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IITRI-G6001-6
Quarterly Report No. 2

PHYSICAL PROPERTIES OF REFRACTORY MATERIALS

Systems Engineering Group (RTD)
Wright-Patterson Air Force Base, Ohio
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ABSTRACT

This report presents much of the available JTA graphite data and attempts to analyze this information with regard to its uniformity and application to possible design use. The report will attempt to acquaint the reader with information concerning the characterization of JTA, its oxidation resistance, and the following temperature dependent mechanical and physical properties:

1. Tensile strength,
2. Flexure strength,
3. Compression strength,
4. Elastic properties,
5. Thermal expansion,
6. Thermal conductivity,
7. Enthalpy,
8. Specific heat, and
9. Relationship between sonic modulus, density and strength of JTA.

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PHYSICAL PROPERTIES OF REFRACTORY MATERIALS

I. INTRODUCTION

Nose cone, rocket nozzle, and leading edge applications under extreme environmental conditions require materials which will withstand severe thermal and mechanical conditions. Attention has been focused on the refractory composite materials because of their potential high strength at elevated temperatures, thermal insulation, and oxidation resistance. However, most of these materials often exhibit a wide variability in properties used in the design of structures required to resist extreme environments. This research program is designed to correlate the physical and mechanical parameters of a refractory oxidation material, JTA graphite.

Considerable emphasis has been placed on determining the uniformity of JTA from billet to billet and from one size billet to another. Initially (Quarterly Report No. 1, August 16, 1965), material from two (2) 14 in. diameter billets was to be evaluated and the data developed compared as well as establishing the relationship between the new data with previously obtained results. However, due to processing difficulties which have arisen in the fabrication of two uniform 14 in. billets, the scope of the program has been modified to study one (1) 14 in. billet and two (2) 7 in. billets. However, since satisfactory material has not yet been delivered, an analysis of available data will be given in this quarterly report. This information will be used for analyzing and comparing data obtained during this program with that developed on the other programs.

II. MATERIAL CHARACTERIZATION

Grade JTA graphite composite is a development of the Carbon Products Division of the Union Carbide Corporation. The composition as stated in its literature, is 48% carbon, 35%

zirconium, 8% boron, and 9% silica. The raw materials are hot pressed in an inductionally heated graphite mold.

Little information has been published as to the grain and phase structures of the JTA composites, or concerning processing and raw material parameters. The lack of this type of information requires that characterization studies be conducted to establish:

1. Variability in constitution and density from batch to batch, as well as internal uniformity within specimens.
2. Microstructure and phases present prior to testing.
3. Nature of oxidation products on exposure to air at elevated temperatures.
4. Effect of time and temperature on phase constitution and microstructure.

The nature of the dispersion of phases in the graphite matrix will be dependent on the raw materials used in fabrication. The grain sizes of these phases should be noted and their growth at high temperature monitored and related to oxidation resistance.

III. PROPERTY EVALUATIONS

A. Oxidation Resistance

Grade JTA graphite is a complex material containing four elements capable of forming a great variety of compounds and solid solutions (ZrC, SiC, BiC, SuB_2, SiB_4). On oxidation, a considerable number of oxides may form. At elevated temperatures, phase changes may occur within the material, some constituents will volatilize, and oxygen diffusion will occur at the surface, resulting in compositional gradients.

One of the important properties of JTA graphite as a refractory material is its resistance to oxidation in a high temperature oxidizing environment. A material with excellent

properties such as good high temperature strength and thermal shock resistance would be worthless as a structural material if its effective cross section is readily eroded due to oxidation processes.

During dynamic oxidation tests at Union Carbide[1], JTA specimens in flowing air lost 6.5% of their weight on heating from 750° - 1100°C at 10°C/min, and then gained weight on heating further to 1450°C with a slight loss in weight on continued heating to 1500°C. Rapid coating build-up appears to occur at 1100° - 1450°C.

Upon heating JTA graphite for 20 min at 1700°C, 4% of its weight was lost, 7% weight loss occurring after 10 min of 1800°C, with little further loss after 20 min. Ordinary graphite will lose 7% of its weight in approximately 3 min at 1200°C; the rate is linear with time.

The oxidation rate does not appear to be affected by ambient pressure at 1600°C and below. At 1800°C, where volatilization rates are higher, a maximum rate (14% in 10 min) occurs at 0.5 atmospheres.

General Electric[2] has compared the loss behavior of JTA with RVA graphite, a fine grain conventional graphite of uniform properties. They found that at moderate heating rates (280 and 400 BTU/ft^2/sec) JTA exhibited outstanding oxidation resistance compared to unpurified RVA (JTA exhibited 1/20 the recession of RVA under identical test conditions) at surface temperatures below the melting part of protective oxides (~2000°C). Above these temperatures, the resistance to shape change demonstrated at lower temperatures is lost. Thus, JTA by virtue of its oxidation resistance in the moderate surface temperature range, is suited for consideration as a candidate for leading edge applications of lifting re-entry vehicles. However, no mechanical property data has been uncovered which

shows any relationship between rate of oxidation and strength. The future work of this project should provide some of this data.

B. Data Analysis

Mechanical property data for JTA is limited, and due to its recent development, most of the information that is available is experimental in nature. This report will attempt to evaluate available data for tension, flexure and compression strength, elastic modulus data, coefficient of expansion and the relationship between sonic modulus and flexure strength. The origin of the data presented is referenced for each series of curves on the various figures showing a particular property relationship.

Table I provides a comparison for JTA graphite obtained under ambient (R.T.) conditions. The temperature dependent relationships are exhibited in the following manner: flexure strength, figures 1 and 2; tensile strength, figure 3; compressive strength, figure 4; thermal expansion, figures 5 and 6; relationship of thermal expansion to thermal stress, figure 7; sonic modulus, figures 8 and 9; relationship of sonic modulus and density to strength, figure 10; thermal conductivity, figures 11 and 12; enthalphy, figure 13; specific heat, figure 14.

The information presented in Table I shows that the ratio of tension to flexure agrees reasonably well with established rule-of-thumb relationships [3] (1 to 1.4 - 1.6) the tension to compression ratios are somewhat below those anticipated in graphite materials (1 to 3). It appears that the measured compressive strength is the same or only slightly higher than the flexure strength in the with-grain orientation, while the compression strength is about twice the flexure strength in the across-grain orientation. The across-grain elastic modulus in compression and flexure are about the same

however, the with-grain orientation exhibits a lower compression modulus than flexure modulus. The tension elastic modulus indicates a similar relationship to the flexure modulus as that shown by the strength ratios. Past work [4,5] with JTA and ATJ graphite displays similar trends for these materials.

A possible explanation of these phenomena is that the graphite crystallites in the with-grain orientation are held together with weak van der Waal's forces. The tension forces introduced due to Poisson's ratio will overcome these bonds and allow considerably greater lateral deformation than normally expected. This would, of course, cause greater vertical deformation per unit load which would be reflected in a flattened stress-strain curve, i.e., a lower elastic modulus. Under tensile loading this phenomenon would not occur; Poisson's ratio produces compression in the lateral direction, and relatively higher elastic moduli can be expected in tension and flexure for the with-grain orientation. However, for the across-grain orientation, the forces developed due to Poisson's ratio are pulling against the van der Waal's forces which will cause larger than normally expected deformations per unit load, resulting in a lower measured elastic modulus. This behavior can cause serious performance problems if not given due consideration in the design phase when the material is to be used as a structural member.

Data for the flexural strength of JTA graphite is more extensive than either tension or compression. However, there appears to be a large spread in the data, about $\pm$ 1500 psi for an average across-grain strength of 8500 psi at room temperature and $\pm$ 3500 for an over average across-grain strength of 12,500 psi. These relationships appear to hold for the with-grain flexure strength, except the average strengths are about twice the across-grain strengths. The within group variability for the two crystal orientations show statistically significant differences between data obtained at different times or by

different organizations.

The flexure strength curves show typical graphitic behavior; at about 1800° to 2000°F there is a sharp rise in strength, which peaks at about 3000°F and begins to fall off rapi ly after 3400°F. The variability in present data is probably due to the experimental nature of the material tested. A major phase of the present program is to attempt to establish variability of material which is considered commercial.

The tensile strength-temperature relationship conforms to the tensile strength-flexural strength previously discussed for the more recent data acquisitions. Earlier data [6] exhibits ratios which are well above (2.5) the 1.4 to 1.6 values normally expected. It appears that the newer data begins to show greater uniformity and conforms closer to established relationships for graphitic material.

Compression strength temperature dependence shown in Figure 4 is an estimated value determined by Carbon Products Division of Union Carbide Corporation [7]. The information does not conform to the flexure and tension strength curves obtained from actual measurement. This plot should be considered questionable until measured data can be developed which will either confirm or reject this information.

The more recently obtained thermal expansion data, as previously noted for other properties, exhibits close agreement. The with-grain orientation produces a linear expansion relationship with temperature while the across-grain expansion is approximately linear up to about 2700°F and then rises steeply to above 4000°F, the end point of most measurements. Considering the predominance of data, the with-grain data from Union Carbide Corporation quarterly report dated 11/63, appears questionable. Analysis[8] of the effect of temperature and strength upon the temperature difference which will cause failure in different graphites is shown in figure 7. Although

there may be strength increases with temperature, the change in expansion for the across-grain (weak strength direction) nullifies any strength advantage and the critical temperature difference remains almost constant.

Sonic modulus measurements have been used in the past as an indication of mechanical strength trends for a particular material. Examination of the sonic modulus curves reveals material variable similar to that exhibited by the flexure strength curves. However, it is the writer's opinion that this information does not provide the necessary data to adequately evaluate the relationship between sonic modulus and strength.

A series of experiments (figure 10) were performed in which the room-temperature sonic modulus of the flexure specimens was obtained before destructive tests were performed. The sonic modulus data were then compared to the flexure strength of the individual bars. While the test populations are not large, a trend can be established.

Grouping due to orientation and billet are readily discernible, and it is obvious that there is a relationship between sonic modulus and strength. However, the small population size of the groups does not allow a real definition of strength vs. sonic modulus within the groups.

A similar comparison of bulk density measurements with the room-temperature strengths reveals that the densities of the specimens from billet No. 1 are the same. The strength difference shown for the with-grain and across-grain orientation is due to the anisotropic behavior of the graphite crystal, whereas the difference in strength between billets No. 1 and 2 is due to the lower density of the material. These comparisons point up the fact that sonic moduli reveal not only strength differences due to different densities of the material, but also strength differences due to crystal orientation. Bulk density measurements cannot provide the latter information.

The thermal conductivity data exhibits low variability except for the Union Carbide quarterly report dated 11/63. An average value curve drawn through the points shown should provide an adequate measure of the thermal conductivity for JTA graphite for both the with and across grain orientations.

The curves for enthalphy and specific heat of JTA graphite are from a single series of experiments made at IITRI and need no interpretation since no other data is available for comparison.

Table II provides data on the emittance of JTA graphite and for the same reason given above no comparisons can be made.

IV. SUMMARY AND FUTURE WORK

This report has attempted to evaluate the available information on grade JTA graphite. The information presented is probably the most complete compilation of JTA data available. The experimental effort of this project is to obtain additional information to verify data analysis which have been attempted, and establish the variability of data within carefully made and fully characterized JTA material.

Latest estimates on the arrival of the JTA graphite for use on this program is December 12, 1965. Once the material is available for evaluation, experimental work will be begun and we should be able to confirm or reject some of the relationships given in the tentative analyses we have attempted in this report.

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3. Currie, Hamister and MacPherson (National Carbon Company) "The Production and Properties for Reactors," paper presented at Atomic Energy Conference, Geneva, Switzerland, August 6-20, 1955.

4. "Improved Graphite Materials for High-Temperature Aerospace Use," Union Carbide Quarterly Progress Report, August 1. to October 31, 1963, BPS No. 6899-7350-735002, Contract No. AF 33(657)-11171, November 15, 1963.

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7. Bowman, et al, "Improved Graphite Material for High Temperature Aerospace Use," Vol. IT, Development of Graphite-Refractory Composites ML-TRD-65-125 October 1964.

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TABLE I

PROPERTIES OF JTA GRAPHITE

(14 in. Diameter Billets)

Property	With Grain				Across Grain			
	No.of Tests	Avg. X	Error ρ%	Billet No.	No.of Tests	Avg. X	Error ρ%	Billet No.
Room Temperature								
Bulk, density, g/cc	22	2.966	23	1	8	3.028	1.1	1
	21	2.854	3.5	2				
Coefficient of expansion, in/in/°C: RT to 1500°	2	5.6		1,2	2	6.0		1
1500°-2000°C	2	5.6		1,2	2	11.0		1
Tensile strength, psi	4	10,010	7.0	1				
Tensile elastic modulus, $x10^6$ psi (from Ref.4)		5.6				3.6		
Flexure strength, psi	5	17,750	4.7	1	5	9,592	5.2	1
	5	12,784	5.6	2				
Flexure elastic modulus,	5	9.1		1	5	4.[illegible]		1
$x10^6$ psi	5	7.1		2				
Compressive strength, psi	3	15,330	2.6	1	5	22,160	8.7	1
	5	12,592	11.2	2				
Compressive elastic modulus $x10^6$ psi	5	2.9		1	5	3.6		1

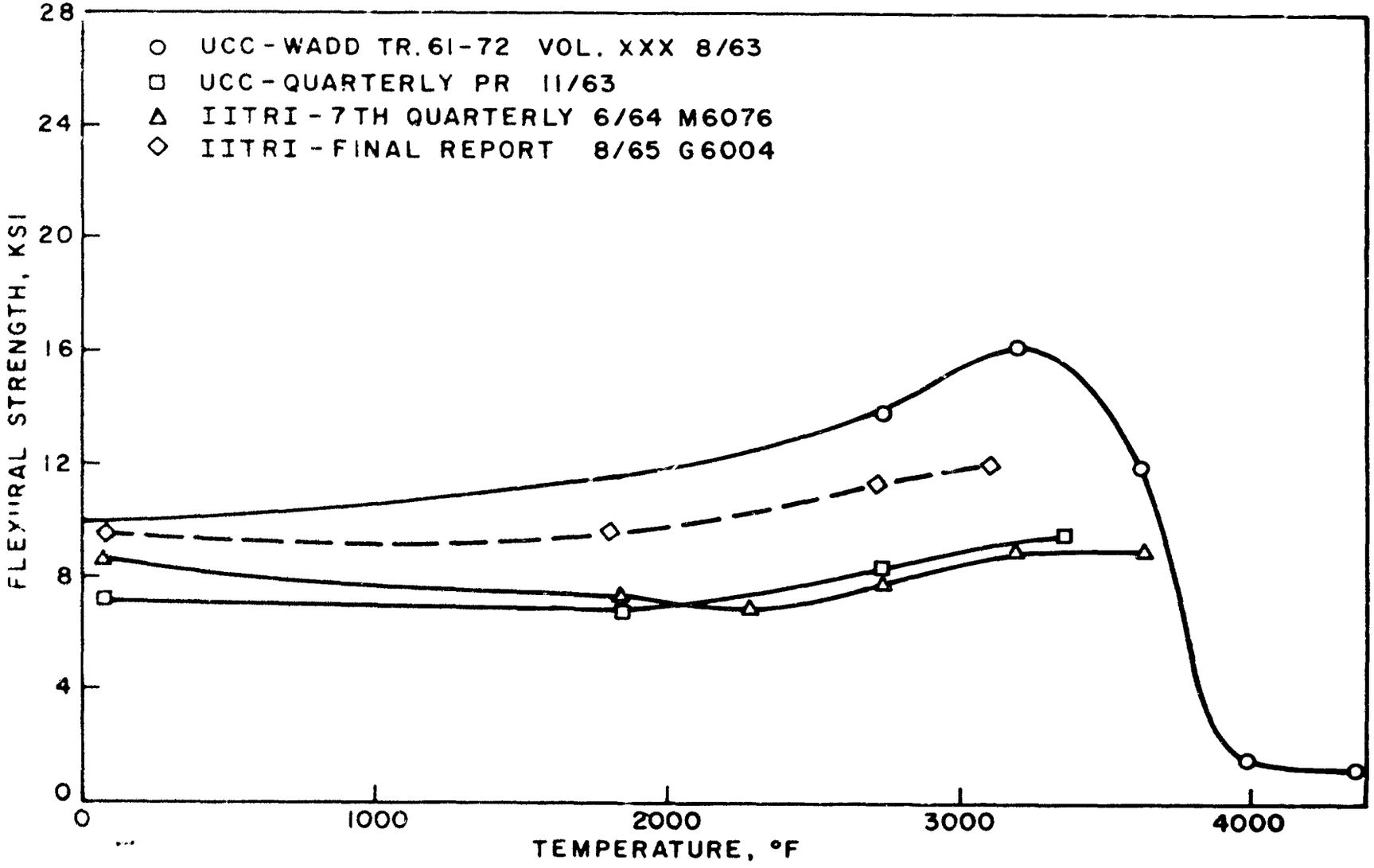

FIG. 1 - FLEXURAL STRENGTH JTA GRAPHITE
(ACROSS THE GRAIN)

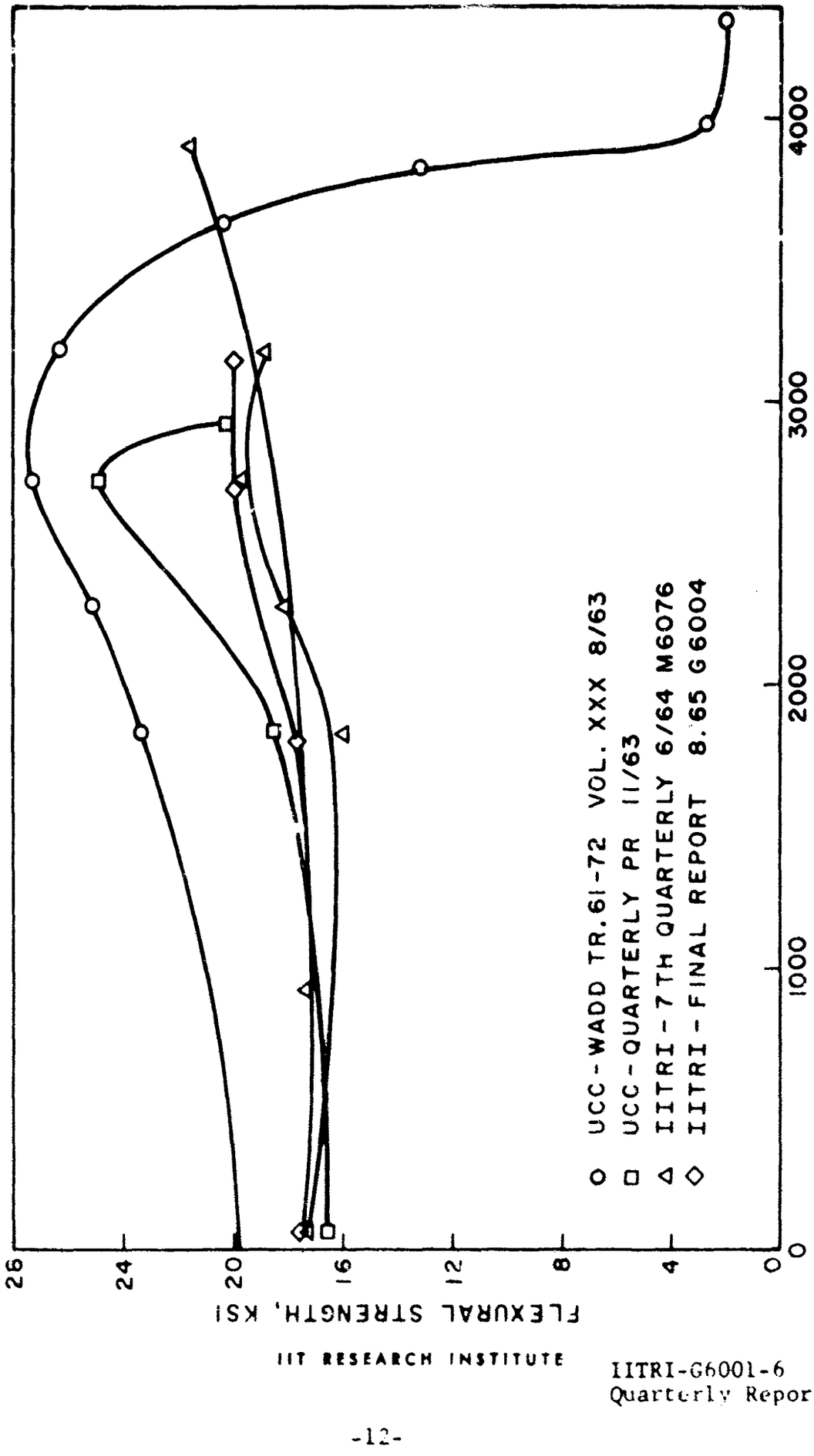

FIG. 2 - FLEXURAL STRENGTH JTA GRAPHITE (WITH THE GRAIN)

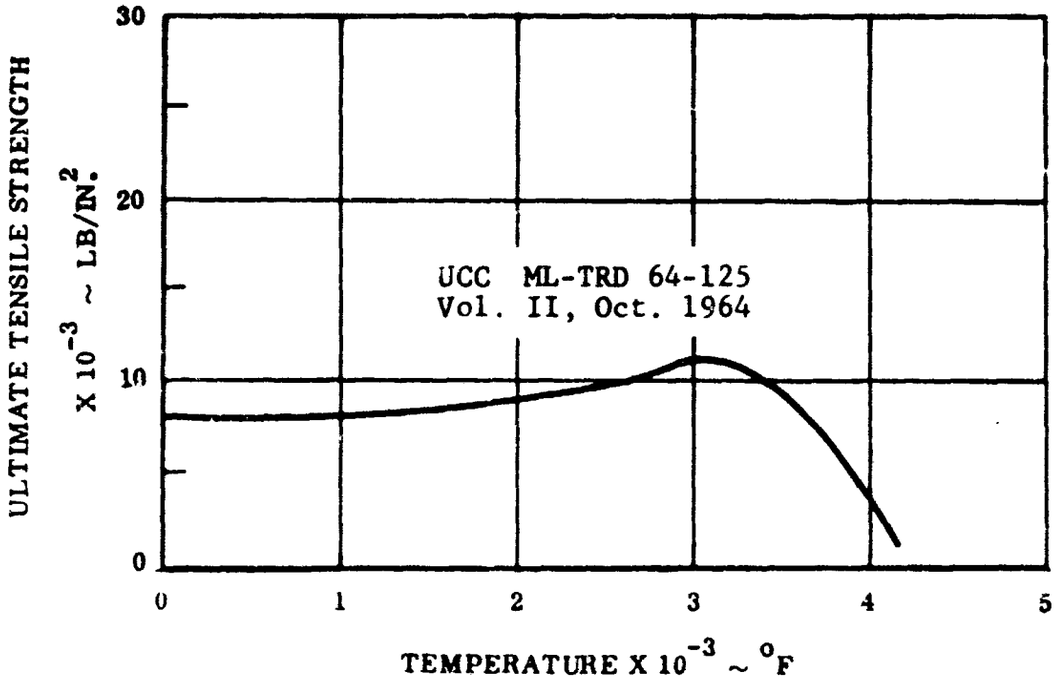

FIG. 3 - ULTIMATE TENSILE STRENGTH FOR JTA

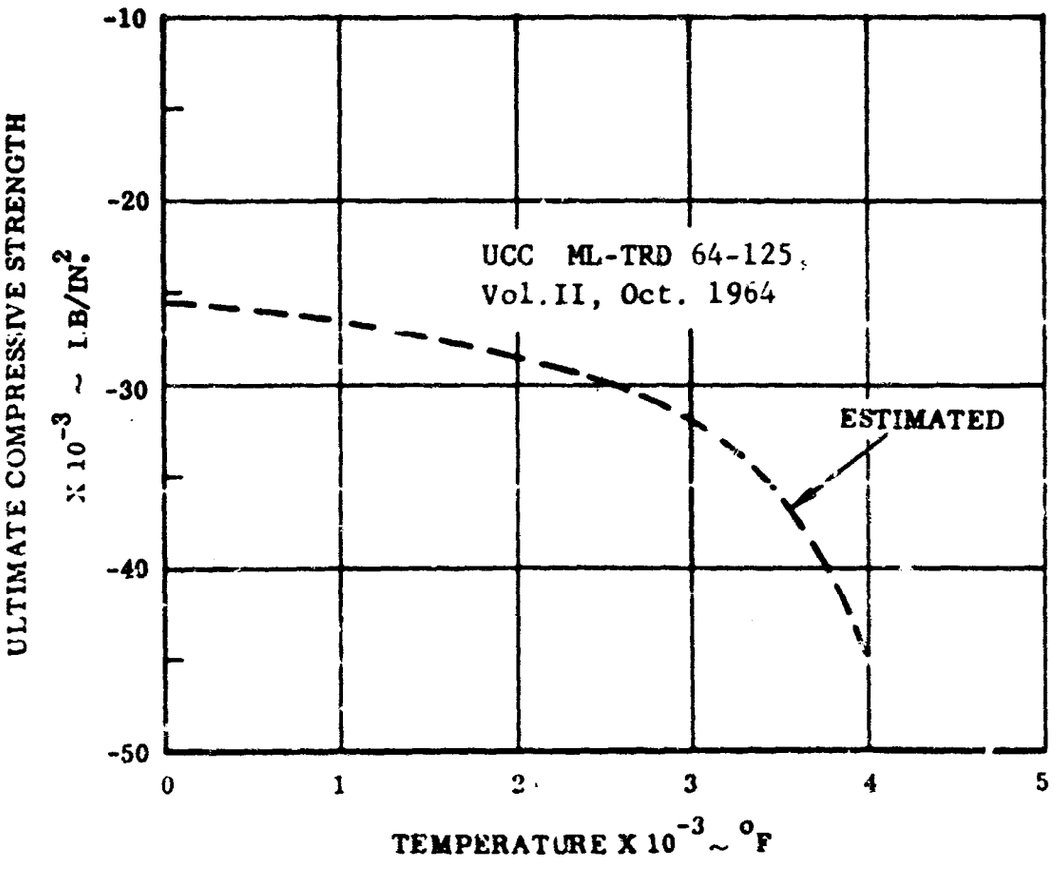

FIG. 4 - ULTIMATE COMPRESSIVE STRENGTH FOR JTA

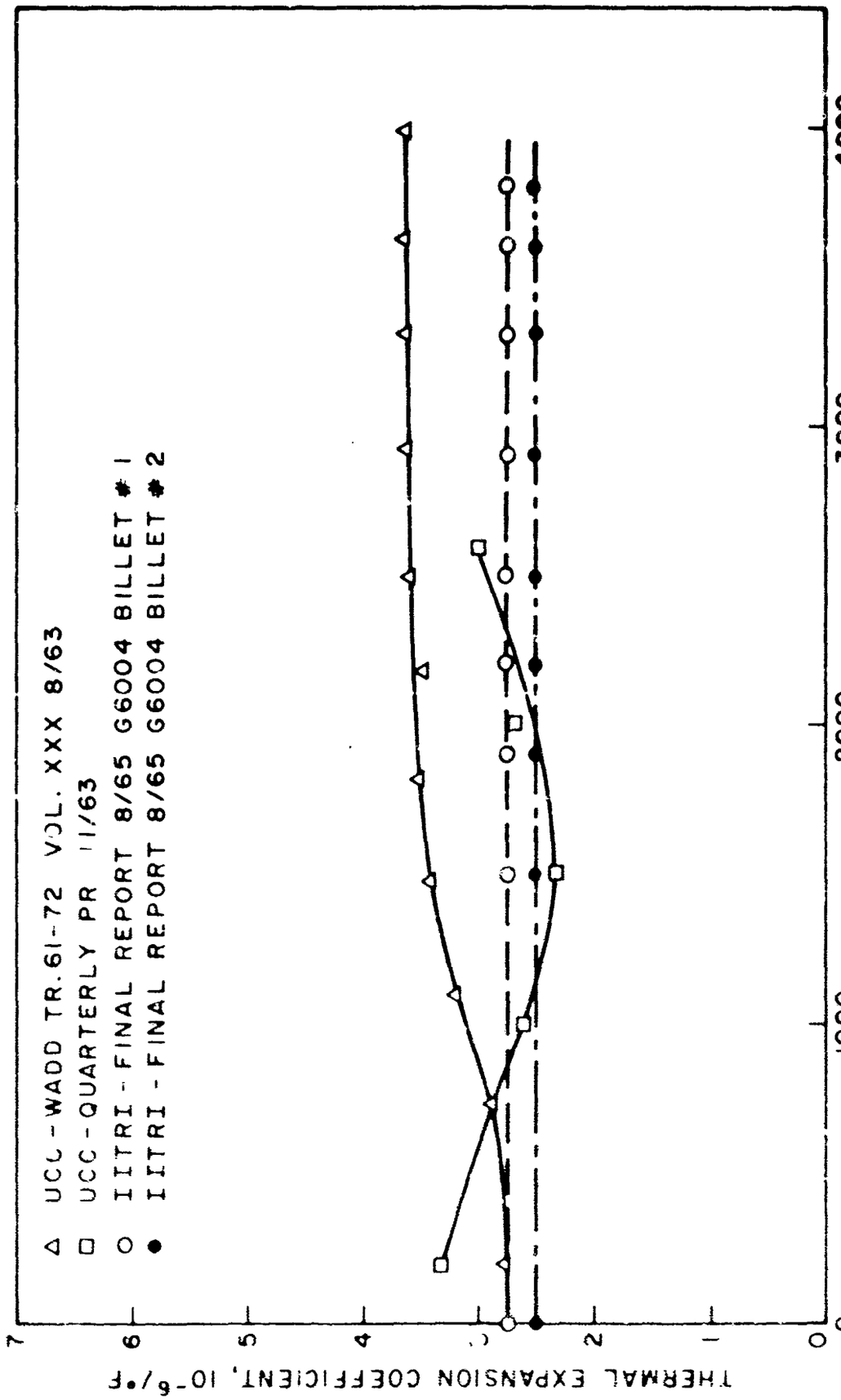

FIG. 5 - THERMAL EXPANSION COEFFICIENT JTA GRAPHITE (AVERAGE) WITH THE GRAIN

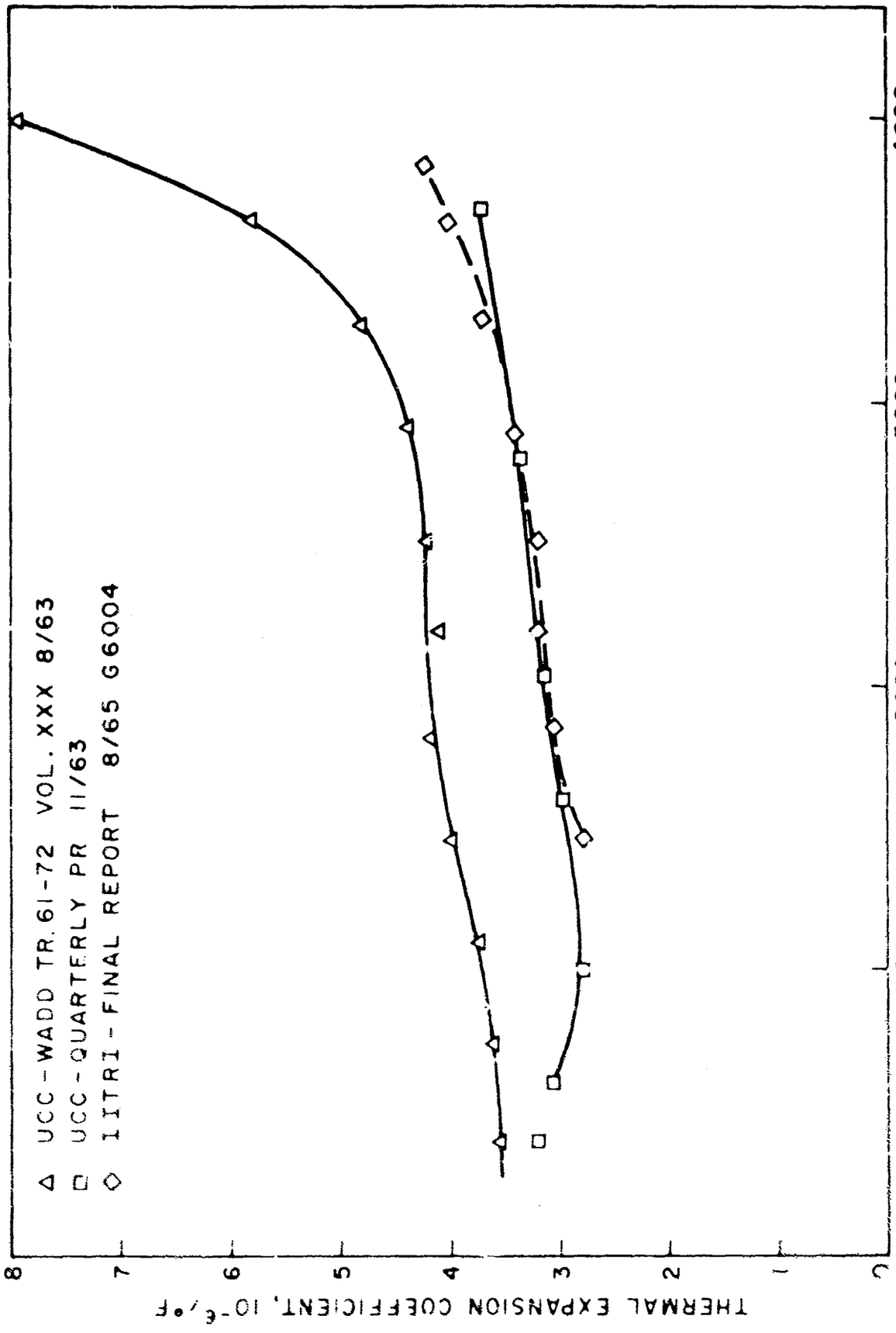

FIG. 6 - THERMAL EXPANSION COEFFICIENT JTA GRAPHITE (AVERAGE) ACROSS THE GRAIN

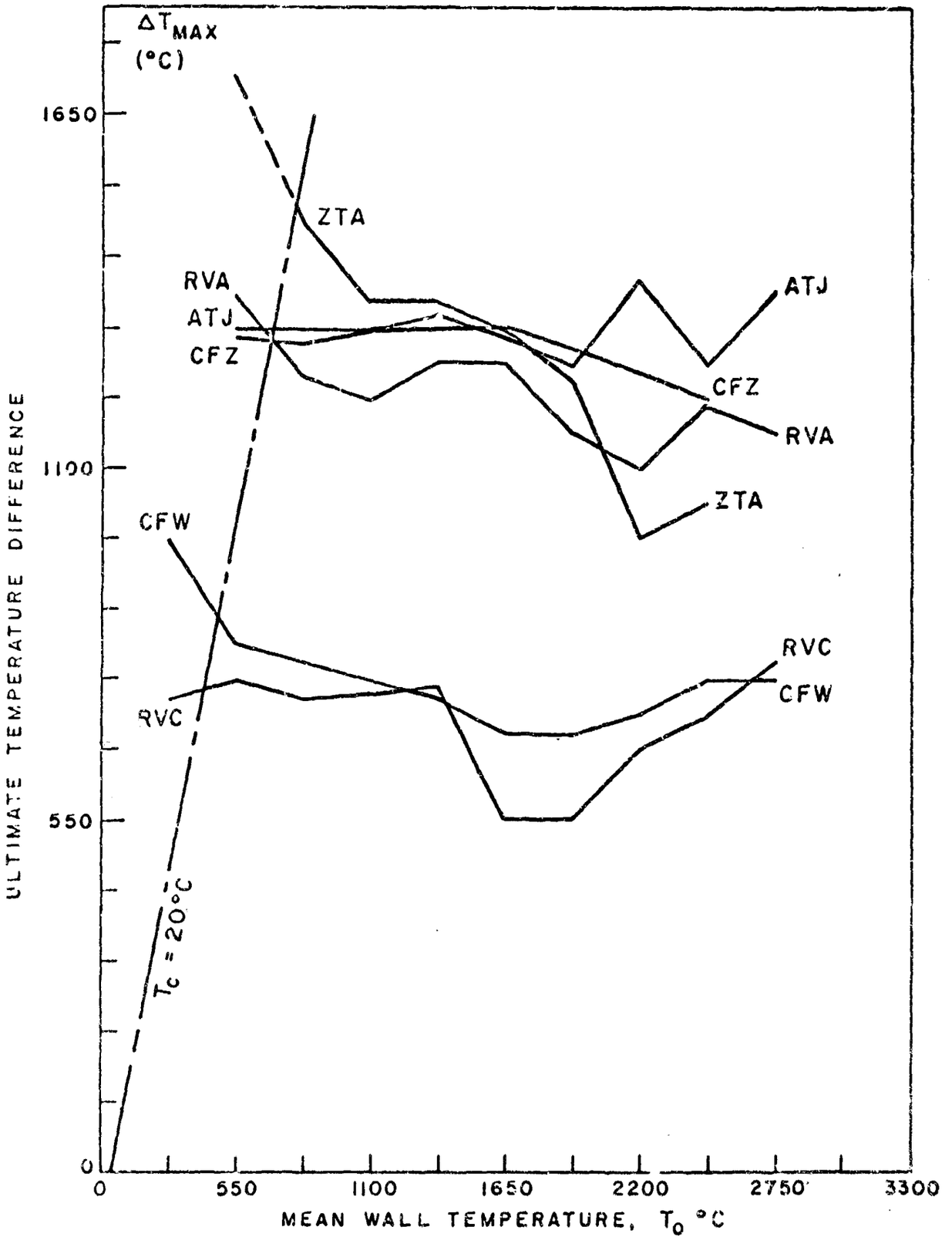

FIG. 7 - SUMMARY OF ULTIMATE TEMPERATURE DIFFERENTIAL IN GRAPHITE CYLINDERS STRESSED WITH GRAIN

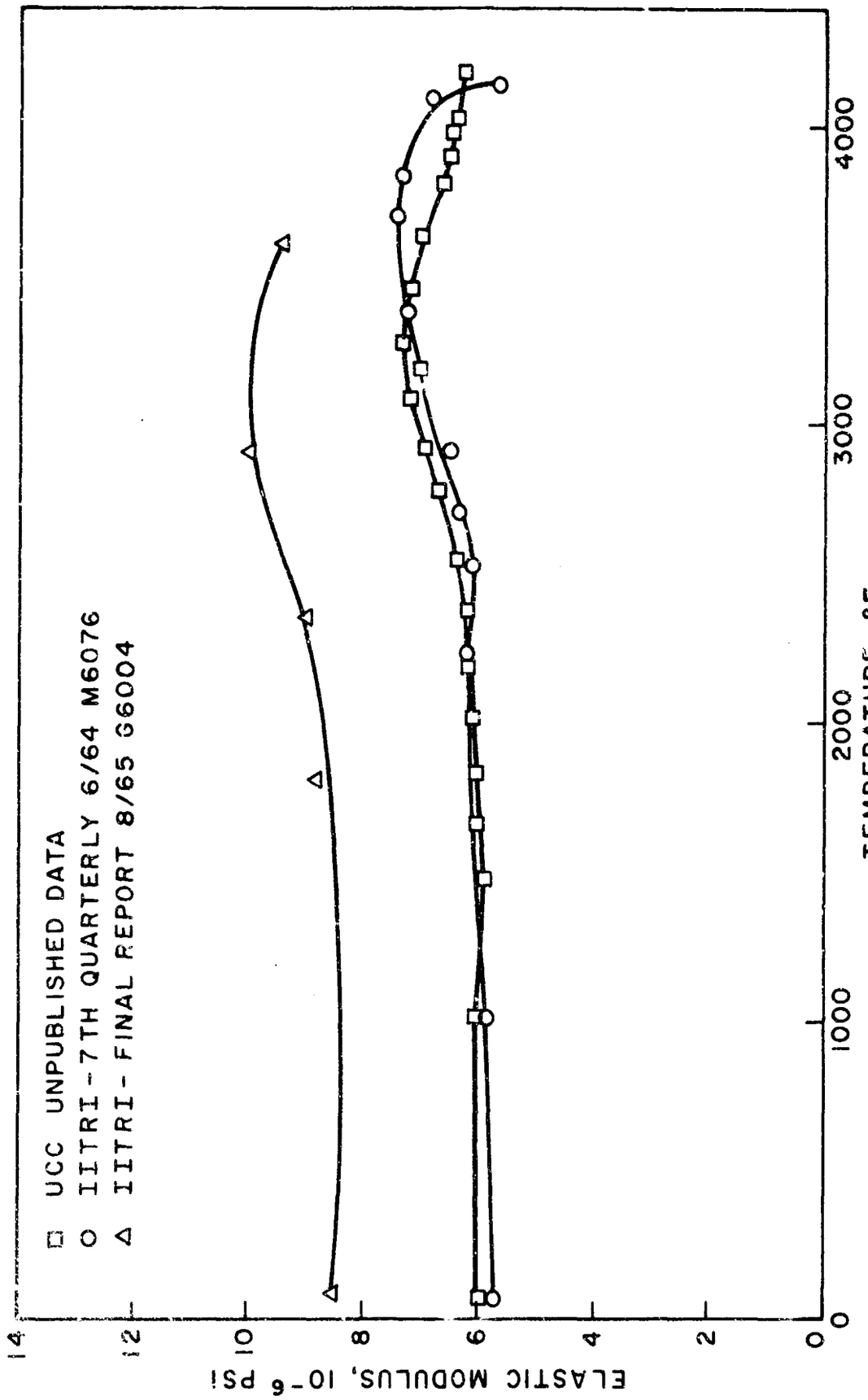

FIG. 8 - SONICALLY DETERMINED ELASTIC MODULUS OF JTA GRAPHITE (ACROSS THE GRAIN)

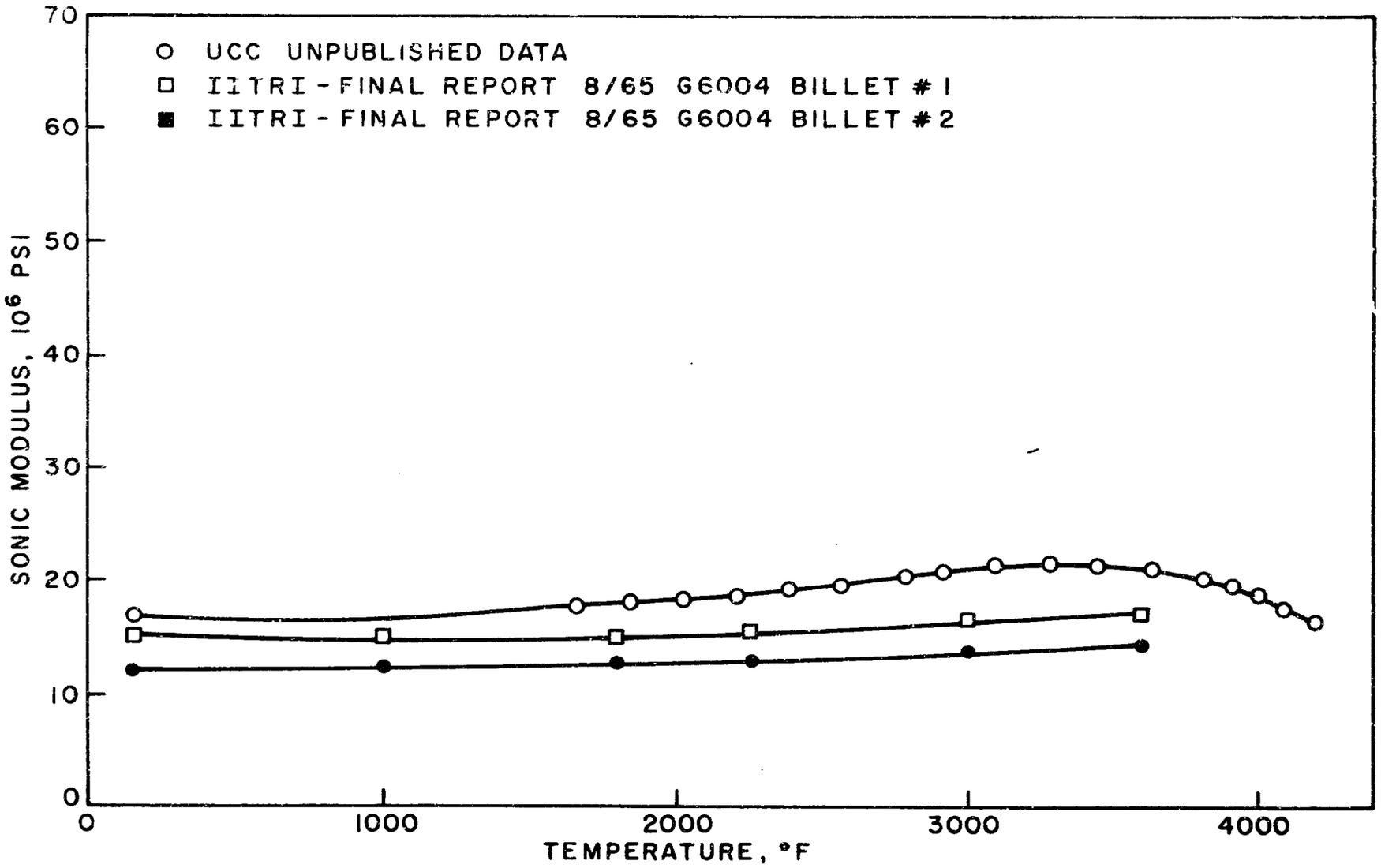

FIG. 9 - SONIC MODULUS VS TEMPERATURE FOR GRADE JTA (WITH THE GRAIN)

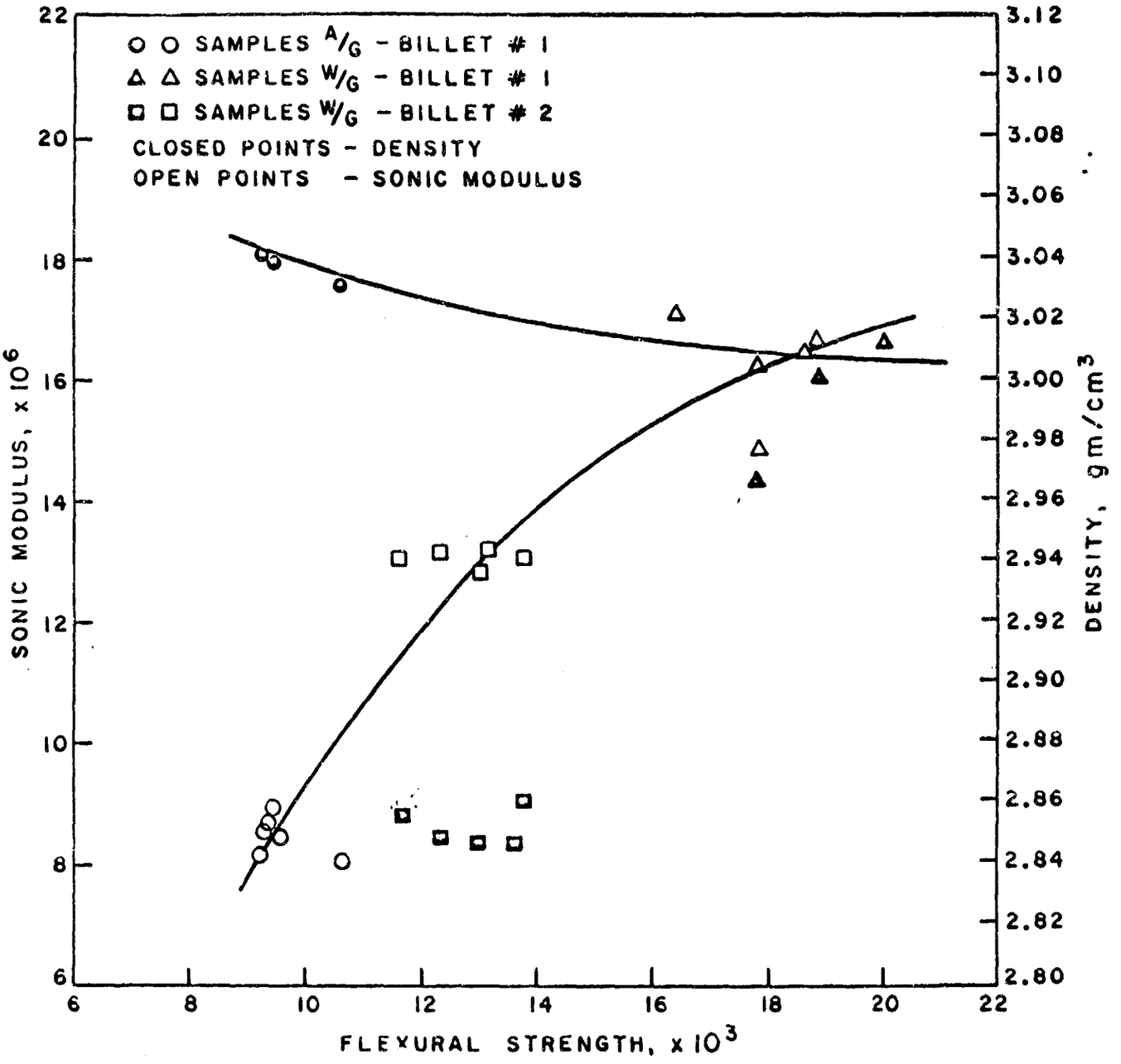

FIG 10 - CORRELATION OF SONIC MODULUS AND DENSITY WITH FLEXURAL STRENGTH OF ROOM-TEMPERATURE JTA GRAPHITE

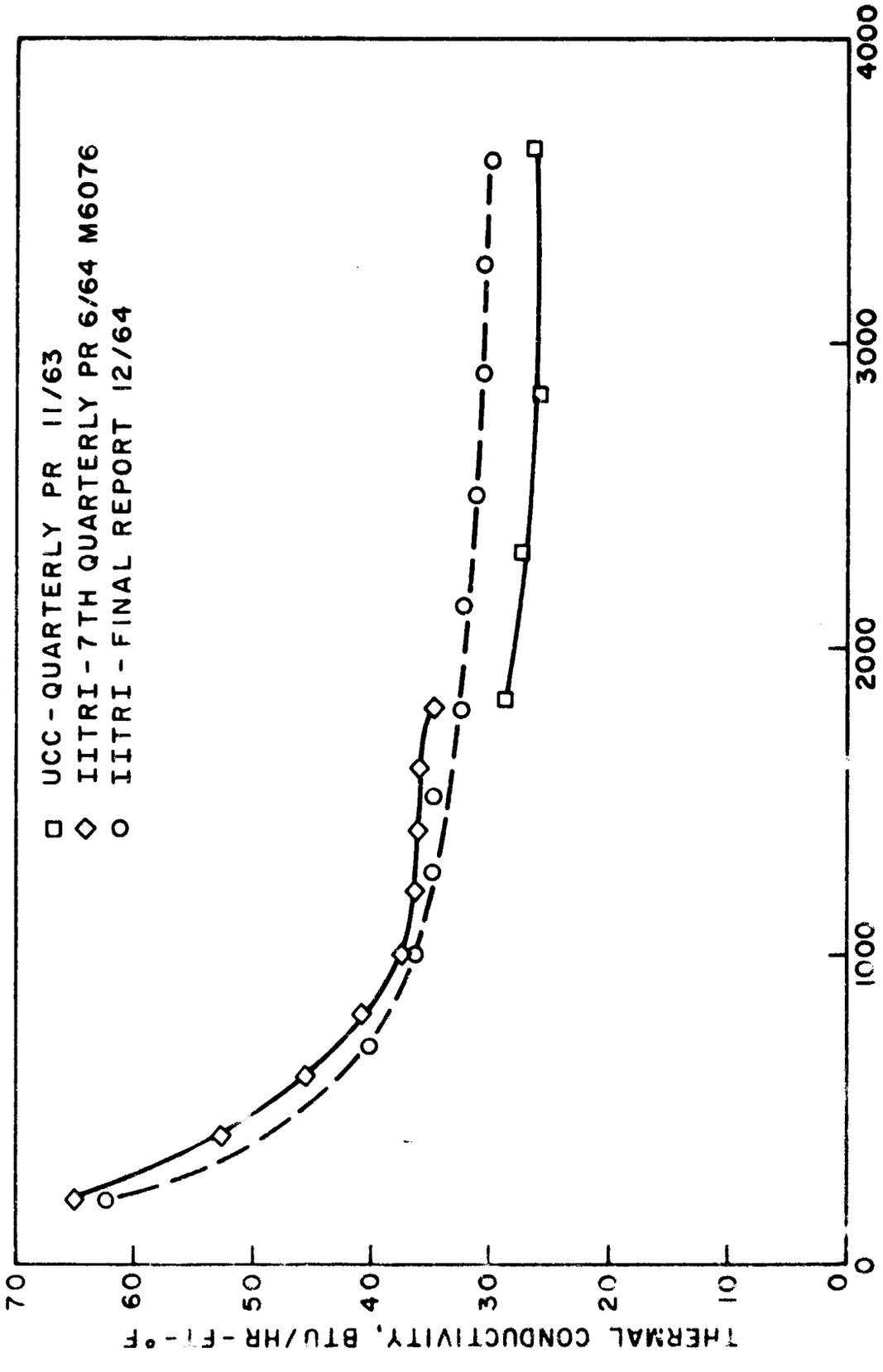

FIG. 11 - THERMAL CONDUCTIVITY JTA GRAPHITE (WITH THE GRAIN)

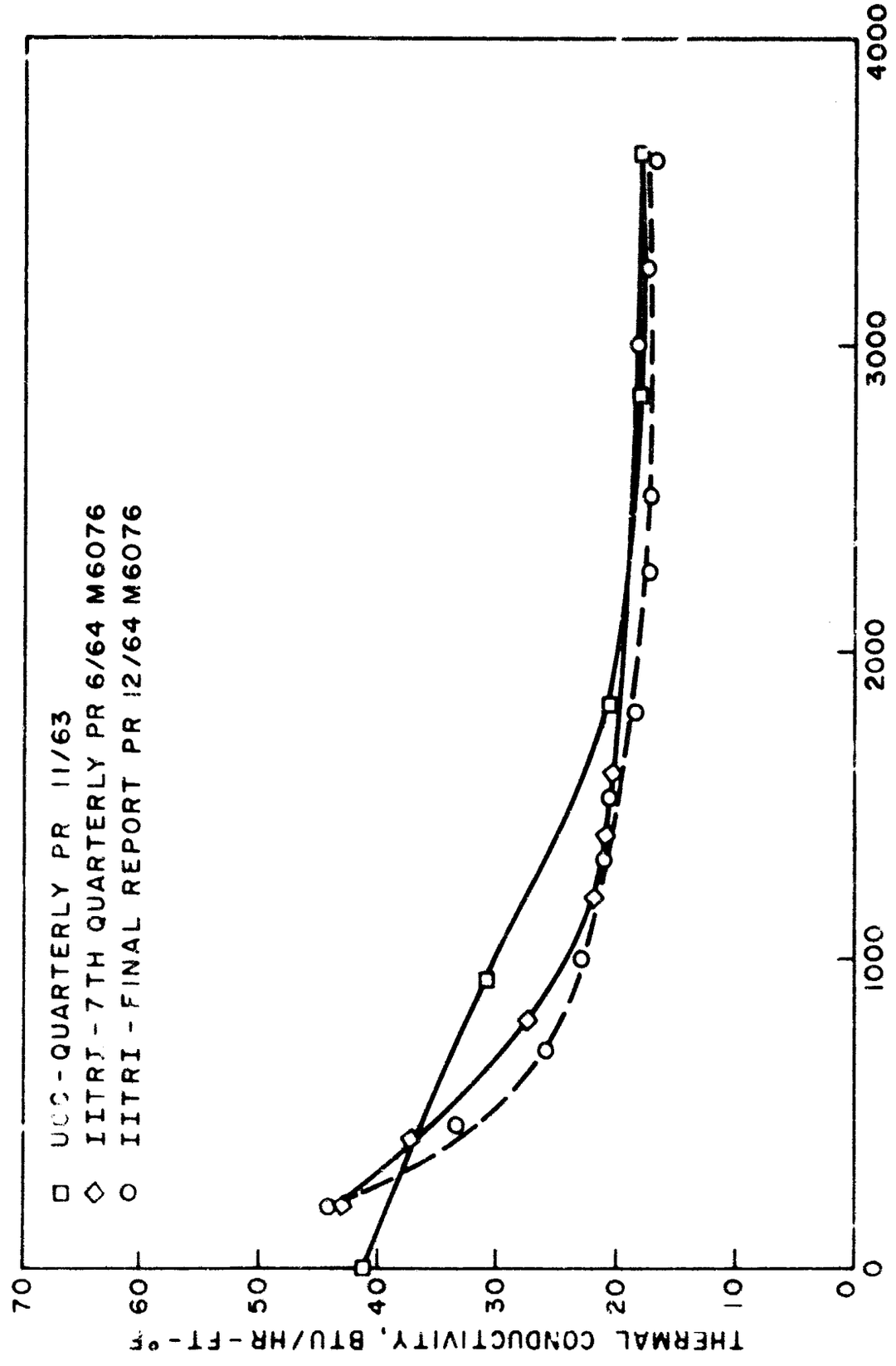

FIG. 12 - THERMAL CONDUCTIVITY JTA GRAPHITE (ACROSS THE GRAIN)

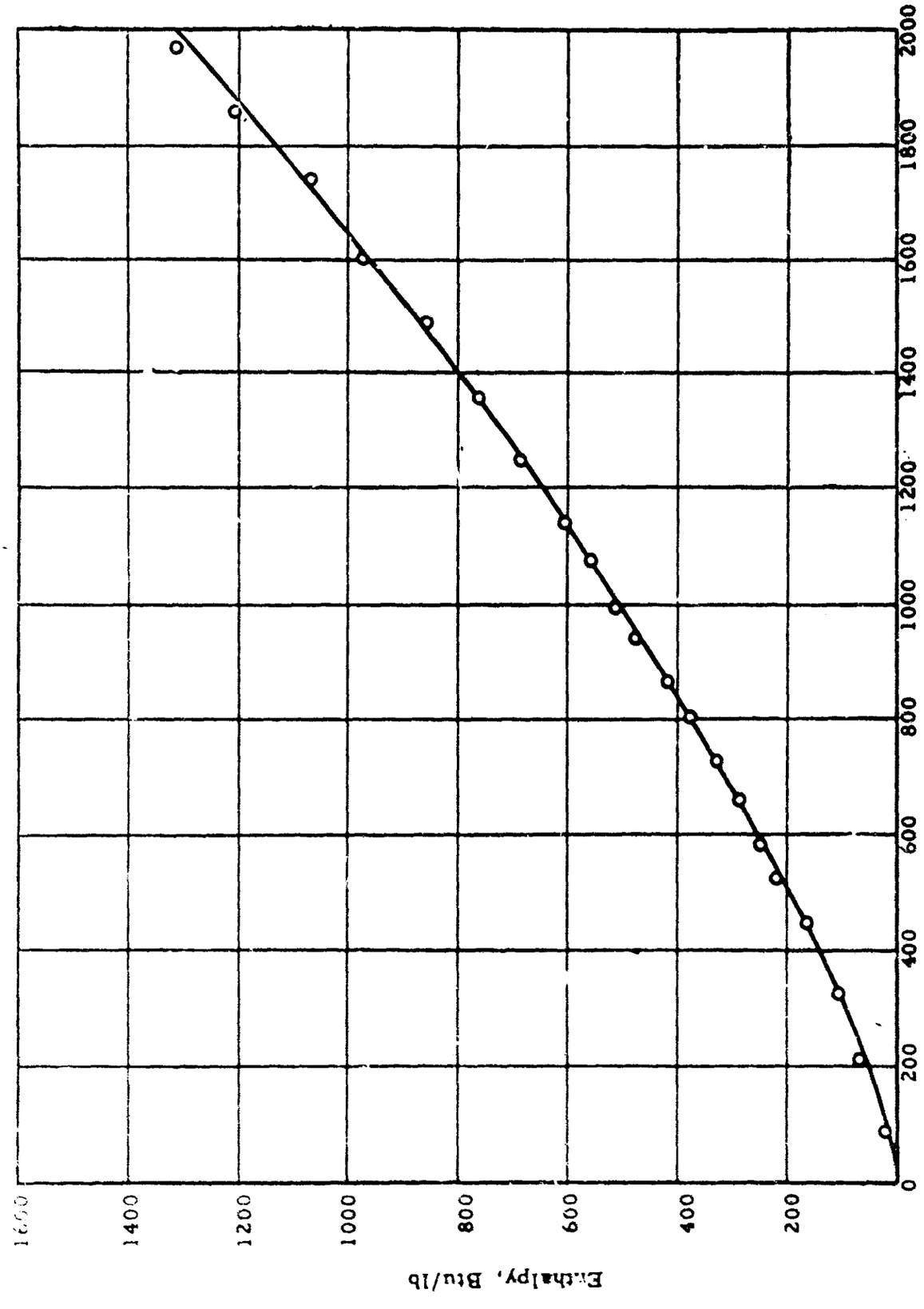

FIG 13 - ENTHALPY OF JTA GRAPHITE.

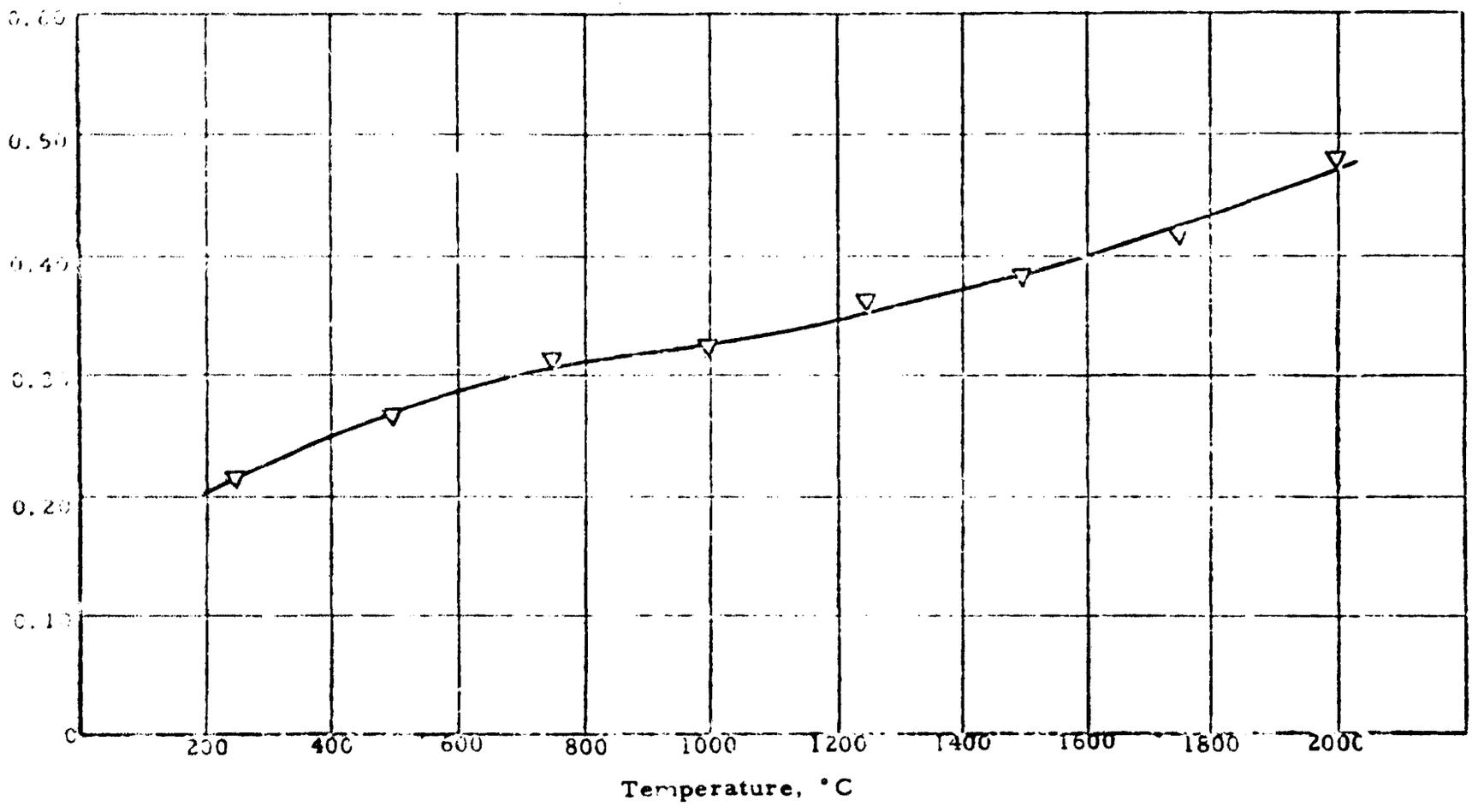

FIG. 14 - SPECIFIC HEAT OF JTA GRAPHITE

TABLE II
TOTAL NORMAL EMITTANCE OF JTA GRAPHITE

	Time After Startup (hr)	Temp (°F)	Emittance
Initial Run	2 3/4	2570	0.92
	4	3020	0.88
	5 3/4*	3495	0.89
Rerun	4 1/4	3500	0.86
	5 1/4	3750	0.86
	5 3/4	3800	0.88
	6	3905	----**

*Sample smoked badly. After cooling overnight thickness had decreased by 1/32 inch.

**Results erratic because of heavy white smoke. After cooling overnight, sample had apparently lost all of the graphite and was white and very porous.