q was obtained from a steady-state creep test where the stress was held constant and a step change in temperature occurred.

The solid curve in Fig. 2 represents $Q = TQ_c/T_i$ for $T \leq T_i$, and $Q = Q_c$ for $T \geq T_i$, using the constants given in Table 1. This curve does a reasonable job of correlating the data over the entire temperature range, except in the neighborhood of $\sim 0.6 T_m$ where there is a dramatic reduction in Q . The investigators who performed these experiments attribute this reduction to the presence of an additional diffusion mechanism, *i.e.* diffusion along dislocation pipes [11, 12]. However, other researchers do not find experimental evidence to support this conclusion [4, 13, 14, 15, 16]. It has also been suggested that this intermediate activation energy is associated with the mechanism of cross slip [13, 14, 15, 16]. Consequently, pipe or core diffusion is not incorporated into our formulation, and a satisfactory explanation of these data remains to be given.

The activation energy *vs.* temperature re-

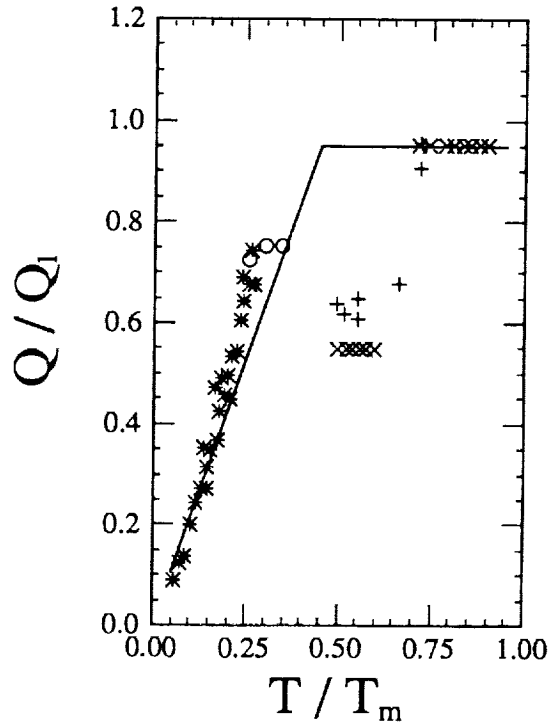


Figure 2: Temperature dependence of the activation energy for creep of copper. Data are from TIETZ & DORN [9] (o), LANDON *et al.* [10] (*), FELTHAM & MEAKIN [11] (+) and BARRETT & SHERBY [12] (x).

lation presented in Fig. 2 is not unique, but is known to depend upon the average of the strain rates used to obtain the activation energies [2]. A strain-rate sensitive transition temperature is not considered, as this seems to be an unnecessary complication in applications.

3 Models for Creep

Two different methods for modelling creep are presented. The first is a theory based on dislocation kinetics. The second is a phenomenological approach to creep. The capability of each method in correlating creep data is explored. These two approaches use combinations of the three activation energies just discussed to describe thermal activation.

3.1 Dislocation Theory – Based Model

At the higher temperatures and lower stresses, the well-established and prevailing mechanism for creep is diffusion-assisted dislocation climb [5], which evolves according to the relation

$$\dot{\epsilon}_c = A_c \frac{D\mu b}{kT} \left(\frac{\sigma}{\mu}\right)^n \quad (6)$$

where

$$D = D_0 \exp\left(\frac{-Q_d}{RT}\right)$$

is the lattice diffusion coefficient with D_0 defining the frequency factor. This diffusion coefficient uses Eqn. 3 as its expression for the free energy. Here μ is the elastic shear modulus, A_c is the creep coefficient for climb, b is the magnitude of the Burgers vector, k is the Boltzmann constant (*i.e.* $k = 1.381 \times 10^{-23}$ J/K), and n is the power-law creep exponent. The quantities σ/μ and $kT/\mu b^3$ are normalized variables for stress and temperature.

At the intermediate temperatures and higher stresses, obstacle-controlled dislocation glide is the prominent mechanism controlling creep [1, 5], which evolves according to the relation

$$\dot{\epsilon}_g = A_g \left(\frac{\sigma}{\mu}\right)^2 \exp\left[\frac{-\Delta F}{RT} \left(1 - \frac{\sigma}{\tau}\right)\right] \quad (7)$$

where A_g is the creep coefficient for glide. The exponential in this expression is the probability function for the occurrence of an equilibrium fluctuation associated with the stress-dependent free energy of Eqn. 4. The pre-exponential term, $(\sigma/\mu)^2$, arises from the variation of mobile dislocation density with stress. Except at low stress levels, the exponential stress dependence dominates the flow behavior of dislocation glide.

Following the simplified approach of NIX & ILSCHNER [17], the creep rate is taken to be given by the sum

$$\dot{\epsilon} = \dot{\epsilon}_c + \dot{\epsilon}_g \quad (8)$$

which is analogous to the classical decomposition of strain-rate into creep, *i.e.* $\dot{\epsilon}_c$, and plasticity, *i.e.* $\dot{\epsilon}_g$, contributions. However as NIX *et al.* [17, 18] point out, this simple relation is not a very accurate representation for creep; a better approach is to consider a cellular model composed of hard and soft regions of high and low dislocation densities, respectively. We have begun the study of such a model, but our results are preliminary to date and are not ready to be reported on.

The ability of Eqns. 6 and 7, *i.e.* Eqn. 8, to correlate experimental creep data for Cu and LiF-22%CaF₂ is illustrated in Figs. 3 and 4. From the vast wealth of copper data that is present in the literature, data were selected for four evenly spaced temperatures where reported strain-rates can be found that span nine to twelve decades. Contrary to copper, only one data source is available for the

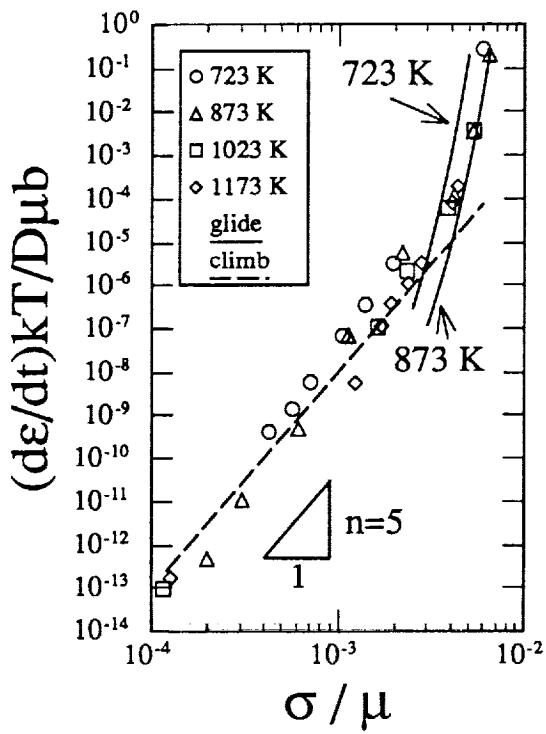


Figure 3: Theoretical creep response of copper. Data are from BARRETT & SHERBY [12], ALDER & PHILLIPS [19], PAHUTOVÁ *et al.* [20] and SAMANTA [21].

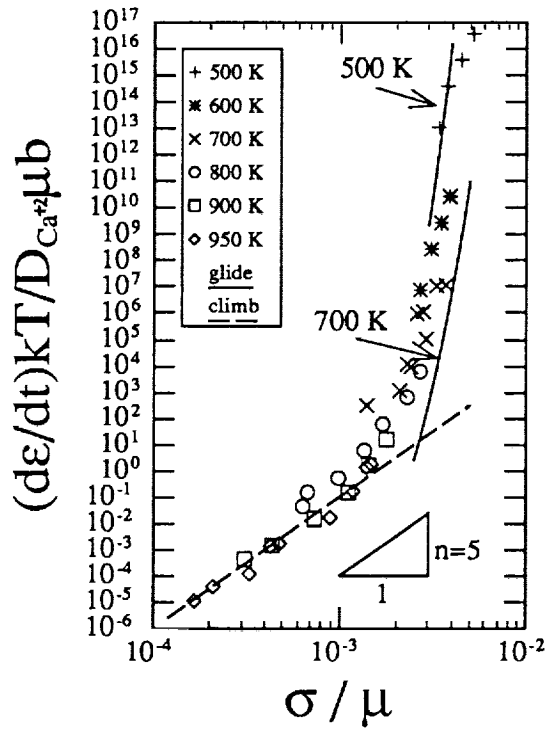


Figure 4: Theoretical creep response of LiF-22%CaF₂ hypereutectic salt. Data are from RAJ & WHITTENBERGER [3].

LiF-22%CaF₂ salt. The diffusion coefficient used in Fig. 4 is for the diffusion of Ca⁺² in CaF₂, i.e. D_{Ca⁺²}, as this appears to be the diffusion process which governs the rate of dislocation climb in LiF-22%CaF₂ [3].

Values for the constants associated with Eqns. 6 and 7, as represented in Figs. 3 and 4, are given in Tables 1 and 2. The exponential creep or glide response is temperature dependent in these figures. This is because the creep rate is normalized for dislocation climb (not dislocation glide) in these figures. This is true for both the experimental data and the correlations. The ability of Eqn. 7 to correlate these data in the exponential creep domain may be considered to be satisfactory, but it is certainly not exceptional, especially for the salt. In particular, Eqn. 7 does not predict the correct slope for the data given in Fig. 4. As we shall now see, a phenomenological creep model does a better job of correlating these same data.

3.2 Phenomenological Model

The phenomenological model for creep combines GAROFALO'S [22] expression for stress dependence with MILLER'S [8] expression for temperature dependence. Here Eqn. 2 is given by¹

$$\dot{\epsilon} = A \theta \sinh^n \left(\frac{\sigma}{C} \right) \quad (9)$$

¹This creep model is the basis upon which at least two different viscoplastic models have been developed. One is the model of MILLER [8]; the other is the model of FREED & WALKER, which is published in these conference proceedings.

where A is the creep coefficient, C is the power-law breakdown stress, and

$$\theta = \begin{cases} \exp \left(\frac{-Q_c}{RT} \right) & T_m > T \geq T_i \\ \exp \left\{ \frac{-Q_c}{RT_i} \left[\ln \left(\frac{T_i}{T} \right) + 1 \right] \right\} & T_i \geq T > 0 \end{cases}$$

accounts for the thermal diffusivity. This formulation uses Eqn. 3 at the higher temperatures and Eqn. 5 at the lower temperatures as expressions for the free energy. At stresses less than power-law breakdown, Eqn. 9 reduces to a power-law expression like Eqn. 6; whereas, for stresses greater than power-law breakdown, Eqn. 9 becomes an exponential expression similar to Eqn. 7.

The correlative capability of this model is demonstrated in Figs. 5 and 6 using the constants given in Tables 1 and 2. The capability of $\dot{\epsilon}/\theta$ vs. σ (found in Figs. 5 and 6) to collapse the experimental data onto a master curve with less scatter than one obtains with $\dot{\epsilon}kT/D\mu b$ vs. σ/μ (found in Figs. 3 and 4) distinguishes the two approaches. This is particularly true in the domain of exponential creep, and especially true for the LiF-22%CaF₂ hypereutectic salt. By not normalizing the stress with the shear modulus, and by using θ instead of $D\mu b/kT$, data distributions with less scatter are observed over the entire range of stress (not just the range of power-law behavior).

We know of no physical explanation for why the temperature-dependent free energy expression of Eqn. 5 correlates experimental creep data in the exponential domain better than the stress-dependent free energy expression of Eqn. 4, but that seems to be the case.

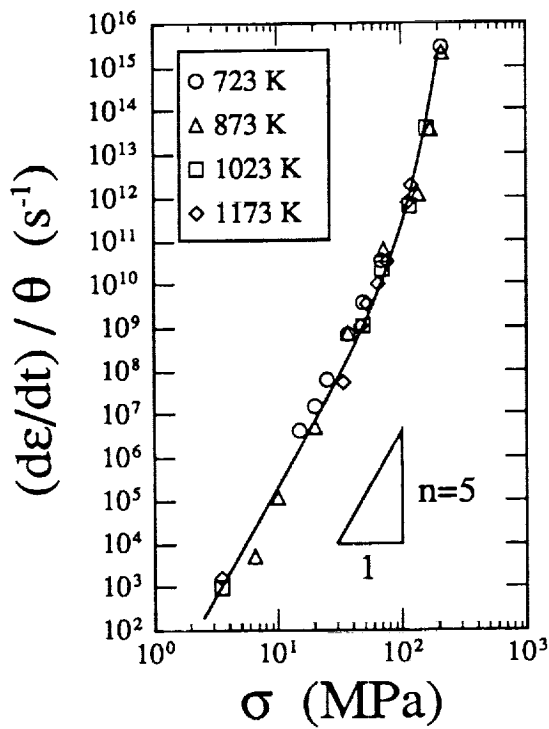


Figure 5: Phenomenological creep response of copper. Data are from BARRETT & SHERBY [12], ALDER & PHILLIPS [19], PAHUTOVÁ *et al.* [20] and SAMANTA [21].

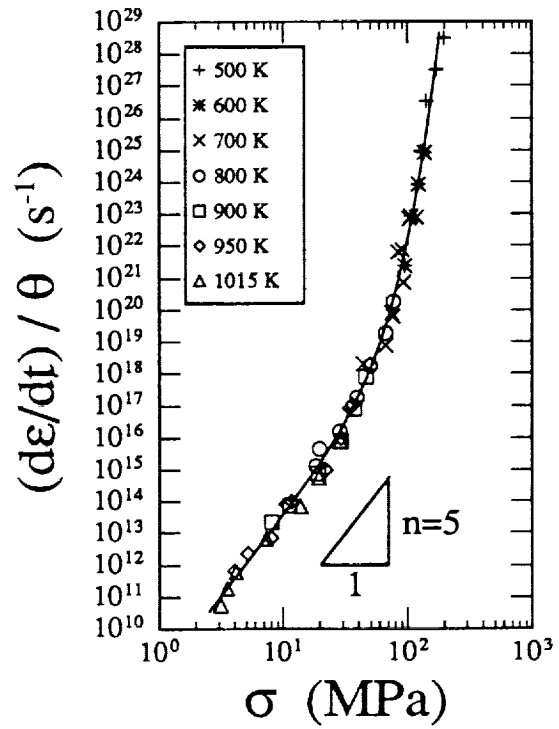


Figure 6: Phenomenological creep response of LiF-22%CaF₂ hypereutectic salt. Data are from RAJ & WHITTENBERGER [3].

4 Summary

The capability of both stress and temperature dependent Gibbs free energies in correlating exponential creep behavior has been investigated. For polycrystalline copper and a LiF-22%CaF₂ hypereutectic salt, the phenomenological, temperature-dependent, free energy derived by MILLER [8] seems to do better than the theoretical, stress-dependent, free energy associated with obstacle-controlled dislocation glide [1] in correlating experimental data. The ability of a cellular model (such as that proposed by NIX *et al.* [17, 18]) to correlate data of this type is being investigated.

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