# On the correlation between Fe concentration and the activation energy for superplastic deformation in Zn-22 pct Al

J.A. Montemayor-Aldrete[1], J.D. Muñoz-Andrade[2*] and A. Mendoza-Allende[1]
[1]*Instituto de Física, Universidad Nacional Autónoma de México*
*Apartado Postal 20-364, 01000 México, D.F., México.*

[2]*Departamento de Materiales, DCBI Universidad Autónoma Metropolitana*
*Unidad Azcapotzalco, Ave. San Pablo 180, Col. Reynosa-Tamaulipas,*
*02200 México, D.F.*

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For the first time, an expression for the apparent activation energy for superplastic deformation in Zn-22 pct Al doped with Fe impurities, which exhibits in an explicit fashion the Fe-concentration has been obtained. Such expression allows to describe all the experimental data previously reported. The range of Fe-concentration for which the Mohamed's model remains valid is established.

*Keywords:* Activation energy; superplasticity; threshold stress; segregation

Se presenta una expresión para la energía de activación aparente para la deformación superplástica en Zn-22 pct Al con impurezas de Fe, en la cual por primera vez aparece de manera explícita la concentración de Fe. Esta expresión permite describir todos los datos experimentales previamente reportados. Asimismo, se delimita el intervalo de concentraciones en que sigue siendo posible aplicar el modelo de Mohamed.

*Descriptores:* Energía de activación; superplasticidad; esfuerzo umbral; segregación.

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## 1. Introduction

From long time ago [1-21], considerable attention has been devoted to the Zn-22 pct Al eutectoid superplastic alloy because this material has numerous potential applications, it is readily available and it is known to exhibit very high elongations to failure under optimum conditions [3]. It is well documented [22,23], that for structural superplasticity in metallic alloys a stable and equiaxied grain size, d, of less than about 10$\mu$ m is required. The grain size of materials remains without change on size or morphology during superplastic deformation [24]. For this phenomenon, the experimental data on Zn-22 pct Al eutectoid alloy [4,5] revealed the presence of a sigmoidal curve in a double logarithmic plot between the applied true stress, $\sigma$, and the steady state strain rate, $\dot{\in}$, at constant temperature. Such a sigmoidal relationship have three regions: region I (low stress region), region II (Intermediate-stress region or superplastic region), and region III (high-stress region).

Recent and systematic investigations performed by Mohamed and coworkers [12,13, 15-21] on the superplastic flow in Zn-22 pct Al doped with Fe impurities have shed new light into the origin of region I. According to Mohamed [12], region I behavior probably arises from the presence of a threshold stress, $\tau_o$, whose origin is related to impurity segregation at grain boundaries whose temperature dependence is given by the following empirical equation

$$\tau_o/G = \beta_o \exp(Q_o/RT), \tag{1}$$

where $G$ is the shear modulus, $\beta_o$ is a constant, $Q_o$ is an activation energy, $T$ is the absolute temperature, and $R$ is the gas constant.

By using Eq. (1) together with the definition of the activation energy for deformation, Yang and Mohamed [16] obtain the following phenomenological expression for the apparent creep activation energy:

$$Q_a = Q - \frac{nRT^2}{G}\,\frac{\partial G}{\partial T}\left[1 + \frac{1}{(\tau/\tau_o) - 1}\right] + \frac{nQ_o}{(\tau/\tau_o) - 1}, \tag{2}$$

where $Q$ is the true activation energy for the superplastic deformation process, $n$ is the stress exponent, $\tau$ is the applied shear stress and $\tau_o$ is the threshold shear stress at grain boundaries.

On the following paragraphs a brief discussion due to Mohamed *et al.* [16] about the range of validation of Eqs. (1) and (2) to describe the superplastic behavior of the Zn-22 pct Al eutectoid alloy doped with Fe impurities will be made.

According to Mohamed *et al.* [16], the apparent activation energy for creep in Zn-22 pct Al for different Fe impurities concentrations as a function of the applied shear stress $\tau$, appears in their Fig. 4, (see the same data in our Fig. 1). Also, in Fig. 2, a plot of the logarithm of $\tau_o/G$ as a function of $1/T$ for different Fe impurities concentrations in the Zn-22 pct Al alloy (as experimentally obtained by Mohamed *et al.* [16], like their Fig. 5 in Ref. 16), is presented.

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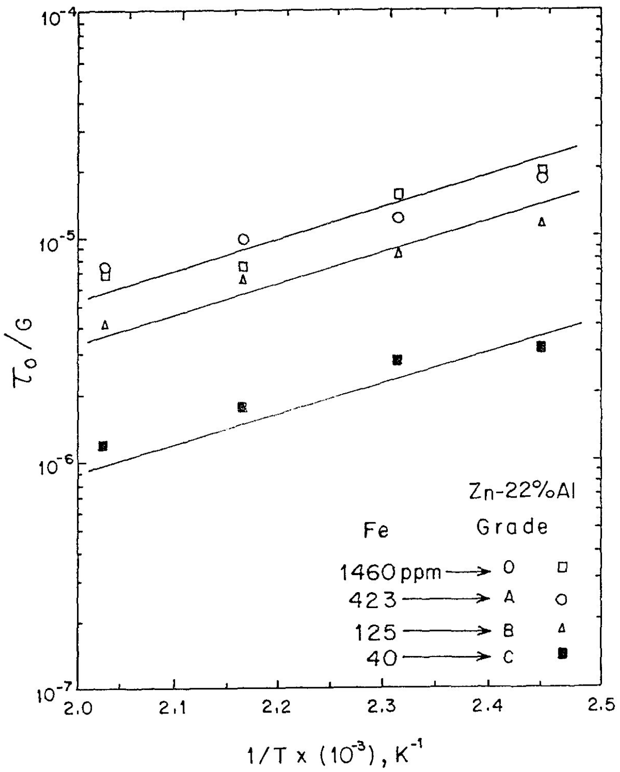

FIGURE 1 A plot of the logarithm of $\tau_o/G$ as a function of $1/T$ for grades 0,A,B, and C of Zn-22 pct Al having a grain size of 2.5$\mu$m and containing 1460, 423, 125 and 40 ppm of Fe, respectively (Mohamed *et al.* [16], their Fig. 4).

Also, Mohamed *et al.* considers [16] that: “For superplastic flow in Zn-22 pct Al at intermediate stresses, where region II (the superplastic region) is observed, $Q = Q_{gb}$ and $n = 2.5$ Since the values of $\tau_o$ for both grade 0 (1460 ppm Fe) and grade A (423 ppm Fe) are indistinguishable (Fig. 4), it is expected on the basis of Eq. (2) that $Q_a$ for both grades would be the same. However, according to Fig. 5, $Q_a$ for the former grade is higher than that for the latter grade over the entire stress range. It is possible that the difference in the values of $Q_a$ for the two may reflect a genuine increase in $Q_{gb}$ for grade 0 due to the presence of a high level of Fe (1460 ppm).”

The main goal of this work is to obtain a phenomenological expression for the apparent activation energy for superplastic deformation of the Zn-Al eutectoid alloy in which the Fe concentration effect appears in an explicit form; and, at the same time such expression allows to describe all the experimental data without any exception.

## 2. Analysis

In this section a simplified phenomenological equation for the apparent activation energy will be used to describe the experimental data for the Zn-22 pct Al alloy doped with Fe impurities.

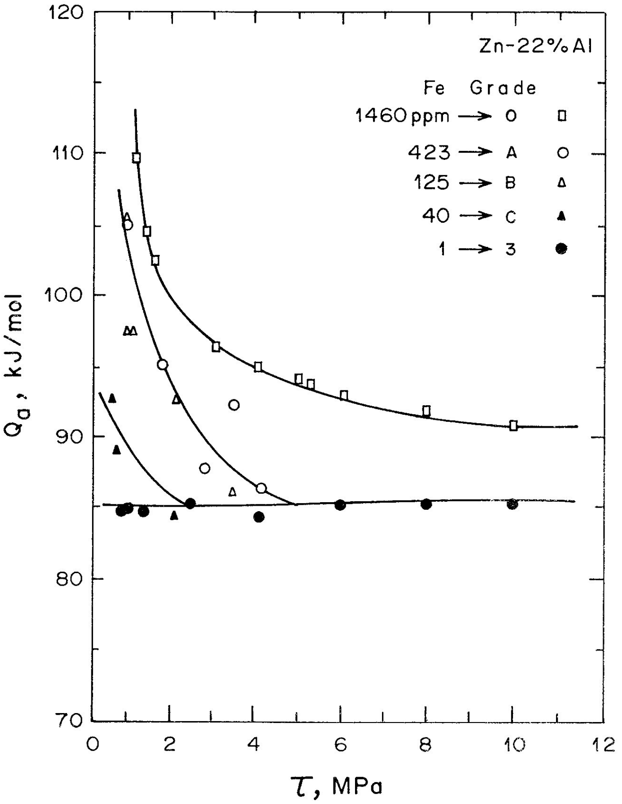

FIGURE 2 The dependence of the apparent activation energy for superplastic flow on applied shear stress for grade 0 of Zn-22 pct Al (1460 ppm of Fe) with a grain size of 2.5$\mu$m. Also, previously reported data for grades A,B,C and 3 containing 423, 125, 40 and 1 ppm of Fe (high-purity grade), respectively, are included for the purpose of comparison (Mohamed *et al.* [16], their Fig. 5).

Under the condition $\tau/\tau_o \gg 1$, Eq. (2) reduces to

$$Q_a = Q_{gb} + \frac{\eta}{\tau}, \qquad (3.a)$$

where the compatibility condition is

$$\eta \equiv nQ_o\tau_o, \qquad (3.b)$$

and $Q = Q_{gb}$ (where $Q_{gb}$ is the activation energy at the grain boundary) as supposed previously by Mohamed *et al.* [16]. After an analysis, it is clear that the inequality $\tau/\tau_o \gg 1$, in Eq. (2) means a physical condition where the segregated impurities at the grain boundary give rise to an increase in the activation energy for plastic deformation, relative to the material free of impurities; but without any change in the fundamental behavior of the pure alloy, because equations resembling Eq. (3.a) has been reported before for creep in some hexagonal close-packed metals like Zn or Mg [25,26], and also is not different from the following equation that has been mentioned in Ref. [13]:

$$Q_a = Q_{gb} + nQ_o/(\tau/\tau_o - 1), \qquad (4)$$

provided that our condition $\tau/\tau_o \gg 1$ has been used.

The experimental data for $Q_a$ in Zn-22 pct Al with Fe impurities as a function of the applied shear stress due to Mohamed *et al.* [16], which appear in Fig. 1, could be adjusted with Eq. (3.a). From Fig. 3 it is clear that the agreement between Eq. (3.a) and all the experimental data reported by Mohamed and coworkers is good, not only for region I but also for region II.

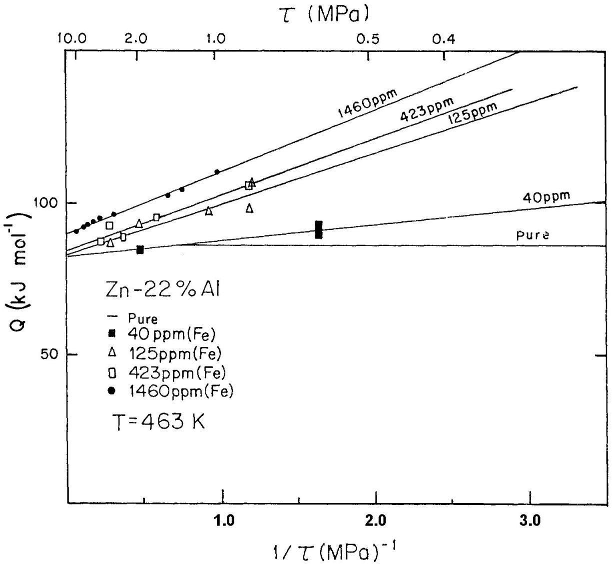

FIGURE 3 The dependence of the apparent activation energy for superplastic flow as a function of the inverse of the applied shear stress for grades 0, A, B and C of Zn-22 pct Al having a grain size of 2.5$\mu$m and containing 1460, 423, 125, 40 and 1 ppm of Fe respectively.

In Fig. 4, a plot for $\eta$ as a function of Fe impurities concentration is shown. It is straightforward that such experimental parameters for the alloy doped with Fe impurities (denoted by solid points) can be described by the following expression,

$$\eta(c) = \eta_s \left[ 1 - \exp(-c/c_c)_{\mathrm{Fe}} \right], \tag{5}$$

where $c$ is the Fe-concentration, $\eta_s$ is a saturation value of $\eta(c)$ equal to 20 kJ MPa/mol, $C_c$ is a critical Fe concentration equal to 116 ppm, and subscript Fe in Eq. (5) it is for Fe. The continuous line is for Eq. (5).

By using Eq. (5) it is clear that Eq. (3.a) appears like,

$$Q_a = Q_{gb} + \eta_s \frac{[1 - \exp(-c/c_c)_{\mathrm{Fe}}]}{\tau}, \tag{6}$$

where, for the first time in an expression for the apparent activation energy for superplastic deformation (of Zn-22 pct Al doped with Fe impurities), the Fe-concentration appears in an explicit way.

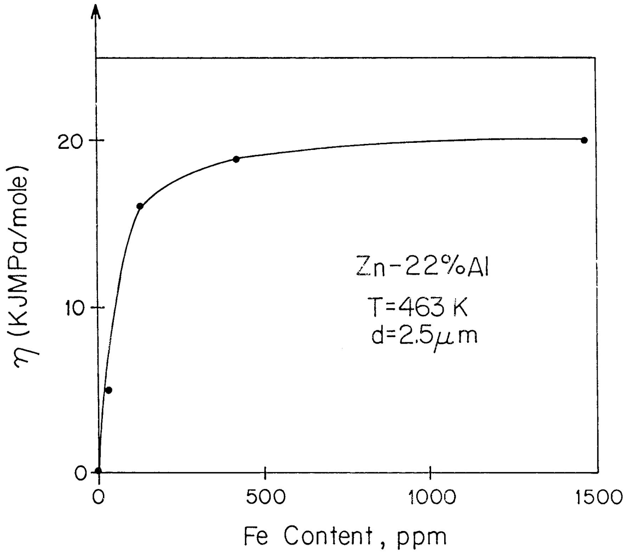

FIGURE 4 A plot of $\eta$ as a function of the Fe impurities concentration of Zn-22 pct Al alloy deformed samples with a grain size of 2.5$\mu$m and T=463 K.

We make note that by using Eqs. (3.a) or (6), all the experimental data for the apparent activation energy as reported by Mohamed *et al.* [16] are fully described. Also, from Eq. (3.a) it is straightforward that $\eta(c)$ has units of activation energy times a shear stress. Therefore by using Eqs. (3.b) and (5) a threshold shear stress at the grain boundary can be defined by the following expression:

$$\tau_o = \frac{1}{nQ_o}\eta(c) = \frac{\eta_s}{nQ_o}\left[ 1 - \exp(-c/c_c)_{\mathrm{Fe}} \right], \tag{7}$$

with the use of this equation, the saturation of $\eta(c)$ at high Fe concentrations it is easy to understand; because such behavior means that $\tau_o$ tends to a saturation limit as the Fe impurities grows. In other words, $\tau_o$ tends to become a constant because the interaction between Fe precipitates and dislocations at the grain boundary arrives to an upper limit. According to Professor Mukherjee [27] expression (7) could be used as a general phenomenological expression to describe the interaction between precipitates at grain boundaries and dislocations in such regions during deformation processes in other system alloys.

## 3. Discussion

Here, we consider that is appropriate to highlight some implications of the results obtained in the previous section, which are relevant to the analysis of superplastic behavior in Zn-22 pct Al alloy doped with Fe impurities.

Usually, equations of the Friedel-type [28-30] has been used to describe the interaction between strengthening particles and dislocations, when such particles offer resistance to dislocation gliding. This type of model give expressions for the critical resolved shear stress, $\tau_F$, which depends on the square root of the volume fraction of the precipitates [30].

It can be shown that for the case of grain boundary Fe-precipitates in an Zn-22 pct Al alloy it is possible to arrive at the following expression:

$$Q_a \cong Q_{gb} + \frac{A\sqrt{C_{\mathrm{Fe}}}}{\tau}, \tag{8}$$

where $A$ is a constant.

From Fig. 4 and Eq. (3.a) it is clear that the approximated expression Eq. (8) is only valid for Fe-concentration lower than the critical value of 116 ppm of Fe, this because for higher values of Fe-concentration $\eta$ in Eq. (3.a) is given by Eq. (5) and not by the square root of Fe-concentration. However Mohamed *et al.*, never arrives to an expression like Eq. (8), they take into account fundamental ideas of the Friedel theory about the interaction between strengthening particles and dislocations (to develop their model of threshold stress) which conceptually implies the validation of Eq. (8). In this scheme a failure of the Mohamed *et al.* description is expected for values of Fe-concentration higher than a certain critical concentration, as actually occur.

Finally, the Mohamed *et al.* phenomenological approach is to be at technical disadvantage against our approach because our Eq. (6) for the apparent activation energy explicitly exhibites the Fe-concentration, and Eq. (2) due to Mohamed *et al.* does not, and also our expression describes experimental data which Mohamed expression is uncapable to do.

## 4. Conclusions

The apparent activation energy for superplastic deformation in Zn-22 pct Al doped with Fe impurities as reported by Mohamed *et al.* [12,13,15-21] has been deeply analyzed. From this analysis arise the following conclusions.

1. For the first time an expression for the apparent activation energy which exhibits in an explicit fashion the Fe-concentration has been obtained. Such expression describes all the experimental reported data, not only for region I, but also for region II. The previous expression obtained by Mohamed *et al.* was uncapable to describe all the experimental data.
2. Models of the Friedel-type, which give place to apparent activation energy depending on the square root of the Fe-concentration are valid only for the low range of Fe-concentration (Fe-concentrations lower than 116 ppm).
3. Semi-phenomenological model by Mohamed *et al.* is valid only for the low range of Fe-concentration.
4. A phenomenological expression for the threshold stress as a function of the Fe-concentration has been obtained.

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