APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO THE PROCESSING OF ALUMINUM ALLOYS

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1. INTRODUCTION

The properties of heat treatable automotive alloys depend on their microstructure, which is controlled by alloy chemistry and processing. However, the material is characterized by measuring different properties of the product, while the microstructural state is rarely monitored. Monitoring microstructural changes via microscopic technique can be a time-consuming exercise. It would be useful to develop a more rapid means of relating microstructure to the properties of alloys. The differential scanning calorimetry (DSC) is one means of achieving this goal in a commercial environment. Modern DSC instruments are economical, fast, sensitive, and reproducible. They can be routinely used for quality control, and process and material development, provided appropriate procedures are used. This paper describes the DSC technique and shows, with examples, what can be achieved by this technique in relation to the development of automotive alloys.

2. DSC TECHNIQUE

The DSC cell contains two pans, one is used to heat a reference and the other to heat the sample. The output of the DSC run is the heat flow to the reference relative to the sample as a function of temperature. For isolating the heat effects due to reactions occurring in the alloy, two separate DSC runs are carried out under identical conditions. In the first run high purity annealed aluminum discs are placed in both sample and reference pans, while in the second run the aluminum disc in the reference pan is left undisturbed but a disc of the alloy of interest is placed in the sample pan(1). The heat effect associated with the transformation in the second run are obtained by subtracting the results from those of the first run. The resultant curve is then corrected to account for the differences in the heat capacities of the sample and reference(1). The example shown in Figure 1 is a corrected thermogram obtained during heating a solution treated sample of Al-0.4%Mg-0.28%Si-0.25%Fe alloy at 10°C per minute. The peaks and troughs in the curve represent various precipitation and dissolution processes respectively.

3. APPLICATIONS

Fabrication of heat treatable products, such as extrusions, sheets and castings, involves many thermomechanical processing steps. Each of them is controlled within a narrow processing window to obtain consistent properties in a production environment. Each batch of the product is subjected to a variety of tests to examine the final properties before shipping to the customers. The determination of optimum processing condition for each thermomechanical step and the final product properties is cumbersome and labor intensive. Modern DSC instruments are now used to determine the micro-structural state of the product accurately and economically with a high degree of sensitivity and reproducibility. This is an excellent tool for quality control, process optimization and alloy development.

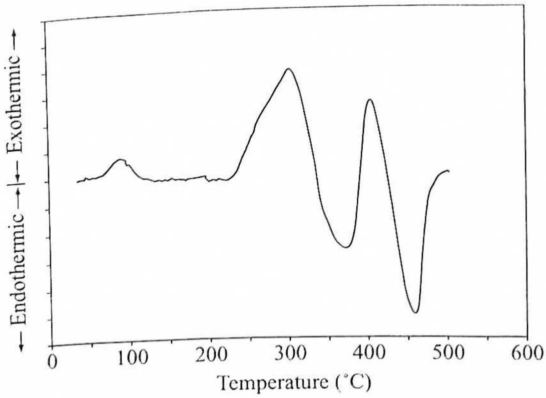

Figure 1. DSC curve of a solution heat treated Al-0.4%Mg-0.28%Si. 0.25%Fe alloy.

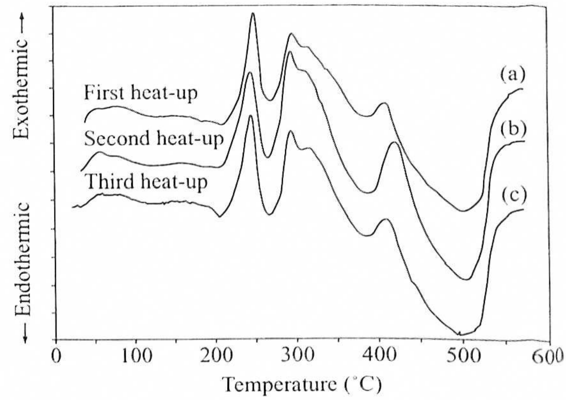

Figure 2. DSC curves of a solution heat treated Al-0.5%Mg-1.2%Si Alloy. Curve (b) and (c) are second and third repeats of curve (a).

3.1.1 Finger Printing Alloys

The DSC thermogram of a sample obtained during heating at a particular heating rate, gives temperature ranges for reactions and the typical shapes of peaks which are characteristics of the material. Repeated DSC experiments give look-alike thermograms, as seen in Figure 2, where three curves a, b and c of the Al-0.5%Mg-1.2%Si alloy, heated at a rate of 10°C per minute, are similar. Such a degree of reproducibility allows this method to provide a fingerprint of the metallurgical state of the alloy. The fingerprint can be used for quality control purposes in the production environment.

3.1.2 Process Optimization

Most of the as-cast automotive alloys can exhibit incipient melting well below the solidus temperature in certain conditions: the DSC curve (a) (Figure 3) of an as-cast Al-1.8%Mg-0.8%Cu-0.5%Si alloy shows nonequilibrium melting close to 500°C. The presence of an incipient melting phase is highly undesirable since it can lead to ingot cracking during hot rolling. By choosing suitable DSC experiments, it is possible to determine homogenization conditions which will eliminate the incident melting as seen in curve (b) for the homogenized alloy in Figure 3.

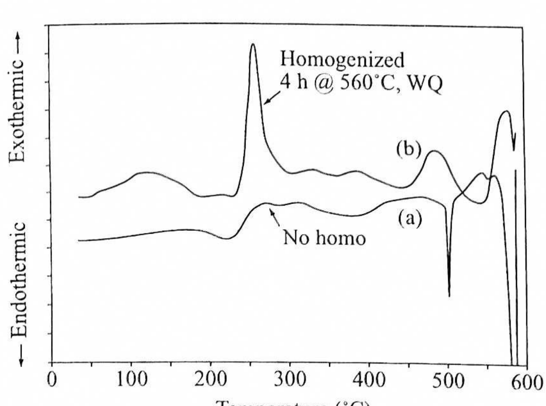

Figure 3. DSC curve of Al-1.8%Mg-0.8%Cu-0.5%Si alloy at 10°C/min (a) as-cast (b) homogenized

The choice of heat treatment conditions such as solution temperature, quenching rates etc. can produce changes in precipitation and dissolution behavior which may be very small. Nevertheless, the DSC can pick up such differences. For example, solutionizing at different temperatures followed by quenching produce different vacancy concentrations which modifies the kinetics of reaction by changing the diffusion rates and substructures. Figure 4 shows how the DSC curves a, b and c of an Al-1.5%Cu-0.75%Mg alloy differ when it is solutionized at 450, 500 and 560°C respectively. Similar changes occur due to differences in quenching rates from solutionizing temperature, and this can also be picked up by DSC as seen in the DSC curves of AA6111 alloy in Figure 5.

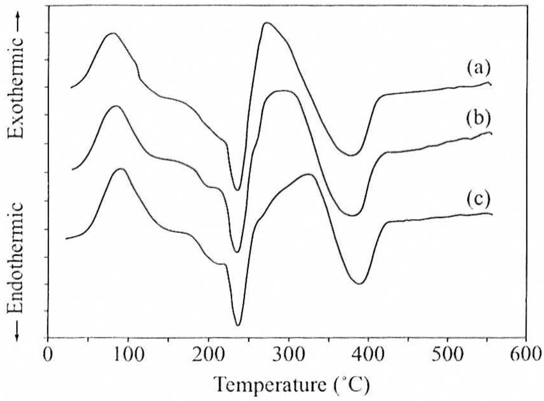

Figure 4. Effect of the solutionizing temperature on the shape of the DSC curve of an Al-1.5%Cu-0.75%Mg alloy. Heating rate 10°C/min (a) 550°C (b) 500°C (c) 450°C

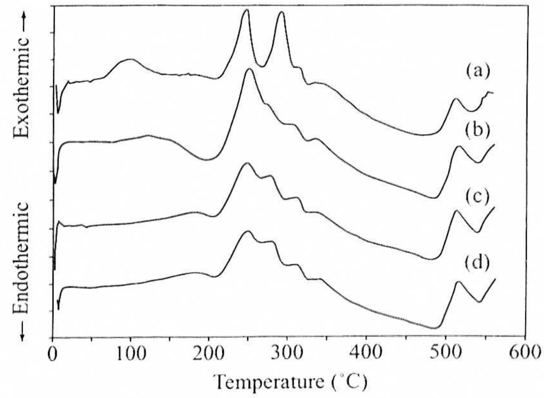

Figure 5. The effect of four different cooling paths on the shape of a solutionized AA6111 alloy

3.2 Alloy Development

3.2.1 Precipitation Sequence

Precipitation hardening in heat treatable alloys occurs due to precipitation of metastable precursors of soluble equilibrium phases. The metastable precipitation process occurs in a particular sequence, and the information regarding the different stages of precipitation is very important in terms of alloy and process development. The general peak arrangement in the DSC curve shows the precipitation sequence and, with the help of transmission electron microscopy (TEM), different precipitates can be identified and associated with the DSC peaks and age hardening curves. Figure 6 shows a DSC curve of a long term naturally aged Al-0.4%Mg-1.2%Si-0.25%Fe alloy along with the microstructure corresponding to different peaks[2]. Various precipitation process identified are:

(i) Trough A: represents dissolution of GP(I) zones and clusters formed during long term natural ageing.

(ii) Peak B: a composite peak representing the formation of three precipitates that are ß"/GP(II) coherent needles, ß' rods, ß' laths and Si particles. The transformation of ß" needles in to ß' also occurs within the peak. Si precipitation continues beyond the peak.

(iii) Peak C: related to the precipitation of ß rods and partial dissolution of ß' and fine Si particles. The precipitation of irregular ß particles continues up to ~500°C.

(iv) Trough F: represents dissolution of all the precipitates. The minor peak E is artificial and represents the net effect of the changes in heat evolution and absorption rates related to the dissolution kinetics of the individual phases.

3.2.2 Effect of Composition

The DSC technique can resolve small peaks which are otherwise difficult to separate by other techniques. This allows one to establish compositional effects on the precipitation process. For example, Figures 7 and 8 show the effect of Mg_2Si content on the appearance of the DSC curve of the balanced alloy in both as-quenched and naturally aged conditions. The precipitation processes between 200 and 350°C are altered by changes in the Mg_2Si level in both Figures 7 and 8.

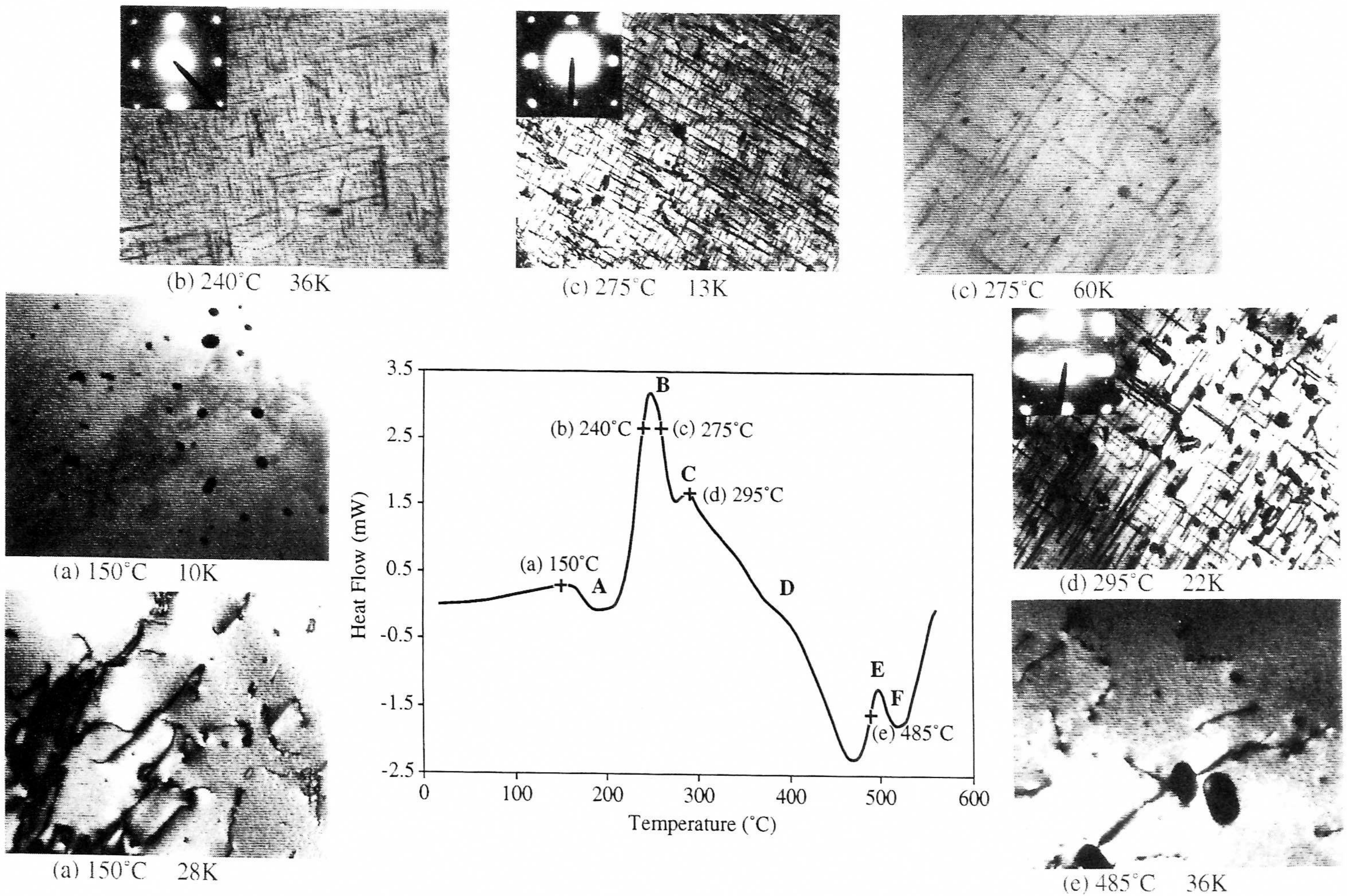

Figure 6: DSC trace of the long term naturally aged AC120 material obtained at 10°C/min. Samples for TEM were obtained by heating the material at 10°C/min in a DSC cell to the desired temperature, holding for 15 minutes and cooling to room temperature.

The effect of alloying elements on the precipitation process can also be established using the DSC technique[3].

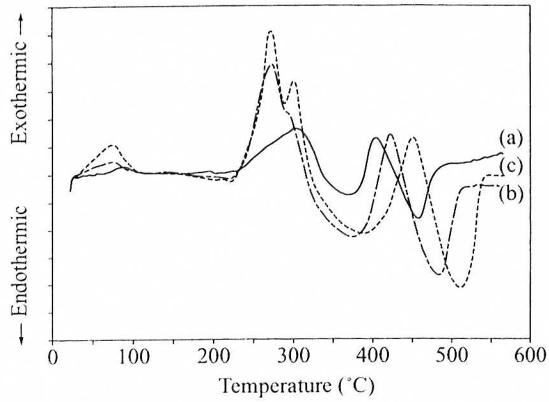

Figure 7. The effect of Mg_2Si level on the DSC curves of solutionized 6XXX alloy (a) 0.63% (b) 0.95% (c) 1.12%

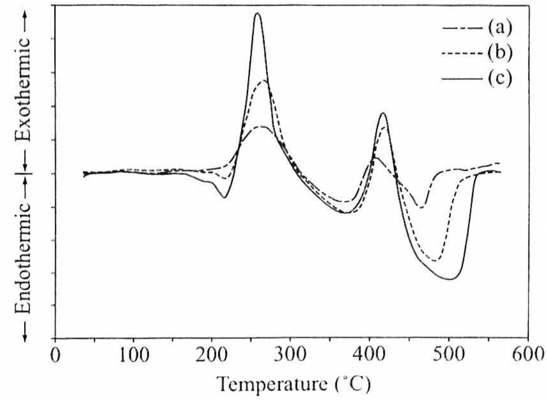

Figure 8. The effect of Mg_2Si level on the DSC curves of naturally aged 6XXX alloys (a) 0.63% (b) 0.95% (c) 1.14%

3.2.3 Quantification of Peaks: Mole Fractions and Reaction Rates of Transformation

Various peaks observed in the DSC curve can be quantified and used for kinetic analysis and alloy design[1].

The heat effect per unit mass, Q(T), associated with any reaction between the initial (T_i) and the final (T_f) temperatures of a peak is obtained by the following equation[1].

$$Q(T) = \frac{EA(T)}{M\phi} \qquad (1)$$

The value of A(T) is obtained from the total area under the peak between T_i and T. The fractional transformation, Y(T), is given by

$$Y(T) = \frac{A(T)}{A(T_f)} \qquad (2)$$

and

$$\left[\frac{dY}{dT}\right] = \frac{\left(\dot{q}_2 - \dot{q}_i\right) - \left(\dot{q}_2 - \dot{q}_i\right)\dot{Q}_0 = 0}{A(T_f)} \qquad (3)$$

Where

$\left(\dot{q}_2 - \dot{q}_1\right)$ = net heat flow due to transformation (mW)

$\left(\dot{q}_2 - \dot{q}_1\right)\dot{Q} = 0$ = correction factor due differences in heat capacities of the Al reference and the sample (mW)

The value of Y(T) and dY/dt can be evaluated, according to equations (2) and (3), from the DSC curve simply by measuring the peak area, A(T), between T_i and T, and the peak height at T and dividing both values by the total area under the peak, $A(T_f)$.

Figure 9 shows the corrected thermograms at 5, 10, 15 and 20°C/min due to formation of GPB zones in Al-1.5% Cu-0.8%Mg alloy. Figure 10 shows the values of Y and dY/dt evaluated from the DSC curves in Figure 9.

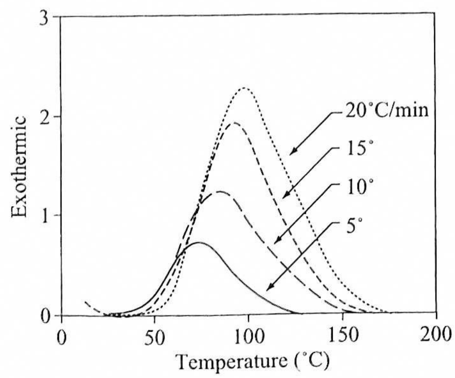

Figure 9. GPB zone precipitation peaks in the solution heat treated Al-1.5%Cu-0.8%Mg alloy at different heating rates

3.2.4 Kinetic Parameters for Reaction

The rate of reaction may be written as[1],

$$\ln\left[\left(\frac{dY}{dT}\right)_{Y}, \phi_j\right] = \ln\left[f(Y')k_0\right] - \frac{Q^*}{R}\left[\frac{1}{T_j}\right] \qquad (4)$$

where,

$(dY/dT)_{Y'}$	=	reaction rate at constant value of Y'
T_j	=	temperature at Y'
ϕ_j	=	heating rate (°C/s)
k_0	=	pre-exponential frequency factor (s^{-1})
f(Y)	=	function of Y only
Q^*	=	activation energy (J/mole)
R	=	gas constant (J/mole K)

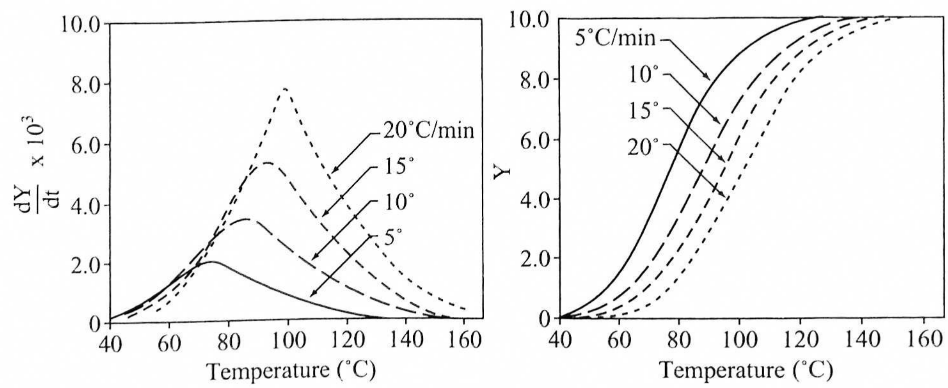

Figure 10. (a) Y vs T plots for GPB zone precipitation peaks, Figure 9, at different heating rates (b) vs T plots at different heating rates

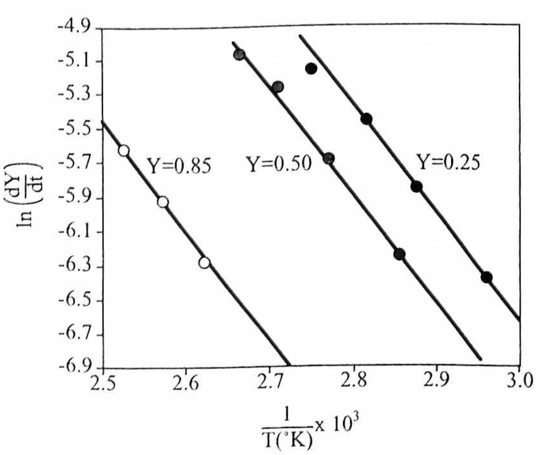

Figure 11. Activation plots for GPB zone precipitation peak from Equation (4)

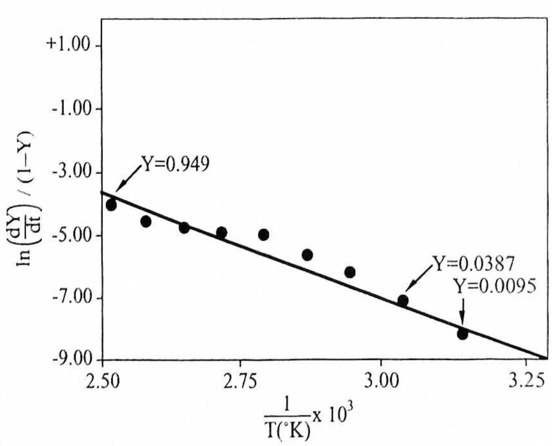

Figure 12. Plot from Equation (5) for determination of f(Y) for GPB zone precipitation

Plots after equation (4) for GPB zone precipitation (Figure 9) are shown in Figure 11. The slope of the best lines for different values of Y are quite close to one another and give an average Q* of 55.60 ± 0.13 kJ/mol which is consistent with the values published in the literature[1].

Figure 12 is plotted after the following equation:

$$ln\left[\left(\frac{dY}{dT}\right)\frac{\phi}{(1-Y)}\right] = ln\,[k_0] - \left[\frac{Q^*}{R}\right]\left[\frac{1}{T}\right] \qquad (5)$$

This figure suggests that $f(Y) = (1\text{-}Y)$

and $K_0 = 5.7 \times 10^5\ S^{-1}$.

Thus, the kinetics of GPB zone precipitation can be described by the following equation

$$\left[\frac{dY}{dT}\right] = (1-Y) * 5.7 * 10^5 * exp\left(\frac{-6687.5}{RT}\right) \qquad (6)$$

3.2.5 Solvus Temperature

The relationship between the solvus temperature and composition is usually complex in multi-component systems. However, suitable relations can be derived for specific systems.

Figure 13 shows the S phase solvus line obtained by deriving appropriate equations and performing the analysis on the DSC thermogram of quenched Al-1.5%Cu-0.8%Mg alloy[4] shown in Figure 3. The results of the analysis fit well with the curve determined by Little et al.[5]

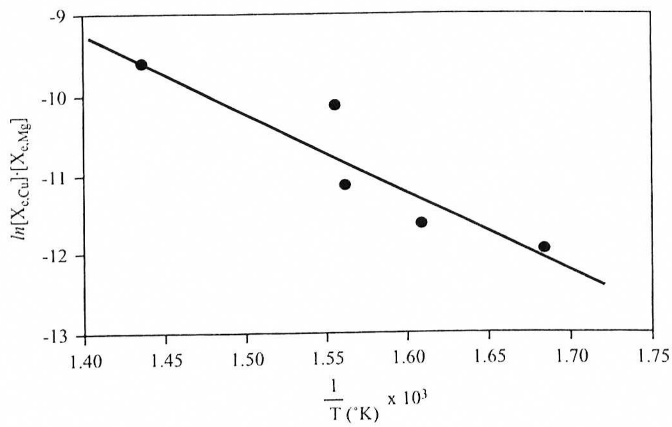

Figure 13. The solvus line of the S phase in an Al-1.5% Cu-0.8% Mg alloy.

4. SUMMARY

From these examples, it is apparent that the DSC technique can be used to quickly obtain qualitative information on the state of microstructure and the precipitation sequence. Moreover, by an appropriate combination of experiment and theory, quantitative information on the kinetics, solvus data and order of reactions can be established.

ACKNOWLEDGEMENTS

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