AD-A171 981 A DIFFERENTIAL SCANNING CALORIMETRY STUDY OF GUINIER PRESTON ZONE FORMATI..(U) NAVAL AIR DEVELOPMENT CENTER WARMINSTER PA AIRCRAFT AND CREW S.. W FRAZIER 1/1

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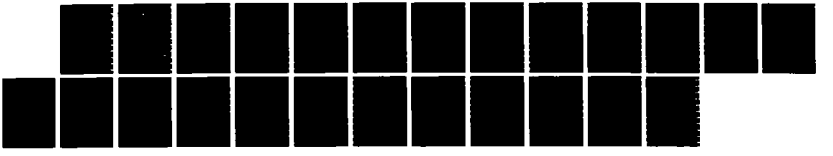

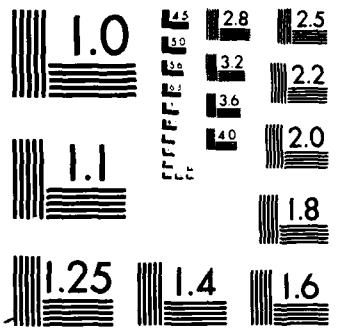
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REPORT NO. NADC-85169-60

(12)

A DIFFERENTIAL SCANNING CALORIMETRY STUDY OF GUINIER PRESTON ZONE FORMATION AND DISSOLUTION IN 7075 AND 7091 ALUMINUM ALLOYS

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30 DECEMBER 1985

FINAL REPORT
Airtask No. A310310A/01B/4F61542000

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Prepared for
OFFICE OF NAVAL TECHNOLOGY
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REPORT DOCUMENTATION PAGE

AD-A171881

1a REPORT SECURITY CLASSIFICATION: Unclassified	1b RESTRICTIVE MARKINGS: N/A
2a SECURITY CLASSIFICATION AUTHORITY: N/A	3 DISTRIBUTION AVAILABILITY OF REPORT: Public Release
2b DECLASSIFICATION DOWNGRADING SCHEDULE: N/A	
4 PERFORMING ORGANIZATION REPORT NUMBER(S): NADC-85169-60	5 MONITORING ORGANIZATION REPORT NUMBER(S): N/A
6a NAME OF PERFORMING ORGANIZATION: Aircraft and Crew Systems Technology Directorate; 6b OFFICE SYMBOL (If applicable): 6063	7a NAME OF MONITORING ORGANIZATION: N/A
6c ADDRESS (City, State, and ZIP Code): Naval Air Development Center, Warminster, PA 18974-5000	7b ADDRESS (City, State, and ZIP Code): N/A
8a NAME OF FUNDING SPONSORING ORGANIZATION: Office of Naval Technology; 8b OFFICE SYMBOL (If applicable): 225	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N/A
8c ADDRESS (City, State, and ZIP Code): Department of the Navy, Washington, DC 20361	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO: See; PROJECT NO: Reverse; TASK NO: Side; WORK UNIT ACCESSION NO:

11 TITLE (Include Security Classification)
A Differential Scanning Calorimetry Study of Guinier Preston Zone Formation and Dissolution in 7075 and 7091 Aluminum Alloys

12 PERSONAL AUTHOR(S)
William Frazier

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Final	FROM _____ TO _____	1985 December 30	20

16 SUPPLEMENTARY NOTATION

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
7091 Aluminum; RST; Powder Metallurgy; High Strength Aluminum; Extrusion

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The aging behavior of P/M 7091 and IM 7075 aluminum were studied by DSC; also hardness and conductivity. The energy associated with the formation and dissolution of Guinier Preston zones is correlated to mechanical and physical properties; equations for conductivity and hardness as a function of heat of reaction are presented. The activation energy for GP dissolution was established by differential scanning calorimetry (DSC) and values for ΔH^*, ΔG^*, and ΔS^* were calculated using absolute reaction rate theory. The activation energy calculated for GP dissolution in 7075-T6 is equivalent to the activation energy reported for the diffusion of Zn in aluminum.

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20 DISTRIBUTION AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL: William Frazier	22b TELEPHONE (Include Area Code): (215)441-1301; 22c OFFICE SYMBOL: 6063

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

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INTRODUCTION

Aluminum 7075 and 7091 are two important precipitation hardening alloys. The precipitation process is complex and involves a series of interdependent steps . SSS → GP → n'' → n' → n; where SSS is the supersaturated solid solution, GP stands for Guinier Preston zones, n'' and n' are semi-coherent hexagonal precipitates of Mg and Zn, and n is the thermodynamically stable incoherent precipitate, $MgZn_2$. Differential scanning calorimetry (DSC) in conjunction with transmission electron microscopy (TEM) has been used to characterize the precipitate morphology (1, 2). A good correlation exists between DSC thermograms and the precipitation behavior of 7000 series alloys but models relating mechanical and physical properties to the DSC thermograms are lacking (3, 4).

Both 7075 and 7091 are used in two tempers: peak strength (T6) and overaged (T7). An essential part of the aging process involves a four day natural aging step which develops a homogeneous distribution of GP zones. The GP zones are extremely small clusters of Mg and Zn atoms. Those formed at room temperature are reported to be 20-30 x 10^{-10}m in diameter. The GP zones are the nuclei from which the more stable precipitates can grow. The microstructure of the peak strength tempered aluminum has been reported to consist of 5% n' and 95% GP zones of 30-60 x 10^{-10}m diameter with a density of 10^{12} GP/mm^3 (5, 6). Thus, the GP zones represent the predominant precipitate in the T6 tempered material and make a significant contribution to the alloy's excellent mechanical properties.

This investigation centers on the formation and dissolution of GP zones during the natural aging process. DSC work was done in order to determine the stability of fully developed GP zones by establishing their activation energies for dissolution. GP zone formation was studied using DSC, electrical conductivity, and hardness measurements made at periodic intervals during the natural aging process. This permitted correlation to be made between heat of formation/dissolution, and the electrical conductivity and hardness response of these alloys.

EXPERIMENTAL PROCEDURE

Coupons of 7075 and 7091 (1/2" x 1/2" x 1/4") were solutionitized at 482°C. for two hours and cold water quenched. Electrical conductivity was measured in units of %IACS (international annealed copper standard) using an eddy current conductivity meter. Both hardness (Rb) and conductivity were measured periodically during natural aging.

Thermal analysis was performed on a DuPont 1090 Thermal Analyzer employing a DSC module. Discs of 7075 and 7091 were heat treated in the same manner as the conductivity specimens. The power required to heat the 7075 and 7091 alloys was electronically subtracted from the power needed to heat a disc of pure aluminum of similar mass. Periodically during the aging process, DSC runs were performed at a heating rate of 10°C./min. Specimens naturally aged a minimum of 12 days were thermally analyzed at heating rates of 2, 10, and 20°C./min.

RESULTS

The results are divided into two categories: 1. the thermodynamic quantities for GP dissolution obtained for 7091 and 7075 naturally aged 12 days, and 2. the relationships between heat of reaction, electrical conductivity and hardness for naturally aged 7075 and 7091 aluminum.

The Differential Scanning Calorimetry (DSC) plots for 7075 and 7091 aged at room temperature are shown in Figures 1 and 2. The thermograms for 7075-T6 and 7091-T6 are shown in Figures 3 and 4. The graphs of the naturally aged material are divided into three regions: 1. GP formation/dissolution (50-150°C.), 2. n' formation/dissolution and n formation (150-280°C.), and 3. n dissolution (> 280°C.). (3,4) The term "heat of reaction" as used in this report refers to the area under the first peak occurring between 50-150°C. They are plotted in Figure 5. The curve has a sigmoidal shape initially positive, and as aging progresses becomes negative.

RELATIONSHIP BETWEEN HARDNESS, CONDUCTIVITY AND HEAT OF REACTION

The hardness vs. log time and conductivity vs. log time plots also appear sigmoidal. Upon naturally aging, hardness increased from R_B 40 to R_B 78 and conductivity decreased from 32 to 27% IACS as shown in Figures 6 and 7. Figures 8 and 9 show the conductivity and hardness data plotted against the heat of reaction. Both relationships appear linear, and regression analysis yields the following relationships:

7091

$$B = 1.41\,\Delta H + 66.4 \quad (1)$$

$$s = 0.13\,\Delta H + 28.29 \quad (2)$$

7095

$$B = 0.82\,\Delta H + 67.2 \quad (3)$$

$$s = 0.13\,\Delta H + 24.4 \quad (4)$$

Where B is hardness in R_B units:

s is electrical conductivity in % IACS

ΔH is the heat reaction in Jg^{-1}

The coefficient of correlation, r, is shown in each figure.

ACTIVATION ENERGY FOR GP ZONE DISSOLUTION

The activation energies for GP dissolution were determined, according to ASTM E 698-79 (6) by determining the slope of $\log \beta$ vs. $1/T$ as shown in Figure 10, 11, and 12. The slope was calculated by a regression analysis where β is heating rate in °C. $min.^{-1}$ and T is the peak temperature in K. The peak temperature is that temperature where the reaction rate is maximum.

The activation energy (E*) was calculated using:

$$\text{(ref. 7)}\quad E^* = 2.19R\,\frac{\Delta \log B}{\Delta (1/T)} \quad (5)$$

The value of E* was refined by using an iterative technique presented in ref. 6. The specific rate constant can be calculated by:

$$k = ko \exp \frac{[-E^*]}{RT} \quad (6)$$

Where the term ko is given by:

$$ko = B\,E^*\,\exp\frac{[E^*]}{RT}\,(RT^2)^{-1} \tag{7}$$

THERMODYNAMIC POTENTIALS

From absolute reaction rate theory,

$$K = \frac{RT\exp(-\Delta G)}{hN\quad RT} = \frac{RT\exp}{hN}\,\frac{(-\Delta H)\exp}{RT}\quad\frac{(\Delta S)}{R} \tag{8}$$

where

R is the universal constant
h is Plank's constant
N is Avogadros number

Rearranging equations 6, 7, and 8 produces (ref. 3)

$$\Delta H = E - RT \tag{9}$$

$$\Delta G = RT\,1n\,\frac{(KhN)}{RT} \tag{10}$$

$$\Delta S = \frac{(\Delta G - \Delta H)}{T} \tag{11}$$

The value of ΔG, ΔH, ΔS, and E are presented in Table 1. The free energy of activation of 7091 and 7095 naturally aged and in the T6 condition are similar; the value of ΔG for the dissolution of GP zones in the T6 temper is at 130.9 KJ mol^{-1} substantially higher, reflecting its greater strength and higher thermal stability of the precipitate formed during artificial aging.

DISCUSSION OF RESULTS

Mechanical and physical properties depend a great deal on the microstructure of an alloy. Supersaturated solid solutions, obtained by rapid quenching from solution heat treatment temperatures, generally have low electrical conductivity and are soft compared to age hardened aluminum. The increase in yield strength and hardness during natural aging is directly related to the precipitation of coherent/semicoherent particles.

CONDUCTIVITY

Classical physical metallurgy principles state that electrical conductivity should increase during aging since solute atoms are removed from the matrix. In this study, 7075 and 7091 alloys exhibit a decrease in conductivity with natural aging commonly called "the resitivity maximum". This is a consequence of the complex precipitation process. During room temperature aging, only a fraction of the solute is removed from the matrix, perhaps not enough to significantly increase conductivity. The GP zones that precipitate are of a size and distribution that interferes with the standing waves of the conduction band electrons. The GP zones formed have significant strain

fields and these apparently contribute more toward impeding electron movement than does the decrease matrix solute to increase electron mobility, hence, decreased electrical conductivity.

This study has shown electrical conductivity and hardness to be functions of the heat of reaction. This appears reasonable, since during mechanical deformation processes energy is required to pass dislocations through the material, breaking atomic bonds; and the heat of reaction is a measure of the quantity and stability of the strengthening precipitates. During the initial few minutes of natural aging, few GP zones have nucleated, and so the material's resistance to deformation is small. A DSC thermogram made at this time yields a large exothermic peak corresponding to GP zone nucleation (Figures 1 and 2). After several thousand hours of natural aging, the majority of GP zones have nucleated and grown. These zones then provide a great deal of resistance to dislocation motion and require thermal energy to dissolve. This absorption corresponds to the endothermic peaks on the DSC thermographs of Figures 1 and 2.

FREE ENERGY OF ACTIVATION

The GP zones formed at room temperature in 7075 and 7091 have similar free energies of activation: 107 KJ mol^{-1}. The entropy contribution to the free energy of activation is slightly larger for 7091 than it is for 7075 (Table 1). Aging 7075 and 7091 to the T6 condition stabilizes the GP zones. This is reflected by the increase in free energy of activation from 106 to 131 KJ mol^{-1}. This value corresponds well with the value of 137 KJ mol^{-1} previously reported (2).

The activation energy calculated for GP dissolution in 7075 is 119 KJ mol^{-1}. This figure compares well with the reported value of the activation energy for the diffusion of Zn in aluminum, 120 KJ mol^{-1} (7). This is reasonable since Zn is a major constituent of the precipitated phase.

CONCLUSIONS

1. The heat of reaction for GP zone formation/dissolution as determined by DSC analysis is linearly related to hardness and electrical conductivity.

2. Conductivity decreases with room temperature aging due to the formation of GP zones.

3. The free energy of activation for 7075 and 7091 are similar when naturally and artificially aged.

4. The activation energy for GP zone dissolution in 7075-T6 is similar to the activation energy for the diffusion of zinc in aluminum.

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TABLE 1

THERMODYNAMIC QUANTITIES FOR G.P. ZONE DISSOLUTION

Alloy	ΔG^* (KJ mol^{-1})	ΔH^* (KJ mol^{-1})	ΔS^* (J $mol^{-1}K^{-1}$)	E^* (KJ mol^{-1})
7075-T6	130.9	115	-34.2	119
7075 - Nat. Aged	106.0	92.3	-36.5	95.4
7091 - Nat. Aged	106.1	87.1	-50.8	90.2

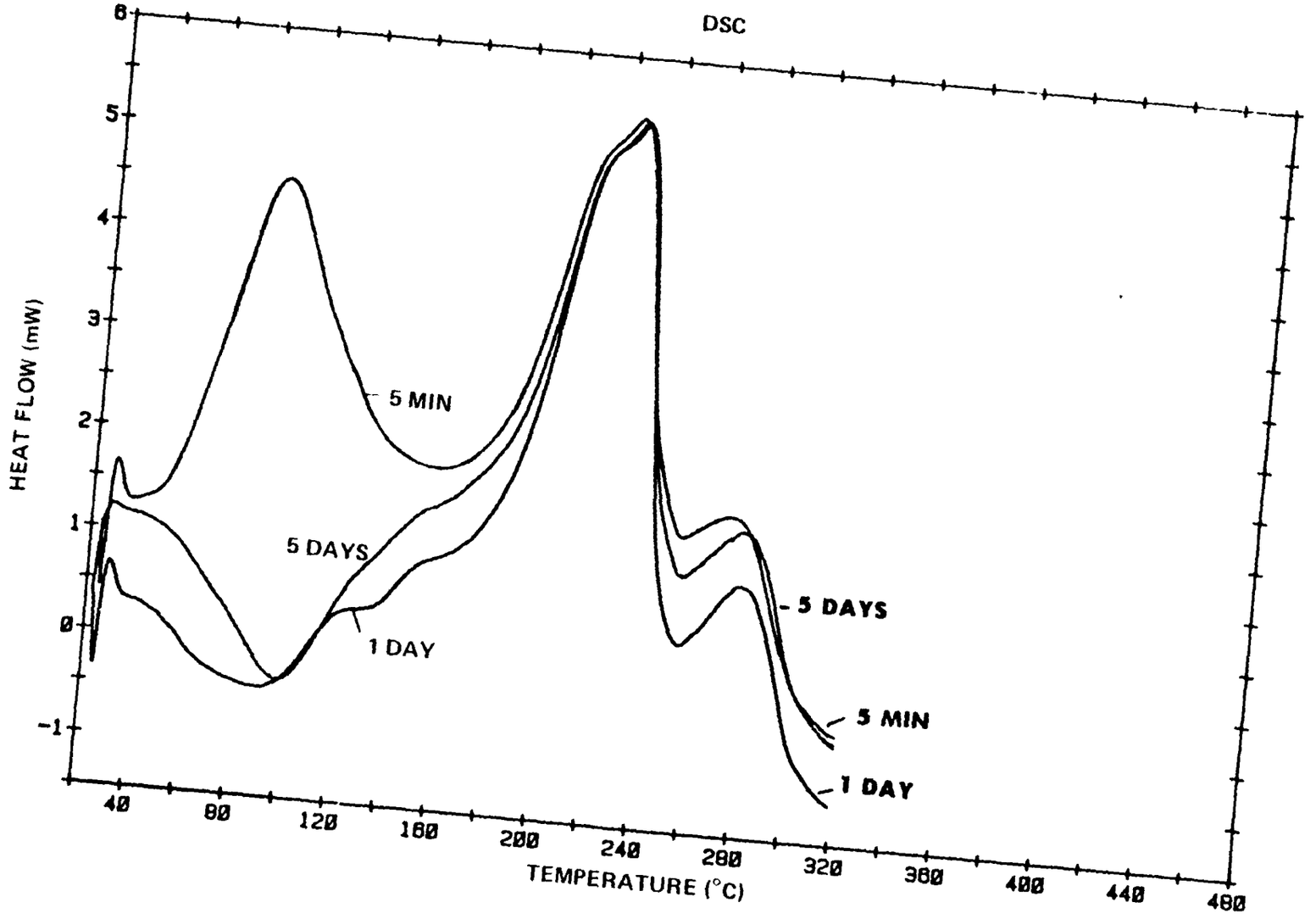

Figure 1. DSC of Naturally Aged 7091 Aluminum Alloy

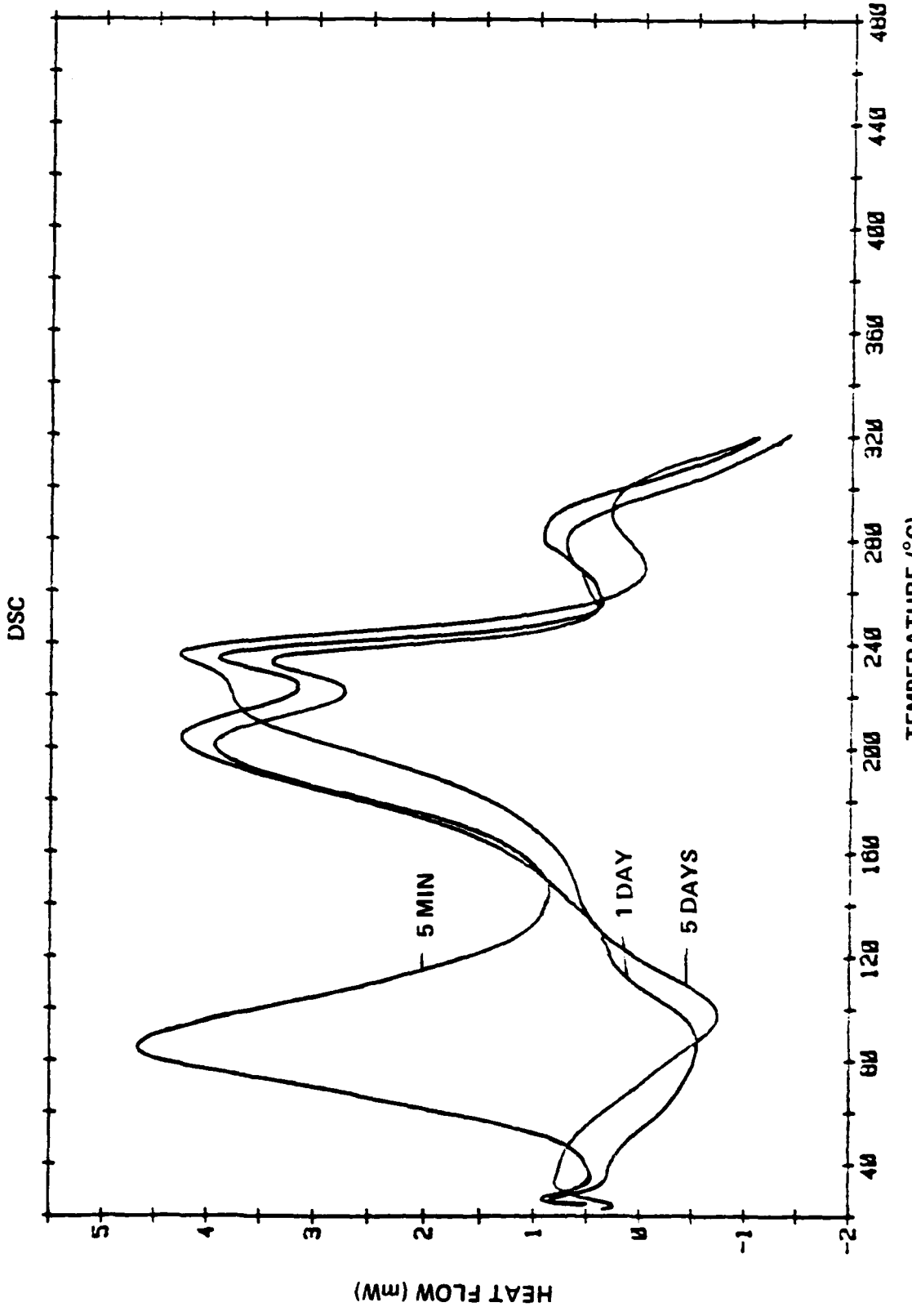

Figure 2. DSC of Naturally Aged 7075 Aluminum Alloy

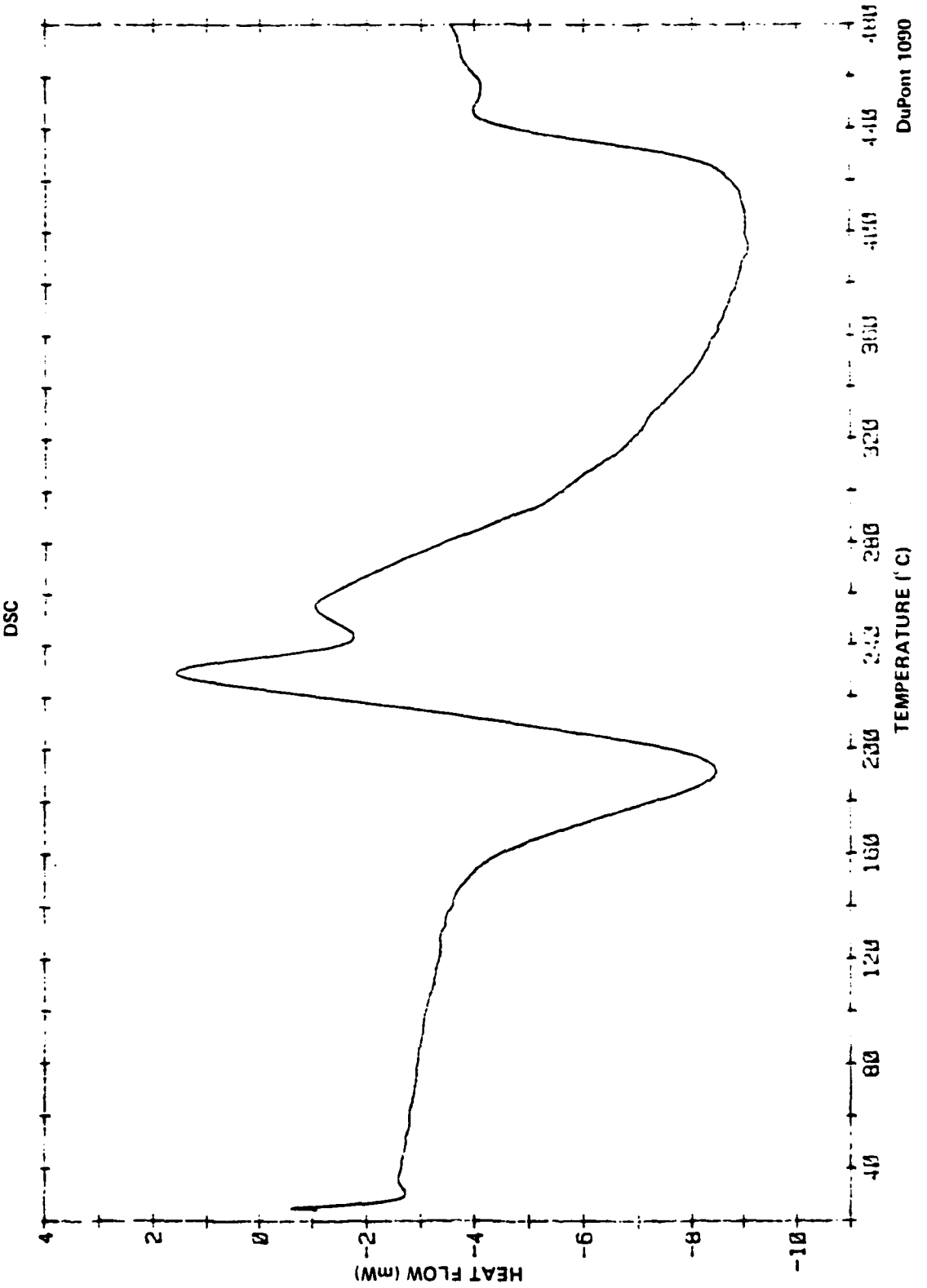

Figure 3. DSC of 7075-T6 Aluminum Alloy

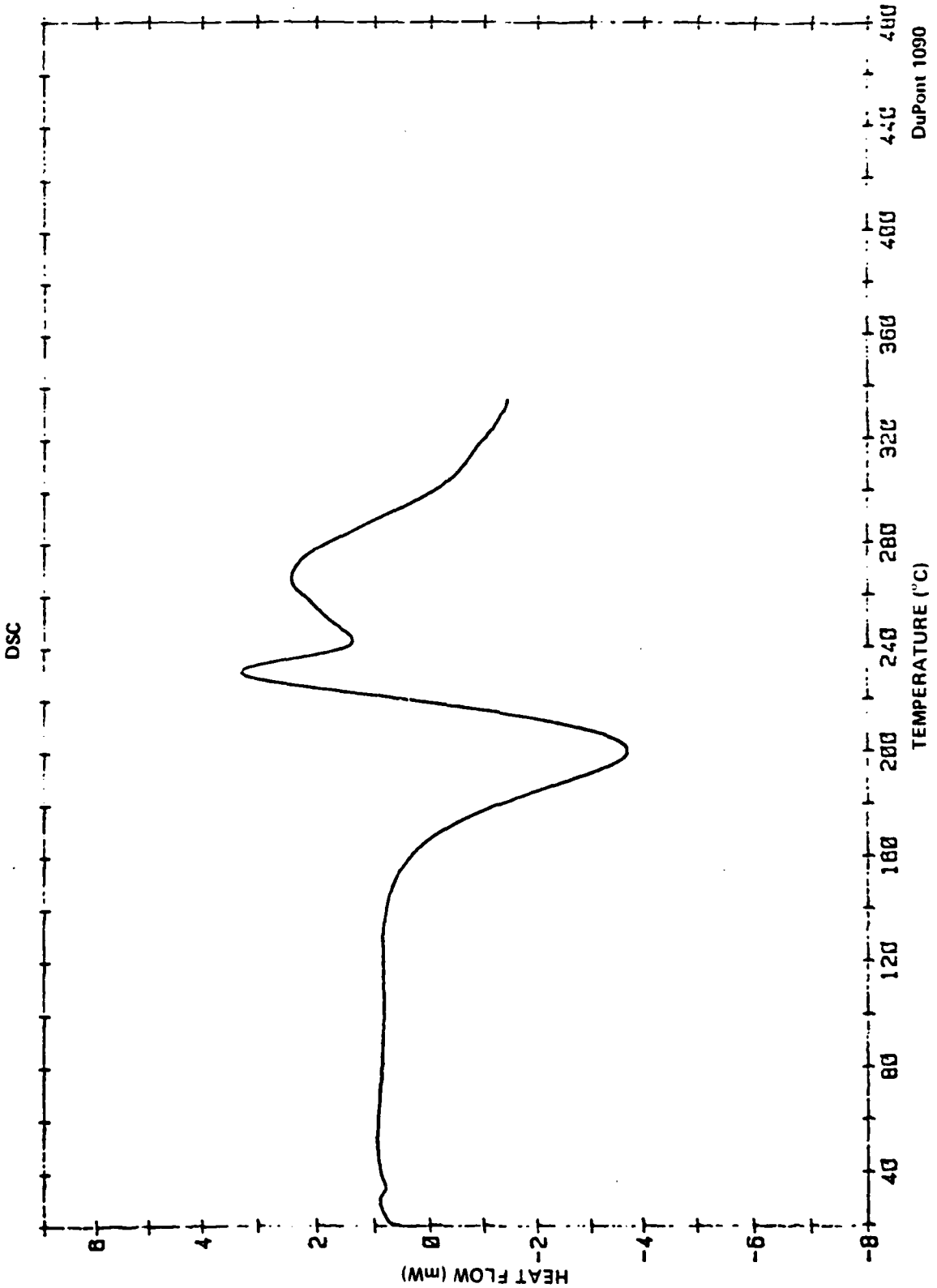

Figure 4. DSC of 7091-T6 Aluminum Alloy

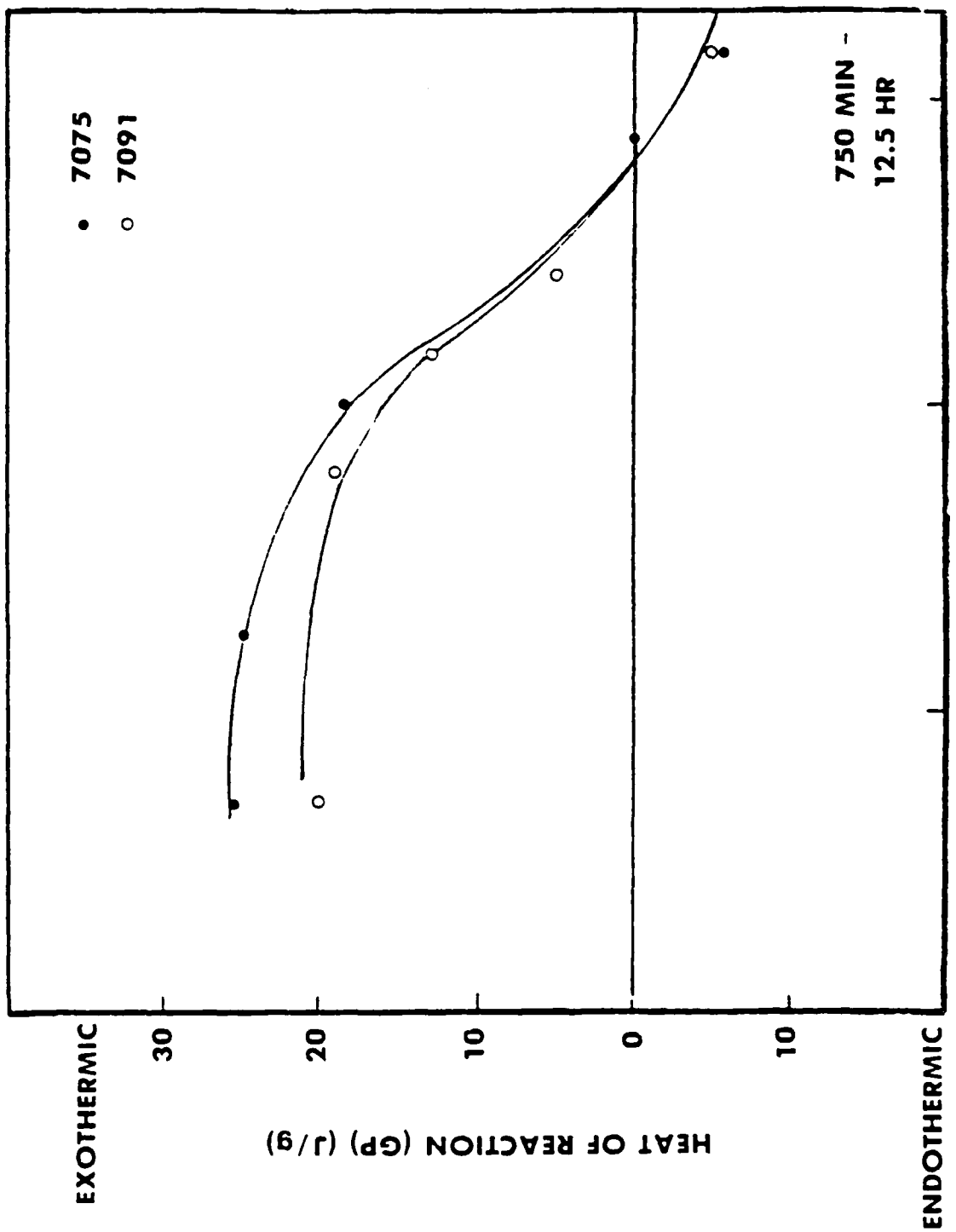

Figure 5. Naturally Aging Effect on the Heat Reaction During GP Zone Formation Dissolution

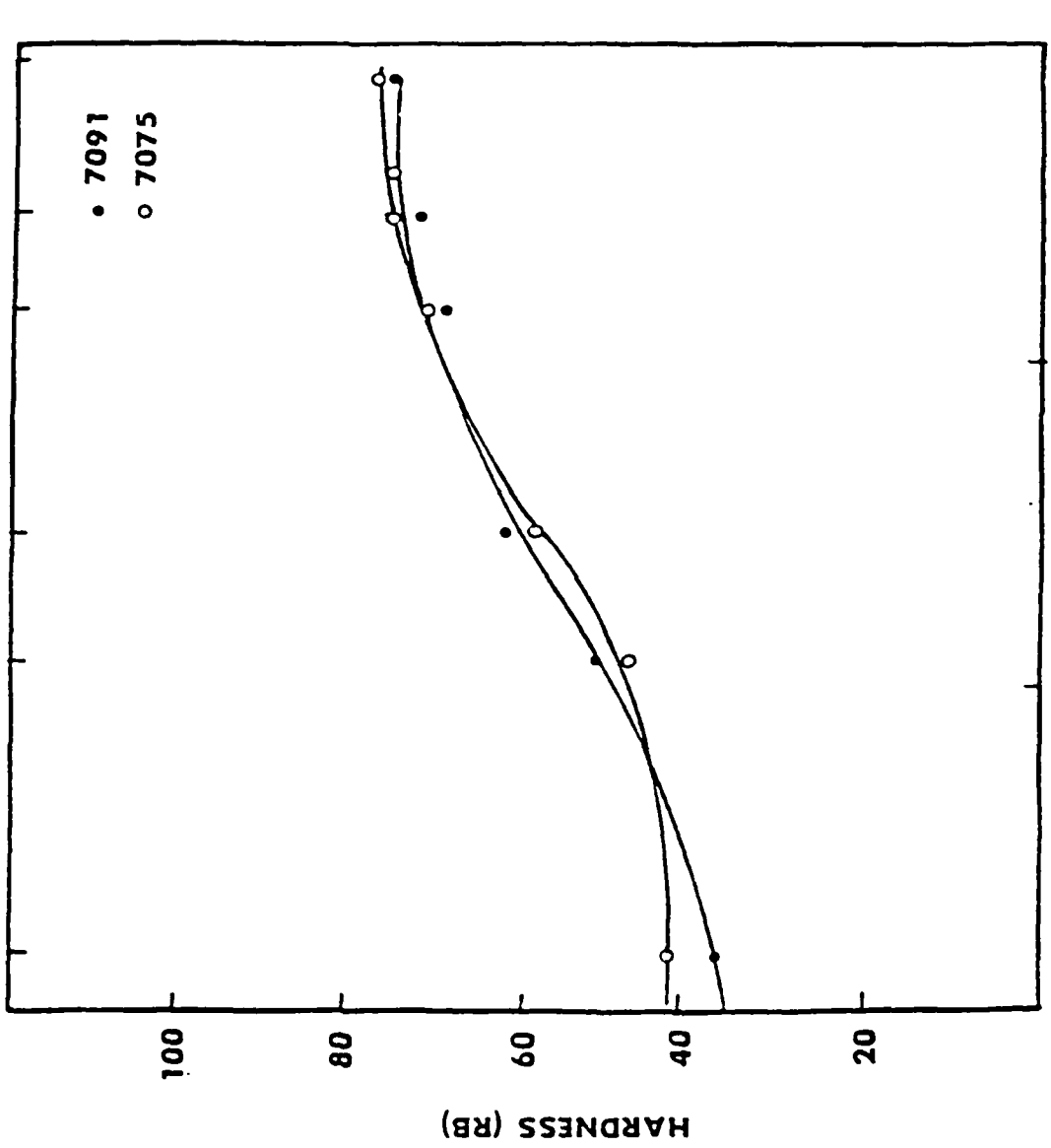

Figure 6. Hardness Profile of Naturally Aged 7091 and 7075 Aluminum Alloy

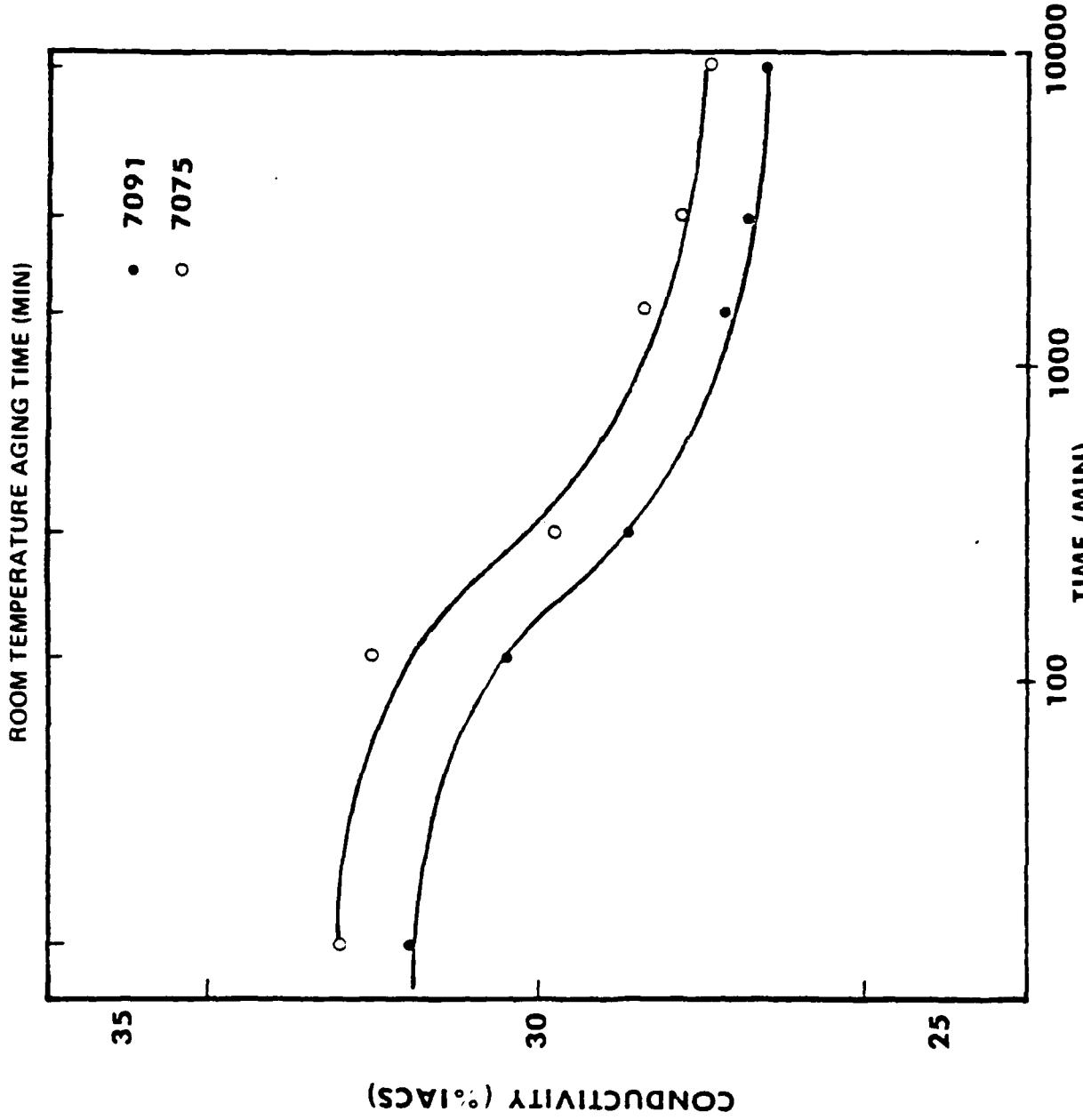

Figure 7. Conductivity Profile of Naturally Aged 7091 and 7075 Aluminum Alloy

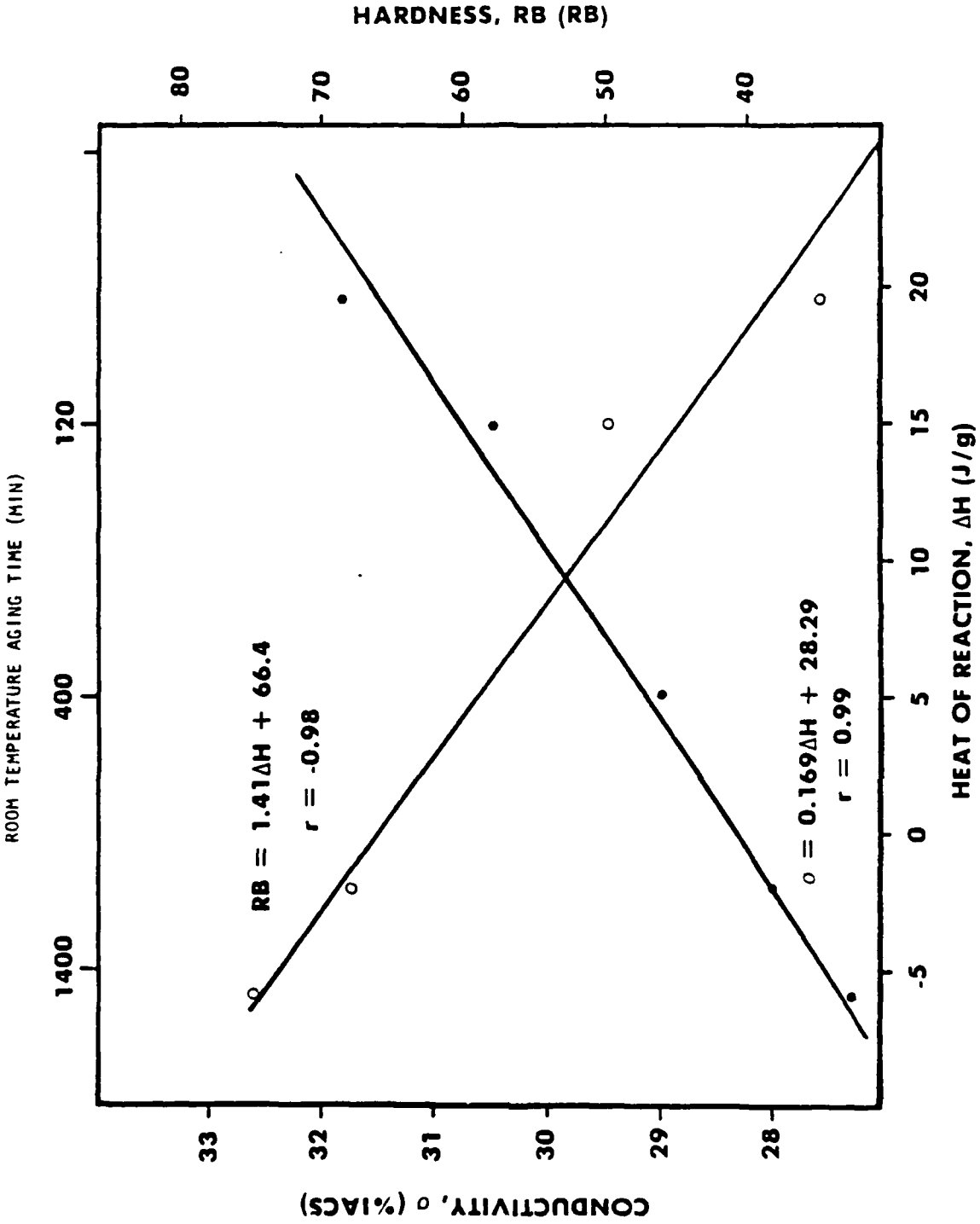

Figure 8. Linear Relationship Between the Heat of GP Dissolution, Conductivity and Hardness in 7091 Aluminum

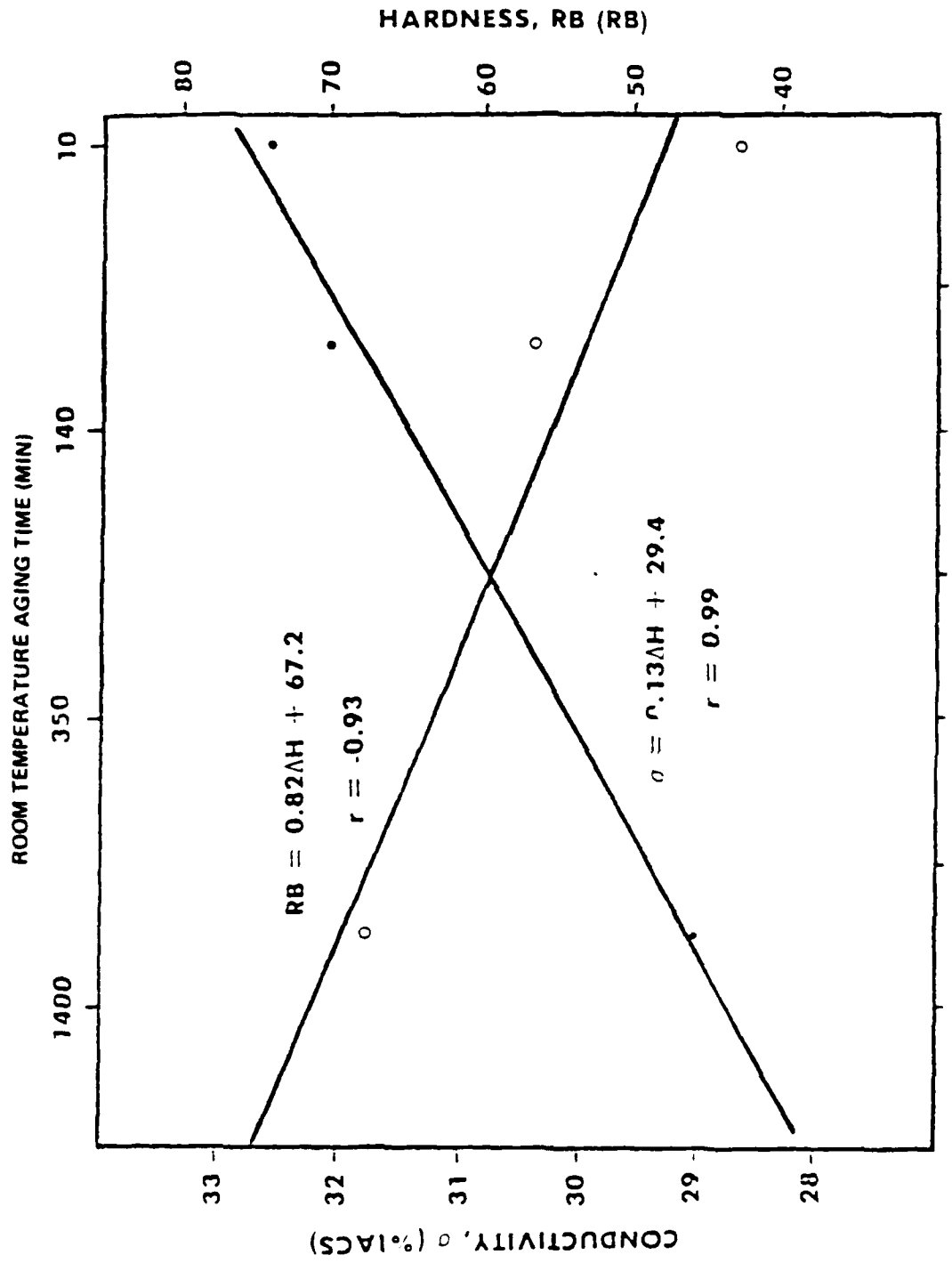

Figure 9. Linear Relationship Between the Heat of GP Dissolution, Conductivity and Hardness of 7075 Aluminum

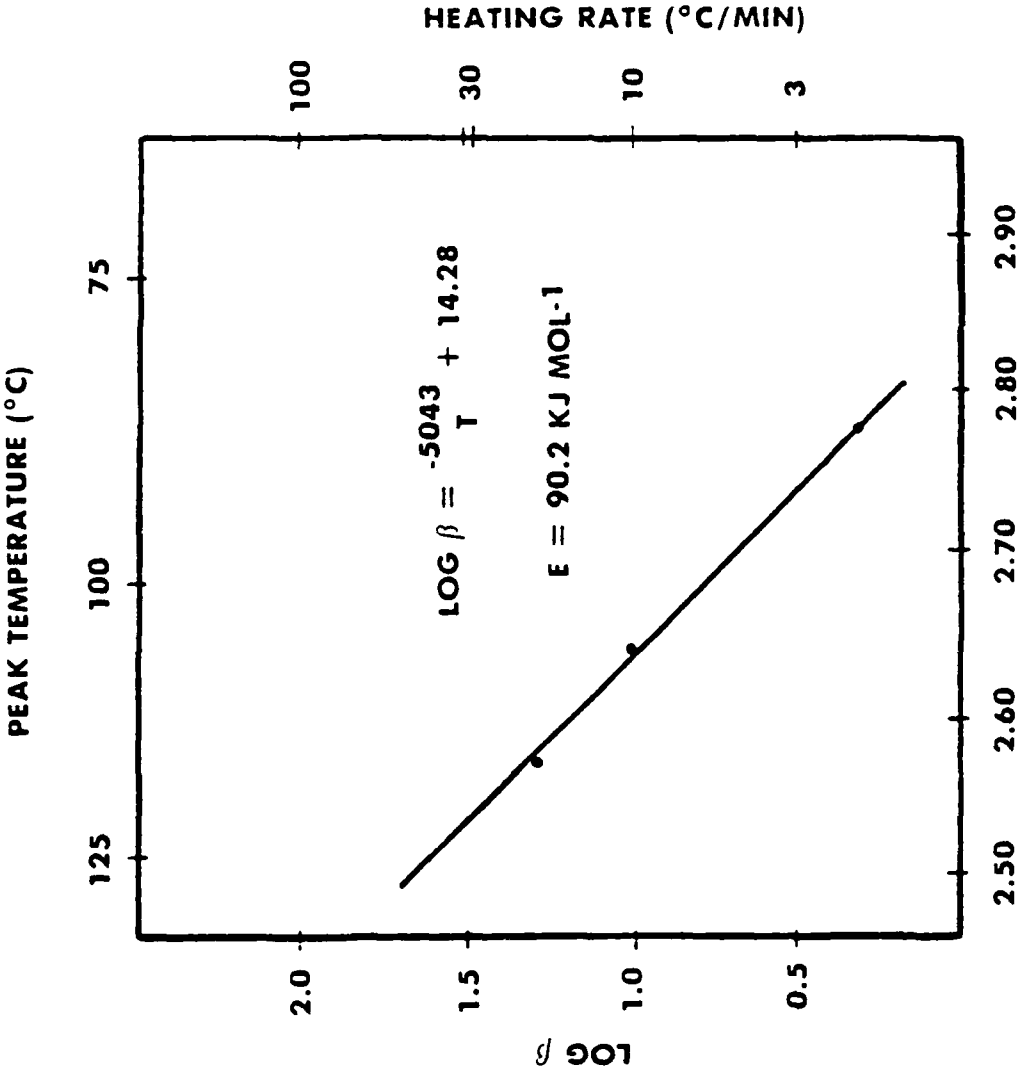

Figure 10. Thermal Data for GP Dissolution in 7091 Aluminum

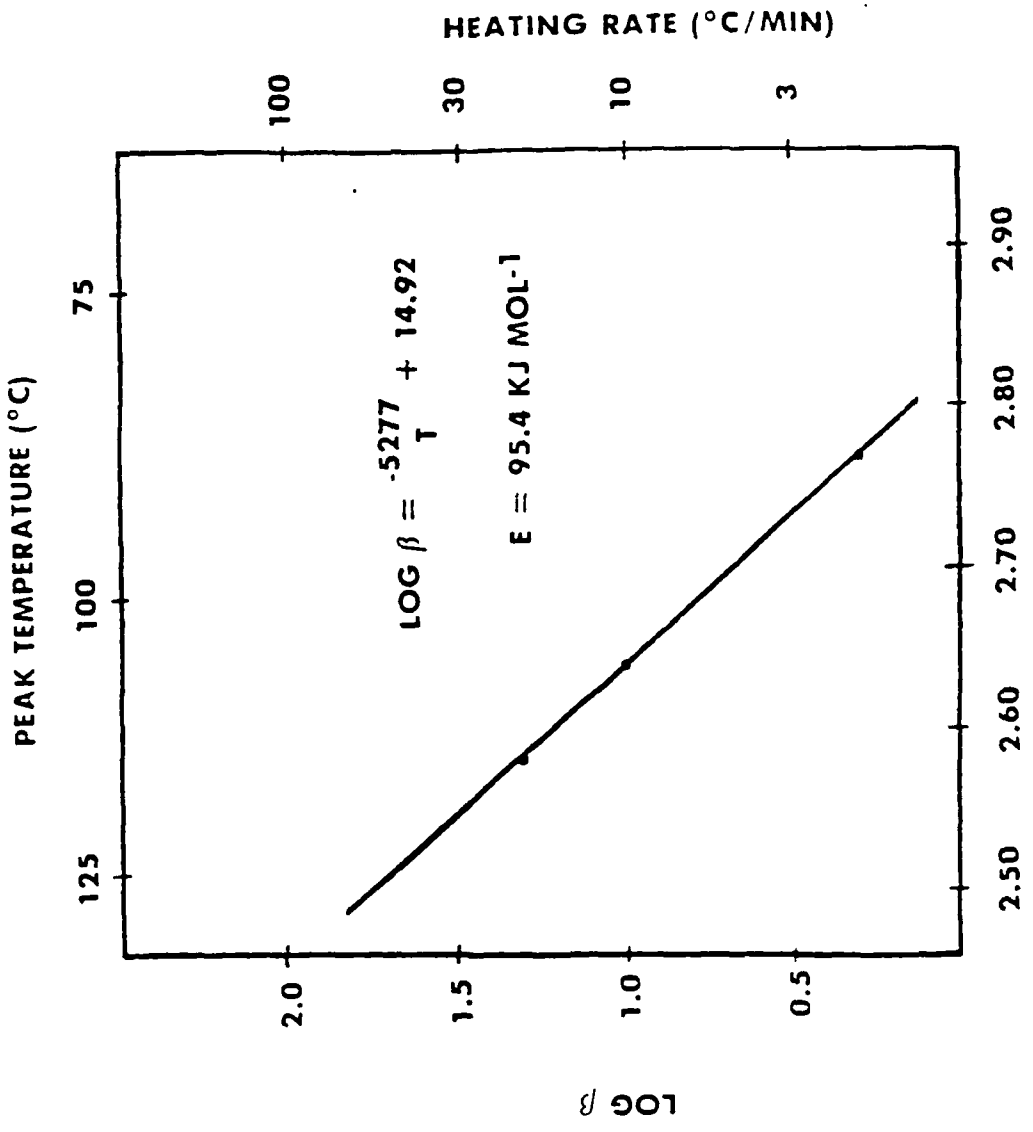

Figure 11. Thermal Data for GP Dissolution in 7075 Aluminum Alloy

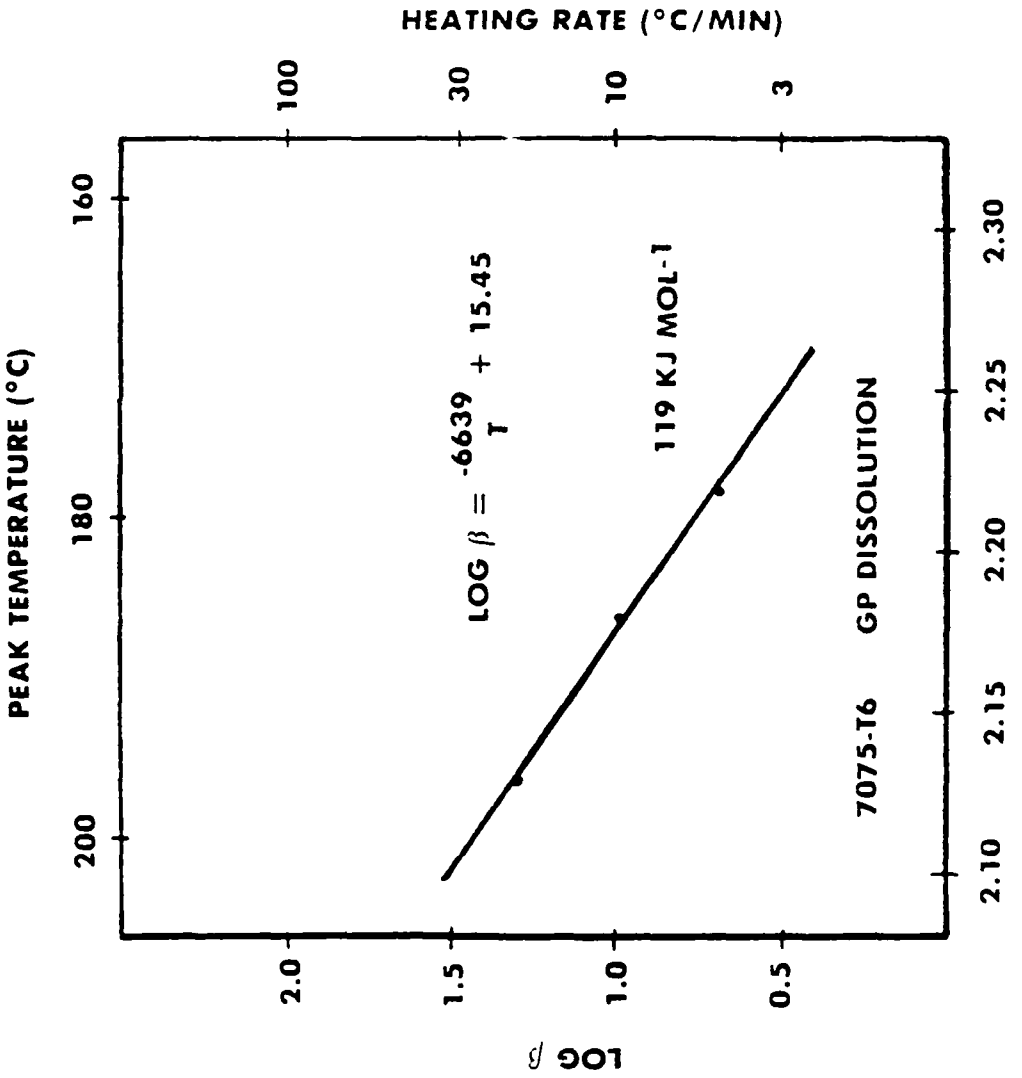

Figure 12. Thermal Data for GP Dissolution in 7075 T6 Aluminum Alloy

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