STRUCTURAL CHANGES ACCOMPANYING COKE CALCINATION

M. P. Whittaker, F. C. Miller and H. C. Fritz

Great Lakes Research Corporation

INTRODUCTION

Although a voluminous number of articles have been published on the structural changes occurring in carbons upon heat treatment over a wide 1200°C-2800°C temperature range, similar information for the narrow 500°C-1200°C calcination range is rather sparse. A few articles[1-4] have been written in which properties such as density, electrical resistivity and pore structure have been correlated with temperature of calcination and time at maximum temperature. It is, however, difficult to relate the various experimental results and conclusions reported. In this study the progression of structural changes occurring during the calcination of four raw coke samples from different sources was followed using high temperature microscopy techniques. Concurrent with the examination of the topographical features, the transformation of the microstructure of the carbons was studied by means of x-ray diffraction and mercury porosimetry.

EXPERIMENTAL

The high temperature microscopic examinations were performed using a Leitz Ortholux microscope equipped with a Leitz vacuum heating stage. Thin polished sections (≈0.03" thick) of the cokes were placed on a hollow graphite cylinder encompassing a Pt + 10% Rh vs. Pt thermocouple which had been calibrated against the melting points of several pure compounds. The sample and sample holder were then radiantly heated at a rate of ca. 30°C/minute in an inert atmosphere. A holding time of 5-10 minutes was allowed at each temperature to establish thermal equilibrium. Two representative areas were selected from each sample and photographed at a magnification of 35X with parallel and crossed nicols in the raw state, 300°C and at increments of 100°C to 1000°C. The dimensional and structural changes were obtained from 100X photographic enlargements.

In a complementary microscopic study relatively large lumps of the raw cokes were polished, and suitable areas were selected and photographed at 10X. These samples were then successively heated from 500°C to 1200°C in 100°C increments at a rate of 5°C/minute.

A 15,000 psi Aminco mercury porosimeter was used to obtain micropore volume distribution in representative samples of each coke as a function of heat treatment. The samples were crushed to 10/20 mesh particle size and duplicate measurements made on 0.5 g. samples.

X-ray diffraction studies were carried out employing a recording diffractometer using monochromatic Cu Kα radiation. Crystallite size values were obtained using the Scherrer formula with KCl as an internal standard.

RESULTS

A total of four cokes was studied in this investigation. As indicated by the characteristics of the four cokes listed in Table I, these samples are representative of an anisotropic coke (sample A&B) and an isotropic coke (sample C&D). The ash and sulfur contents and real densities of the raw cokes represent the range of values generally encountered with commercial cokes.

The type of changes in topographical features which the cokes underwent during calcination as revealed under the hot stage microscope are illustrated in Figure 1. The structure of the raw coke could be determined only with the aid of polarized light. Heating to 700°C produced very little change in the appearance of the polished surface of the samples except, perhaps, a slight increase in the width of existing cracks. Suddenly at 800°C, the detailed structure of the coke could be observed under parallel nicols. Further increase in temperature resulted in progressive opening of existing cracks, apparent creation of a few small cracks, and an obvious overall shrinkage. However, the basic macrostructure of the calcined coke was essentially the same as observed in the raw coke under polarized light. The two isotropic cokes had areas of pitch and mesophase which melted upon heating above 500°C producing voids lined with highly anisotropic carbon.

The magnitude of the dimensional changes observed as a function of temperature are illustrated in Figure 2 representing results typical of an anisotropic coke and in Figure 3 for a coke with an isotropic structure. The curves were plotted from data obtained with the hot stage (micro) and from ambient temperature measurements on the coke lump samples (macro). Considering the high temperature microscopy experiments, it should be noted that the dimensional changes recorded include the reversible thermal expansion of the carbon as well as shrinkage. The 1.0% to 2.5% linear expansion observed in all of the coke samples upon heating to 500°C is a manifestation of the reversible expansion. Contraction of the coke begins after 500°C with the maximum rate of dimensional change occurring between 700°C and 800°C. It is also significant to note in this same temperature range the marked shrinkage in the direction perpendicular to the needle structure as compared to that occurring parallel to the needle structure for the anisotropic cokes.

The information derived from the larger samples at room temperature correlates well with the high temperature measurements. The two sets of curves are similar in shape and the cross-over point of the shrinkage perpendicular and parallel to the flow structure occurs, within experimental error, at the same temperature. The weight losses calculated from these experiments suggest, as one would expect, a general direct relationship with the volatile content. Of more interest is the change in slope observed in the curves representing weight loss as a function of temperature which occurs in the 700°C to 800°C temperature range. This information for the two anisotropic and two isotropic cokes is given in Figure 4.

Mercury porosimetry measurements of 10/20M fractions were used to determine the accessible pore volume at each of the heat treatment temperatures. Pore volumes were determined in two pore size ranges, V_2 for pore diameters between 65 and 12μ and V_1 for diameters between 12 and 0.015μ. Although a gradual increase in V_2 with increasing

temperature was noted for all of the cokes, the results were usually erratic and appeared to reflect gross, non-uniform structural changes. The V_1 porosity behavior, as illustrated in Figure 5, is generally the same for both types of cokes. There is an overall increase in accessible porosity with increasing temperature. This increase in porosity is considered to be due to the formation of shrinkage cracks resulting primarily from loss of volatiles during calcination. As shown in Figure 5, three of the four cokes exhibited a relatively abrupt increase in porosity beginning at about 900°C, which would appear to be indicative of a significant structural change.

Changes in apparent density measured by mercury displacement were also determined concurrent with the porosity measurements. Figure 6 displays the trends in density change vs. temperature for the two types of coke studied. The A. D.'s of the cokes were observed to remain constant until 700°C-800°C at which point a sudden increase in density occurred. These results correlate well with the hot stage microscopy measurements where a significant linear shrinkage of the samples was observed to occur in this temperature range.

The (002) x-ray diffraction peak intensities were measured on the four cokes and plotted as a function of temperature. The peak intensity measurements reflect the progressive ordering of the graphitic planes during calcination. Figure 7 illustrates the extreme cases of the anisotropic cokes compared with the isotropic cokes. In all cases the peak intensity appears to increase at a logarithmic rate with temperature; however the anisotropic cokes maintain peak intensities of a higher magnitude throughout the calcination range than the isotropic cokes.

The d-spacing, which is classically a measure of the graphitic nature of carbon, was obtained for all samples as a function of temperature. As might be expected, d-spacings were found to decrease with increasing temperature. This is illustrated in Figure 8, where it is of interest to note that while the isotropic cokes have large d-spacings at the outset, the d-spacings of the anisotropic and isotropic cokes are essentially equivalent by 1100°C. The low initial d-spacings of the isotropic cokes are believed to be due to the amorphous material contributing mainly to the background of the diffraction curve. Only the highly graphitic portions of the sample are detectable, which result in low d-spacing values not truly representative of the entire sample. On the other hand, less amorphous material is present in the anisotropic cokes, and a broader spectrum of crystallite perfection is detectable. Therefore, the total value of the d-spacings appears large. Other experiments conducted beyond the 1200°C range have shown that the d-spacings of isotropic cokes maintain higher values than the anisotropic cokes, which is in agreement with the cross-over point at 1100°C in Figure 8.

The change in crystallite size along the c crystallographic axis as a function of temperature was very similar for all cokes. This relationship, presented in Figure 9 for the four cokes, is characterized by a significant decrease in size between 500°C and 900°C; after which a steady increase is observed up to 1200°C. Since the Lc values represent an average of all detectable crystallites for a given sample, it is believed that the initial decrease in Lc is due to the appearance of a large number of extremely small crystallites which have grown to a detectable size. This pronounced decrease in

Lc values at 600°C-700°C corresponds with the onset of the rapid shrinkage of the coke samples. It seems reasonable, therefore, to presume that the coke structure shrinkage is in part a result of its conversion to a more compact crystalline structure.

CONCLUSIONS

With only minor exceptions, the general overall structure of the calcined coke is predetermined in the raw state. With respect to microstructure, the dominant recurring theme running through our experimental data is the sudden changes which occur in the 600°C to 900°C temperature range. The sharp observed increase in dimensional shrinkage results from the loss of volatile constituents as well as ordering and growth of the polycrystalline structure. The increased microporosity represents the creation of shrinkage cracks as well as pores formed due to the escape of volatile components.

REFERENCES

1. P. L. Walker, Jr., F. Rusinko, Jr., J. F. Rakszawski, and L. M. Liggett. Proceedings of the Third Conference on Carbon, University of Buffalo (1957) p. 643.

2. C. F. Stout, M. Janes, and J. A. Biehl: WADD Technical Report 61-72, Vol. 36 (1964).

3. E. Barrillon, Carbon, 5, 167-171 (1967).

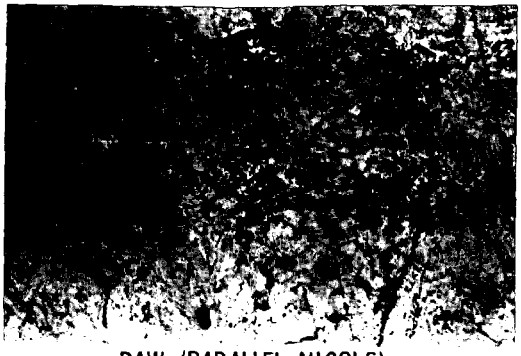
4. P. Rhedey, Transactions of the Metallurgical Society of AIME, 239 1084 (1967).

TABLE I
CHARACTERIZATION OF THE RAW COKES

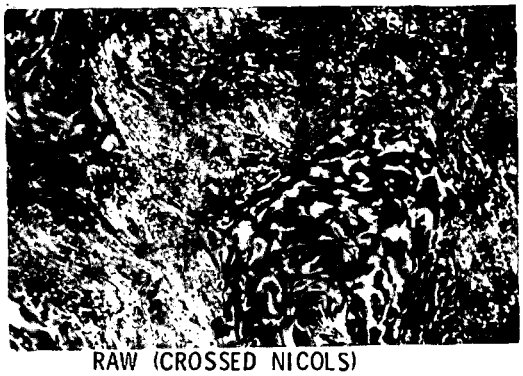
Sample	Volatile Matter (%)	Ash (%)	Sulfur (%)	Real Density (g/cc)	002 Peak Intensity (c/s)	d-Spacing (Å)	X'tal Size Lc (Å)
Coke A	5.90	0.110	0.72	1.437	115	3.5131	25.6
Coke B	6.43	0.085	0.70	1.397	178	3.7745	23.6
Coke C	15.71	0.086	1.32	1.345	111	3.5186	30.1
Coke D	21.46	0.281	1.28	1.314	117	3.5118	32.6

FIGURE 1

STRUCTURAL CHANGES ACCOMPANYING
COKE CALCINATION

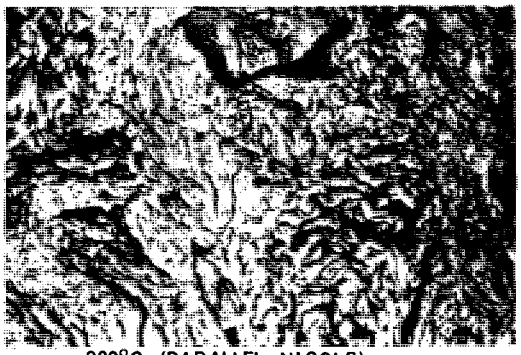


RAW (PARALLEL NICOLS)



RAW (CROSSED NICOLS)

700°C (PARALLEL NICOLS)



800°C (PARALLEL NICOLS)

1000°C (PARALLEL NICOLS)

1000°C (CROSSED NICOLS)

100 μ

FIGURE 2
DIMENSIONAL CHANGES OF AN ANISOTROPIC COKE

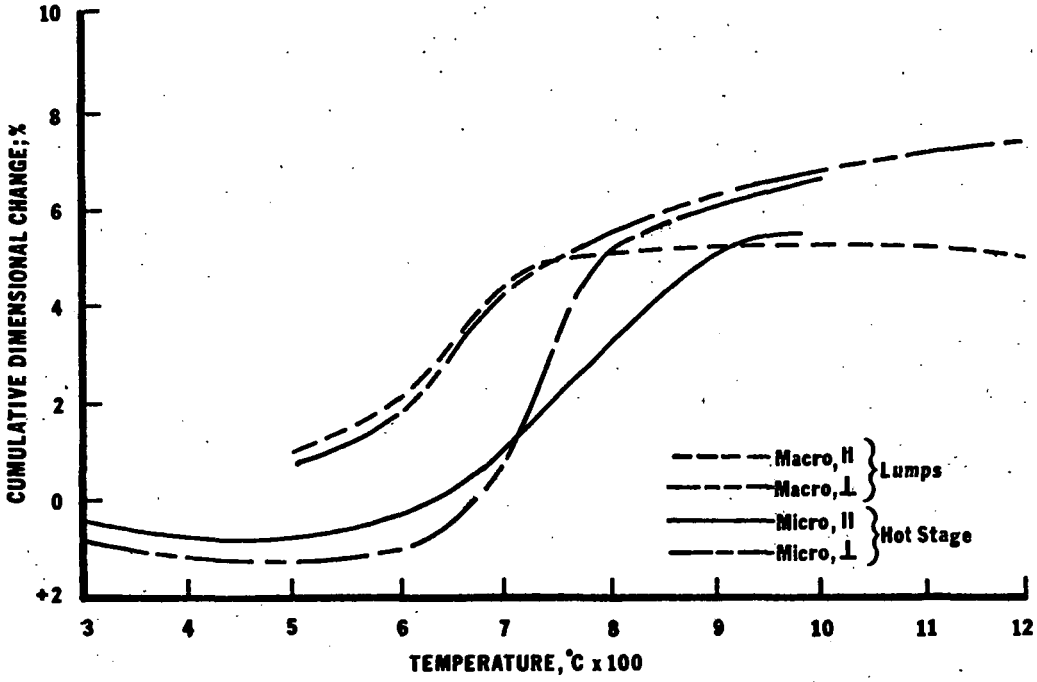


FIGURE 3
DIMENSIONAL CHANGES OF AN ISOTROPIC COKE

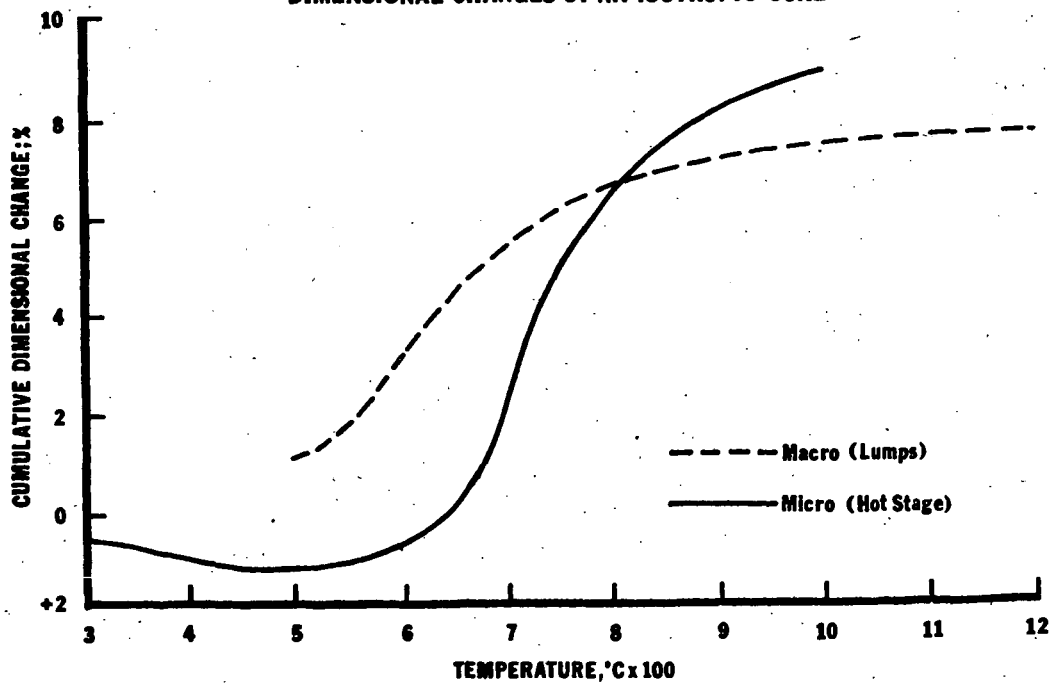


FIGURE 4
WEIGHT LOSSES vs TEMPERATURE

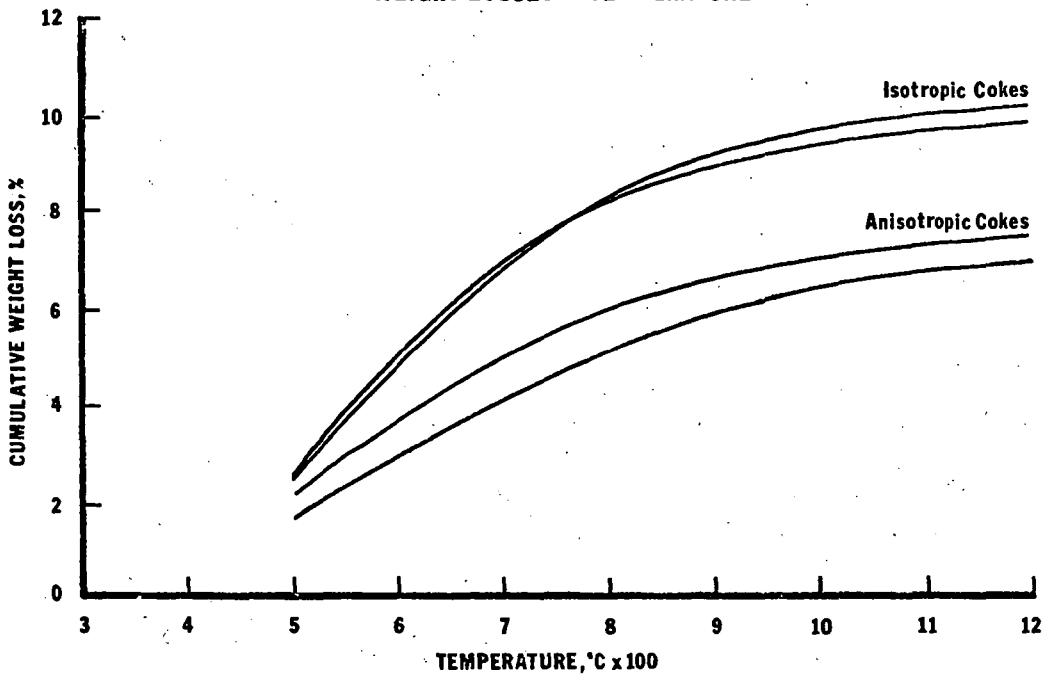


FIGURE 5
POROSITY vs TEMPERATURE OF VARIOUS COKES

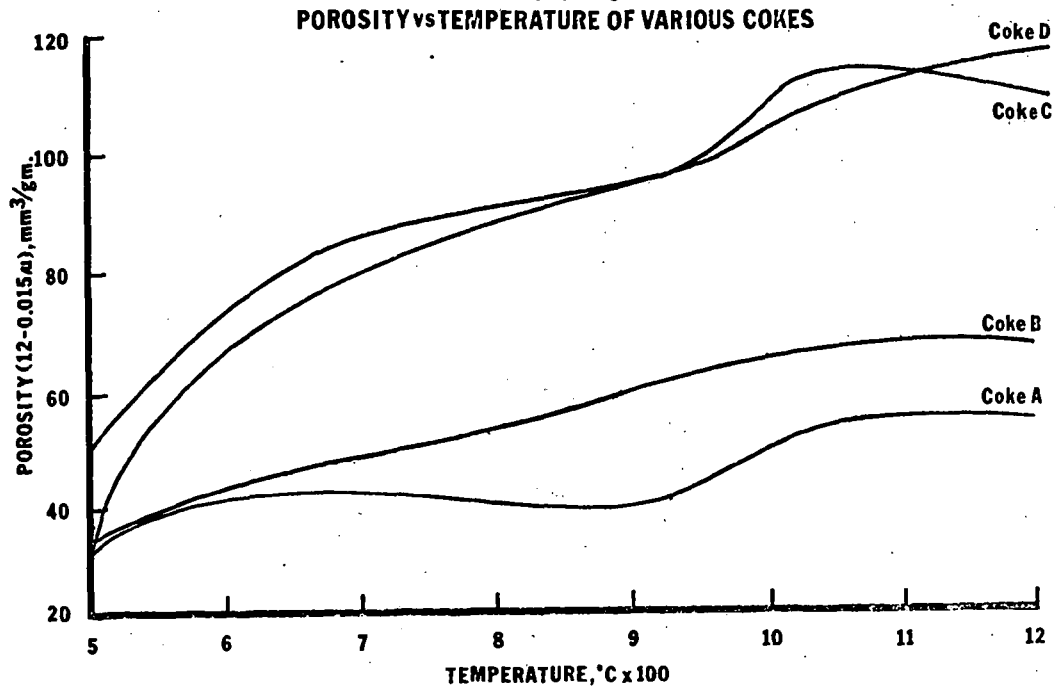


FIGURE 6
DENSITY vs TEMPERATURE

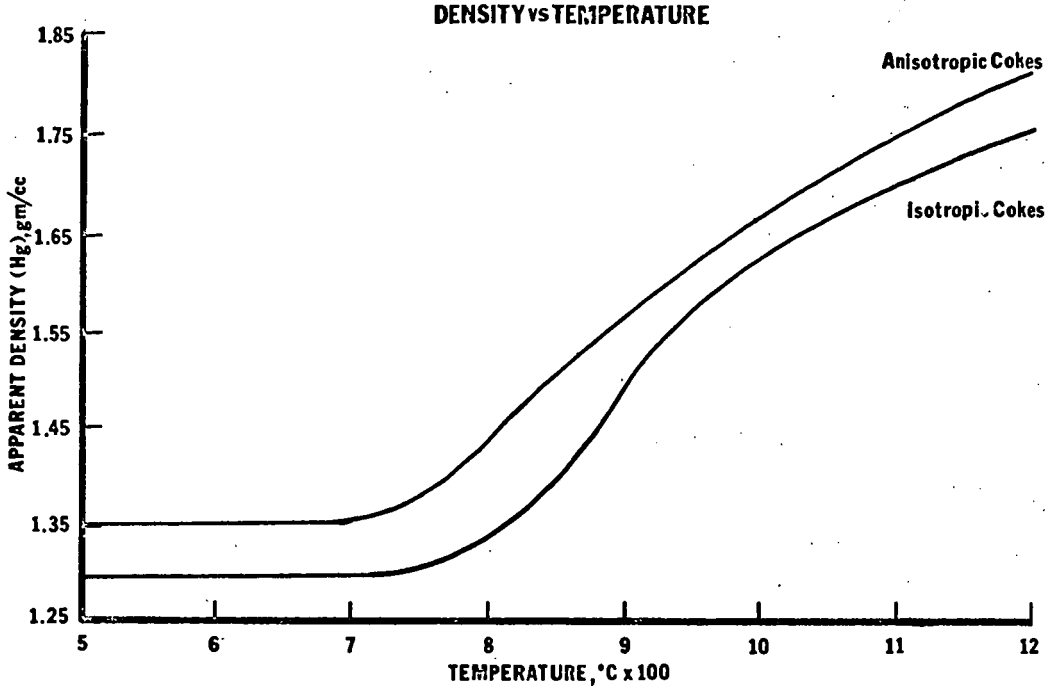


FIGURE 7
PEAK INTENSITY vs TEMPERATURE

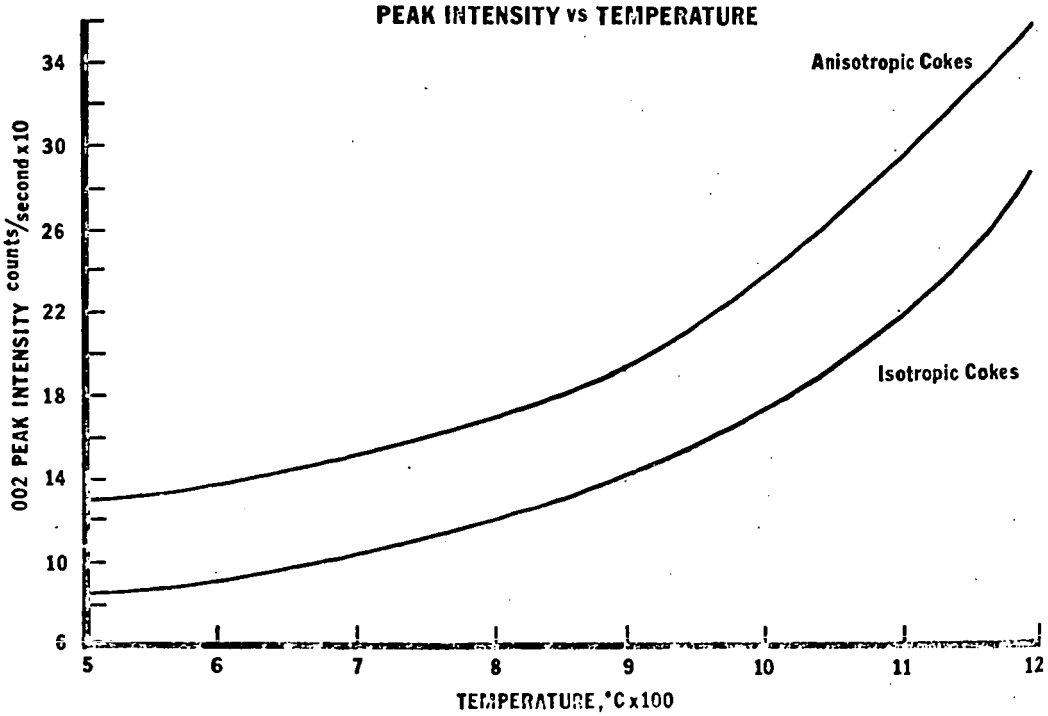


FIGURE 8
D-SPACING vs TEMPERATURE

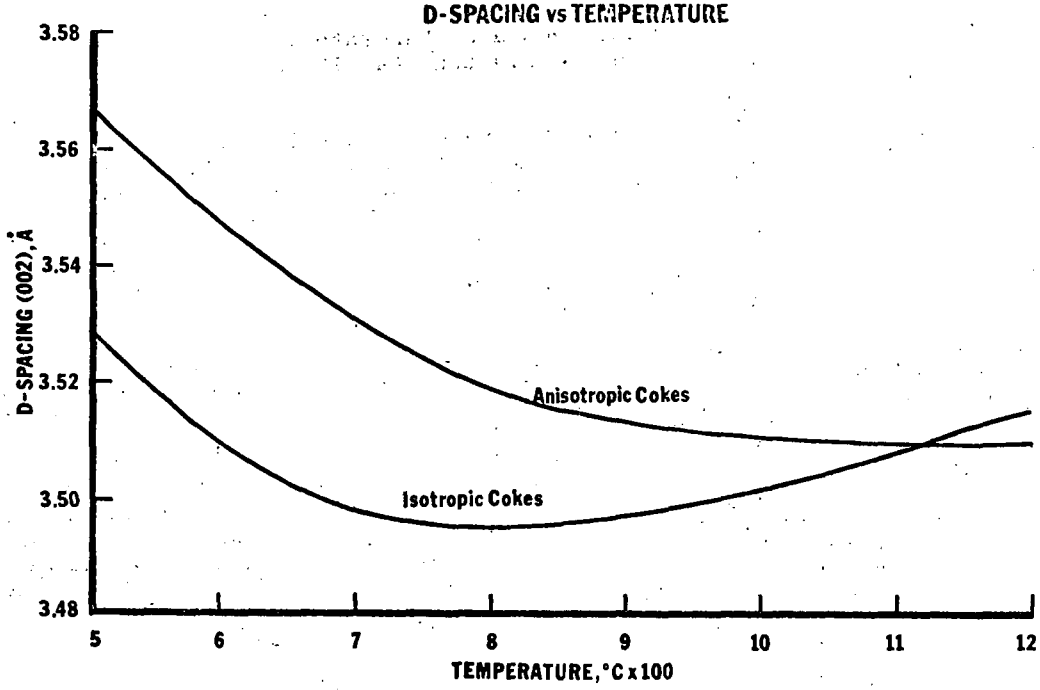
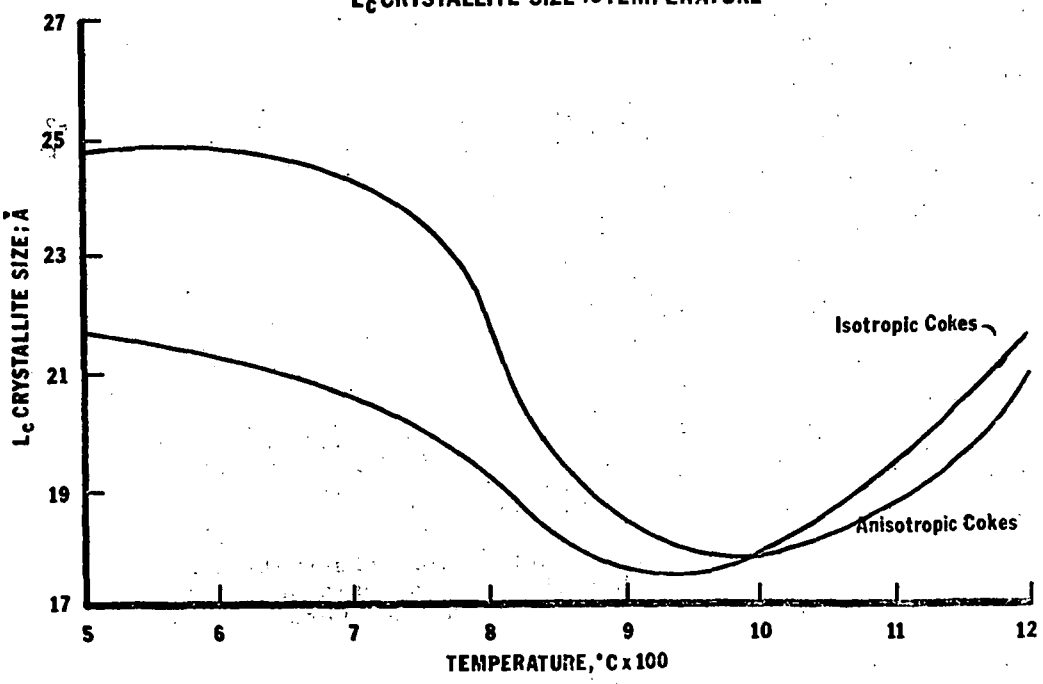



FIGURE 9
L_c CRYSTALLITE SIZE vs TEMPERATURE