JOURNAL OF MATERIALS SCIENCE 30 (1995) 4101-4102

The stability of the Johnson–Mehl–Avrami equation parameters

R. MAGNANI, A. T. ADORNO
Instituto de Química-UNESP, Departamento de Físico-Química 14800-900 Araraquara, SP-Brazil

The stability of the parameters of the Johnson–Mehl–Avrami equation was studied using two parametrizations of the sigmoidal function and its fit to some kinetic data. The results indicate that one of the forms of the function has more stable parameters and only for this form it is reasonable to use, as an approximation, the linear regression theory to analyse the parameters.

1. Introduction

The kinetics of heterogeneous solid-state reactions can, in general, be described by the Johnson–Mehl–Avrami equation [1]

$$h(t) = 1 - e^{-\gamma t^{\delta}} \quad (1)$$

where h is the transformed fraction in the time t.

In most cases, it is not possible to obtain the transformed fraction at each time, but one can measure a suitable physical property of the metal, y, and define

$$h = \frac{y - \beta}{\alpha - \beta} \quad (2)$$

where α and β are the values of y at the end and at the beginning of the transformation, respectively. This leads to

$$y = \alpha - (\alpha - \beta) e^{-\gamma t^{\delta}} \quad (3)$$

called [2] the Weibull-type function or just the Weibull function. Another form of this function [3, 4], often used, is

$$y = \alpha - (\alpha - \beta) e^{-(kt)^{\delta}} \quad (4)$$

which is a reparametrization of Equation 3, with $\gamma = k^{\delta}$, and δ and γ (or k) are empirical parameters useful for the description of the isothermal transformation kinetics.

The estimation of α and β can be done graphically and then, by the linearization of Equation 3 or 4, δ and γ (or k) are estimated by the mean square method.

In this work, it is suggested that these estimations can be improved by some iterative process of non-linear estimation. Also, considering that in both forms, Equation 3 or 4, the Weibull function gives the same deviation from the experimental values in spite of the presence of two distinct parameters γ and k, the behaviour of these two parameters is compared, from its physical interpretation and its statistical properties.

2. Experimental procedure

The experimental data, shown in Fig. 1, were obtained by Adorno [5] from the measurement of microhardness isothermical changes with time, in a copper-based alloy.

The statistical analysis of the parameter estimators of the Weibull function was made using the additive error regression model in the form

$$y_i = f(t_i, \boldsymbol{p}) + \varepsilon_i \qquad (i = 1, 2, \ldots, n) \quad (5)$$

where the components of the vector $\boldsymbol{p}$ are the parameters to be estimated and ε_i are the random errors, with a supposed zero average normal distribution and σ standard deviation. The function $f(t, \boldsymbol{p})$ has the form of Equation 3 or 4. The minimum square estimate, $\hat{\boldsymbol{p}}$, of the parameter vector $\boldsymbol{p}$ was obtained by the linearization iterative method [6].

When n is small, the statistical properties of the mean square estimators, for a non-linear model, are unknown, but the linear model properties may be valid as approximations, depending on the degree of non-linearity. According to Bates and Watts [7], the non-linearity quantification of a model can be done by means of two components: the intrinsic non-linearity, depending only on the form of the model and on the previously fixed values set, and the non-linearity of the parameters effect, which can be decreased, sometimes drastically, by a reparametrization of the model function.

3. Results and discussion

Table I shows the parameter estimates of the Weibull sigmoidal function, in the forms of Equations 3 and 4 and the standard deviation of the parameter estimates. As expected, only the γ and k estimates differ.

Fig. 1 shows the experimental points and the Weibull function curve. The plot is the same for the two function forms. The parameter estimate variability can be evaluated by its relative error, defined by the standard deviation and the parameter

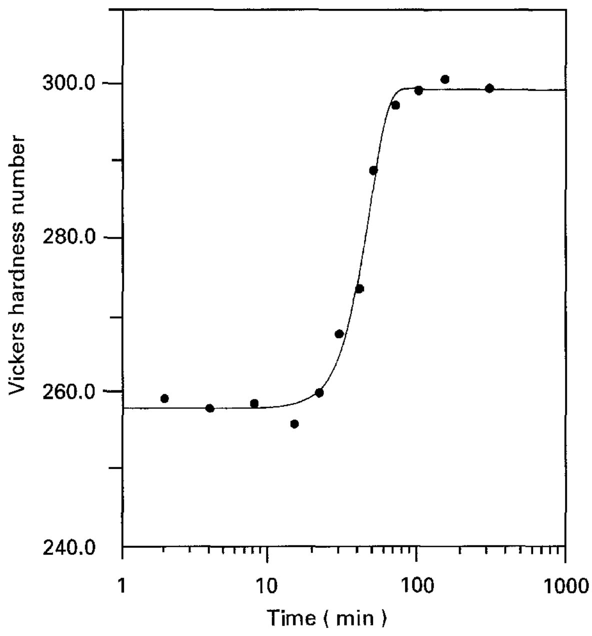

Figure 1 Weibull function curve and the experimental points.

TABLE I Parameter estimates of the Weibull sigmoidal function (Equations 3 and 4) and estimated standard deviation

Parameter	Estimate	Standard deviation
α	299.68	0.9368
β	257.78	1.3460
δ	3.609	0.5036
γ	0.0000009	0.000002
k	0.0211	0.0006

estimate ratio. This ratio, calculated for the estimates in Table I, in percentage, gives more than 200% for $\hat{\gamma}$ and just 2.8% for $\hat{k}$, indicating that k is a more stable parameter than γ.

The Bates and Watts intrinsic non-linearity measurement, for the two forms of the Weibull function, is equal to 0.19, because this non-linearity component is not affected by the reparametrization. The obtained value is lower than the minimum level of significance, given by $1/2F^{1/2} = 0.25$, where F is the Snedecor distribution value with $p = 4$ degrees of freedom at the numerator and n–p degrees at the denominator, with 5% of significance. This minimum level represents the value from which the non-linearity degree is significantly high. In this study, this degree is not significant and so the linear regression procedures can be used to get inferences about the expected values for y.

The Bates and Watts measurements for the non-linearity of the parameter effects were 31.26 for the form of Equation 3 and 0.21 for the form of Equation 4, indicating that Equation 3 has an excessively high non-linearity degree, due to the presence of the γ parameter. This degree is lowered to an acceptable value (lower than the significance minimum 0.25) when Equation 4 is used.

Therefore, one can see that just for the statistical model with additive error, which adopts the Weibull function in the form of Equation 4, it is reasonable to use the linear regression theory as an approximation and, for instance, the reliability interval for the parameter estimates can be calculated by

$$\text{parameter estimate} \pm t_0 \text{ (estimate standard deviation)}$$

where t_0 is the t Student distribution value with n–p degrees of freedom, and the standard deviation is given in Table I.

4. Conclusion

The form of Equation 4 of the Weibull function seems to be more suitable for the study of transformation kinetics in metals. Contrary to Equation 3, Equation 4 has more stable parameters and a satisfactorily low non-linearity degree, intrinsic and for the parameters effect, allowing the use of the linear regression theory, as an approximation.

Acknowledgements

The authors thank FAPESP and FUNDUNESP for financial support.

References

1. J. CHRISTIAN, "The Theory of Transformations in Metals and Alloys-Part I", 2nd Edn (Pergamon, Oxford, 1975).
2. D. RATKWOWSKI, "A non-linear regression modeling" (Marcel Dekker, New York, 1983).
3. J. BURKE, "The kinetics of phase transformations in metals" (Pergamon, London, 1965).
4. E. J. MITTEMEIJER, *J. Mater. Sci.* **27** (1992) 3977.
5. A. T. ADORNO, unpublished results.
6. N. R. DRAPER and H. SMITH, "Applied regression analysis", 2nd Edn (Wiley, New York, 1981).
7. M. D. BATES and D. G. WATTS, *J. R. Statist. Soc. B* **42-1** (1980) 1–25.

Received 11 July 1994
and accepted 3 February 1995