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ANISOTHERMAL VERSUS ISOTHERMAL KINETICS: THE TRANSFERABILITY OF KINETIC PARAMETERS

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ABSTRACT

An important assumption of anisothermal calorimetry is that kinetic parameters are transferable, that is, kinetic parameters obtained from anisothermal experiments should also be valid to describe isothermal kinetics (the opposite should also hold). This will be hereafter referred to as the transferability principle. Recently, the present authors have shown that the only way to fulfil this principle is to use the same rate equation for iso- and anisothermal kinetics. In this paper this conclusion is further illustrated on two largely different reactions, namely, recrystallization in a commercial aluminium alloy (AA1145) and curing of an epoxy resin.

INTRODUCTION

An important assumption underlying the use of anisothermal calorimetry to study the kinetics of phase transformations is that kinetic parameters are transferable. That is, kinetic parameters obtained from non-isothermal data for a given reaction can be also used to describe the isothermal kinetics for that reaction; the opposite should also hold. The question is whether the methods used to analyze experimental data do or do not lead to similar results. kinetic parameteres obtained from different schemes need not coincide, but rather the reaction kinetics should be similar and in agreement with experimental data.

Although the literature on thermal analysis shows a general consensus on how to analyze experimental data obtained from isothermal techniques (1, 2), several quite different methods have been suggested for the study of anisothermal kinetics (3-6). The fundamental difference between these methods does not lie in the various analytical expressions assumed for the fraction reacted, but rather it concerns what iso- and anisothermal kinetics have in common. Specifically, whereas some methods assume that the same reaction rate equation holds for the two kinetics (5), others take the same fraction reacted (4) and, more recently, it has even been assumed that neither the fraction reacted nor the reaction rate follow the same equation for iso- and anisothermal kinetics (6). The subject has been recently discussed by the present authors

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(7) concluding that in order to fulfil the transferability principle the same rate equation has to be used for iso- and anisothermal kinetics.

The purpose of this paper is to present further evidence to support the aforementioned conclusion. Anisothermal experimental data for recrystallization in a cold-rolled aluminium alloy and curing of an epoxy resin will be presented and analyzed; kinetic parameters obtained from these data will be shown to be valid to describe both iso- and anisothermal kinetics. The rate equation assumed for the two kinetics is that proposed by Avrami (1); although this expression has not been widely used for describing the curing of organic resins (8), it will be accurate enough for our purposes. The expression given by Avrami (1) can be written as,

$$\frac{d\alpha}{dt} = n\,(1-\alpha)\left[-\ln(1-\alpha)\right]^{\left(\frac{n-1}{n}\right)} g\,(T) \qquad (1)$$

α being the fraction reacted, n the reaction order and g (T) the Arrhenius relation, that is,

$$g\,(T) = \nu \exp(-\Delta E/RT) \qquad (2)$$

where ν is the frequency factor, ΔE the activation energy and R the gas constant.

Both ν and ΔE will be calculated by means of Kissinger method (1), which as already proven by the present authors holds for DSC (7). Instead, n will be adjusted to fit the fraction reacted given by the DSC curves. The expressions for the fraction reacted given by eqn. (1) for the iso- and anisothermal cases can be found in ref. (5).

EXPERIMENTAL PROCEDURES

The commercial aluminium alloy was the AA1145 continuously cast as an slab 8 mm thick. Atomic absorption gave the following composition in wt pct: 0.31 Fe, 0.11 Si, 0.05 Mn, 0.01 Mg, 0.02 Zn, 0.015 Ti and 0.015 Cu. The alloy was 60% cold rolled, annealed at 673ºK for 2 h to avoid interference with precipitation reactions (9), and 85% cold rolled. The epoxy resin was supplied by Buehler Ltd., the trade name being Epomet TM.

DSC measurements were carried out in a Perkin-Elmer DSC-2C apparatus. Runs were carried out at heating rates in the range 5-100 deg/min under dynamic argon atmosphere (1 l/h). Isothermal experiments were performed in the same DSC equipment. All precautions required to obtain reliable isothermal data were taken

RESULTS AND DISCUSSION

As mentioned above the kinetic parameters were obtained in two steps. First, Kissinger (3) method was used to obtain ν and ΔE, and then the reaction order was adjusted to fit the fraction reacted given by the DSC curve. Table 1 reports the kinetic parameters and Fig. 1 illustrates the adjusting procedure for the epoxy resin

Table 1 - Kinetic parameters for the two reactions studied in this work

	ΔE (kJ/mol)	ν (min^{-1})	n
AA1145	204.3	3.6×10^{17}	2.5
Epomet	66.4	1.07×10^{8}	1.2

Isothermal kinetics were then analyzed by means of the kinetic parameters given in Table 1. The experimental and calculated values for the time at which the isothermal reaction rate is maximum are reported in Table 2. The agreement is highly satisfactory indicating that the procedure utilized in this work does not violate the transferability principle. In a recent work the present authors showed that, instead, a method which assumes the same fraction reacted for iso- and anisothermal kinetics (4) does not preserve the above mentioned principle. This suggests that the only way to fulfil the transferability principle is to use the same rate equation for iso- and anisothermal kinetics.

Table 2 - Experimental and calculated values for the time at which the isothermal reaction rate is maximum (t_m)

AA1145			Epomet		
T (ºK)	t_m (min)		t_m (min)		T (ºK)
	Exp.	Calc.	Exp.	Calc.	
580	4.7	5.4	5.3	4.9	370
590	1.9	2.7	3.5	3.7	375
-	-	-	1.6	2.1	385
-	-	-	0.9	1.3	395

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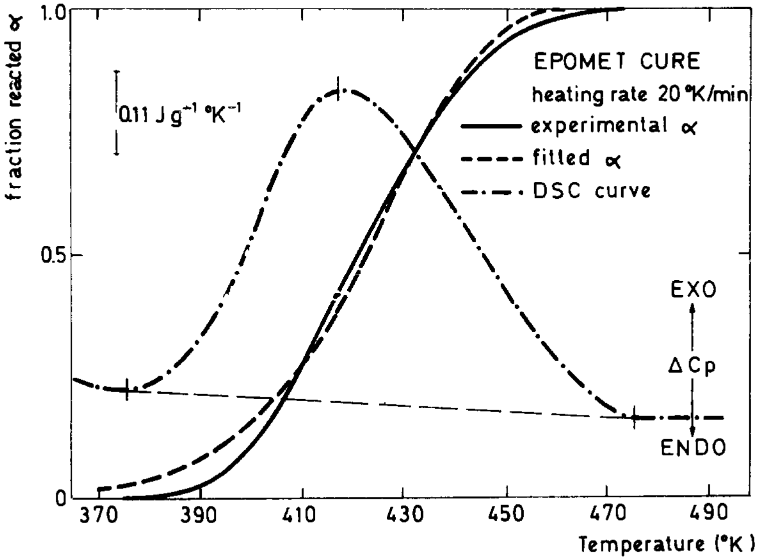

Figure 1