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FINAL REPORT

TRANSIENT DETERMINATION OF THE THERMAL CONDUCTIVITY OF A LOW DENSITY PHENOLIC NYLON CHAR

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FOREWORD

This work was conducted by the Re-Entry Systems Department of the General Electric Company, under NASA Contract NAS1-2979-1. The contract was administrated under the direction of the NASA Langley Research Center with Mr. R. G. Wilson acting as Contract Monitor.

The work covered in this report was under the overall technical direction of Mr. E. J. Nolan, Program Manager, with Mr. R. A. Tanzilli acting as Project Engineer. Mr. J. Brazel conducted the experimental program and authored the final report. Acknowledgement is also given to Mr. B. Kennedy who fabricated and instrumented the test models and Mr. P. Dubin who performed the data reduction and graphical illustrations.

TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	2
DISCUSSION OF RESULTS	5
RECOMMENDATIONS	6
REFERENCES	7
APPENDIX	8
LIST OF FIGURES	9
FIGURES 1 TO 12	10

SUMMARY

Four transient thermal conductivity determinations have been made on a low-density phenolic-nylon char submitted by the NASA Langley Research Center. The transient technique has yielded significantly lower thermal conductivity values than those obtained by steady-state means. This is attributed in part to the "non-heat-treated" nature of the char and its continuing pyrolysis during severe transient heating. The inconsistency of attributing thermophysical parameters based on steady-state measurements to the operational performance of ablative heat shield systems is pointed out.

INTRODUCTION

In the design and analytical description of high-performance thermal-protection systems, performance of a system is critically dependent upon the adequacy of thermophysical characterization. When thermally degradable materials are chosen because of their ability to absorb great amounts of heat energy by physical-chemical transformation processes, the thermophysical parameters assume an irreversible, time-variant nature. As a consequence of this behavior, conventional laboratory techniques for the measurement of such a parameter as thermal conductivity must be interpreted in terms of a plot similar to figure 1. This series of steady-state measurements reported by Mrozowski (reference 3) shows the effect of temperature history on the thermal conductivity function of a sample of pressed carbon. For each measurement establishing the curves, steady heat flow conditions were established. By definition, this precluded further kinetic effects at that temperature. This plot is typical of the hysteresis function of a thermally degradable material in the steady-state plane, i.e., for time at temperature much greater than the reaction kinetics time. However, in operational use the degradation process is (by design) incomplete and a three-dimensional plot including kinetic effects must be considered. The actual, dynamic application of these materials, under conditions of severe heating, with coupled mechanical-thermal effects and exposures measured in orders of seconds, has indicated the desirability of measuring thermophysical parameters under conditions closely simulating their actual use.

This sensitivity of analytic models to materials characterization has been discussed in general in reference (1) and for phenolic nylon, the subject of this report, by Kratsch (2) in a correlation of the flight performance of RVX-1 Thor-Able vehicles. In this particular study, Kratsch et.al. found it necessary to "perturb" the value of the residual weight fraction for phenolic nylon chars. That is, a less severe degree of degradation at given temperatures was required to obtain a lower thermal conductivity function in order to match flight data to their analytic model. For a similar experience at GE-RSD, where a discrepancy was noted between steady-state data and the results of the GE-Reaction Kinetics Program, see "Discussion of Results", below. Since variations of an order of magnitude in thermal conductivity are observed across the degradation range - for constant temperature - the correct specification of the operational, i.e. dynamic, char degradation state is far more significant than static determinations on laboratory samples.

The final design target of any materials characterization program must be the design specifications of the shield: the weight, shape, and thickness. The thickness for a given material and hence the vehicle weight can be reduced significantly if realistic values of the actual, operational thermal conductivity are available for design computations, as is evidenced, for example, in reference (1) and the Kratsch study (reference 2).

Because of the importance of this problem, a transient thermal conductivity technique has been developed at GE-RSD to obtain values of the thermal conductivity useful for the design of charring ablators undergoing hypersonic entry.

The application of this technique to a low-density phenolic-nylon char is described in this report.

EXPERIMENTAL PROCEDURE

Samples were taken from the charred layers on the discs of material submitted for measurement. These were shaped to fit in the containment canister shown in figure 2. This measure provided a greater degree of structural integrity to the very fragile char structure so that it could be drilled and handled during instrumentation and test. The canister assembly could then be directly inserted into the test fixtures regularly utilized in this laboratory's program for transient determination of thermal conductivity. Due to the cracked, irregular, and porous surface of the material, a .010" disc of tantalum was fitted over the canister assembly of models 1 and 2, holding the char in compression to insure good thermal contact. A photograph of model 4, sectioned to show the internal dimensions and sensor installation is presented as figure 3. Figure 4 shows an x-ray view of model 4. The details of individual model assembly are presented below in tabular form.

TABLE 1

Model	Sensors; Spacing	Heating Source	Notes
1	W-W/26 Re; .040", .065" Pt-Pt/10 Rh; .090" C-A; .120", .150".	a. Shroud arc (He) b. oxy-acetylene torch	Plasma discharge caused noisy thermocouple traces although successful for other types of chars; switched to oxy-acetylene source after 1-second run. (.010" thick tantalum disc used on surface to prevent penetration.)

TABLE 1 - cont'd.

Model	Sensors; Spacing	Heating Source	Notes
2	Pt-Pt/10 Rh; .030", .050" C-A; .070", .090", .110", .140" Spurious readings from couples at .090", .110".	Oxy-acetylene torch	This model (and #3) was tested in addition to programmed #1 and #4 to get improved statistical sample and further examine behavior before running other government funded model (.010" thick tantalum disc on surface).
3	Pt-Pt/10 Rh; .030", .050" C-A; .070", .110", .140"	"	Instead of a protective disc, char filings were used to fill in the surface crevices.
4	W-W/26 Re; .020", .040" Pt-Pt/10 Rh; .060", .080" C-A; .100", .125"	"	An ATJ graphite cap (.010" thick) was used to protect the surface. Peak temperature of 3600°F was reached at first sensor station .020" beneath char surface.

The experimental temperature responses of the four tests (figures 4-8) provide a record of the material's performance under simulated atmospheric entry. The traces shown represent a certain increment of time during the transient heating period and were selected for ease of calculation. Together with the model dimensions (x) the responses can be used to compute the terms in the non-linear differential equation of heat conduction:

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \frac{\partial k}{\partial x}\left(\frac{\partial T}{\partial x}\right) \qquad (1)$$

An example of the values which were deduced graphically and then used in the computation for model #4 is given below in tabular form for t = 0.5 sec.

TABLE 2

x(ft)	T(°F)	$\frac{\partial T}{\partial t}\left(\frac{°F}{s}\right)$	$\frac{\partial T}{\partial x}\ \frac{°F}{ft}$	$\frac{\partial^2 T}{\partial x^2}\left(\frac{°F}{ft^2}\right)$	$C_p(T)\left(\frac{Btu}{lb\text{-}°F}\right)$	$\rho\left(\frac{lbs}{ft^3}\right)$
1.67×10^{-3}	2670	1160	-153×10^{4}	$+2880\times10^{6}$	.52	13.1
3.33	1850	1020	-24.96	+129.60	.52	13.1
5.00	1530	1080	-19.68	-20.16	.52	13.1
6.67	1120	940	-29.76	-57.60	.52	13.1
8.33	680	720	-20.64	103.68	.50	13.1
10.00	480	520	- 2.88	100.80	.42	13.1

These values are used as input to a computer code which utilizes a Runge-Kutta approximation scheme. This numerical solution transforms the differential equation into one for k and $\partial k/\partial T$, in effect computing the k(T) function necessary to allow the temperature response experienced by the test material. The thermal conductivity functions required for each of the four responses are given in figure 10.

It is seen mathematically that the accuracy of the transient thermal conductivity technique is primarily dependent upon the accuracy of the temperature and positioning terms inserted in equation (1) above. The positioning of sensors is verified by x-ray photographs (figure 3) and in few cases has deviated more than .003" from the nominal dimensions specified. These are verified for each determination and the actual dimensions are used.

An obvious approach for obtaining maximum temperature measurement accuracy is to install probes of the finest diameter available along the anticipated isotherms of the test model. A computer simulation of this geometry was performed in an earlier analysis conducted under a different program. At that time probes of .032" diameter were used and a nominal conductivity of 1×10^{-4} BTU/ft-sec-^{o}F was assumed for the char. For a surface cold wall flux of 2000 BTU/ft^2-sec after 1 second, the temperature of the homogeneous material would be 4653^{o}R, but the temperature at the thermocouple tip located at the same position would be 3800^{o}R, some 17% lower. This would be a worst case - a .032" diameter thermocouple .020" deep leaves only a .004" skin of the test material above it! The present design uses thermocouples of .008" maximum diameter so that a pessimistic linear extrapolation would indicate a 5% maximum error for the sensor closest to the surface, attaining the highest temperature. The platinum and chromel-alumel thermocouples used at depths corresponding to lower temperatures were of .006" to .007" diameter.

To relate this temperature-measurement error to the conductivity error produced through its use, a similar computer computation was made to determine the unperturbed temperature distribution in a similar char model. A temperature measurement error of minus 10% was then hypothesized and the apparent conductivity then recomputed. This resulted in a maximum positive error in thermal conductivity of 13% at 4500^{o}R. It would appear that an upper limit of ±10% error in the conductivity determination can then be assumed for errors in temperature measurement.

DISCUSSION OF RESULTS

The family of curves generated for the low density phenolic nylon char obviously differs from the previously reported steady state result supplied for comparison. In addition to the difference in magnitude of the functions, a large variance is seen in the transient results. This variance is primarily due to the fragmentary, loose structure of the char samples. Experience with thermally degradable materials has shown that variations from sample to sample in density, structure and localized heat treatment can yield variations approaching this magnitude. In addition, the nature of the transient technique- fast temperature response, short measurement times and small sample size - would definitely increase this variance, especially in the presence of incompletely degraded material. The presence of any energy absorbing mechanism would contribute a heat-capacity effect, an accordingly steeper gradient and, therefore, indicate a lower thermal conductivity. The mean value of the four functions, smoothed at the low end to represent only the significant trend, is presented in figure 11 and compared to the steady state result supplied by NASA. It drops from initial agreement demanded by the use of the steady state curve as "k_o" (see experimental procedure) in the beginning of the computer code run. Thus the transient technique, based on the more severe than anticipated gradients, "seeks" a lower thermal conductivity level. The experimental function is plotted (solid) out to 2400°F and linearly extrapolated out to 4000°F.

The lower slope and magnitude of the transient determination are similar to results noted in two other measurements. Mrozowski[3] has observed that when samples of pressed carbon are slowly cycled through successively higher temperature ranges, the resulting thermal conductivity curve approaches that for bodies of polycrystalline graphite (fig. 1). Each new maximum temperature generates its characteristic curve until, at some very high temperature, crystallization of the amorphous carbon into polycrystalline graphite is achieved and the upper limit is reached. In the present experiments the temperatures had been achieved for times of less than 120 seconds (see notes on char preparation in appendix) so that very short heat soaking times had prevailed for the grain growth effects to occur. The range of conductivities involved for these chars falls under the lowest trace of figure 1. Therefore, excursions of temperature for even moderate periods of time (10^2 seconds) should produce order of magnitude changes in transport parameters as any increase in the order of the structure occurs.

A second instance, in which these variations have been observed for another important thermal shielding system, has been reported earlier (1). In reference 1, a discrepancy had been cited between the thermal conductivity function generated in a quite competent steady state measurement, and the "required" function incorporated in a reaction kinetics simulation of the complete charring ablator performance. It was seen that the transient function much more closely approximated the physical simulation "REKAP", General Electric Reaction Kinetics Ablation Program, prediction.

In the design of the foregoing experiment, a model identical in dimensions to that utilized in previous determinations on materials of similar thermal parameters was used. The thermocouple spacings given in Table I were designed for a surface temperature in excess of 4000°F and internal temperatures above 3150°F at the .020" and .040" stations. Accordingly, tungsten thermocouples were used at these positions. However, a much lower and slower temperature response was observed upon heating. This can now be interpreted as a continuing ablative process as the pyrolysis of the sample proceeded. In particular, the government-furnished char preparation description cites a maximum surface temperature of 3000°F. This was exceeded in all four of the transient runs, so that a new maximum temperature was achieved throughout the char body. The resulting data spans a lower than expected temperature range because of this heat sink effect and actual measurement is only indicated up to 2600°F in figure 10.

RECOMMENDATIONS

It is recommended that the data be considered as more validly representing the thermal transport properties of the char under heating conditions similar to those encountered during atmospheric entry. It is further recommended that the heat treating effects noted above be studied by two complementary approaches:

1. An extension of the transient thermal conductivity technique to a more thoroughly instrumented program. This would include calorimetric determination of the heat flux levels to further corroborate the experimental boundary conditions, a char characterization program to determine the effects of continuing pyrolysis of the incompletely degraded material and a much larger statistical sample of models to improve the experimental precision.

2. A more thorough study of the char system, using a conventional steady state apparatus with its concomitant measuring precision. This would entail designing instrumentation and experiments to reduce the present long soaking times which drastically alter the character of the char from that which it would display in operational use. Particularly, the effects noted by Mrozowski should be studied in char systems as discussed in reference 3.

REFERENCES

1. Brazel, J., "Final Report on Thermal Conductivity of Refractory Reinforced Chars", General Electric Company Re-Entry Systems Department TIS report 65SD251 (conf.), April 30, 1965. Work conducted under United States Air Force Contract AF04(694)473.

2. Kratsch, K.M., Hearne, L.F., and McChesney, H.R., "Thermal Performance of Heat Shield Composites During Planetary Entry", presented at AIAA-NASA National Meeting, Sept. 30 - Oct. 1, 1963, Lockheed Missiles and Space Company.

3. Mrozowski, S., "Thermal Conductivity of Carbon and Graphite", letter to the editor, Physical Review, v. 86, No. 2, April 15, 1952.

4. Peters, Roger W., and Wilson, R. Gale, "Experimental Investigation of the Effect of Convective and Radiative Heat Loads on the Performance of Subliming and Charring Ablators." NASA TN D-1355, 1962.

APPENDIX

As required in the task order for NASI-2979 (CRD), the government-furnished data on thermal conductivity (steady state), density, specific heat and a brief description of the char preparation are incorporated in this report.

Thermal Conductivity (steady state)

This function has been presented in figures 9 and 10 for comparison with the results of the transient technique.

Density

A uniform density of 13.1 lbs. was used for the computations, as entered in table 2.

Specific Heat

This function is reproduced in figure 12.

Description of Char Preparation

The low-density phenolic-nylon char was produced by thermal degradation of a low-density phenolic-nylon material. The low-density phenolic-nylon consisted of 25 percent by weight of Union Carbide Bakelite BRP-5549 phenolic resin, 25 percent by weight of Union Carbide Microballoons (formulation BJO-0930), and 50 percent by weight of DuPont Zytel 103 nylon powder. The mixed materials were hot-pressed while in vacuum and at a temperature of 320°F (433°K) for about 2 hours. Ram stops on the molding press were used to limit the molding pressure and thus achieve a pre-determined and reproducible density of the molded material. The material was cooled in the mold under mechanical pressure and in vacuum to room temperature. After removal from the mold, the material was post-cured according to the following temperature cycle:

a. Start at 100°F (311°K), hold 1 hour

b. Increase temperature 10°F/hr (5.5°K/hr) to 200°F (366°K), hold 10 hours

c. Increase temperature 5°F/hr (2.8°K/hr) to 240°F (333°K), hold 10 hours

d. Increase temperature 5°F/hr (2.8°K/hr) to 300°F (422°K), hold 10 hours

e. Decrease temperature 25°F/hr (14°K/hr) to 200°F (366°K), hold 4 hours

f. Decrease temperature 25°F/hr (14°K/hr) to ambient temperature

The low-density phenolic-nylon char was produced by exposing 3-inch-diameter (7.6 - cm) disks of the low-density phenolic nylon to an arc-heated stream of nitrogen for 2 minutes, the time required to produce a char layer of ¼ - inch (0.63 - cm) thickness. The arc jet, described in reference 1, was operated with a nozzle 2 inches (5.1 cm) in diameter and with arc power of 1000 kilowatts. Under these conditions the arc jet produced a thermal flux of about 100 Btu/ft^2-sec (1.13 MW/m^2) on the phenolic-nylon disks located 2 inches from the nozzle, resulting in a maximum surface temperature of about 3000°F (1920°K). Stagnation pressure on the specimen was slightly greater than 1 atmosphere (0.1 MN/m^2).

FIGURES

1. Observed and Predicted Thermal Conductivities for Variously Heat Treated Carbons as Function of Temperature - after Mrozowski.

2. Char Containment Fixture for Use in Standard Holder.

3. Photograph of Sectioned Transient Thermal Conductivity Model #4.

4. X-Ray View of Internal Thermocouple Installation.

5. Phenolic Nylon Char-Temperature Response for Model No. 1.

6. Phenolic Nylon Char-Temperature Response for Model No. 2.

7. Phenolic Nylon Char-Temperature Response for Model No. 3.

8. Phenolic Nylon Char-Temperature Response for Model No. 4.

9. Phenolic Nylon Char-Temperature Response for Model No. 4 (later time).

10. Transient Thermal Conductivity Functions for Simulated Re-Entry Heating, Steady State.

11. Measured Thermal Conductivity Function For Simulated Re-Entry Heating (Mean).

12. Specific Heat of Phenolic Nylon Char Obtained from NASA TN-2991.

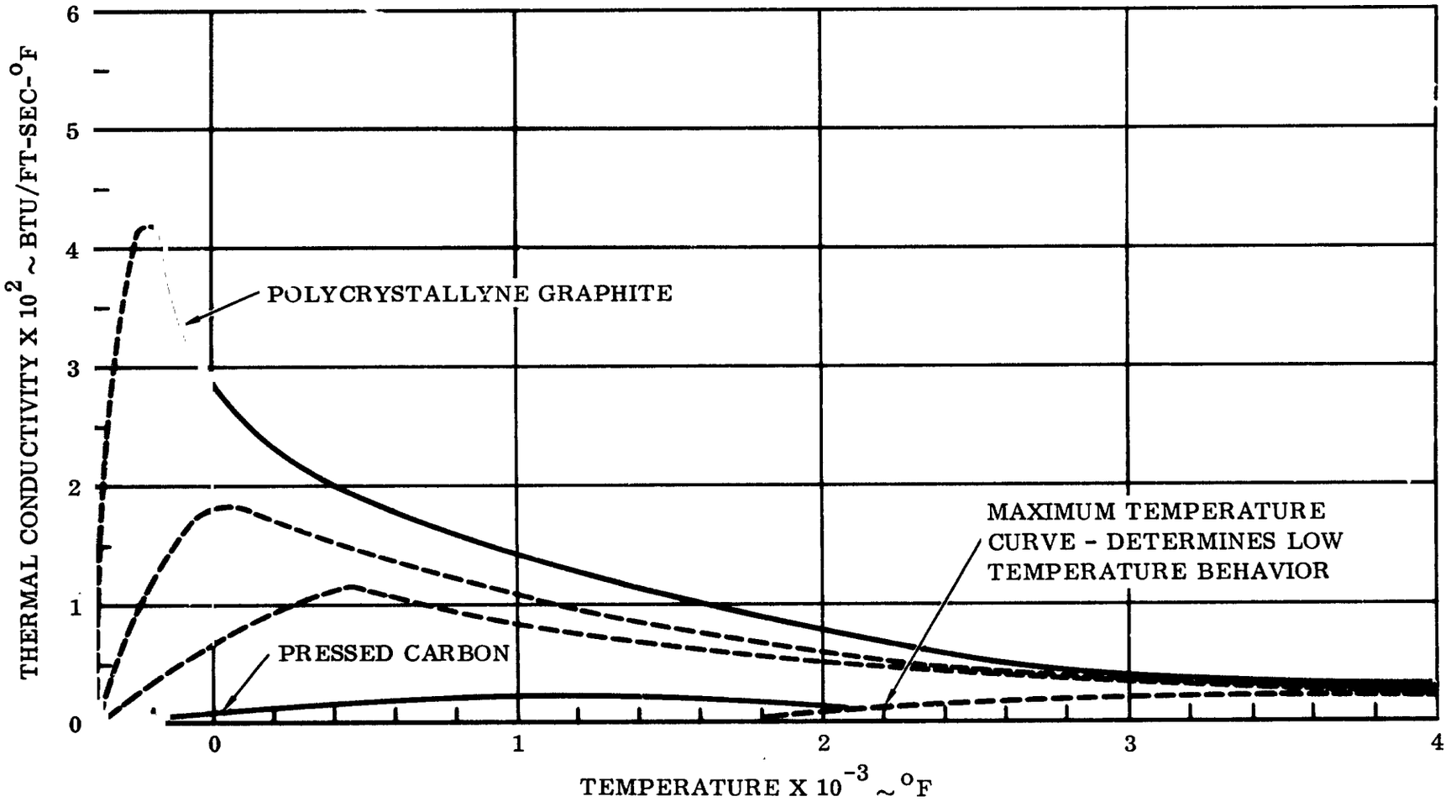

Figure 1. Observed (Solid) and Predicted (Dashed) Thermal Conductivities for Variously Heat Treated Carbons as Function of Temperature - after Mrozowski

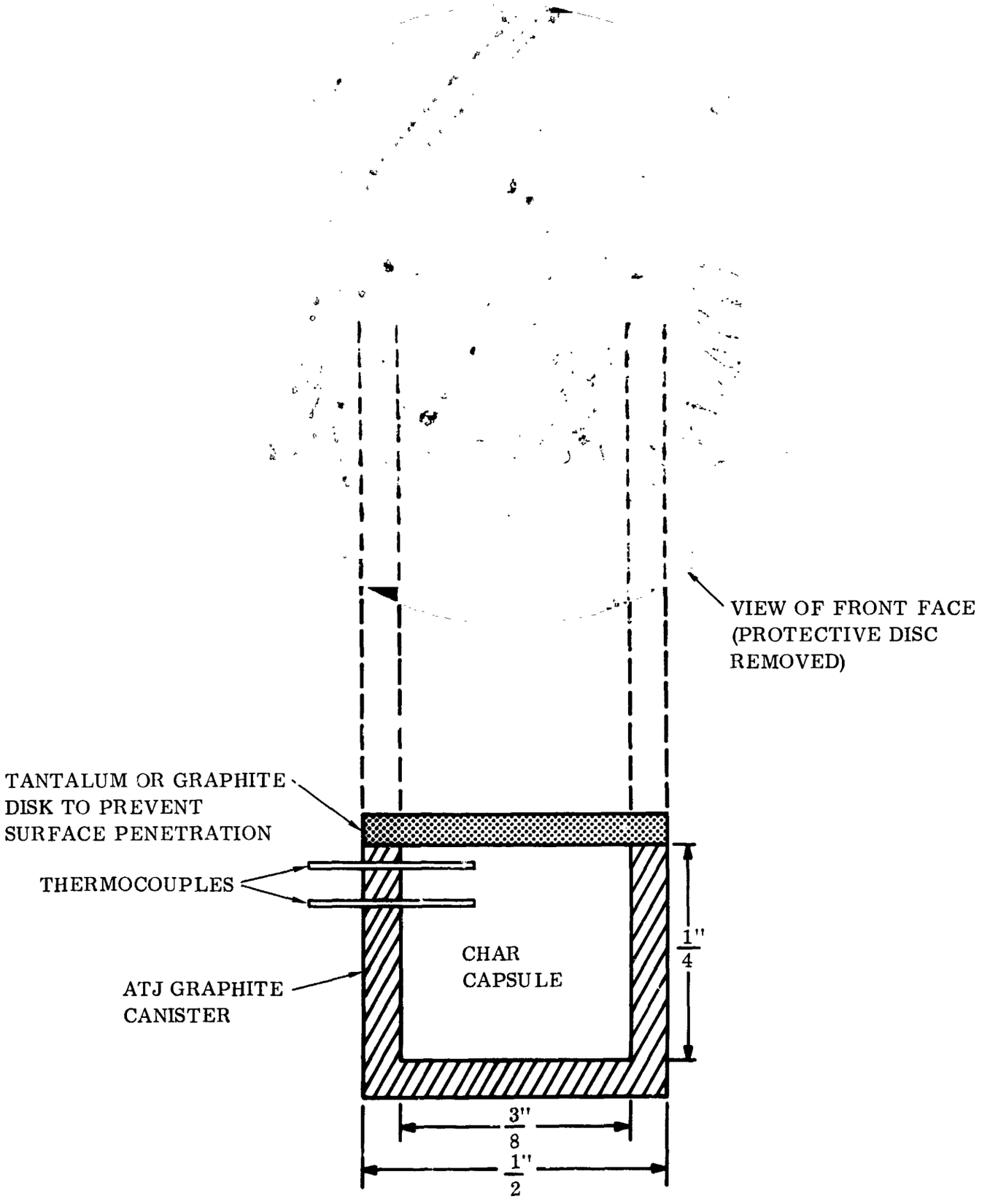

Figure 2. Char Containment Fixture for use in Standard Holder

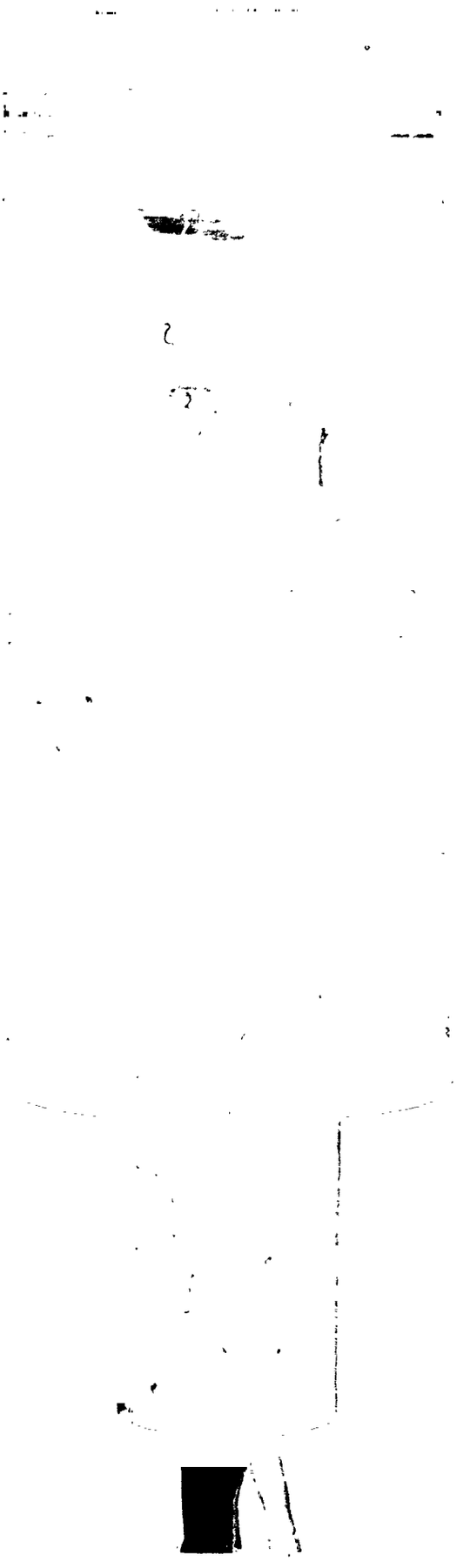

Figure 3. Photograph of Sectioned Transient Thermal Conductivity Model #4

Figure 4. X-Ray View of Internal Thermocouple Installation

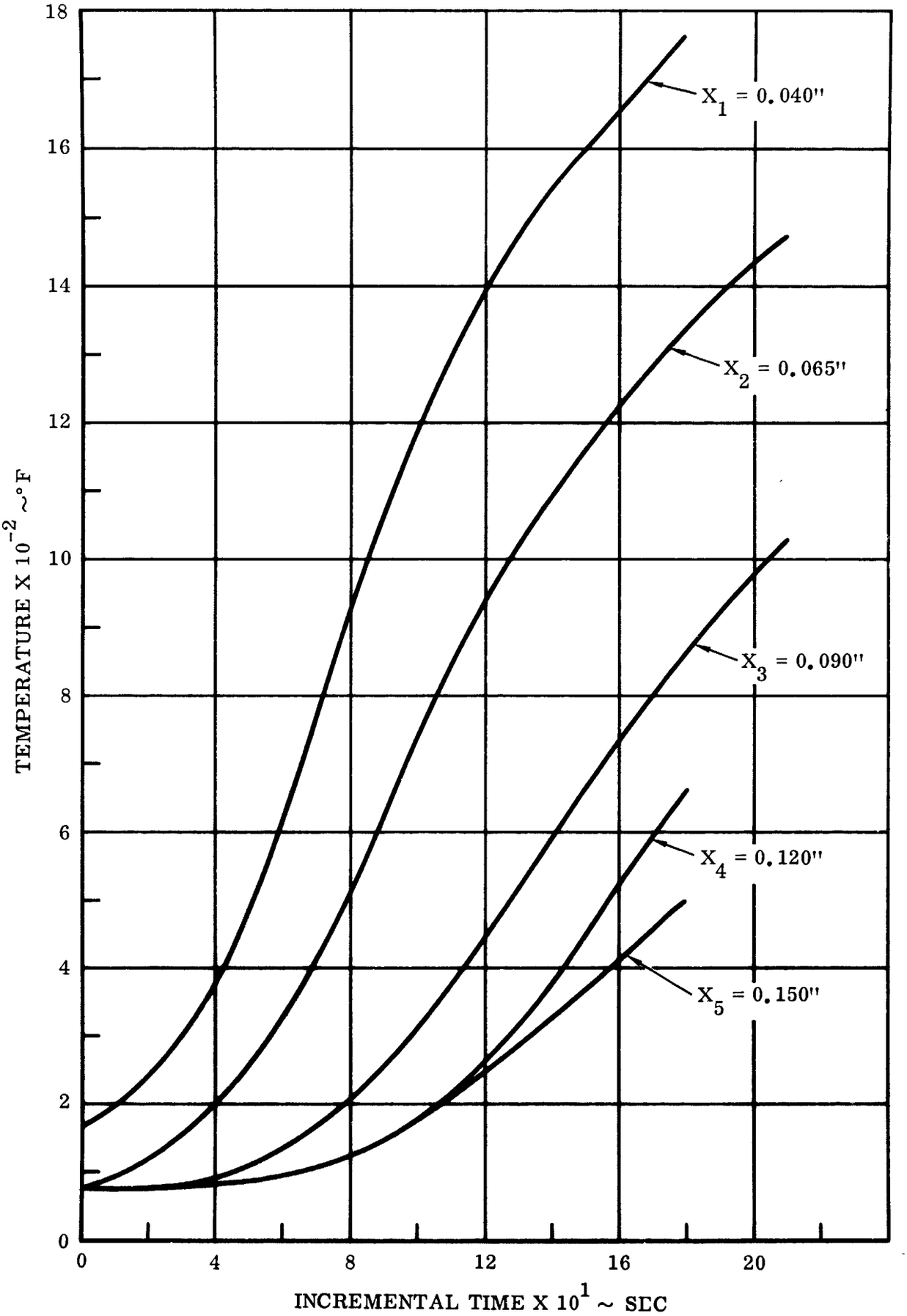

Figure 5. Phenolic Nylon Char - Temperature Response For Model No. 1

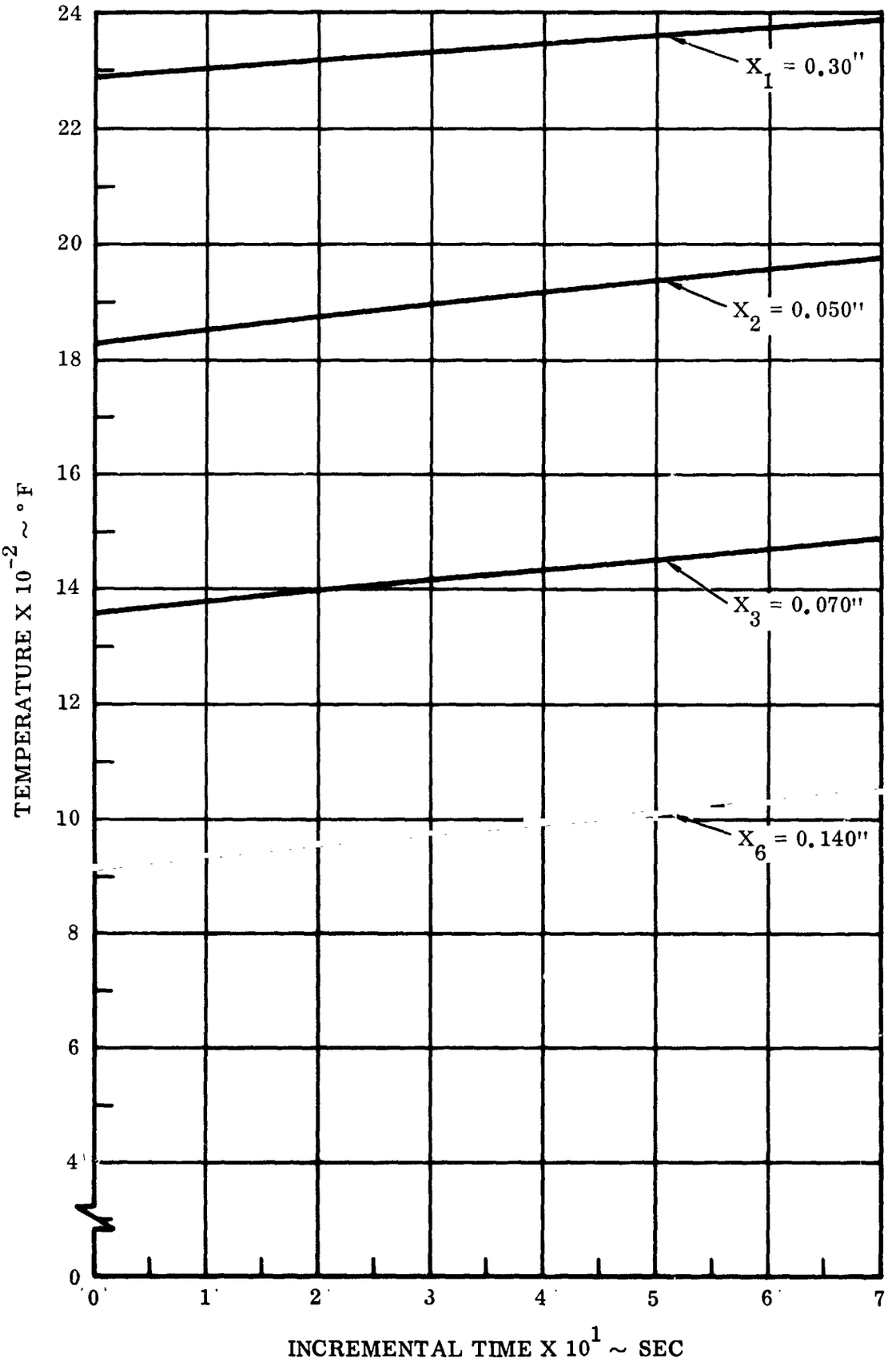

Figure 6. Phenolic Nylon Char - Temperature Response For Model No. 2

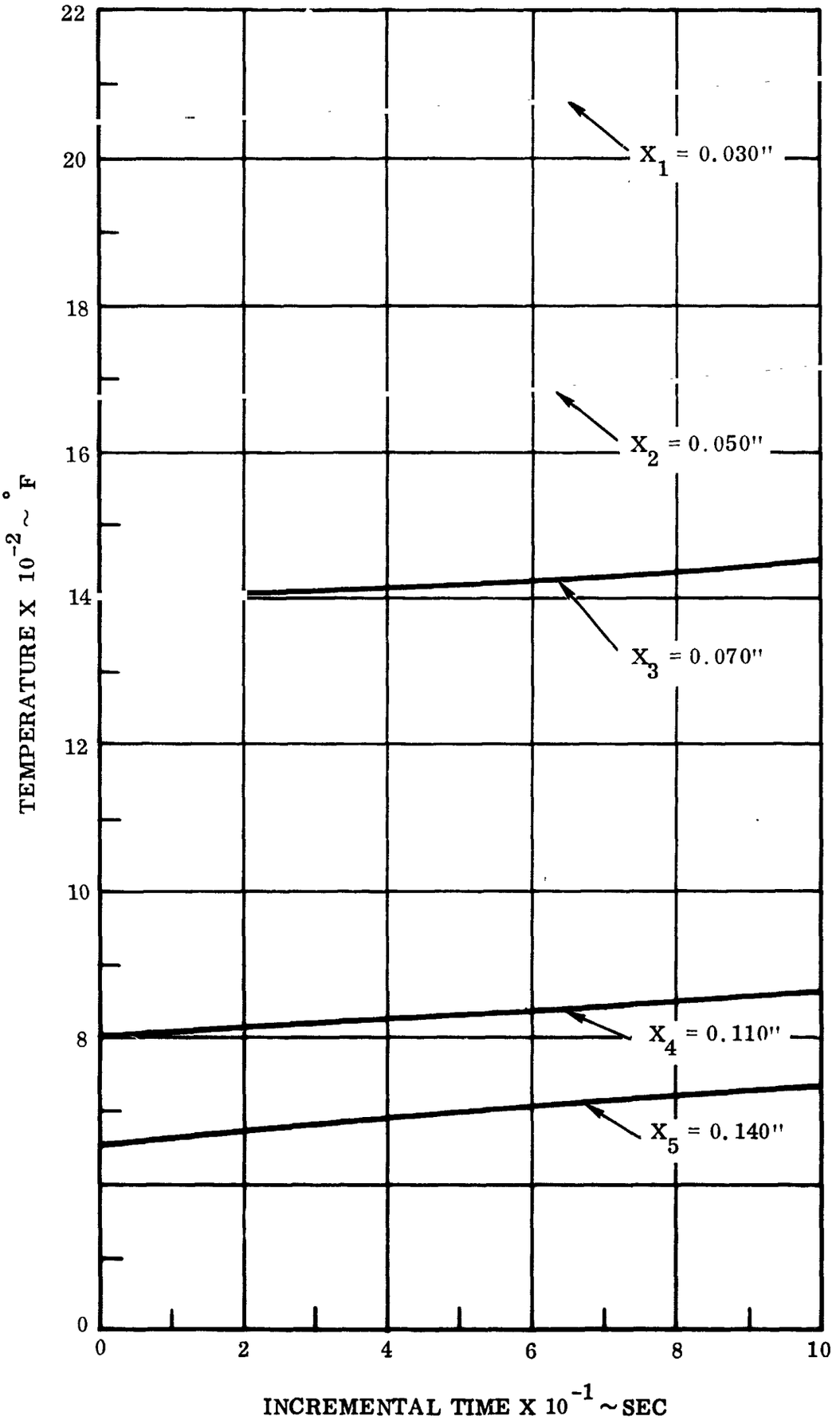

Figure 7. Phenolic Nylon Char - Temperature Response for Model No. 3

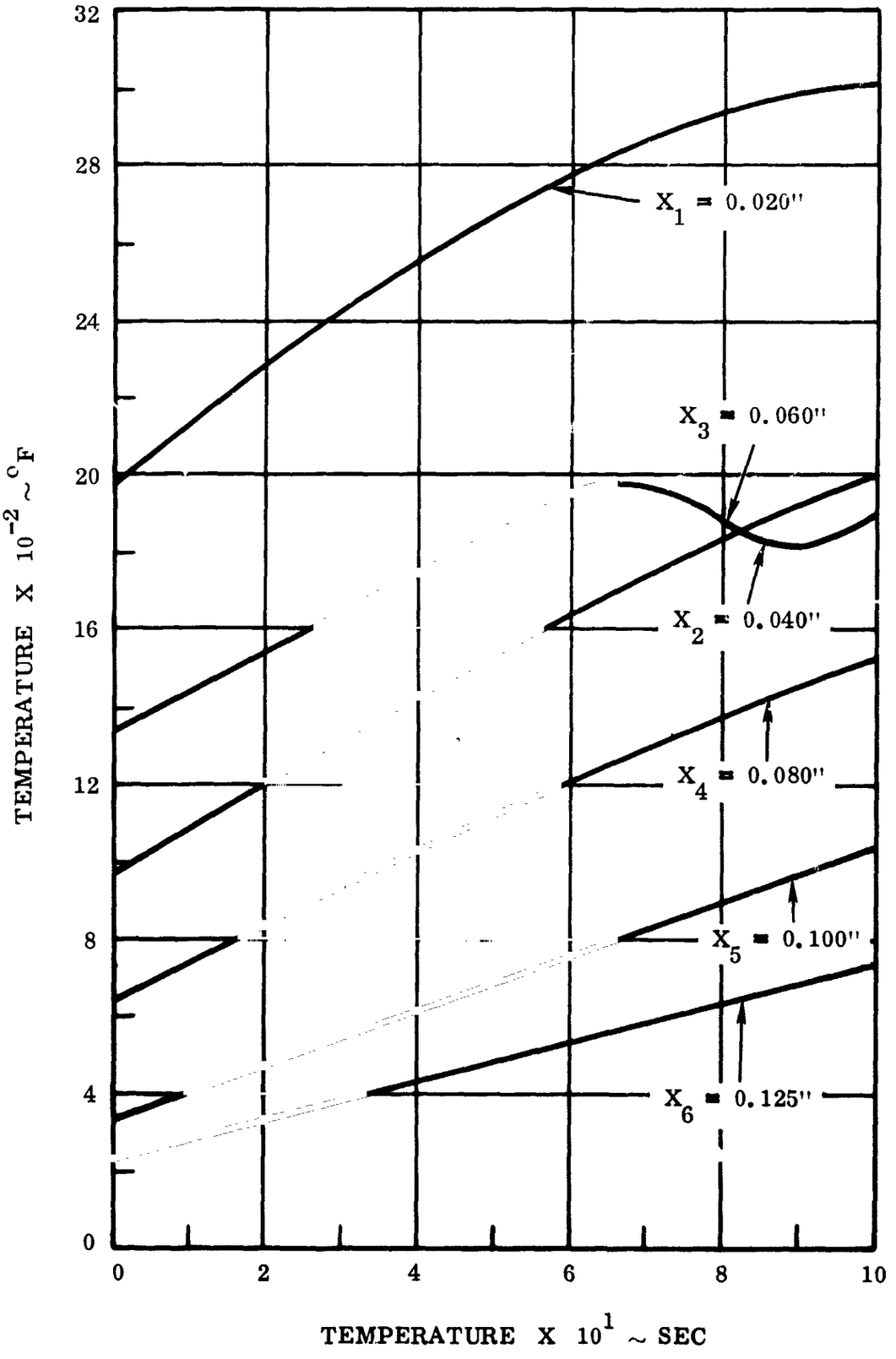

Figure 8. Phenolic Nylon Char - Temperature Response For Model No. 4

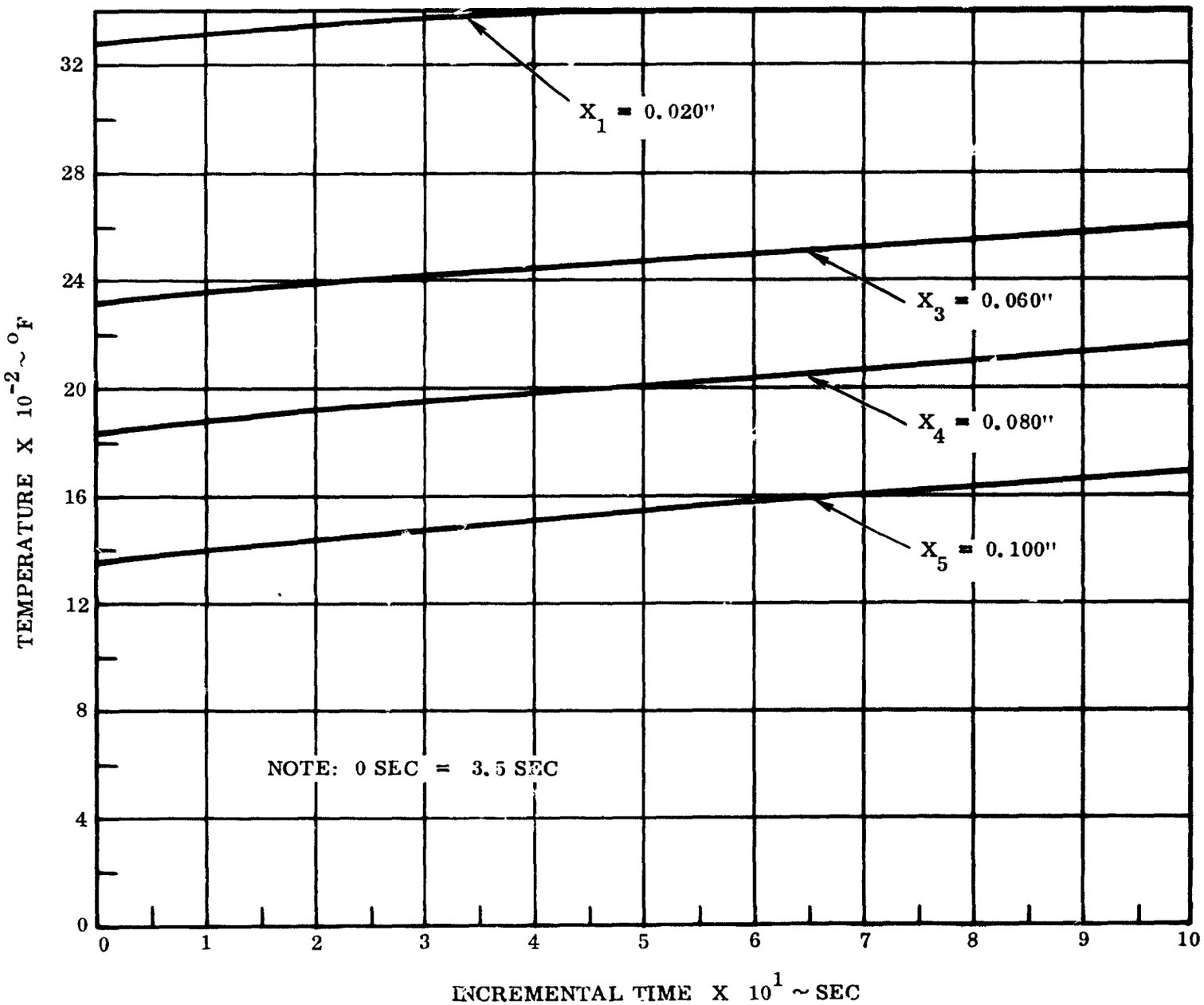

Figure 9. Phenolic Nylon Char - Temperature Response for Model No. 4

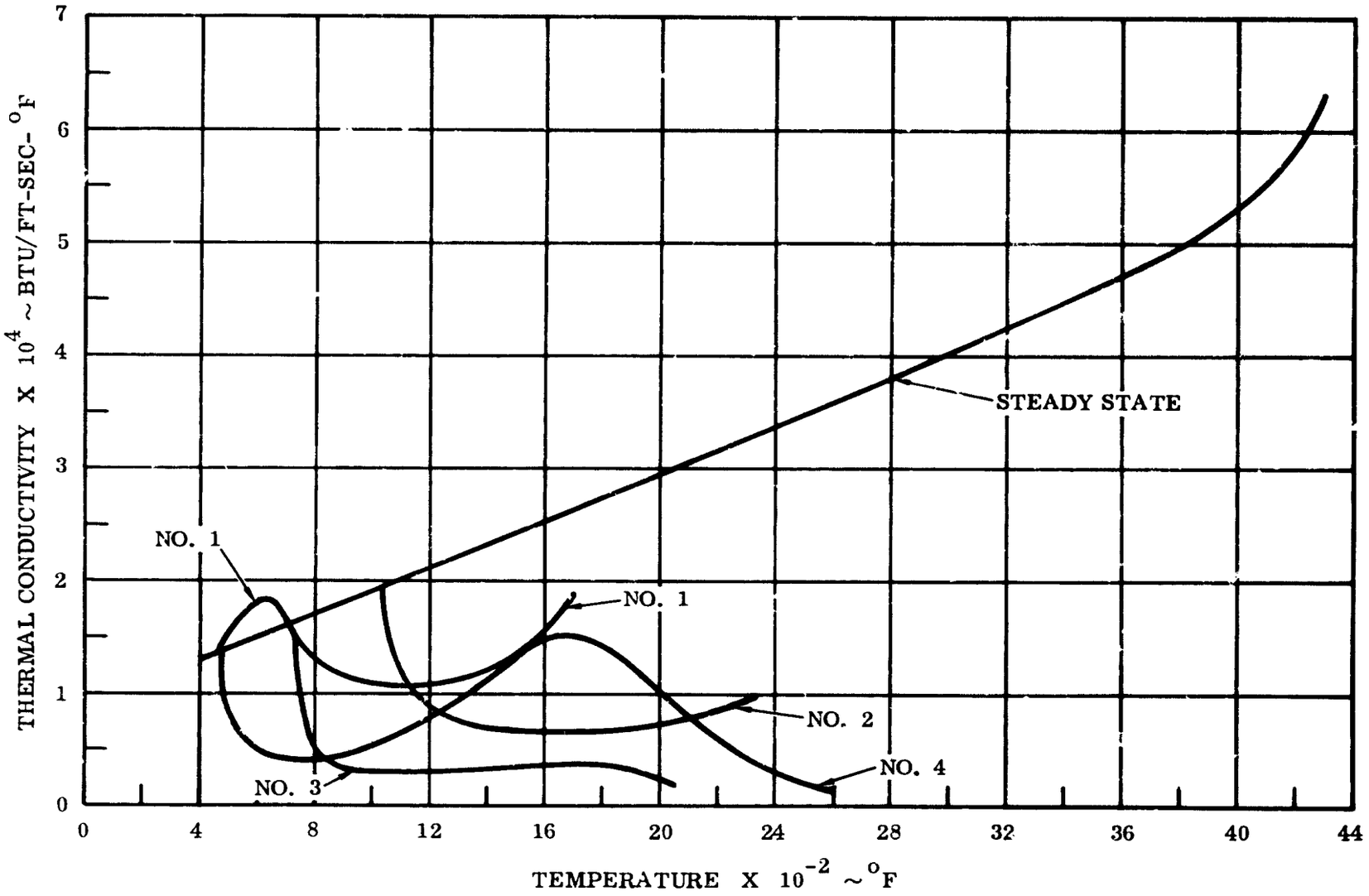

Figure 10. Transient Thermal Conductivity Functions For Simulated Re-Entry Heating Steady State

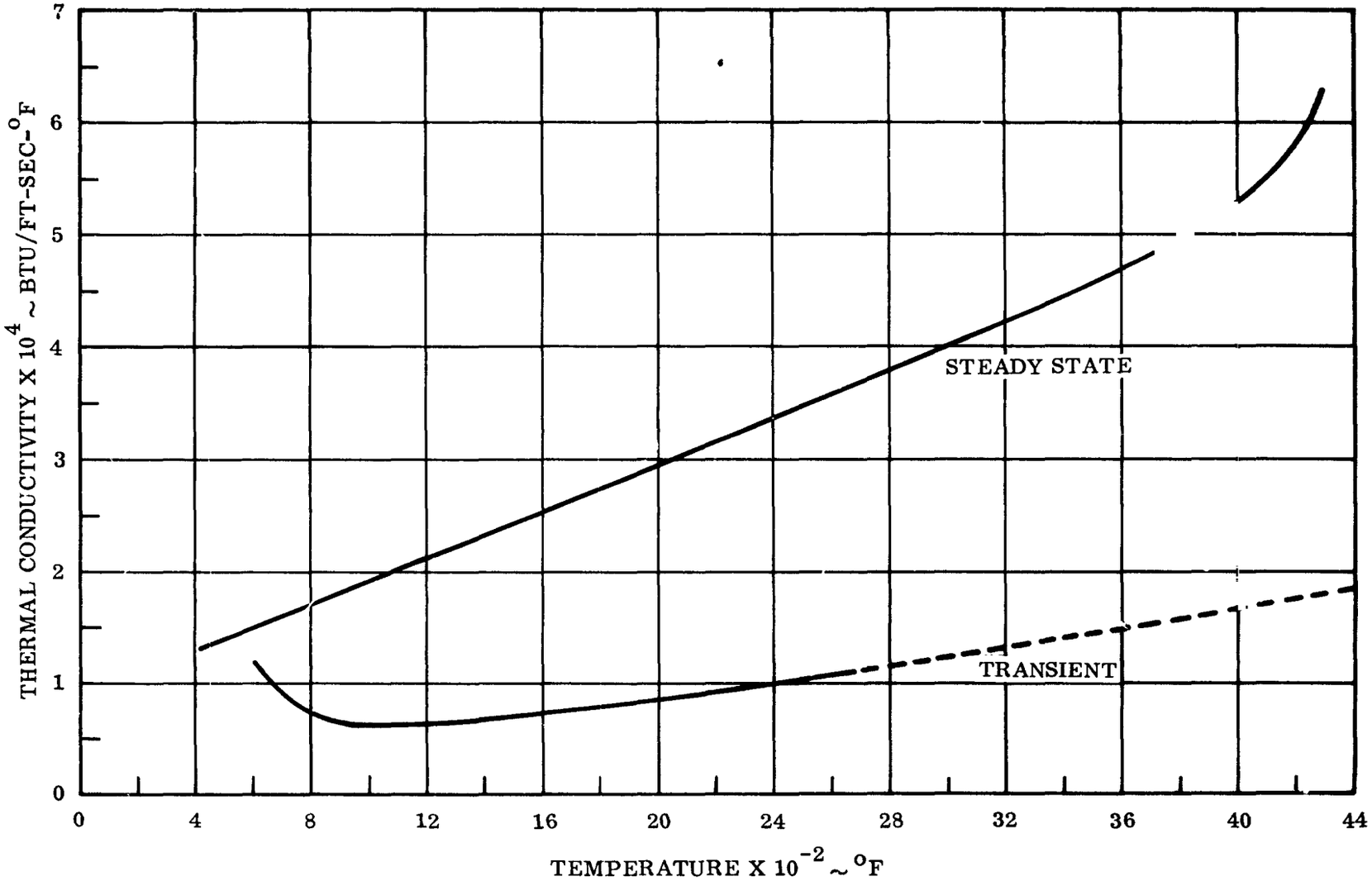

Figure 11. Measured Thermal Conductivity Function For Simulated Re-Entry Heating (Mean)

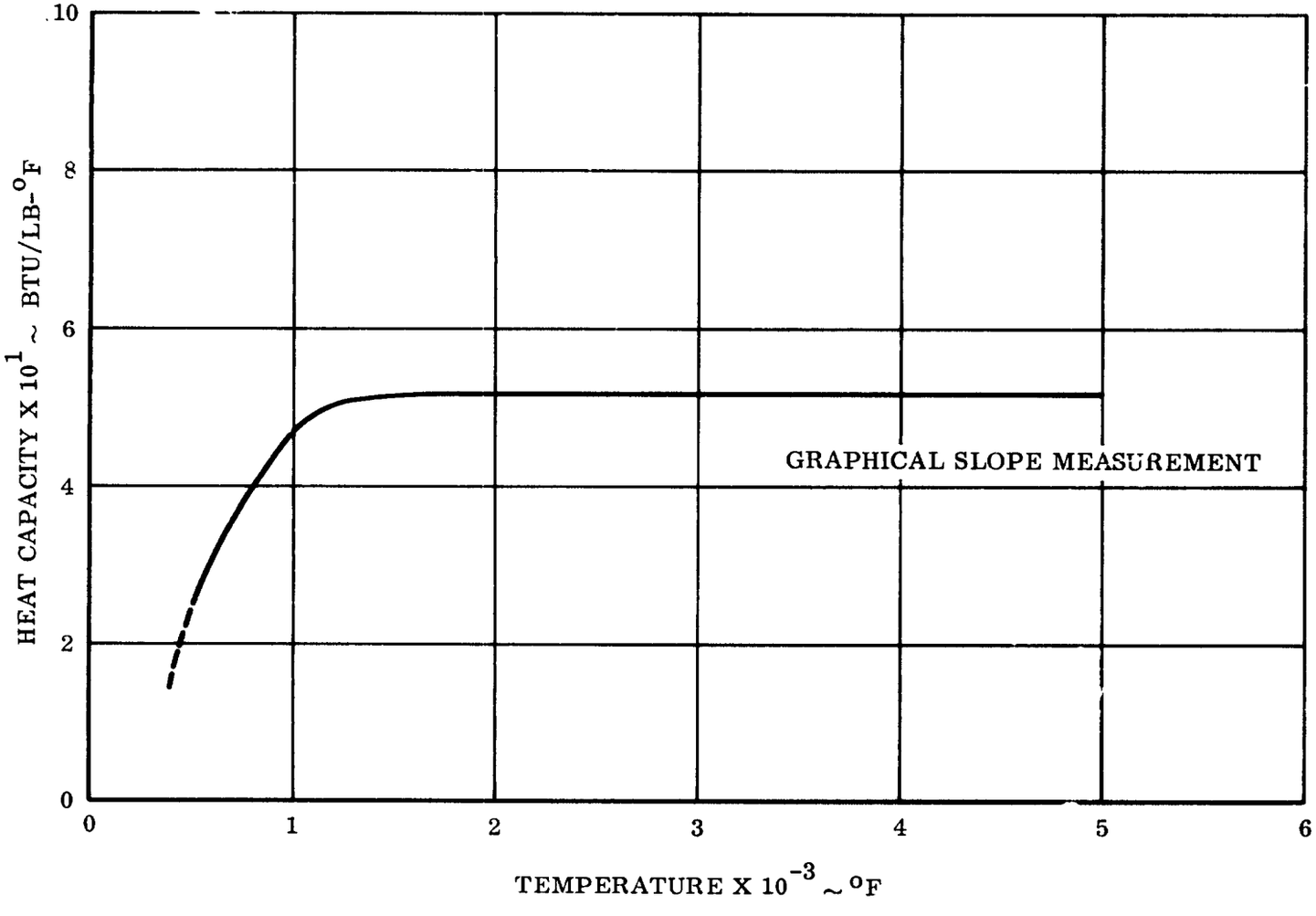

Figure 12. Specific Heat Of Phenolic Nylon Char Obtained From NASA TN-2991