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IRREVERSIBLE DIMENSIONAL CHANGES AND THE INITIAL GRAPHITIZATION KINETICS IN ANNEALED PYROLYTIC GRAPHITE

Technical Report by

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IRREVERSIBLE DIMENSIONAL CHANGES AND THE INITIAL GRAPHITIZATION KINETICS IN ANNEALED PYROLYTIC GRAPHITE

ABSTRACT

The irreversible dimensional changes in the "a" and "c" directions in pyrolytic graphite have been studied as a function of time (up to 4 hours) and temperature (2500 to 2800 C). The change in the "c" lattice parameter has also been studied. Activation energies for the initial stages of dewrinkling and graphitization have been obtained.

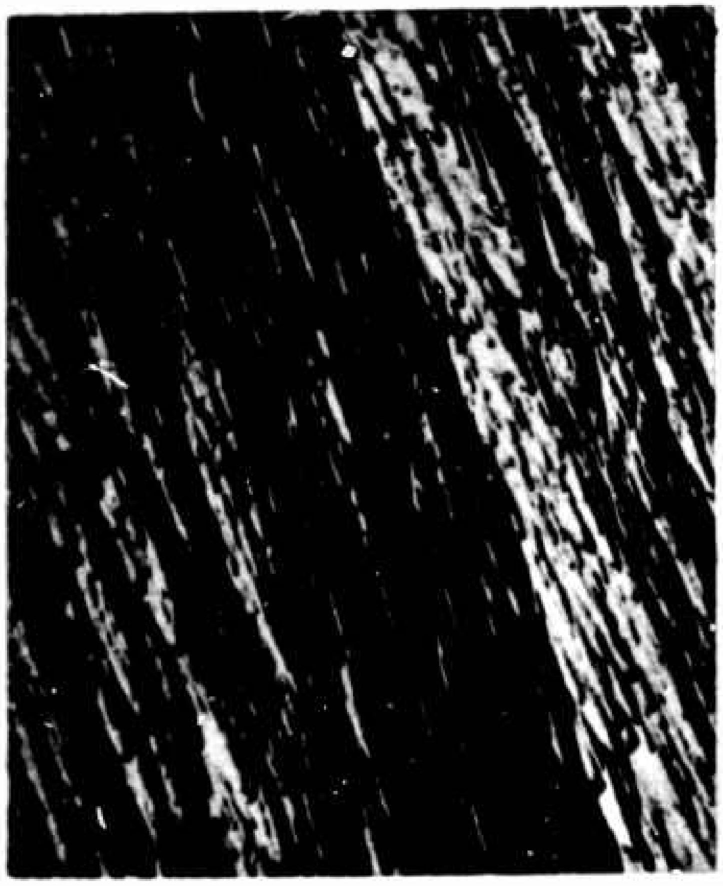
INTRODUCTION

Pyrolytic graphite is known to exhibit substantial irreversible dimensional changes upon prolonged exposure to temperatures above its deposition temperature.[1-5] However, little is known about the kinetics of this process, as the bulk of the measurements of these irreversible dimensional changes have been made after a relatively long time at temperature (> 4 hours).[4] Since irreversible dimensional changes as large as 16 percent have been observed[5] in the "c" direction compared with a maximum possible decrease in this direction due to graphitization (that is, decrease of the interlayer spacing) of about 2.3 percent, the irreversible dimensional change must be due to some mechanism other than graphitization. Generally, this phenomenon has been attributed to the dewrinkling of kinked sheets of graphite.[4,5] The area of the graphitization kinetics of pyrolytic graphite is also one deserving more study. Although many studies of the graphitization kinetics of conventional graphites have been made, only two studies on pyrolytic graphite[5,6] and one on boronated pyrolytic graphite[7] are available. These studies, however, were performed on powdered specimens. Pyrolytic graphite is known to possess large mechanical stresses as deposited and since these stresses have been shown to strongly affect the recrystallization of pyrolytic graphite,[8] it is probable that the behavior of massive pyrolytic graphite should differ from the powdered material in which one may assume that the deposition stresses have been relieved.

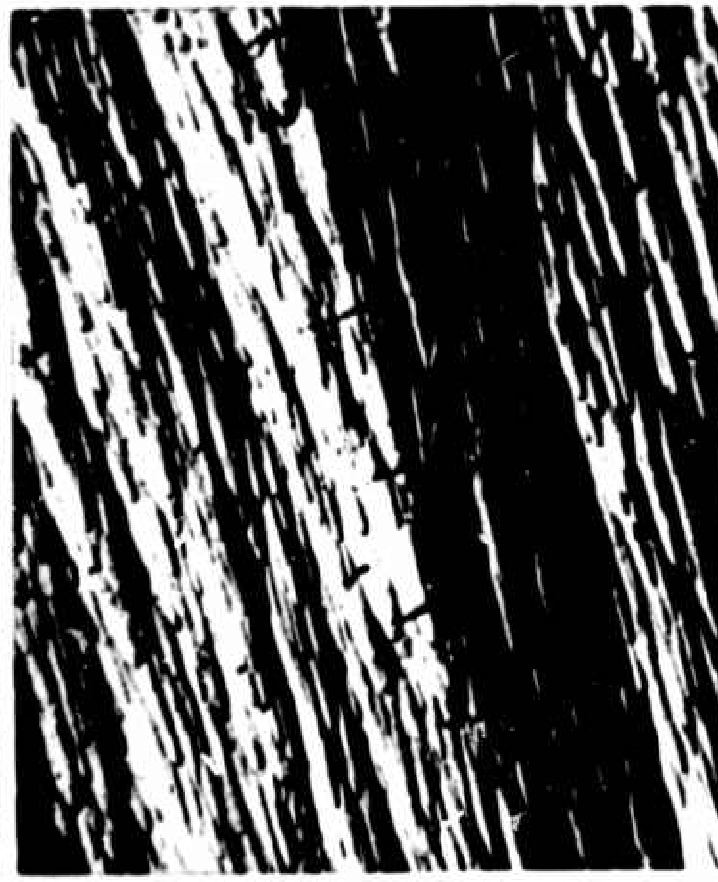
In this paper the authors will present data on the irreversible dimensional changes in pyrolytic graphite in the temperature range of 2500 to 2800 C for times up to four hours. The initial activation energy for the process of dimensional change will be calculated. The changes in the lattice parameter in the "c" direction and the initial activation energy for graphitization will be presented for the same samples.

MATERIAL AND EXPERIMENTAL PROCEDURES

The material used in this study was a continuously nucleated, fine cone pyrolytic graphite deposited at 2000 C, obtained from the Raytheon Company. This material was 98.5 percent of theoretical density; the as-received microstructure is shown in Figure 1. Specimens 2 x 1/4 x 1/4 inch were cut from this material for subsequent measurement. The specimens were then placed in a fixture which allowed the simultaneous heat treatment of six specimens at a given temperature for a given time. Heat treatment was accomplished by lowering the specimens from a quenching tower into a carbon resistance furnace containing an argon atmosphere. After the specimens were in the furnace for the required time, they were withdrawn to the quenching tower and quenched in flowing argon for 1/2 hour. The use of the quenching tower minimized the time the specimens would reside at high temperatures. Typically, a sample would reach temperature in 3 to 5 minutes. All temperatures were monitored by an optical pyrometer and the temperatures quoted are ±20 C. The specimens were measured with a micrometer at their midpoints prior to and subsequent to heat treatment. The specimens were also weighed before and after heat

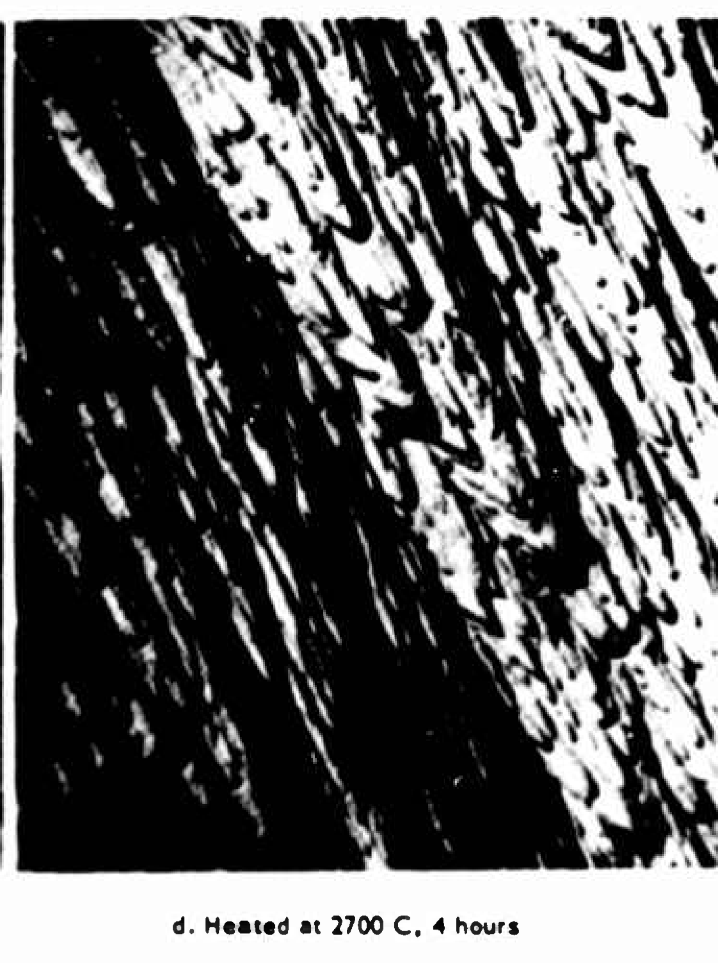


a. As-deposited



b. Heated at 2500 C, 4 hours

c. Heated at 2600 C, 4 hours



d. Heated at 2700 C, 4 hours

Figure 1. MICROSTRUCTURES OF CONTINUOUSLY NUCLEATED PYROLYTIC GRAPHITE
Polarized Light. Mag. 100X

treatment. The maximum weight loss due to vaporization corresponded to a $\Delta c/c$ of 0.04 percent, which is insignificant. Each data point represents the average of six specimens. The X-ray data was obtained on a diffractometer utilizing CuK_{α} radiation and measuring the (002) and (004) peaks.

RESULTS AND DISCUSSION

Figure 2a shows the irreversible percentage decrease in the "c" direction (deposition direction) and Figure 2b shows the irreversible percentage increase in the "a" direction (along the basal plane) for the heat-treated

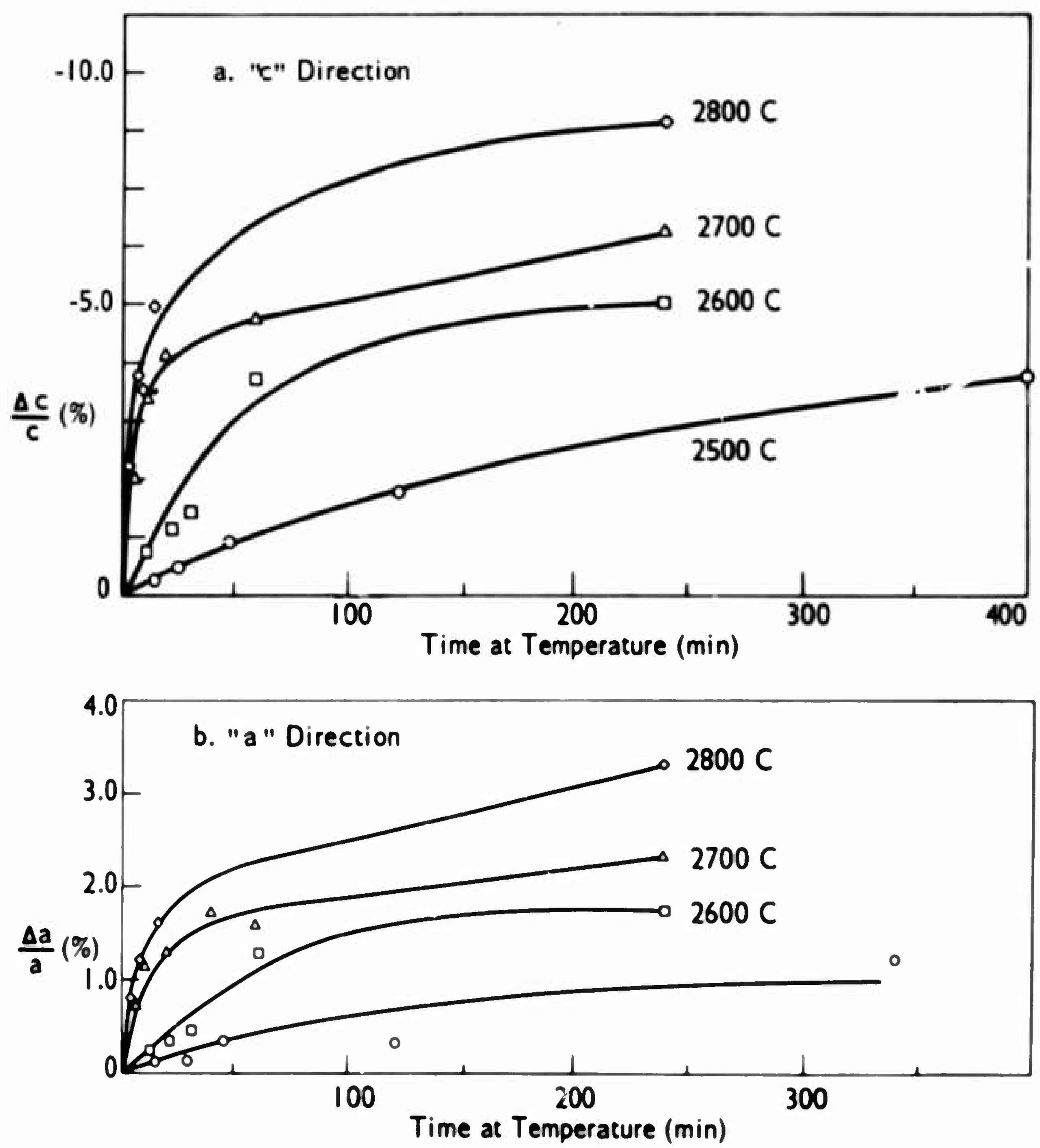


Figure 2. IRREVERSIBLE DIMENSIONAL CHANGES OF PYROLYTIC GRAPHITE AS A FUNCTION OF TIME AND TEMPERATURE

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pyrolytic graphite as a function of time and temperature. Although the rate of dimensional change decreases significantly after the first 50 to 100 minutes, there is no evidence that it will become negligible at times well beyond four hours.

If one plots the irreversible dimensional change versus temperature for a four-hour heat treatment as in Figure 3, it is observed that the current data are in good agreement with those of Richardson and Zehms[1] and Stover[2] but not in close agreement with those of Kotlensky and Martens.[3]

The X-ray data presented in Figure 4 show the decrease in the "c" lattice parameter with time and temperature. Here we notice a limiting "c" spacing of about 6.73 Å being approached with varying degrees of rapidity, depending on temperature. The limiting value seems to be somewhat above the ideal graphite layer spacing of 6.708 Å.

The activation energy for the initial stage of the dimensional change phenomena can be calculated from plotting the logs of the initial slopes of $\Delta c/c$ versus time curves against $1/T$°K. This is done in Figure 5. The activation energy obtained is approximately 281 kcal/mol. In a similar manner one can obtain the activation energy for the initial stage of graphitization from the initial time derivative of the "c" lattice parameter versus $1/T$ as in Figure 6. This value is approximately 180 kcal/mol. Clearly this difference in activation energies indicates a difference in the atomic mechanisms which may be responsible for the two phenomena.

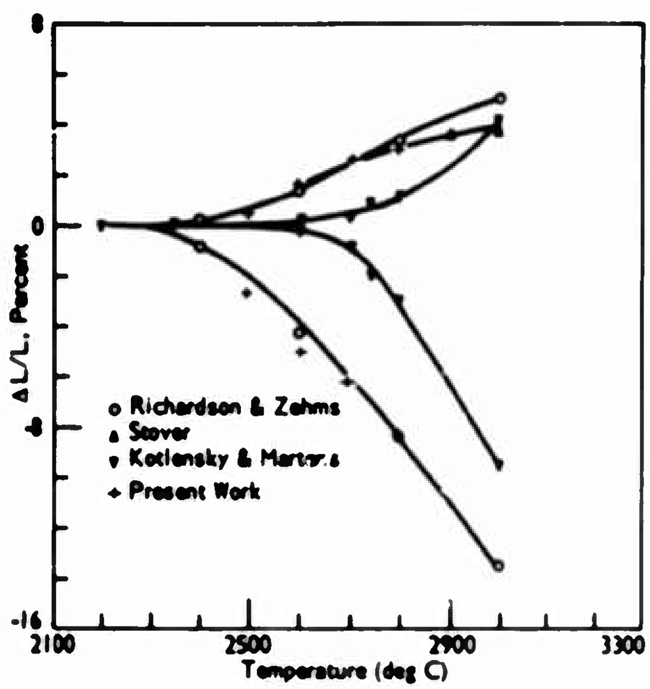

Figure 3. THE IRREVERSIBLE, GROSS DIMENSIONAL CHANGES IN PYROLYTIC GRAPHITE AS A FUNCTION OF TEMPERATURE AFTER A 4-HOUR HEAT TREATMENT (after Richardson & Zehms, Ref. 1)

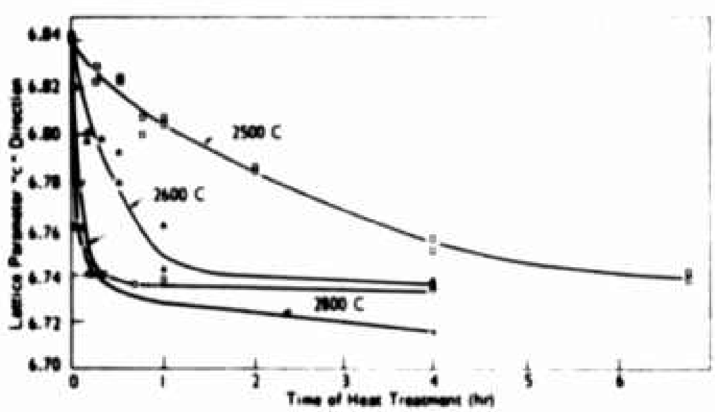

Figure 4. VARIATION IN "c" SPACING WITH HEAT TREATMENT OF PYROLYTIC GRAPHITE

The activation energy associated with the initial stage of graphitization found in this investigation is substantially below the previously reported values of 250 to 270 kcal/mol.[5,6] This discrepancy may be attributed to the different sample preparation involved. Blackman and Ubbelohde[8] have demonstrated the effect that the large residual deposition stresses have on the recrystallization of pyrolytic graphite. They showed that material with the highest degree of residual stress became the most ordered after annealing. Thus one might well suppose that residual stresses aid the graphitization process. The X-rayed surfaces of the bulk samples used in this work were those away from the deposition surface, and thus were areas of high residual stress prior to annealing. This stress presumably aided their graphitization. Powder specimens, on the other hand, would have substantially lost their deposition stresses by mechanical relaxation upon the loss of boundary constraints. These samples would then not have the deposition stress available to aid the graphitization process. To graphitize they would require more thermal energy and thus have a higher activation energy than the bulk specimens.

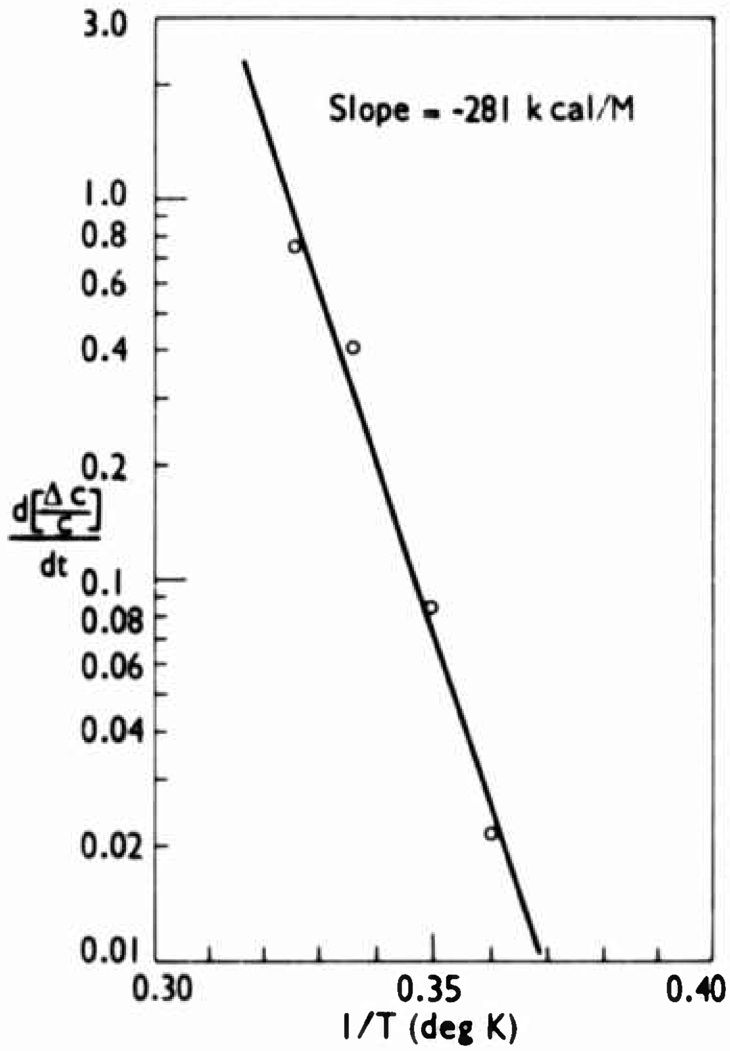

Figure 5. INITIAL SLOPE OF $\frac{d[\text{Irreversible Dimensional Change}]}{dt}$ VERSUS 1/T

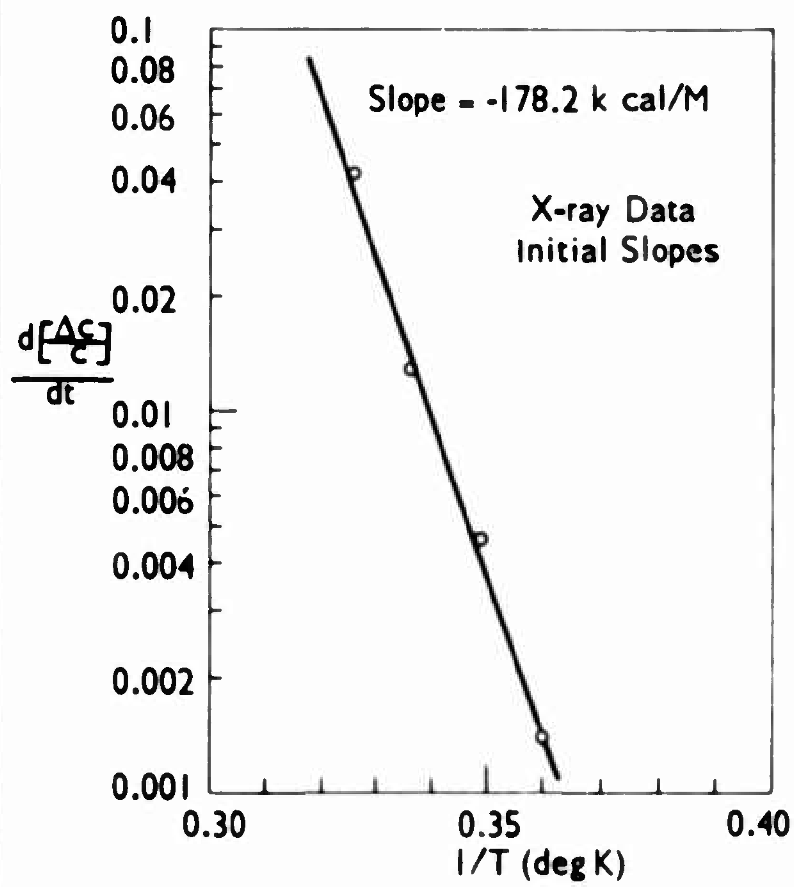

Figure 6. INITIAL SLOPE OF $\frac{d[\text{"c" Lattice Parameter}]}{dt}$ VERSUS 1/T

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