

Quantitative Interpretation of Differential Scanning Calorimetry Heat Effect in A2009 Aluminum Alloy.

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ABSTRACT

The quantitative interpretation of differential scanning calorimetry (DSC) heat effect in A2009 aluminum alloy was investigated. DSC and metallographic techniques have been used to characterize the microstructure and behavior of A2009 alloy. Three models were used to study the kinetic of the precipitation process. Results obtained showed that the microstructure of the Al-Cu-Mg alloy reveals the Al_2CuMg phase in the aluminum matrix. The precipitation and dissolution of GPB zones and the metastable S' and θ' phases are kinetically controlled in the alloy. The kinetic parameters determined for the formation and dissolution of GPB zones using the three models are within the limits of experimental errors. In all the three models Kissinger method has the lower activation energy. Kissinger method has been recommended for studying the precipitation reactions of the alloy in this series.

(Keywords: aluminum alloy, differential scanning, calorimetry, microstructure)

INTRODUCTION

Monolithic Al-based alloys for structural applications are generally strengthened by four basic mechanisms: precipitation strengthening, solution strengthening, grain and subgrain strengthening, and strengthening by dislocations (Aigbodion and Hassan, 2010). The first two mechanisms depend strongly on composition of the alloy and on heat treatment and are generally employed in a metastable state, whilst the latter two mechanisms depend mostly on thermo-mechanical processing routes (Hassan and Aigbodion, 2010).

Differential Scanning Calorimetry (DSC) is a useful technique for the study of phase transformations and has been widely applied to

study precipitation in aluminum alloys, but the results are generally interpreted qualitatively. Quantitative interpretation of DSC experiments on binary and ternary aluminum-based alloys has been attempted (Papazian, 1982), and can improve understanding of their thermodynamics and kinetics of precipitation.

In the present paper a quantitative interpretation of DSC heat effects occurring in A2009 alloy is presented. The aim is to bring together and critically review the published work that is of direct use to researchers working in the field of calorimetry of light metals.

MATERIALS

The materials used in this study are: Copper, high purity aluminum electrical wire which was obtained from Northern Cable Company NOCACO (Kaduna), Magnesium powder, Moulding boxes, Silica sand, Bentonite were obtained from the Foundry Shop of National Metallurgical Development Centre, Jos, Nigeria.

Equipment

The equipment used in this study included: Pyrometer, mechanical stirrer, crucible, electrical resistance furnace, Differential Scanning Calorimeter (DSC) machine and metallurgical microscope with built-in camera.

METHODS

Samples Production

The synthesis of the Al-Cu-Mg alloy that was used in this study was produced using at the Foundry Shop of the National Metallurgical

Development Center, Jos, Nigeria. The samples were produced by keeping the percentage of copper and magnesium constant. High purity aluminum electrical wires was charged in a graphite crucible kept in an electric resistance furnace and 0.01%NaCl-KCl powder was used as a cover for melting the alloy in order to minimize oxidation of aluminum by excluding oxygen and creating a protective atmosphere inside the furnace. After the melting of pure aluminum, the temperature of the furnace was raised to 720°C for the purpose of superheating the aluminum melt. The required quantity of 3.4% copper is added to the melt using ligand (50%Cu-50%Al) the melt was thoroughly stirred, before adding the 1.4% magnesium

With progressive melting, the furnace temperature was raised to 780°C and the melt was held at this temperature for 10 minutes. It was then skimmed to remove the oxides and impurities. The molten metal was continuously stirred in order to ensure a near-uniform distribution of alloying elements and prevent the elements from settling at the bottom due to their higher density. The furnace temperature was controlled between 730 and 740°C and the pouring temperature were controlled to be about 720°C.

A preheated sand mould with diameter 18 mm and 300mm length was used to produce cast bars. After casting, the specimen were homogenized at 550 ± 5 °C for 2 h, and then quenched into iced water [8]. The specimens were then cooled in liquid nitrogen until the DSC runs commenced. The specimens for microstructure study were later aged at 200°C with ageing time of 6 hours (Jena et al., 1989).

Differential Scanning Calorimeter (DSC) Test

DSC was used to investigate reactivity in the Al-Cu-Mg alloy. A Seteram TG-DSC 11, manufactured in France, interfaced with a SETSOFT 2000 software was used in this work. All the samples and crucibles used were weighed using an electronic balance (Schimadzu Corporation, Model AUW120D) (Starink and Mourik, 1992). The DSC was run in the vertical mode in order to create uniform heat distribution in the samples and the reference. The sample, which was 5 mm in diameter and 1mm in thickness, weighed approximately 60 mg, and was placed in one of the pans; the other pan was pure aluminum used as a reference. The output from

the DSC was measured (in J/Kg°C), and the net heat-flow to the reference relative to the sample was recorded as a function of the scanning temperature. The samples were loaded in the DSC at room temperature, and each scan was conducted over a temperature range from 50 °C to 500 °C. A different heating rate of 5, 10, 15, and 20°C/min were used in all scans. Dry nitrogen was introduced and passed through the calorimeter cell to minimize oxidation. The positions of the peak temperatures on the DSC thermograms were determined by direct measurement from the graph.

Three models were used to study the kinetic of the precipitation process they are:-The Kissinger-type expressions used in extract activation energies from data obtained from non-isothermal experiments, since the experiment was non-isothermal heat treatment with a constant heating rate, θ (e.g., DSC experiments). Mittemeijer et al. (1998) approximation, equations below showing an expression between the temperature for a fixed stage of transformation (T_i) and the heating rate, θ , was used as shown below:

$$\ln(T_{y_f}^2 / \Phi) = \frac{E}{RT_{y_f}} + \ln\beta_y$$

where β_{y1} is the state variable fully determining that fixed state of transformation. The activation energy is determined from the slope of the straight line obtained by plotting $\ln(T_i^2 / \Phi)$ vs $(1/T_i)$.

The Augis and Bennett expression for determining the activation energy of the aging process with various heating rates was used and this is given by (Tong and Fang, 1998):

$$\ln(T_p - T_0)/QJ = -\ln K_0 + E/RT_p$$

where T_p is the peak temperature of DSC curves, T_0 is the initial temperature of the DSC experiment, Q is the heating rate, K_0 is the reaction constant, E is the activation energy and R is the gas constant equal to 8.314 J/mol.K. The plot of $\ln[(T_p - T_0)/Q]$ against $1/T_p$ should yield a straight line of slope (E/R) from which the value of activation energy (E) for each precipitation formation in materials can be calculated.

Microstructure Study

Cutting: Most metallographic samples need to be sectioned to the area of interest and for easier handling. Depending upon the material, the sectioning operation was obtained by abrasive cutting. Proper sectioning is required to minimize damage, which may alter the microstructure and produce false metallographic characterization. Proper cutting requires the correct selection of abrasive type, bonding, and size; as well as proper cutting speed, load and coolant. For this research A2009 samples being cut using abrasive cutter.

Mounting: The purpose of mounting is to make sample handling easier in order to run examination. Two different methods of mounting are generally used are hot mounting and cold mounting. In this research, hot mounting is used.

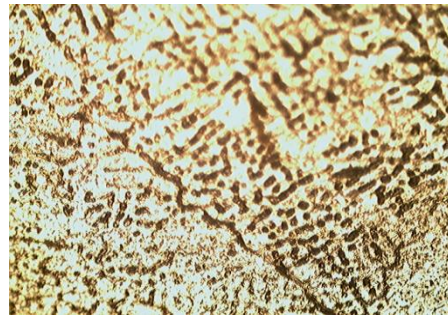
Grinding and Polishing: Grinding purpose is to remove debris and sharp edges during specimen cutting. Proper grinding is needed in order to produce a clean surface of sample. All samples being grind using silicon carbide grinding paper on the grinder. The grid for grinding paper is 120, 180, 320, 400, 600, 800, and 1200. Polishing is final touching before sample can be examined or test. Samples polished by alumina paste. The sample needs to be in mirror surface after polish to obtain clear microstructure.

Etching: Etching is only done when microstructure didn't appear under observation via the microscope (either light microscope or scanning electron microscopy). Etching will remove upper layer of sample so the microstructure will be revealed. For this aluminum alloys etchant that was used is Keller's reagent. This etchant prepared with the addition of several chemical. The chemical are 190ml of distilled water, 5ml of nitric acid, 3ml of hydrochloric acid and 2ml of hydrofluoric acid. This reagent prepared in the fume cupboard. After etching the microstructure was reveal with the help of optical microstructure.

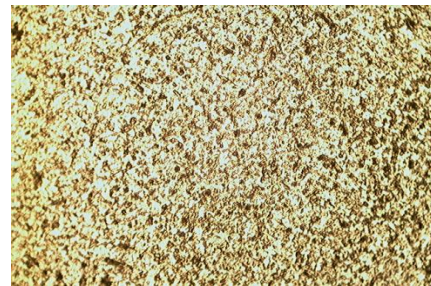
RESULTS AND DISCUSSION

Results

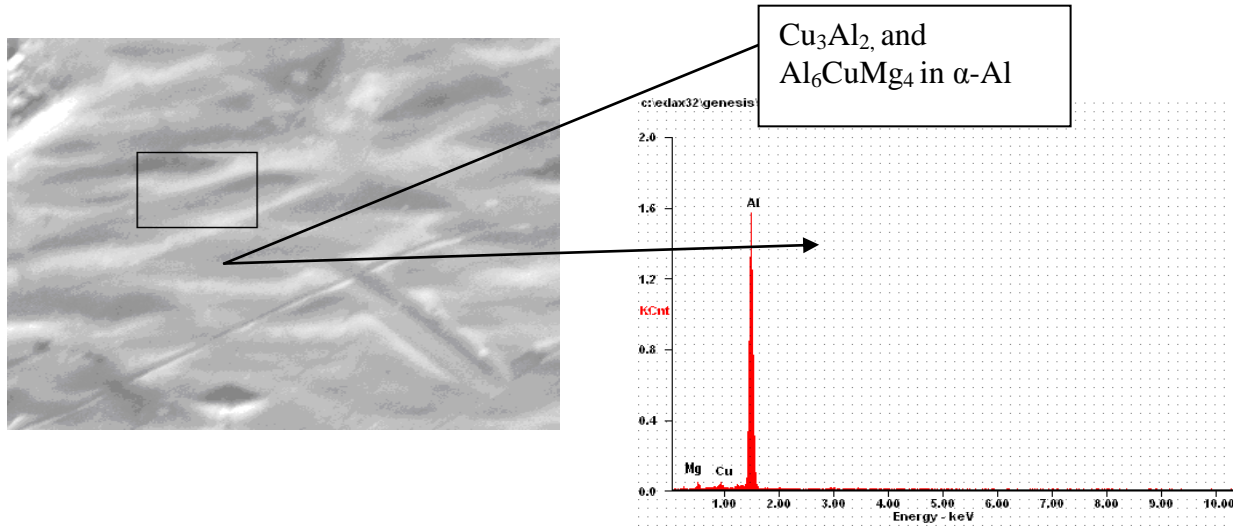
The various microstructures developed for both as-cast and age-hardened are shown in micrographs 1-4. The DSC investigation undertaken to monitor the precipitation reactions in A2009 is presented Figure 1 while the Figures 2-4 shows the plots used in calculating the activation energy. Figure 5 shown the result of the activation energy. Table 1 shown the peaks temperatures.



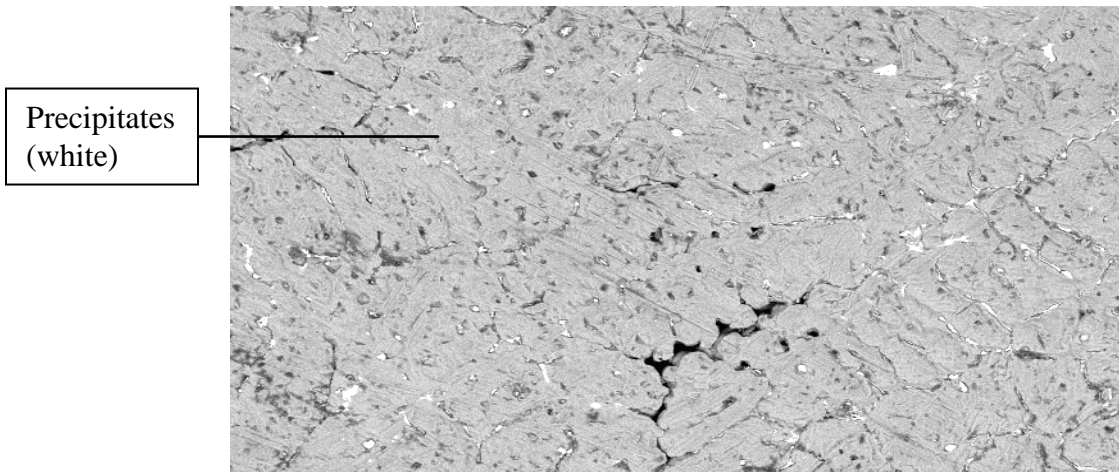
Micrograph 1: Microstructure of the As-Cast A2009 Alloy.



Micrograph 2: Microstructure of the Aged Hardened A2009 Alloy.



Micrograph 3: SEM Microstructure of the Unreinforced Al-Cu-Mg alloy/EDS Spectrum (x400). The structure reveals the presence of Cu_3Al_2 , Al_6CuMg_4 phases in α -Al-matrix(white)



Micrograph 4: SEM Microstructure of the Al-Cu-Mg Alloy after Thermally Aged-Hardened at 200°C after Peak aged (x400). The structure reveals dissolution and precipitation of Cu_3Al_2 , and Al_6CuMg_4 (white) Phases in α -Al matrix .

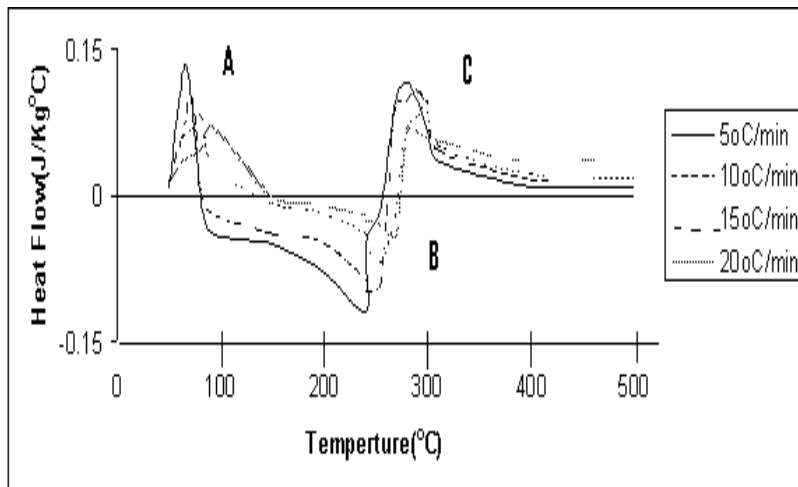


Figure 1: DSC, Thermograms of the Solutionized and Quenched A2009 Alloy at Various Heating Rates.

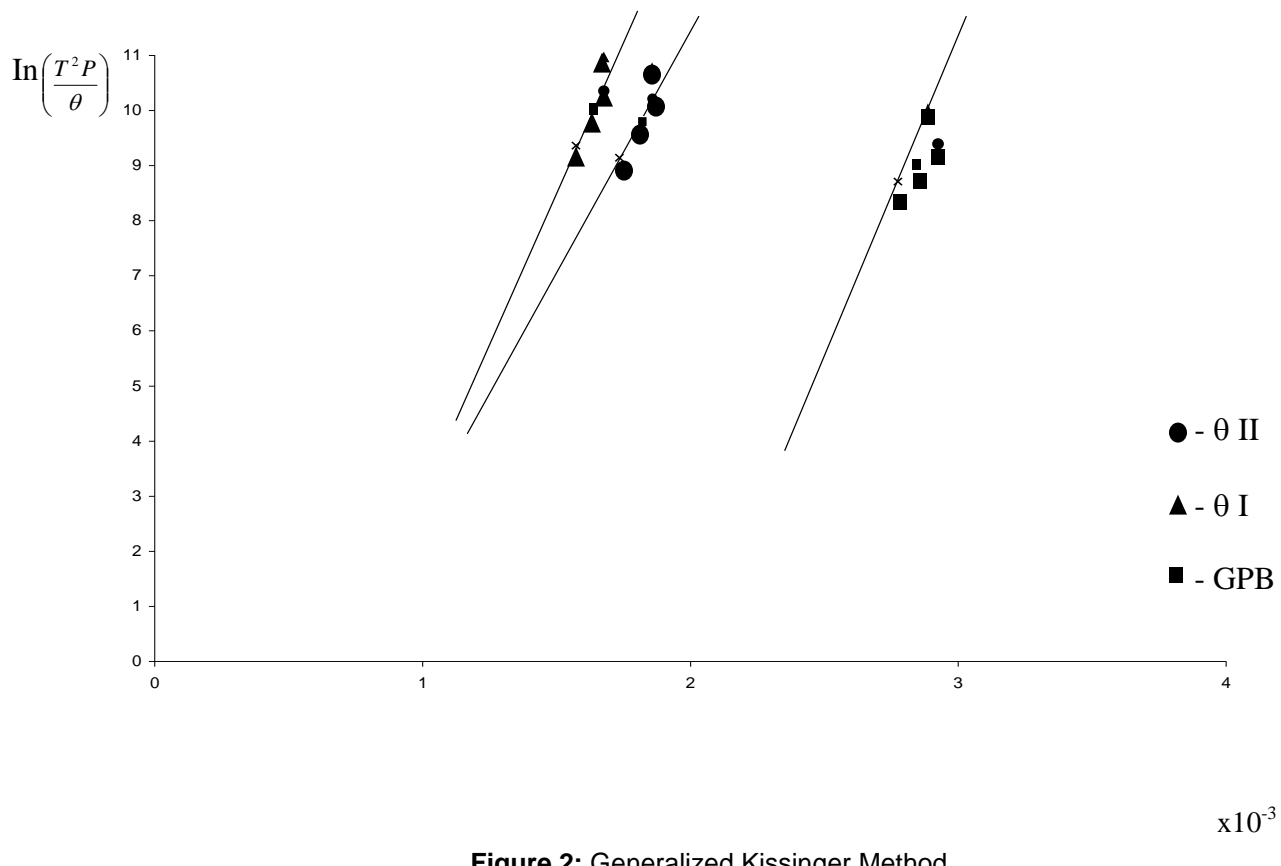


Figure 2: Generalized Kissinger Method.

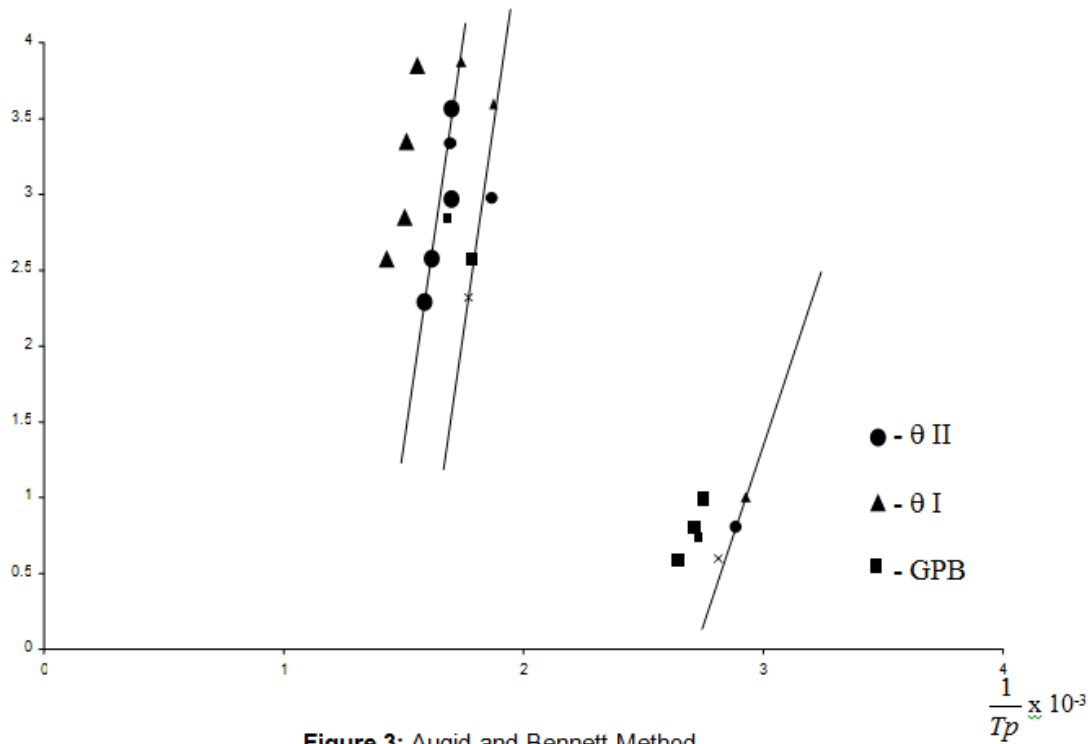


Figure 3: Augid and Bennett Method.

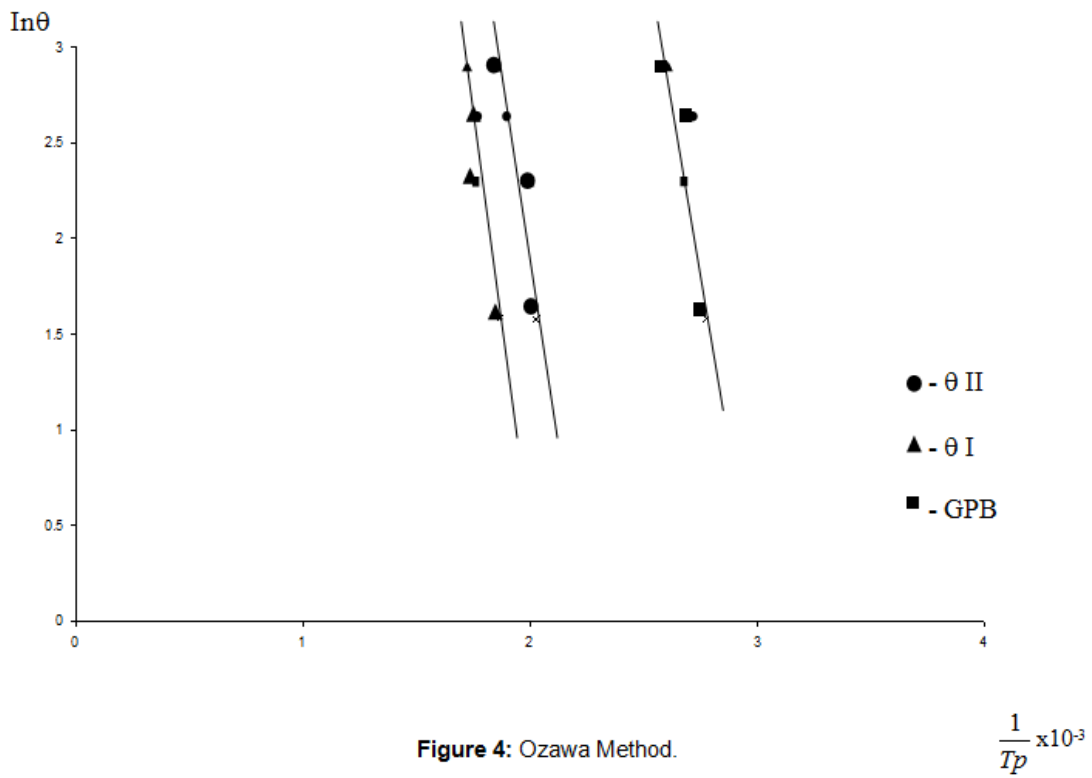


Figure 4: Ozawa Method.

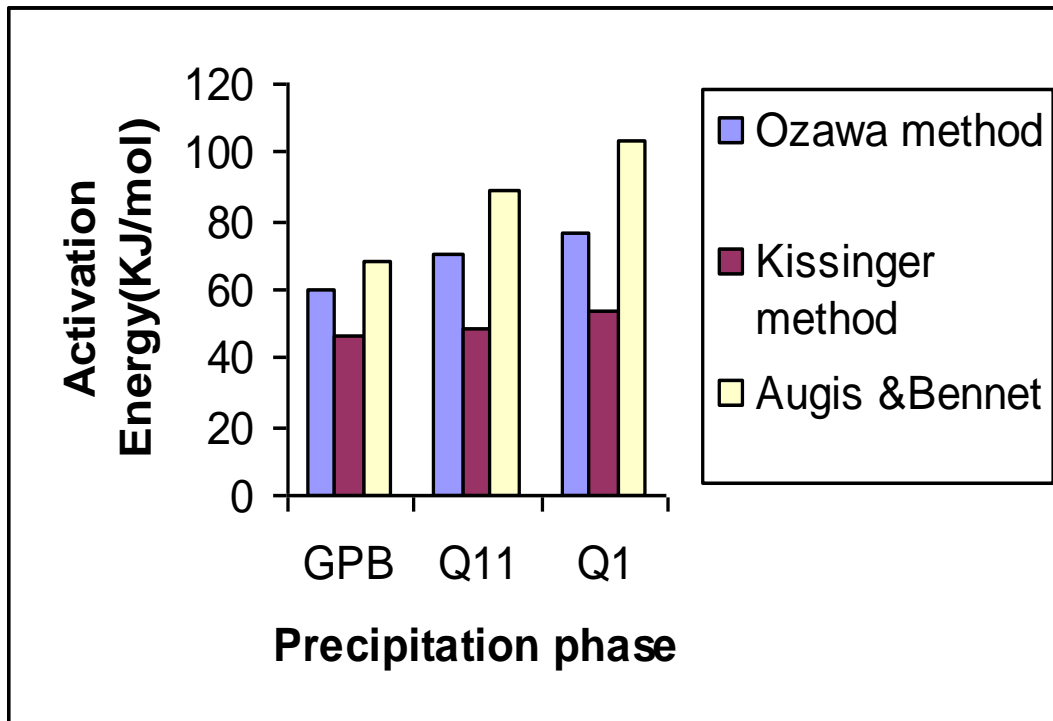


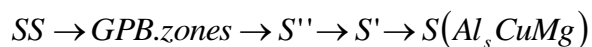
Figure 5: Variation of Activation Energy with Precipitation Phase.

Table 1: The peak Temperature for the DSC, Thermograms.

DSC Peak Temperatures			
Heating rate (°C/min)	Peak A (°C) GPB Zone	Peak B (°C) Θ^{11}	Peak C (°C) Θ^1 & S^1
5	64.00	240.00	280.00
10	72.50	240.70	291.00
15	81.00	255.50	300.08
20	92.90	270.00	310.00

Discussion

Microstructural Study: The microstructure of the Al-Cu-Mg alloy reveals the Al_2CuMg phase in the aluminum matrix (see Micrographs 1 and 3). In the as-cast condition, Cu and Mg is present both in solid solution with the matrix and precipitated as the Al_2CuMg phase that is present both at grain and along the grain boundaries. Ghosh et al. (2004) revealed that the general sequence of precipitation in Al-Cu-Mg alloys with is as follows:



where GPB zones are Cu and Mg containing Guinier-Preston zones, and S' is a slightly strained semi coherent version of the incoherent S (Al_2CuMg).

Since the formation enthalpies of the two variants are the same, S' and S will be considered to be the same phase in this study. The metastable S phase is the predominant precipitate in the Al-Cu-Mg alloy.

Ageing the as-cast material enhances precipitation of the phase (Al_2CuMg) along grain boundaries, formation and distributions of the

precipitates both at grain and along the grain boundaries (see Micrographs 2 and 4).

Differential Scanning Calorimeter (DSC) Study:

The curve in the Figure 2 consists of similar heat effects and the principal features of interest in this study are the two exothermic peaks, A and C, and the one endothermic effects B. Peak A is attributed to GPB zone formation and it is a characteristic thermal effect in the 2xxx series of aluminum alloys. Trough B has been ascribed to the dissolution of GPB zones (Θ^{11}). The second exothermic reaction zone C reveal single peak and has been ascribed (Θ^1). Peak C is not different from the single exothermic peak attributed by various workers to precipitation of the S ($A_{12}CuMg$) phase. Thus, the thermal effects associated with S' \rightarrow S transformation may not be sufficient to exhibit a separate peak during the DSC scan.

In rising-temperature techniques such as the DSC, the extent of transformation at any particular temperature can be controlled by thermodynamic equilibrium or kinetic limitations. In thermally activated processes the heat effects shift to higher temperatures with increasing heating rate. Figure 1 show that the formation and dissolution of GPB zones and the formation and dissolution of the S' and θ' phases are dominated by their reaction kinetics. The average values of the reaction peak temperatures associated with these transformations are shown in Table 1. The peak temperatures correspond to the points of maximum enthalpy of formation or dissolution. The peak temperature for GPB zone formation is less in the material. This suggests that GPB zone formation requires a lower driving force compare to the peak temperatures for GPB zone dissolution and $\theta' + S'$ formation.

The DSC peak A of the alloy at various heating (see Figure 1) due to GPB zone formation. From Figures 2-4 the effective activation energies for GPB zone formation in alloy using the three models were obtained. These values agree fairly well with the results obtained from the AJM (Avrami-Johnson Mehi) analysis. The migration energy of vacancies in Al-Cu-Mg alloys has been reported to be in the range 41-66.9 kJ/mol. The values of activation energy for GPB zone formation obtained in the present study for A2009 using the varying-heating rate method are 59.62, 46.05 and 67.9KJ/mol using Ozawa, Kissinger,

Augis & Bennet methods, respectively. Ozawa, and Kissinger methods are within this range, and are lower than those reported in the literature by Papazian(1982) $E = 61.0 \pm 2.2$ kJ/mol and $E = 53.9 \pm 1.6$ kJ/mol for A8090 using the DSC and resistivity techniques, respectively.

The endothermic trough B in Figure 1 is associated with GPB zone dissolution. Figures 2-4 show the plots using in calculating the activation energy of GPB zone dissolution using the three models. From the plots one can therefore say that, the GPB zone dissolution reaction is kinetically controlled. The dissolution of GPB zones in some aluminum alloys has been attributed to a diffusion-limited mechanism. The value of activation energy obtained for GPB zone dissolution are 69.96, 48.90 and 88.66KJ/mol using Ozawa, Kissinger, Augis and Bennet methods, respectively, all the values are lower than the value of 123.9 kJ/mol and 128.5 ± 3.5 kJ/mol reported in the literature (Miesel and Cote, 1983, Richardson and Charsley, 1998), respectively.

The activation energy for solute diffusion during the GPB zone dissolution reaction includes the activation energy for formation of excess vacancies and that for solute transport. This implies lower effective activation energy for GPB zone dissolution in a vacancy-deficient environment than that in a vacancy-rich environment.

Starink and Mourik (1992) have reported that GPB zone dissolution reaction is essentially a two-step process. After the formation of GPB zone during a DSC scan, at least two reactions can occur on continued heating: (i) GPB zone dissolution (endothermic) and (ii) GPB zone coarsening (exothermic). In the present study, the temperature range of GPB zone dissolution during the DSC scan is conducive for solute diffusion.

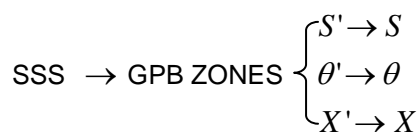
The activation energy for S' and θ' formation A2009 alloy material from the slopes of the plots in Figures 2-4 using the three models are 76.04, 54.04 and 103.93KJ/mol using Ozawa, Kissinger, Augis & Bennet methods respectively, are lower the values reported by previous workers. Jena et al obtained $E = 129.9$ kJ/mol for Al-3wt.%Cu-0.79wt.%Mg alloy, Youdelis and Fang (1994) reported $E = 109.6 \pm 12.4$ kJ/mol, The discrepancy between the results obtained in the present work and the quoted data is attributed to

differences in material composition, mass transfer resistance, and environment (matrix environment). In all these three models study Kissinger method has the lower activation energy (see Figure 5).

CONCLUSIONS

In the present work, DSC and metallographic techniques have been used to characterize the microstructure and behavior of A2009. From the results presented and discussed in the preceding section, the following conclusions can be made:

1. The ageing sequence of the alloy does alter from those of others aluminum alloy in this series.
2. The microstructure of the Al-Cu-Mg alloy reveals the Al_2CuMg phase in the aluminum matrix.
3. The precipitation and dissolution of GPB zones and the metastable S' and θ' phases are kinetically controlled in the alloy.
4. The kinetic parameters determined for the formation and dissolution of GPB zones using the three models are within the limits of experimental errors.
5. In all these three models study Kissinger method has the lower activation energy.
6. Since Kissinger method has the lower activation energy, it is recommendation for studying the precipitation reactions of the alloy in this series.
7. A precipitation sequence for the alloy, based on the current DSC investigation, is proposed as: (i) formation and dissolution of GPB zones; and (ii) concurrent formation and dissolution of metastable phases (S' and θ'). That is:



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