

Monitoring the Oxidation of a Carbon-Carbon Composite
Using an Electrical Resistance Measurement

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Exec. Dir., Honors Program _____

Abstract

The aerospace industry among others requires high strength, light weight materials that can withstand high temperatures. Carbon-carbon composite materials fit these requirements, but they are susceptible to oxidation damage when they are subjected to high temperatures in the presence of oxygen. Monitoring this oxidation during material characterization as well as in service is a difficult problem. This study presents data which shows that an electrical resistance measurement could be used to monitor such oxidation. The resistance measurements were correlated with mass loss results from a thermogravimetric mass analyzer and the oxidation behavior was characterized using differential thermogravimetric analysis.

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I. Introduction

All space craft and many airplanes operate at high external skin temperatures. This has required the aerospace industry to seek out and develop materials that maintain their integrity and strength when they are exposed to high temperatures. Carbon-carbon composite materials possess the capability to maintain their strength under these high temperature conditions, but these materials can be degraded when they are exposed to high temperatures in the presence of oxygen. The degradation of the substrate is caused by material oxidation that produces gases from the original solid and gas reactants. The oxidation damage mode is usually investigated before a carbon-carbon material system is considered as a viable option for real world applications.

Carbon-carbon composite materials consist of strong, brittle carbon fibers and a compliant, weaker pyrolyzed resin matrix. In many cases, the carbon fibers are woven into sheets that can be stacked in a variety of orientations. When the material is fabricated, (laid up), sheets of carbon fiber are stacked on top of one another, and the resin matrix is deposited in the carbon textiles. The matrix serves to hold the layers of textile material together and provide the material with better toughness properties. The resulting structure of the material is a composition of matrix pockets and fiber textile, as pictured in Figure 1. The material system used in this study will consist of woven fibers and a phenolic resin matrix.

Carbon-carbon composite material systems have already been used for applications like the leading edges of the space shuttle wings, but they require oxidation protection. The protection is usually provided by an external coating of silicon carbide

that prevents oxygen from penetrating to the surface and consequently the interior of the carbon-carbon material. Additional protection can be provided by inhibitor particles that are embedded in the matrix. These inhibitor particles attract the oxygen molecules more forcefully than the composite material itself, which reduces the extent of oxidation in the interior of the specimen. The inhibitor particles serve as an additional protective reinforcement to the coating system because all of the current coating systems available develop cracks during the material's manufacture and subsequent use. Cracks develop in the coating when thermal mismatch between the material substrate and coating create high internal stresses in the coating. The composite specimens that will be used in this study have both an external coating and internal inhibitor particles composed of boron carbide.

As reviewed in the literature, the oxidation process in carbon-carbon composites was typically studied by measuring the specimen mass either during or after the oxidation process. This type of measurement was adequate for some experimental work, but it was not applicable to two major regimes of interest for design which require knowledge of mechanical and material property degradation. Oxidation monitoring during high temperature tensile testing and, perhaps more importantly, during aircraft operation cannot be accomplished by measuring specimen mass. The purpose of this project is to confirm the viability of using an electrical resistance measurement to monitor the oxidation of a carbon-carbon composite material for subsequent use in mechanical studies. This objective was accomplished by monitoring the resistance across a specimen length while the material was being oxidized at high temperature. With further

refinement, this type of measurement will be extremely useful. Other types of material systems that are electrically conductive could also be tested using this method.

II. Theoretical Motivation

The primary constituents of carbon-carbon composites, carbon fibers and resin matrix, are both electrically conductive. If a rectangular solid specimen of a material is assumed to be homogeneous, it has an electrical resistance which is given by,

$$R = \frac{\rho l}{A} \quad (1)$$

Where ρ is the resistivity, l is the length of a specimen, and A is the cross sectional area of a specimen. When the material is made up of two components, the physical situation is similar to the model for two parallel resistors as shown in Figure 2. The equation for resistance in the material therefore becomes the following.

$$R = \frac{1}{\frac{A_1}{\rho_1 l_1} + \frac{A_2}{\rho_2 l_2}} \quad (2)$$

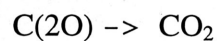
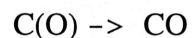
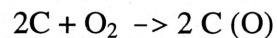
The resistivity properties of the T-300 fibers and the phenolic resin matrix that make up the composite specimens used in this study are known from previous studies to have the values given in the table on the following page.

Property	T-300 Fibers	Phenolic Resin Matrix
Resistivity ($\mu\text{Ohm-m}$)	10.8	3.0

Substituting these resistivity values and the dimensions of the specimen in Equation 2 above provides an excellent approximation to the resistance that the entire specimen exhibits.

Equations 1 and 2 clearly show that the resistance of the material is dependent upon the geometry of the specimen being measured. A.S.D. Wang et al. have exploited this relationship between geometry and resistance to monitor matrix cracking in composite specimens. This was accomplished by sputtering a thin gold film on the tensile surface of a three point bend specimen before loading, and then during loading, monitoring the electrical resistance of the gold film in real time. When matrix cracking occurred on the tensile surface of the specimen, the gold film cracked with the substrate material and caused a sudden increase in electrical resistance. Essentially, the cracking in the gold film reduced the cross sectional area in Equation 1 to produce this effect.

Similarly, if the edges of a carbon-carbon composite specimen are exposed to high temperatures in an oxygen environment, the following processes will result in the desorption of carbon monoxide and carbon dioxide from the specimen surface.



The desorption of gas products from the specimen surface results in a reduction in the cross sectional area of the oxidizing specimen. If the resistance of the conductive carbon-carbon specimen is measured as this oxidation takes place, it will increase as the cross sectional area of the specimen decreases, according to equation 1.

The resistance of the carbon-carbon specimen during the oxidation process will clearly be related to the amount of oxidation taking place. In fact, the resistance is inversely proportional to the cross sectional area of the specimen. This means that if the resistance is measured, the cross sectional area unaffected by oxidation can be determined. Knowledge of this unoxidized area is very useful information that can be used to predict the strength of the material. When the mass change is also correlated to the resistance change in the specimen, the resistance measurement becomes even more useful. This type of measurement is relatively simple to make and can be monitored in real time as the oxidation is taking place. It has particular importance for design engineers because it reflects the change in the geometry of the specimen during the oxidation process. The current method of monitoring specimen mass does not provide this critical information.

III. Specimen Preparation

The carbon-carbon composite specimens that were used in this study were produced by HITCO for high temperature applications. The specimens were cut from plates with a 0-90 lay-up configuration. The specimens were cut using a circular saw with a diamond blade and came from the locations on the plate diagram in Figure 3.

Pigtail wires were required to provide electrical contacts to the specimens that were used in this study. Aremco Pyroduct silver paste coating was used to attach pigtail wires as shown in Figure 4. To obtain the desired contact between the wire and specimen, the coating was painted onto the specimen with the wire in close proximity. The wires were clamped to the specimen while the coating dried at room temperature. The coating was then cured for 2 hours at 60 degrees Celsius to complete the bonding procedure. The clamp ensured that there was direct contact between the wire and specimen. The specimen preparation procedure originally specified that polishing would be required to obtain proper coating adhesion, but it was soon discovered that excellent adhesion could be obtained without polishing.

After the pigtail wires had been attached to the specimen using silver paste, the specimen had the configuration shown in Figure 4, which left two carbon-carbon edges exposed, and four edges protected by silver paste and the silicon carbide coating. The photograph in Figure 5 shows an example specimen after the pigtail wires have been attached. A photomicrograph of the platinum wire bonded to the specimen using the silver paste coating is provided in Figure 6 to illustrate the integrity of the bond between the wire, coating and specimen.

IV. Experimental Apparatus

The high temperature resistance measurements that were made for this study required several specialized pieces of equipment. A quartz stage and quartz rod were designed and fabricated for inserting the specimens into a high temperature furnace. A

quartz tube end cap was also modified for use with the furnace. The following is a list of the equipment used in this study.

1. Kiethley 237 High Voltage Source and Measure Unit, (X2)
2. Marshall Annealing Furnace - Model 1079S (Max capability of 1000 degrees Celsius)
3. Pressurized argon gas
4. Pressurized dry oxygen gas
5. Brooks gas flowmeter, (X2)
6. Quartz Stage
7. Quartz rod with attachment hook
8. Thin gage platinum wire
9. Six inch, four hole ceramic insulators, (X5)
10. Ohaus digital scale

Photographs of the furnace and Kiethley Source and Measure Units are presented in Figures 8 and 9.

V. Experimental Procedure

Each high temperature resistance measurement followed the procedure outlined here in order to maintain compatibility between measurement runs:

1. The initial mass of the specimen is measured.
2. The four wires which carry voltage and current signals from the Kiethley source and measurement units are bonded to the composite specimen pigtail wires using silver paste.
3. The test specimen is introduced into the oven by moving the quartz stage that holds the specimen into the flat temperature zone using the quartz rod. The quartz rod contains the signal wires and remains in the furnace during heating.

3. Argon gas is passed over the specimen at 20 cc/sec to prevent oxidation during the transient heating process.
4. The specimen is heated up to 900 degrees Celsius, (The specimen and furnace are at almost identical temperatures during the heating process).
5. When the temperature reaches 900 degrees Celsius, oxygen is introduced while current is sourced from one Kiethley unit and voltage is measured using the other Kiethley unit. Each Kiethley is calibrated to maintain extremely high accuracy in these measurements.
6. Measurements will continue until a maximum of 2 hours have elapsed.
7. The furnace will be allowed to return to room temperature naturally, while argon gas is again passed over the specimen.
8. The specimen will be removed, weighed and retained for further analysis.

In order to obtain a good correlation between mass loss and resistance measurements made for this study, thermogravimetric mass analysis techniques were used to obtain real time mass loss measurements during oxidation. These measurements were made using a Thermogravimetric Mass Analyzer, (TGA) at Loral Vought Systems. A correlation between mass loss and resistance change was made possible by these measurements and is presented in the results section. The conditions that the specimens were subjected to in the resistance measurements and mass analysis experiments were matched as closely as possible. The primary difference between the resistance and mass loss measurements was that the specimens had to be reduced in size for the mass loss apparatus to accommodate them. A diagram of the TGA used for these experiments is

provided in Figure 9. The TGA apparatus used to make these measurements was also capable of performing differential thermogravimetric analysis, which uses a reference sample to determine whether any thermal activity due to chemical reactions is taking place within the specimen. This information is obtained by comparing the temperature response of a known reference specimen of alumina to the experimental specimen. Thermocouples are attached to both the reference specimen and the experimental specimen to produce this data.

VI. Results and Discussion

The measurements made over the course of this experimental study were informative for engineering purposes and should be viewed in this light. These measurements have provided information that will motivate further development of an electrical resistance measurement to monitor oxidation in carbon-carbon composites. In fact, a proposal to the AFOSR has been submitted and accepted to pursue this as part of Dr. Ochoa's future research program. Three data sets have been obtained to date using the resistance measurement technique and are presented in the graph in Figure 11. Each of the data sets were taken under the same conditions outlined in the procedure section. The specimens in the tests had the following characteristics.

Sample	Width (in)	Thickness (in)	Length (in)
1-1	.200	.159	1.49
1-2	.200	.157	1.50
2-2	.199	.156	1.52

The specimens were placed in the furnace which was preheated to 300 degrees Celsius and were ramped at 20 degrees Celsius per minute until they reached 900 degrees Celsius, which occurred 30 minutes into the test. The temperature was held at 900 degrees until contact with the specimen was lost at the specimen, wire interface. This loss of contact was determined by observing large, irregular fluctuations in the data that resulted from the unstable contact between the wire and the composite material. The change in the resistance with time during the steady state temperature application was quite linear up until the loss of contact with the specimen. When the minor variations in the slope of the resistance versus time data are examined, a relatively sharp change is observed in the first two minutes of oxidation, followed by a five minute slow down. Finally, the resistance measurement changes extremely linearly for the remaining fifteen minutes. These small variations in the resistance measurement are most readily observed in the graph in Figure 12.

The graphs that are pertinent to the TGA experiments are presented in Figures 13 through 20 and the specimen parameters for each of the tests are presented in Figure 10. The graph in Figure 13 displays the temperature versus time and its derivative showing that a very even ramp was used for the tests on specimen 3-2-2 and stable temperatures were maintained. The graph in Figure 14 presents the mass loss in terms of the percent of the sample weight remaining and a differential thermogravimetric analysis, (DTA) plot which shows that there was thermal activity in the specimen during the temperature ramp. The mass loss graph shows that there was very little change in the mass of the specimen during the temperature ramp, showing the percent of the mass remaining in the specimen

as a function of time. After ramping for fifty six minutes, the flow of argon gas was shut off and the specimen began to oxidize and, as a result, the mass of the specimen began to decrease. The mass loss data obtained using the TGA was quite linear, with the exception of an initially varying slope in the mass loss with time. The small variations in the TGA graph's slope were remarkably similar to the variations in the resistance measurement.

The differential thermogravimetric analysis, (DTA) data shows that an exothermic process takes place during the temperature ramp and that very little chemically related thermal activity takes place during the temperature hold period. The cause of the exothermic behavior during the ramping period is difficult to determine, but the lack of thermal activity during oxidation at the hold temperature is expected. The oxidation processes involving carbon should take place spontaneously at the 900 degree temperatures in this experiment. This reaction is not expected to cause a temperature change in the specimen.

Figure 15 includes another mass loss plot and a plot of the mass loss time derivative, which clearly shows the slope variations in the data that were discussed earlier. Figure 16 presents a plot of mass loss versus temperature, which shows that the mass of the specimen remains almost constant during the temperature ramp. The plot in Figure 17 presents the same information Figure 13 did, but this time for another specimen. The trends in the behavior of the specimen remain consistent between these two specimen tests. The plot in Figure 18 is another repetition of the measurements made in Figure 16, but this time on specimen 7-2-1. Finally, Figures 19 and 20 show

measurements that were made on a specimen that was ramped to 800 degrees Celsius to show that the linear mass loss behavior could also be observed in this temperature range.

The graph in Figure 21 shows the mass loss behavior after the argon flow to the system was shut off at fifty six minutes. The linear mass loss behavior and linear increase in resistance, which was expected, can now be correlated by a factor dm/dR , which is the ratio of mass change to resistance change with time. For the specimens tested in this study, this factor has a value of -1.36. Thus, provided with an initial and final resistance value, a mass change value can be predicted for this material for oxidation at 900 degrees Celsius.

It should be noted that all of the TGA data taken in this study is not presented here. This data showed consistent behavior between test runs, and therefore redundant data was not presented. It should also be noted that test 2 used a shorter specimen than test 1 and test 3, which decreased the resistance of the specimen. This is the reason that the trend is the same for the slope for all three tests, but the values are slightly different for test 2.

A Project Spin-off

With the results obtained from the experiments performed in this study, it is clear that this type of measurement has the potential to carry out the functions described in the introduction. A further improvement in understanding the progression of the oxidation into the material could be obtained by using a C-scan nondestructive evaluation technique. An example C-scan of a specimen with oxidized edges is presented in Figure 23. Areas of low density in the material are represented by light shades of gray or white

and areas of high density are represented by dark shades of gray or near black. Excellent correlation between the structurally significant cross sectional area of the material and resistance measurements could be made using this technique. To accomplish this, a series of C-scan images would be made of a material at varying stages of oxidation. The progression of the oxidation into the material could be observed directly using C-scan and referenced back to the resistance measurements that were made in this study.

VII. Conclusion

The demands of the aerospace industry have driven engineers to provide advanced materials which can withstand extremely adverse environments. Testing and characterizing them has become increasingly difficult. The resistance measurement presented here can, with further refinement, allow engineers in the future to predict the material geometry and mass of carbon-carbon composite materials under these adverse conditions. The measurement showed excellent correlation with specimen mass loss during high temperature oxidation. The results of this research will be presented in a scientific paper co-authored by M.L. Scott and Dr. Ozden O. Ochoa at the Japan-U.S. Conference on Composite Materials in Kyoto, Japan on June 19-22, 1995. In the future, the test will allow researchers in the area of carbon-carbon composite materials to understand their materials much more thoroughly.

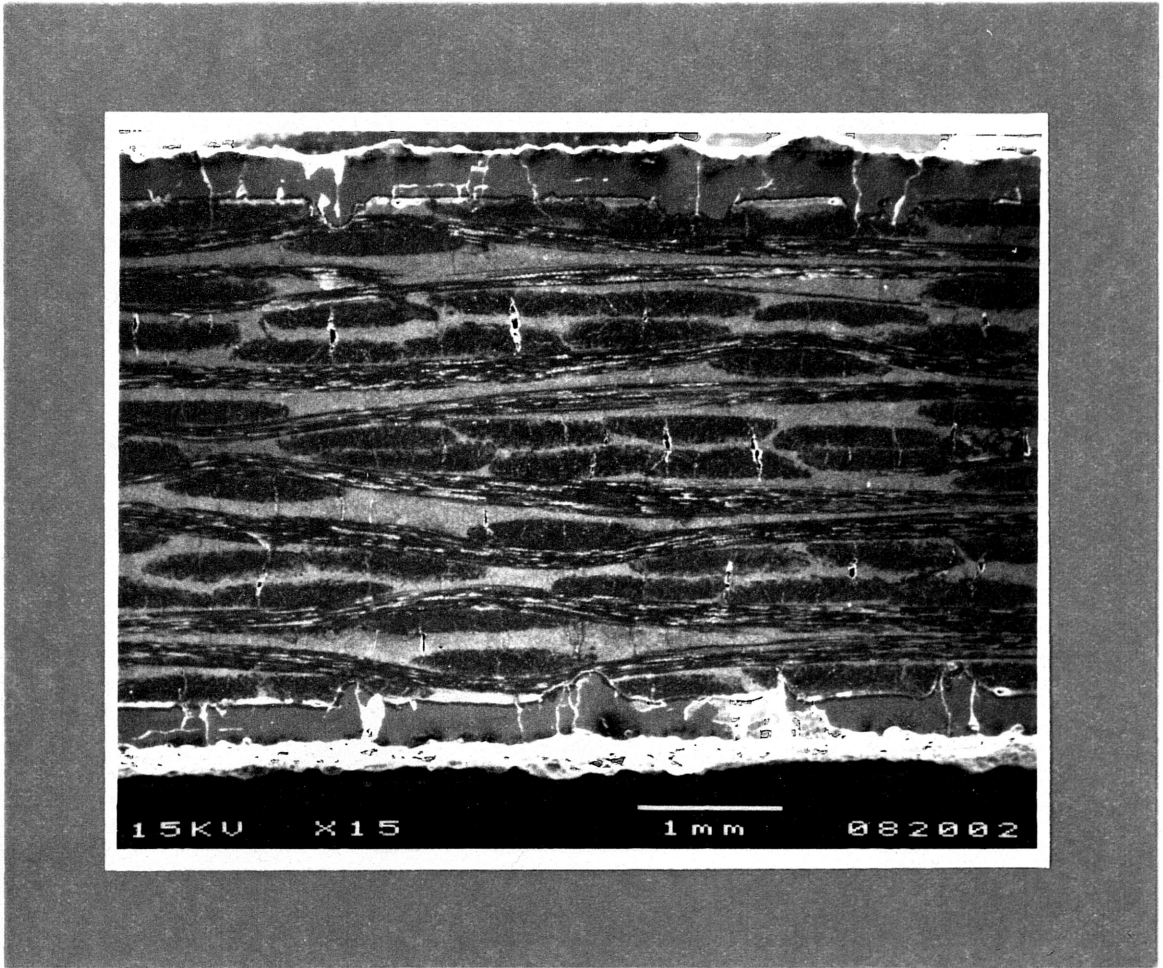


Figure 1: Through the thickness view of a carbon-carbon composite specimen.

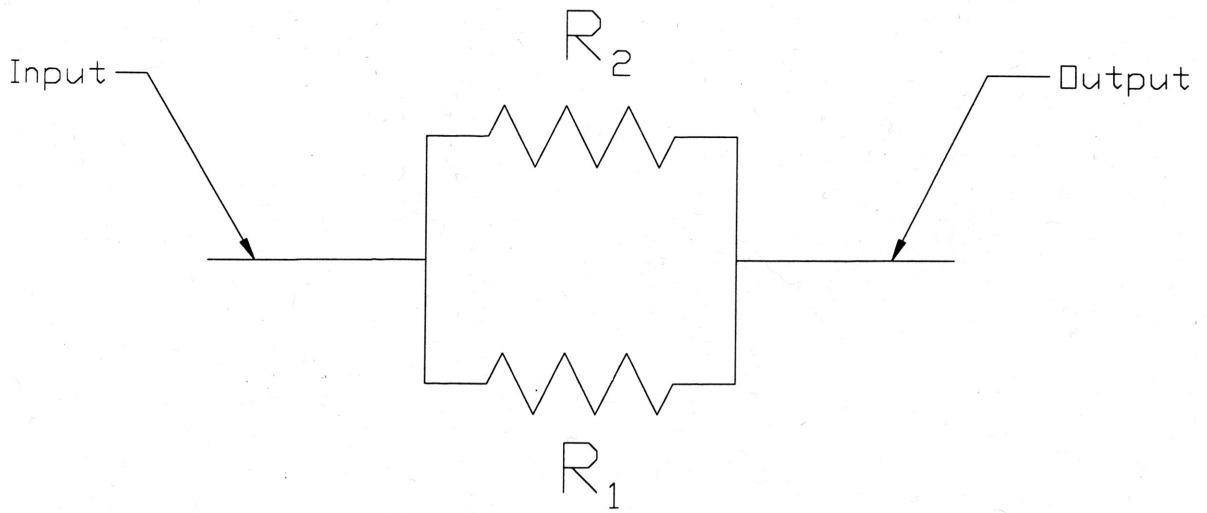


Figure 2: Resistors in Parallel.

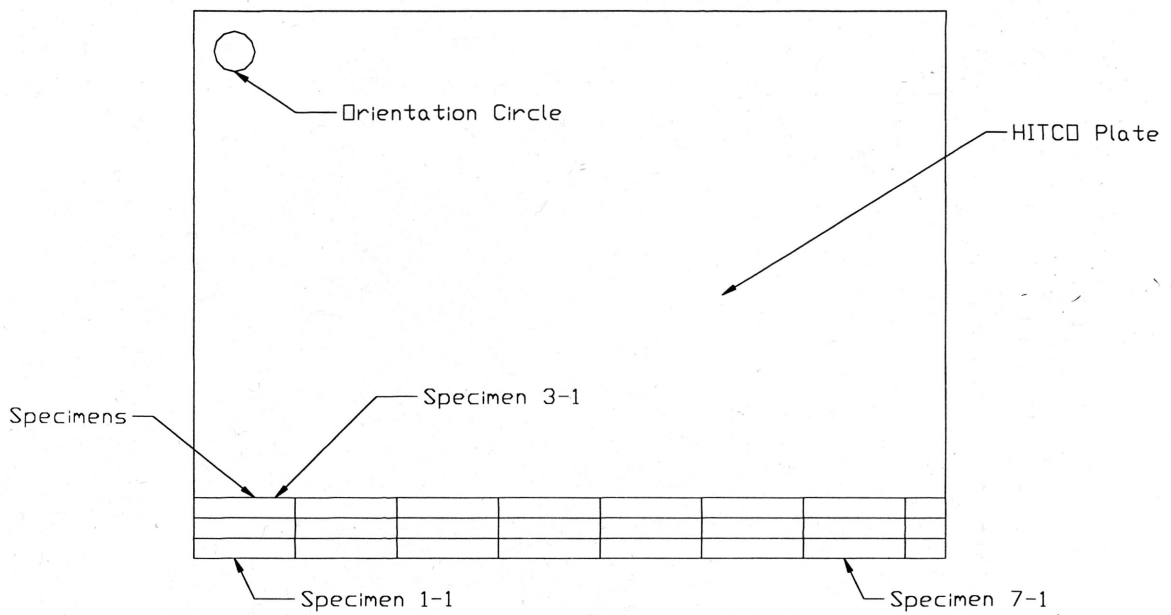


Figure 3: Original HITCO plate with specimen extraction locations.

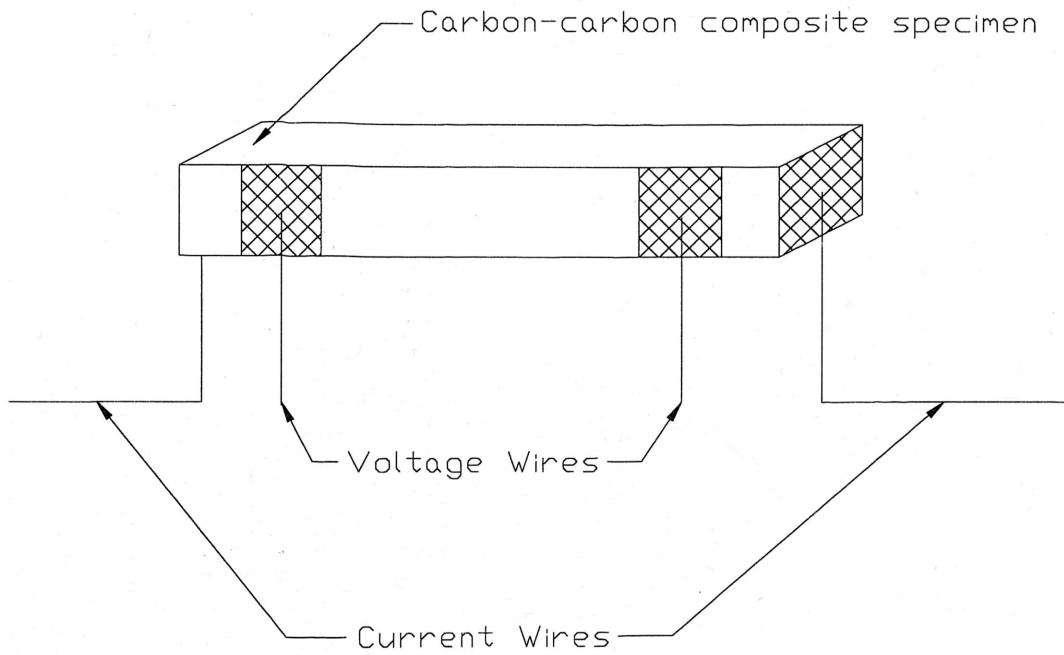


Figure 4: Diagram of the specimen configuration.

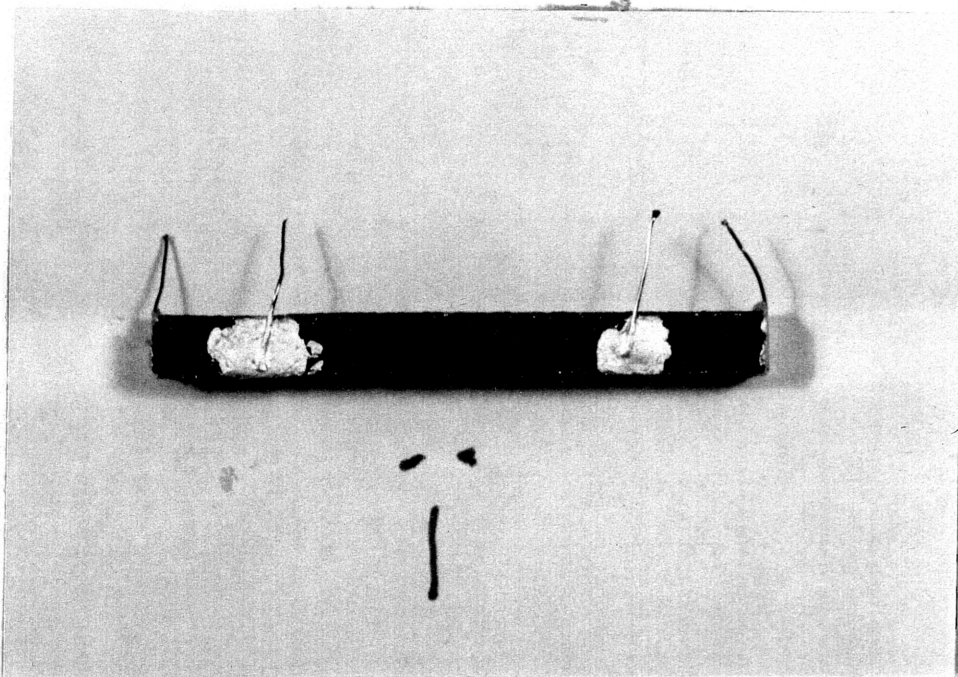


Figure 5: Example specimen photograph.

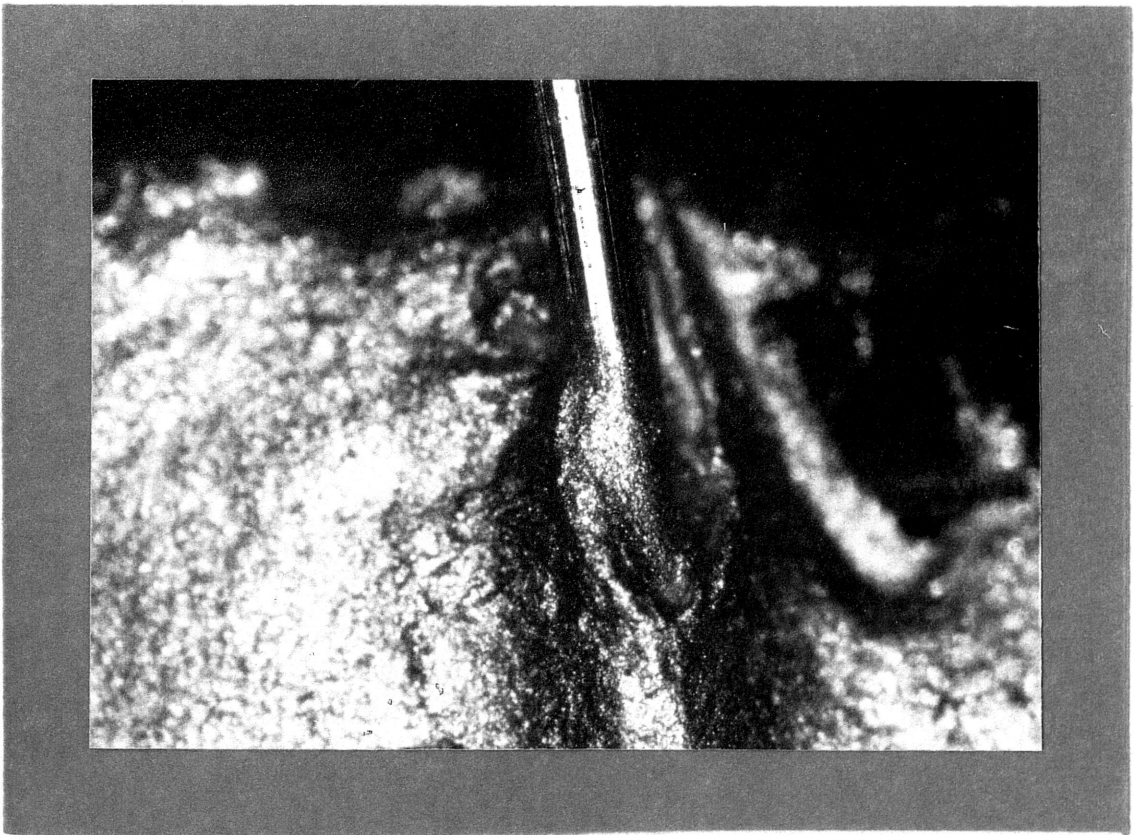


Figure 6: Photomicrograph of the wire, silver paste interface.

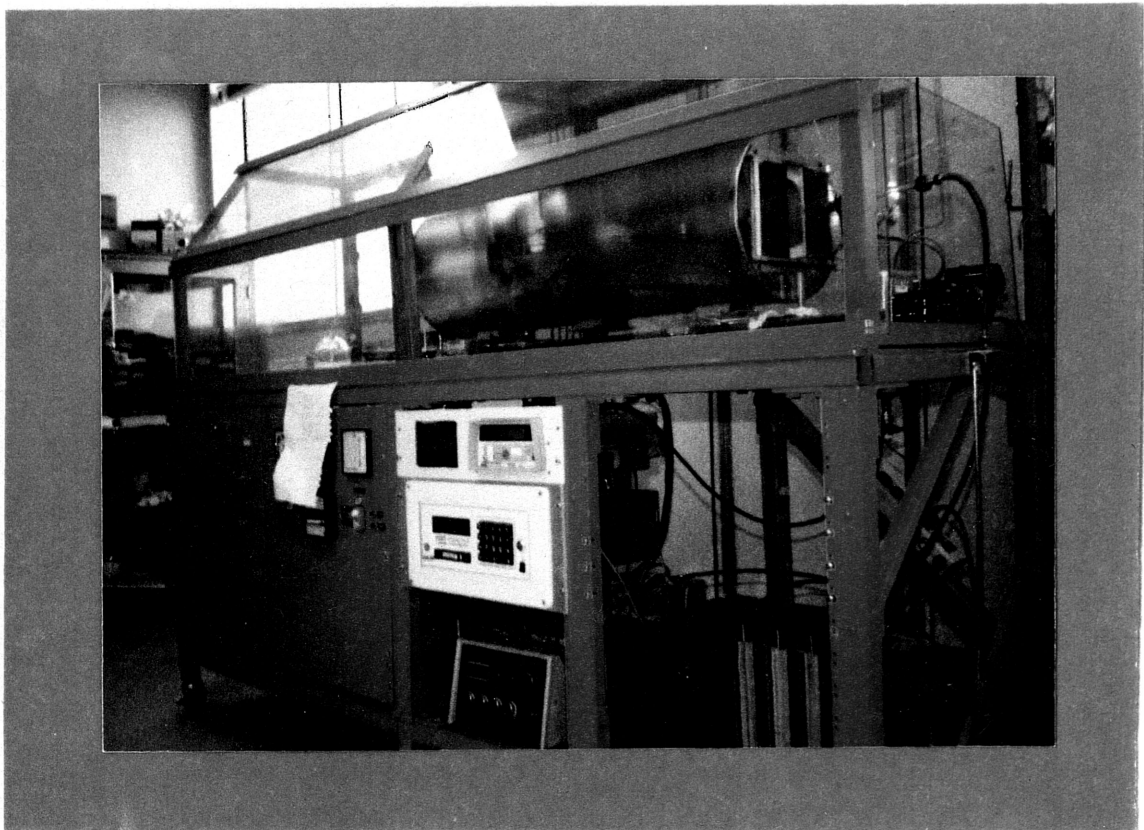


Figure 7: Photograph of the tubular furnace.

TESTING APPARATUS

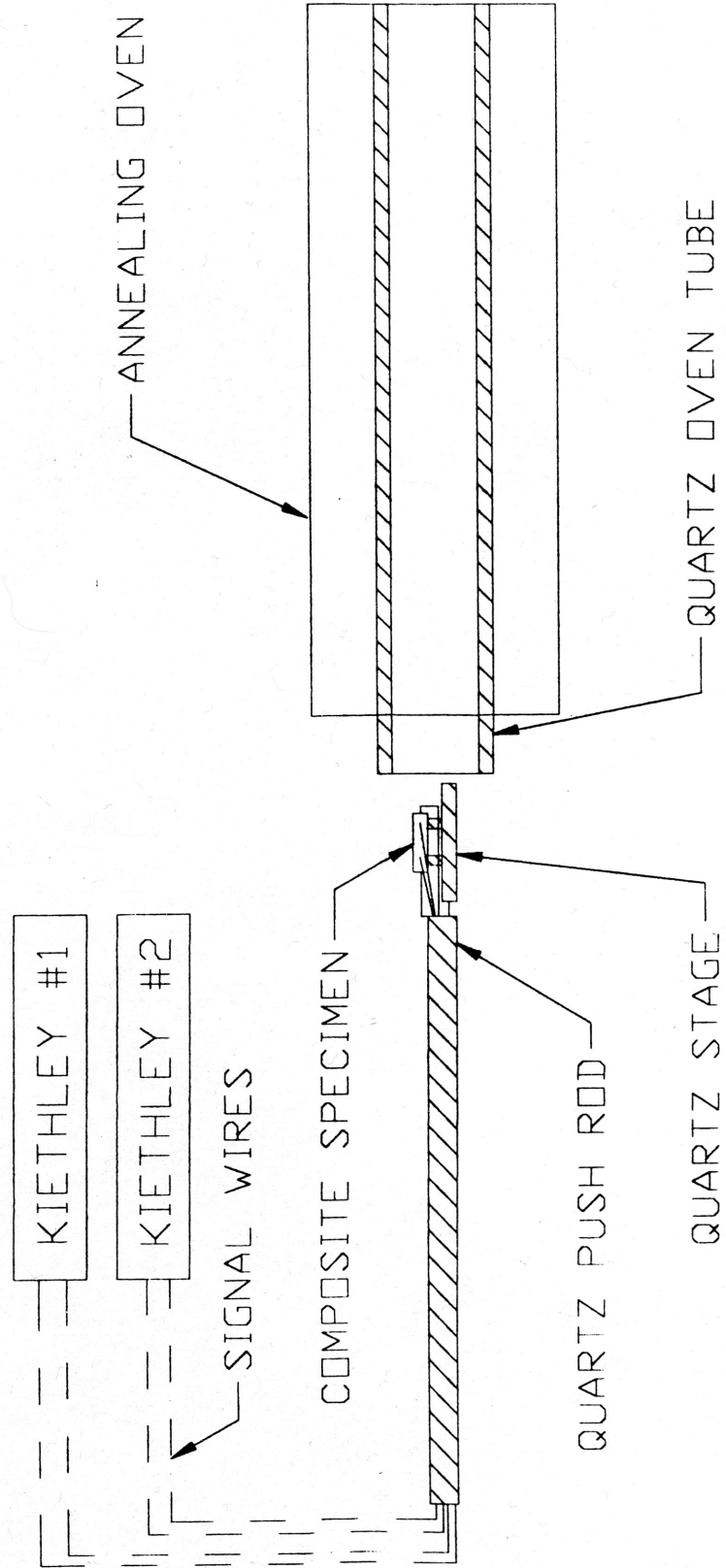


Figure 8: Experimental apparatus diagram.

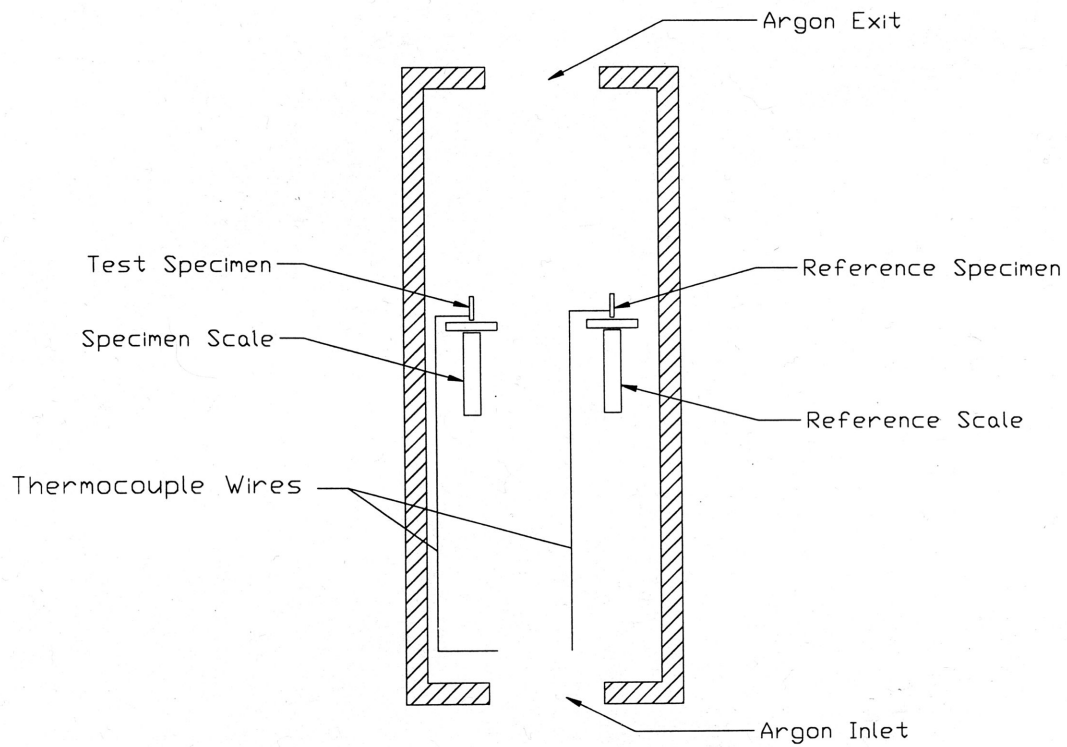


Figure 9: Thermogravimetric Mass Analyzer Schematic Diagram.

TGA SAMPLES AND NOTES									
Sample #	Width (in)	Thickness (thru numbers) (in)	Length (in)	Initial Wt. (mg)	sample holder	sample orientation	SUCCESSFUL	Notes	
3-2-1	0.200	0.158	0.343	324.6	cup	vertical	Y	sanded edges slightly	
3-2-2	0.200	0.158	0.309	288.3	Pedestal	standing on end	Y		
3-2-3	0.200	0.159	0.269	257.5	Pedestal	standing on end	Y		
3-2-4	0.200	0.159	0.472	447.8	Pedestal	flat, numbers up	NO	Data very noisy	
6-2-1	0.198	0.159	0.701	685.7	Pedestal	flat, numbers up	Y		
7-2-1	1.960	1.570	0.593	576.7	Pedestal	flat, numbers up	Y		
1-3-1	0.200	1.520	0.535	512.4	Pedestal	flat, numbers up	NO	Gas late 1:40 left in hold	
2-3-1	0.200	0.155	0.555	539.0	Pedestal	flat, numbers up	Y		
3-3-1	0.202	0.156	0.565	551.2	Pedestal	flat, numbers up	Y	Data report done with and without buoyancy	
3-3-2	0.200	0.156	0.360	346.3	Pedestal	flat, numbers up	Y	Re-run to check repeatability for same sample	
1-3-2	0.200	0.154	0.485	462.9	Pedestal	flat, numbers up	Y	Hold @ 800°C for 2 hr...	
P-1	-----	-----	-----	91.4	Pedestal	flat, numbers up	NO	silver paint sample	
								note : P-1 needs different sample holder, data to follow	

Figure 10: TGA specimen parameters and test matrix.

Resistance vs. Time at 900 C

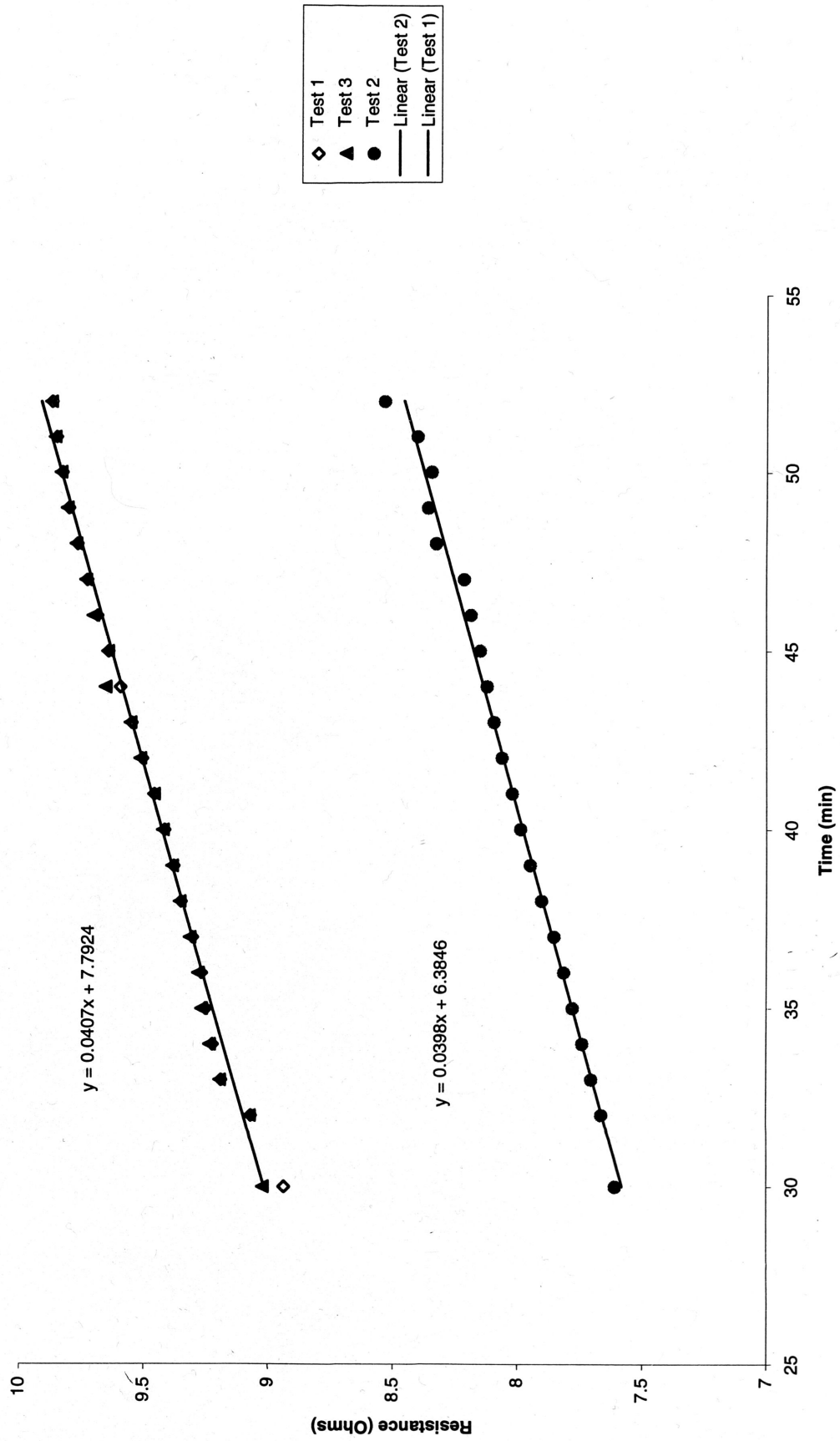


Figure 11: Resistance variation with time for three composite specimens.

Resistance vs. Time

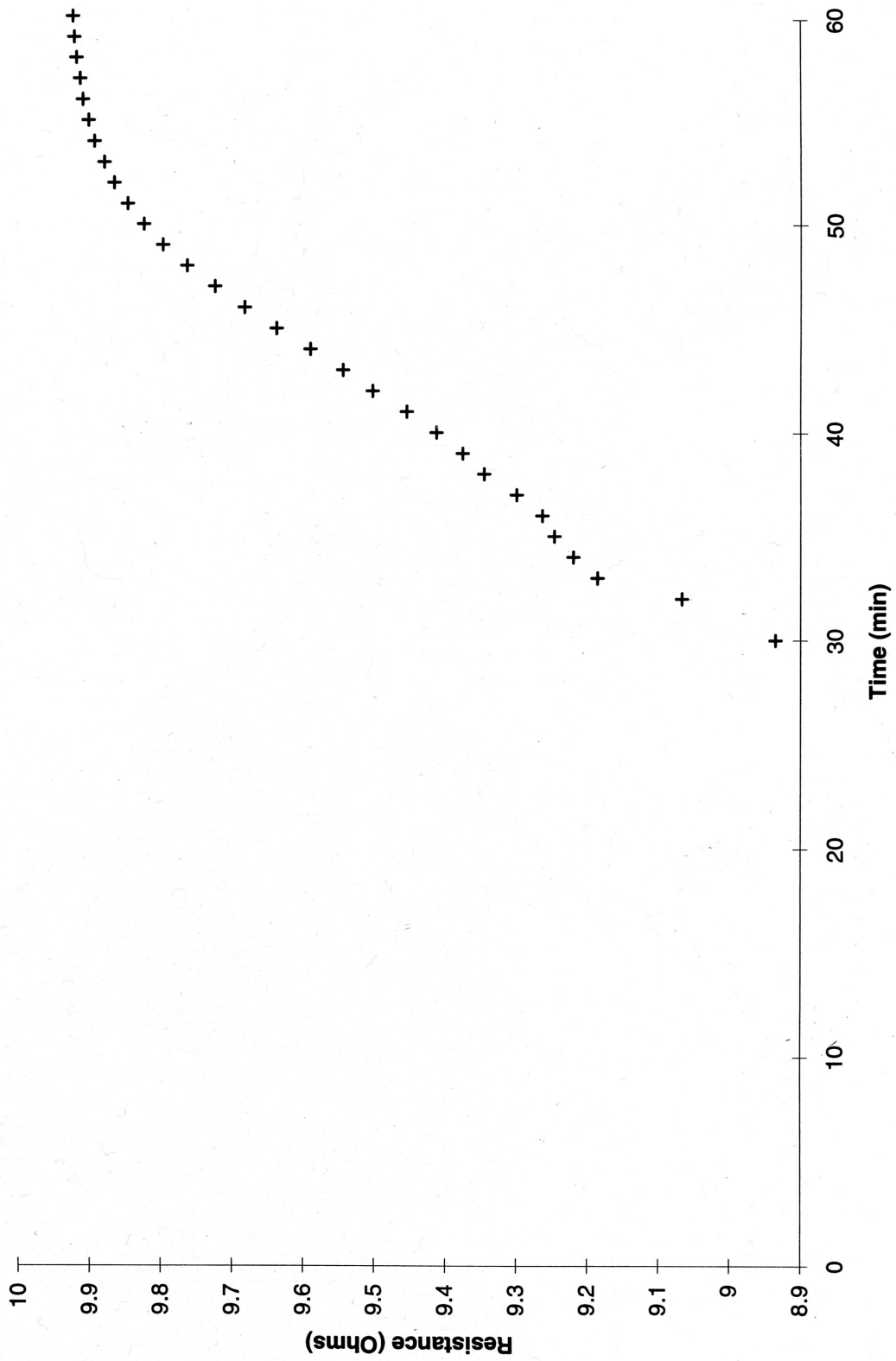


Figure 12: Resistance variation with time for test specimen 1.

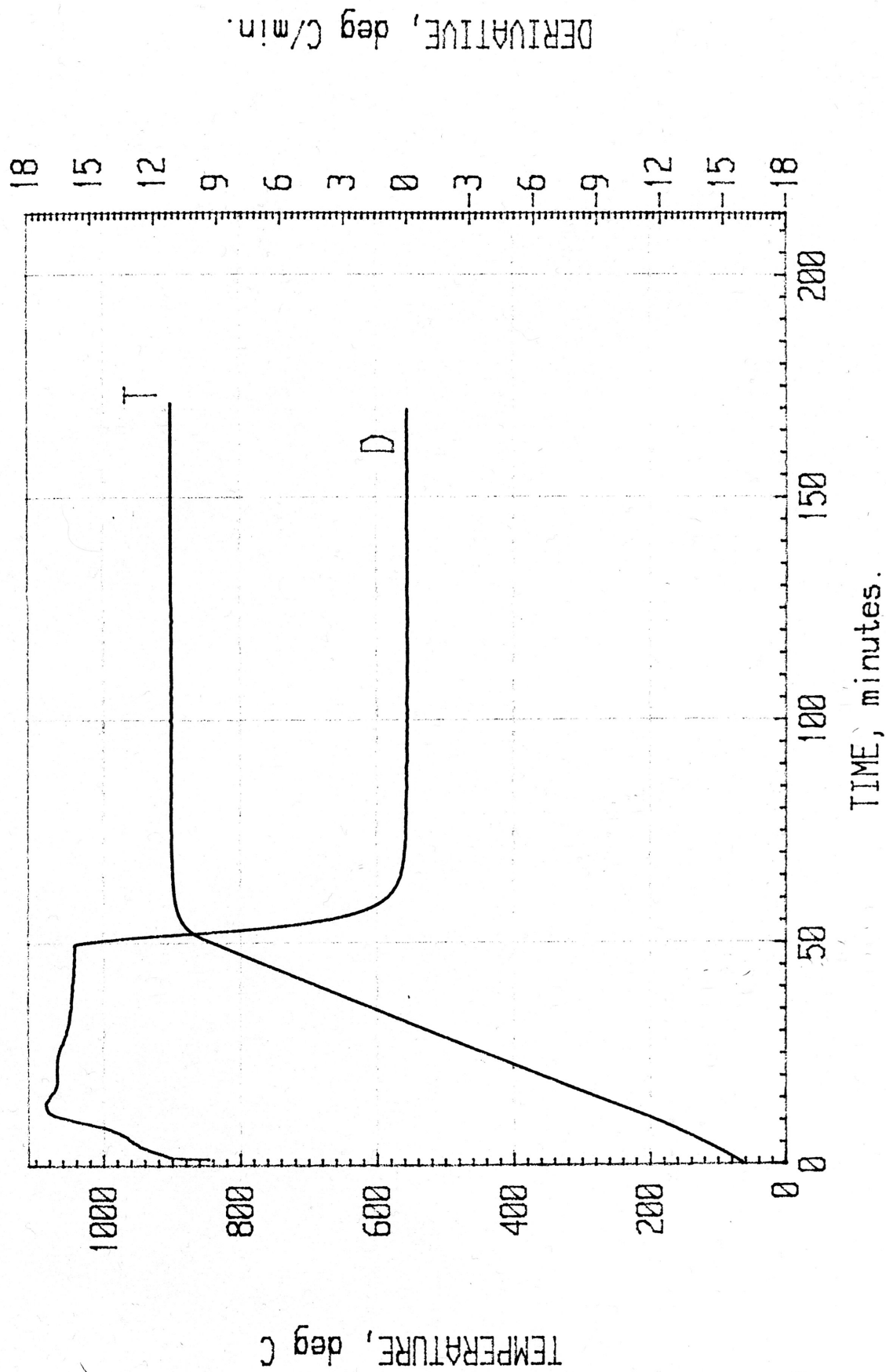


Figure 13: Temperature ramp from room temperature to 900 C along with its derivative.

OPERATOR: JFM
 DATE: 4 Mar 1995
 RUN No. 1
 SAMPLE No. 1
 SAMPLE NAME: 3-2-2

** NETZSCH STA ANALYSIS **
 REFERENCE: Alumina
 CRUCIBLE: Alumina
 FILE NAME: 0-3-2-2
 LOT No. 1

ATMOSPHERE ARGON/AIR
 FLOW RATE, cc/min: 50
 HEAT RATE, deg C/min: 15
 SAMPLE Wt., mg: 288.3
 REFERENCE Wt., mg: 0

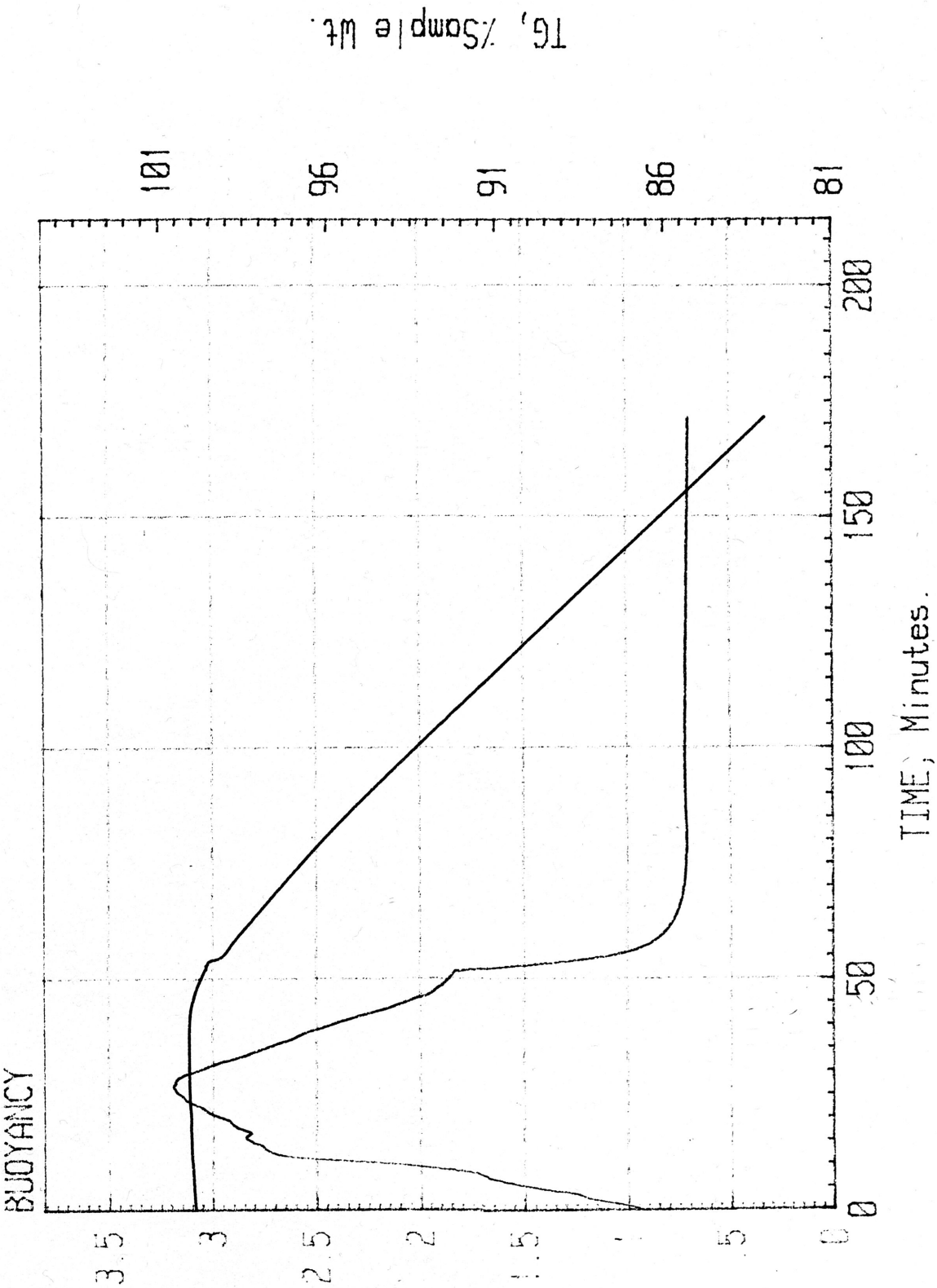


Figure 14: Specimen mass in terms of weight percent as a function of time. The DTA plot for this specimen is also presented.

OPERATOR:	JFM	** NETZSCH STA ANALYSIS **	ATMOSPHERE	ARGON/AIR
DATE:	4 Mar 1995	REFERENCE:	FLOW RATE, cc/min:	50
RUN No.	1	CRUCIBLE:	HEAT RATE, deg C/min:	15
SAMPLE No.	1	FILE NAME:	SAMPLE Wt., mg:	288.3
SAMPLE NAME:	3-2-2	LOT No.	REFERENCE Wt., mg:	0

BUOYANCY

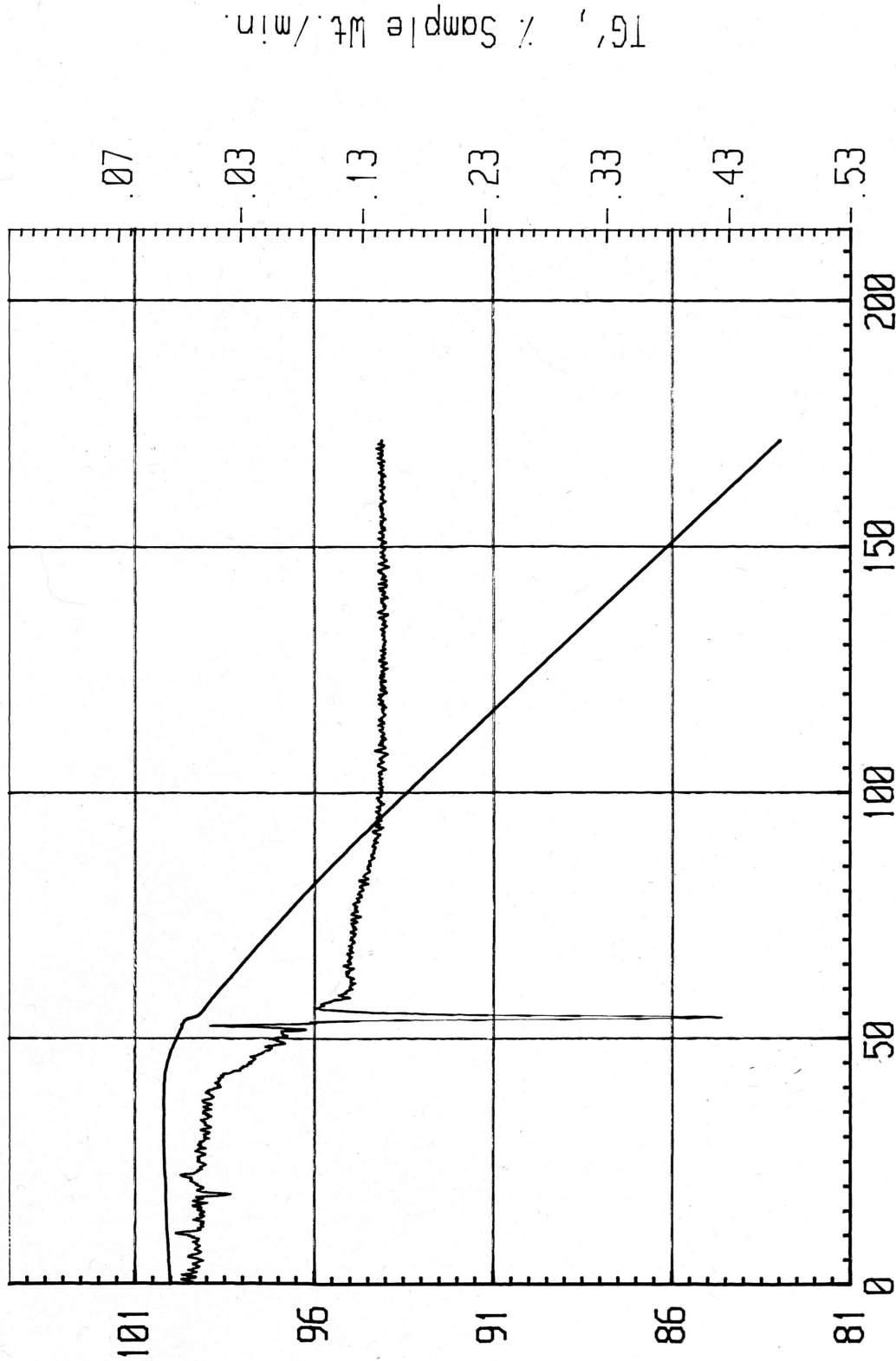


Figure 15: Specimen mass in terms of weight percent as a function of time. The differential of mass loss with time is also presented.

OPERATOR: JFM ** NETZSCH STA ANALYSIS **
 DATE: 4 Mar 1995 REFERENCE: Alumina
 RUN No. 1 CRUCIBLE: Alumina
 SAMPLE No. 1 FILE NAME: 0:3-2-2
 SAMPLE NAME: 3-2-2 LOT No. 1

ARGON/AIR 50
 ATMOSPHERE FLOW RATE, cc/min: 15
 HEAT RATE, deg C/min: 200.3
 SAMPLE Wt., mg: 0
 REFERENCE Wt., mg: 0

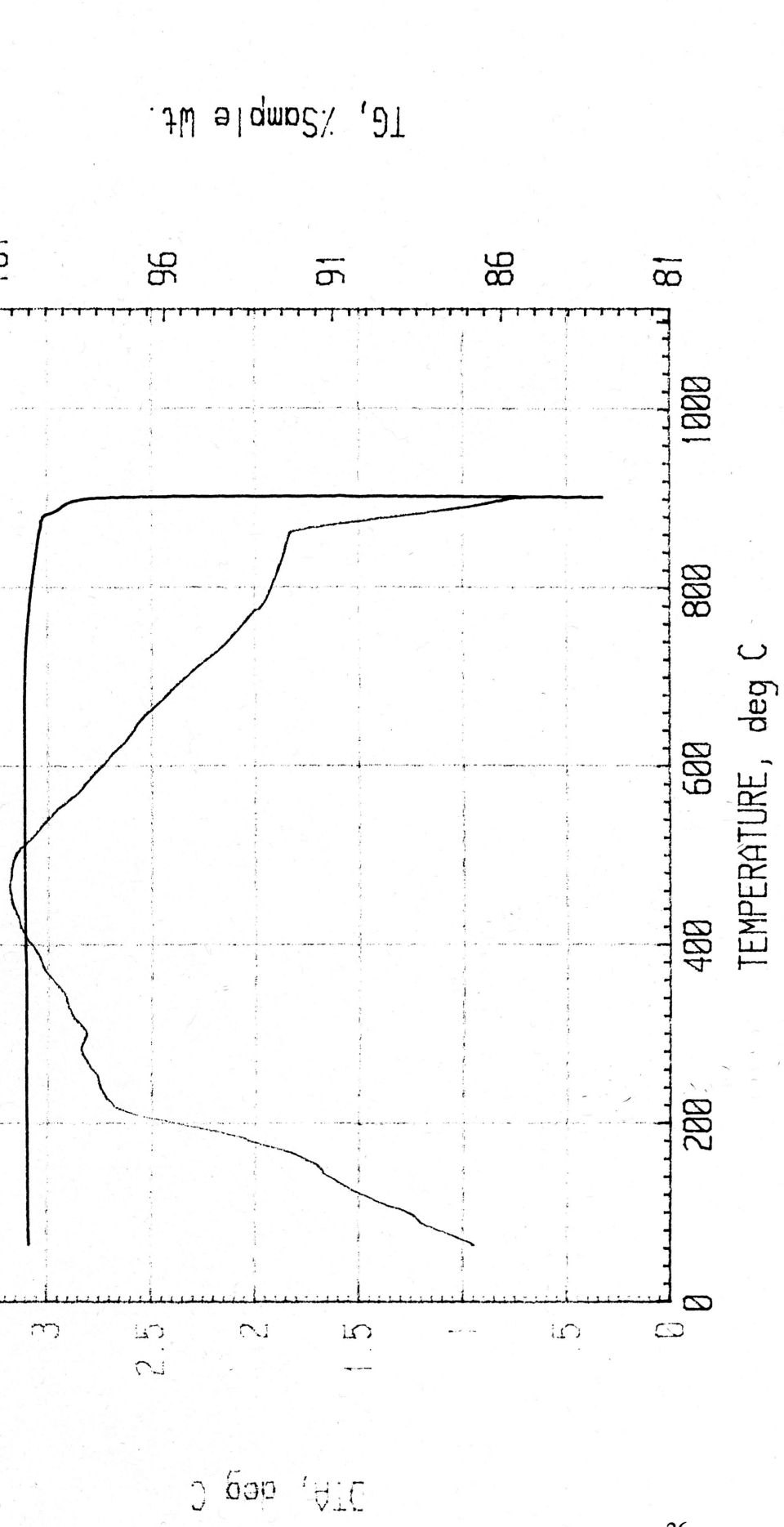


Figure 16: Specimen mass as a function of temperature. The DTA plot for this specimen is also presented.

OPERATOR:	JFM	** NETSCH STA ANALYSIS **	ATMOSPHERE	ARGON/AIR
DATE:	11 Mar 1995	REFERENCE:	FLOW RATE, cc/min:	50
RUN No.:	1	CRUCIBLE:	HEAT RATE, deg C/min:	15
SAMPLE No.:	1	FILE NAME:	SAMPLE Wt., mg:	576.7
SAMPLE NAME:	7-2-1	IDT No.:	REFERENCE Wt., mg:	0

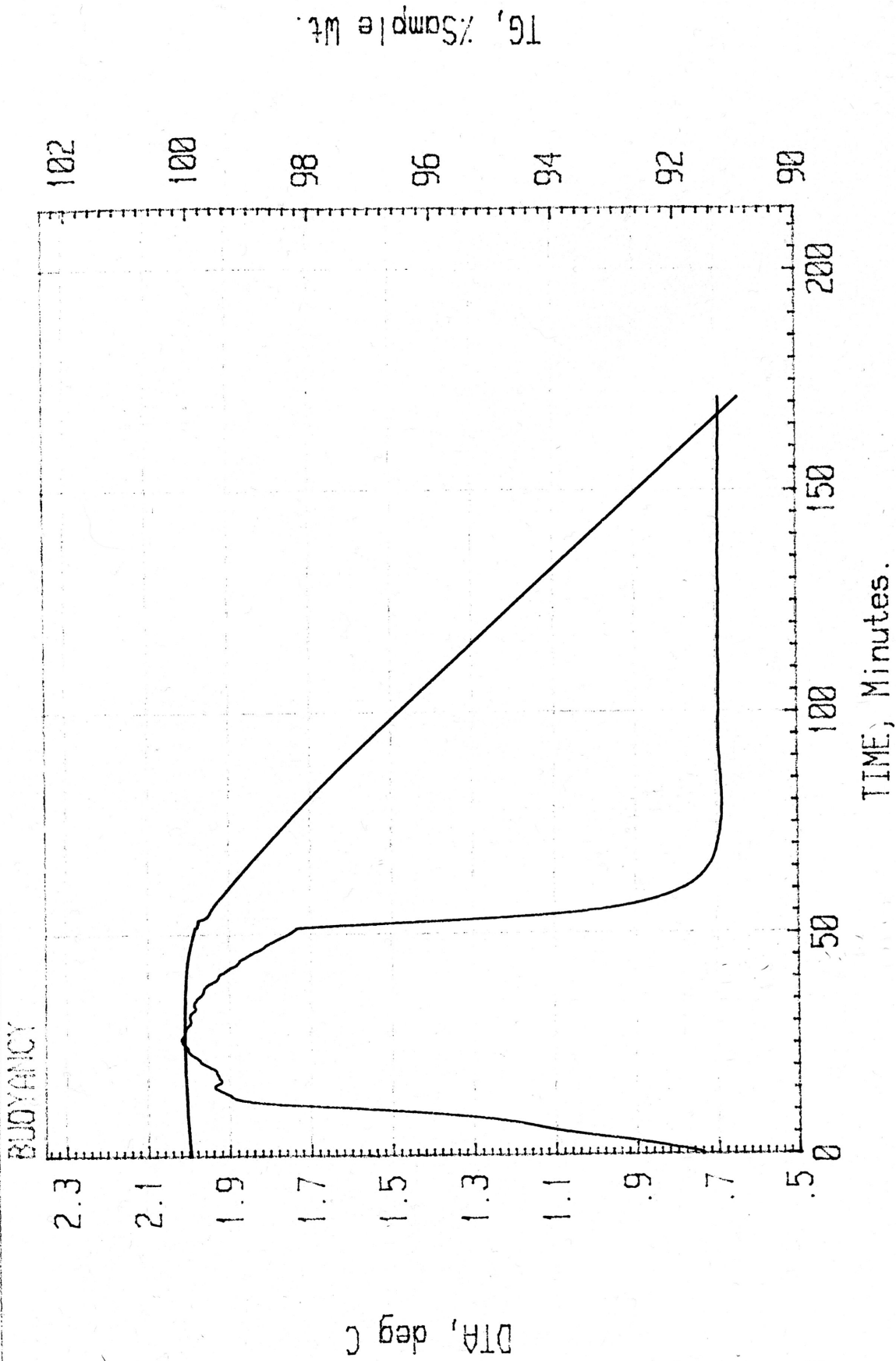


Figure 17: Specimen mass in terms of weight percent as a function of time. The DTA plot for this specimen is also presented.

OPERATOR:	JFM	** METZSCH STA ANALYSIS **	ATMOSPHERE	ARGON/AIR
DATE:	11 Mar 1995	REFERENCE:	FLOW RATE, cc/min:	50
RUN No.	1	CRUCIBLE:	HEAT RATE, deg C/min:	15
SAMPLE No.	1	FILE NAME:	SAMPLE Wt., mg:	576.7
SAMPLE NAME:	7-2-1	LOT No.	REFERENCE Wt., mg:	0

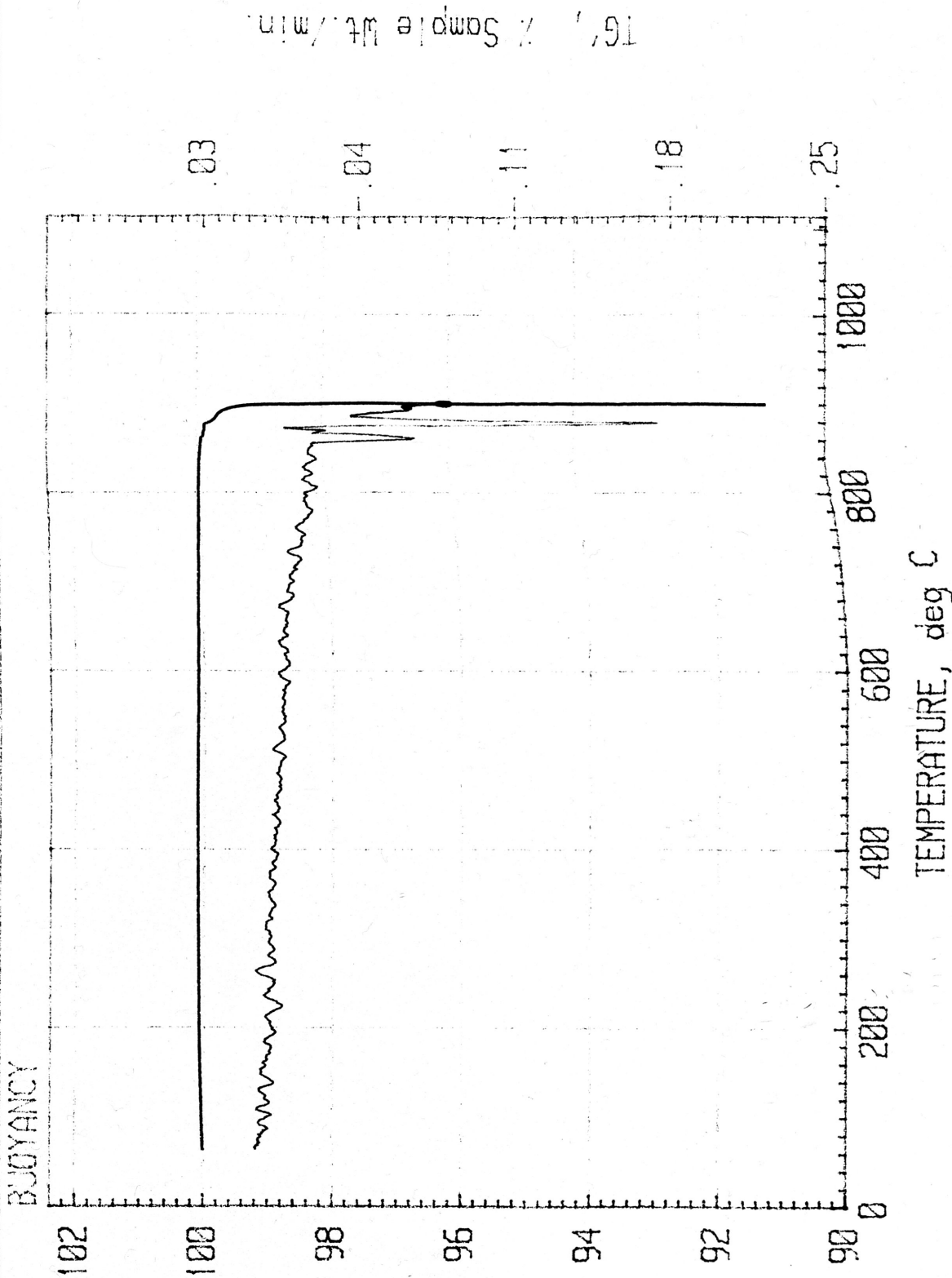


Figure 18: Specimen mass as a function of temperature. The DTA plot for this specimen is also presented.

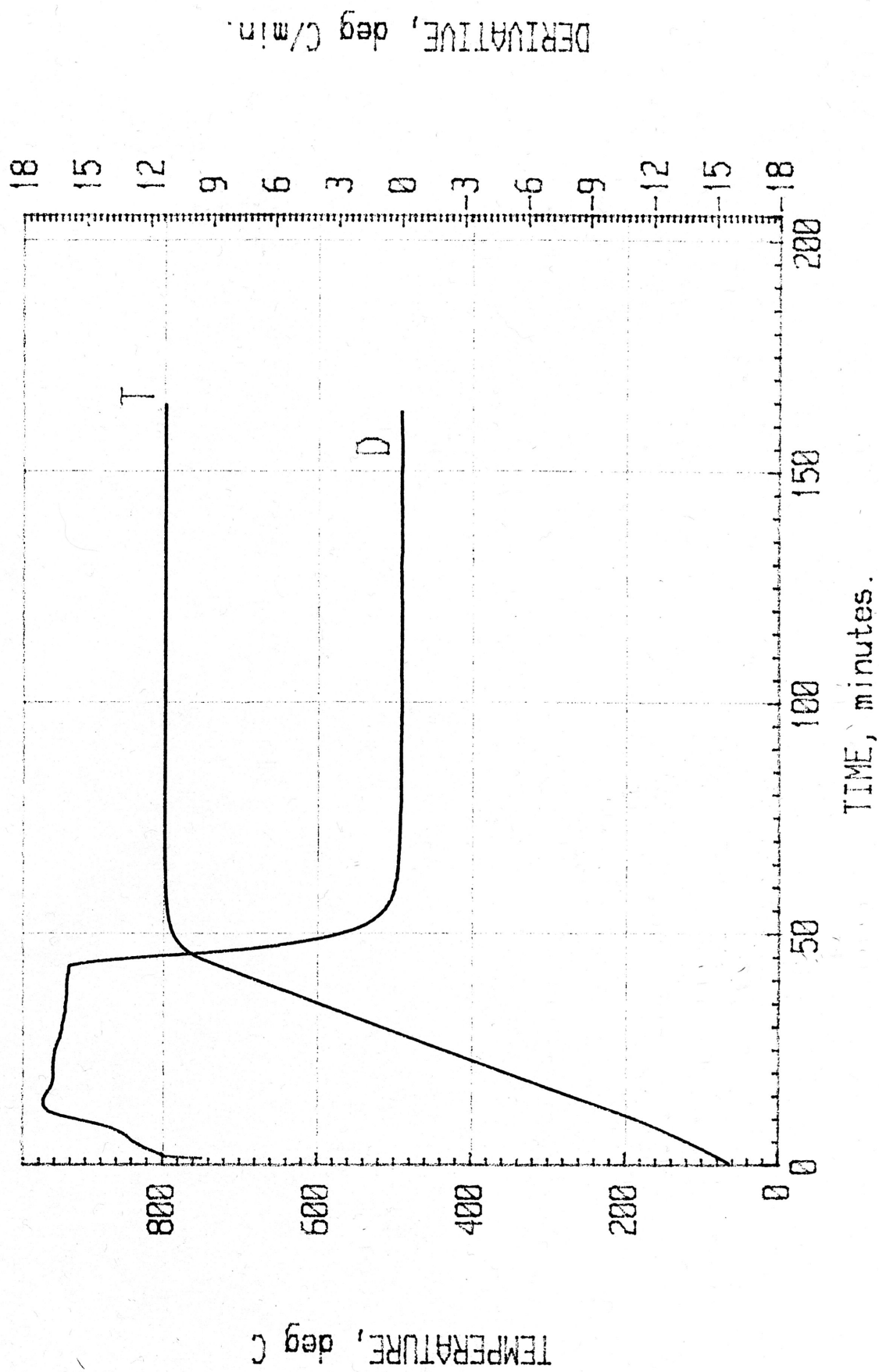


Figure 19: Temperature ramp from room temperature to 800 C along with its derivative.

OPERATOR:	JFM	** NETZSCH STA ANALYSIS **	ARGON/AIR
DATE:	22 Mar 1995	REFERENCE:	50
RUN No.:	1	CRUCIBLE:	Alumina
SAMPLE No.:	1-3-2	FILE NAME:	0:1-3-2
SAMPLE NAME:	1-3-2	LOT No.:	1
			ATMOSPHERE
			FLOW RATE, cc/min:
			HEAT RATE, deg C/min:
			SAMPLE Wt., mg:
			REFERENCE Wt., mg:

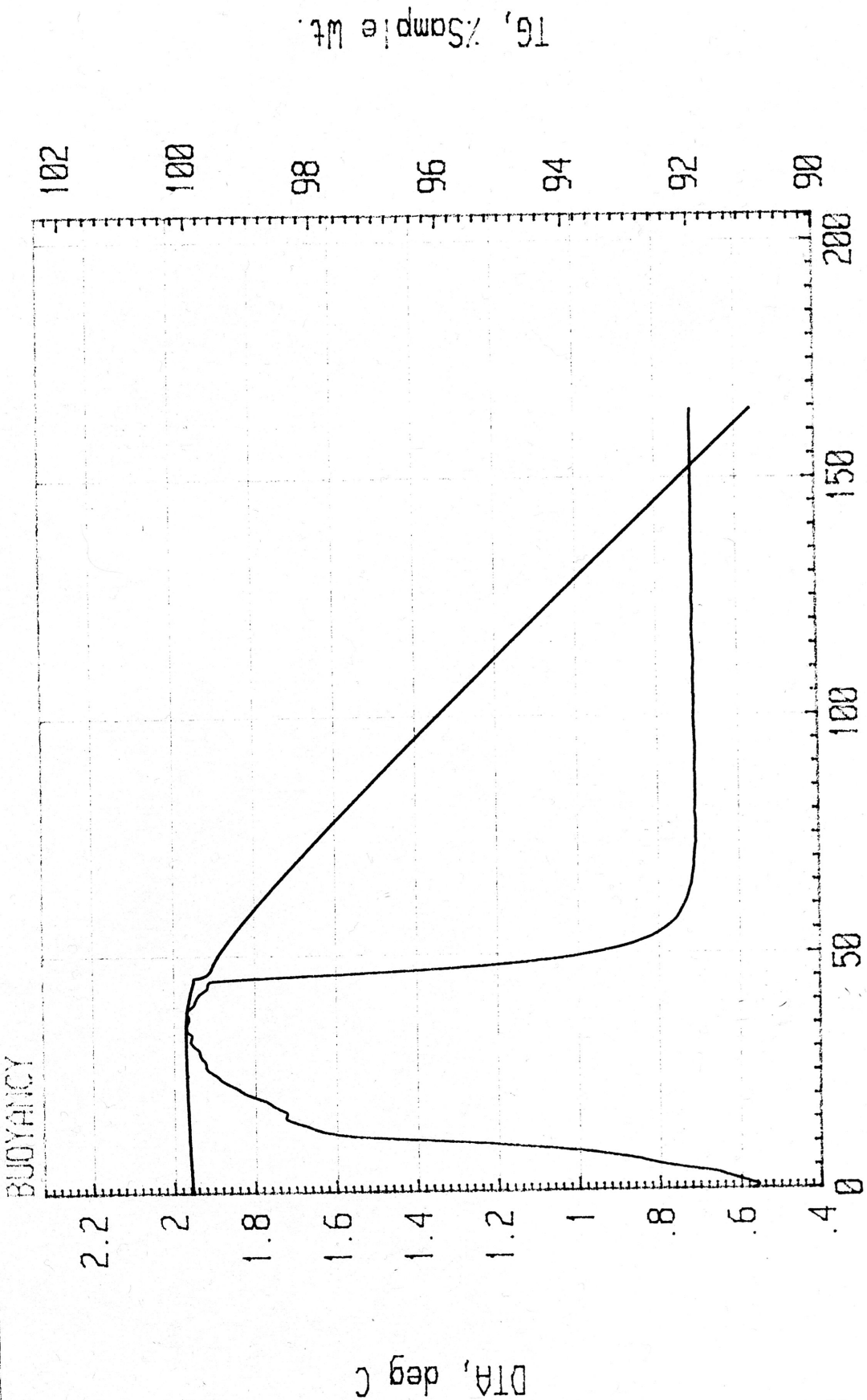


Figure 20: Specimen mass as a function of temperature. The DTA plot for this specimen is also presented.

Mass Loss vs. Time at 900 C

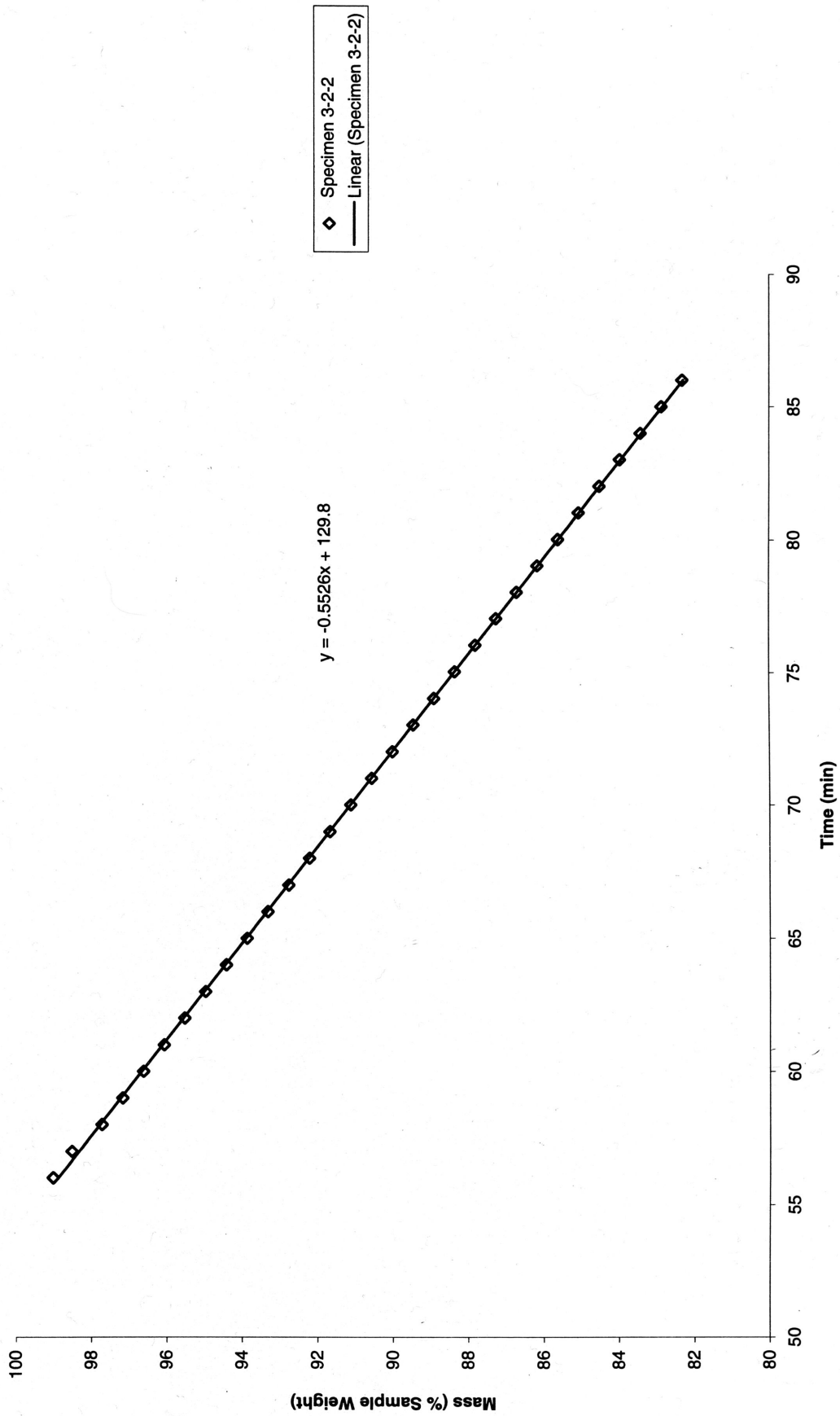


Figure 21: Specimen mass as a function of time in terms of weight percent.

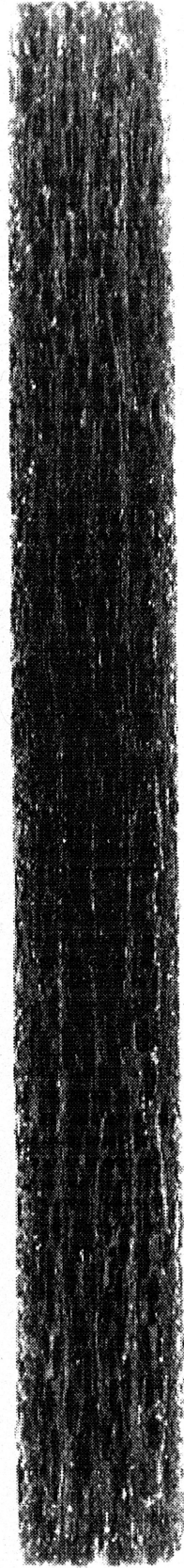


Figure 22: Photograph of an oxidized specimen after 2 hours at 900 degrees Celsius, (Magnification 6X).

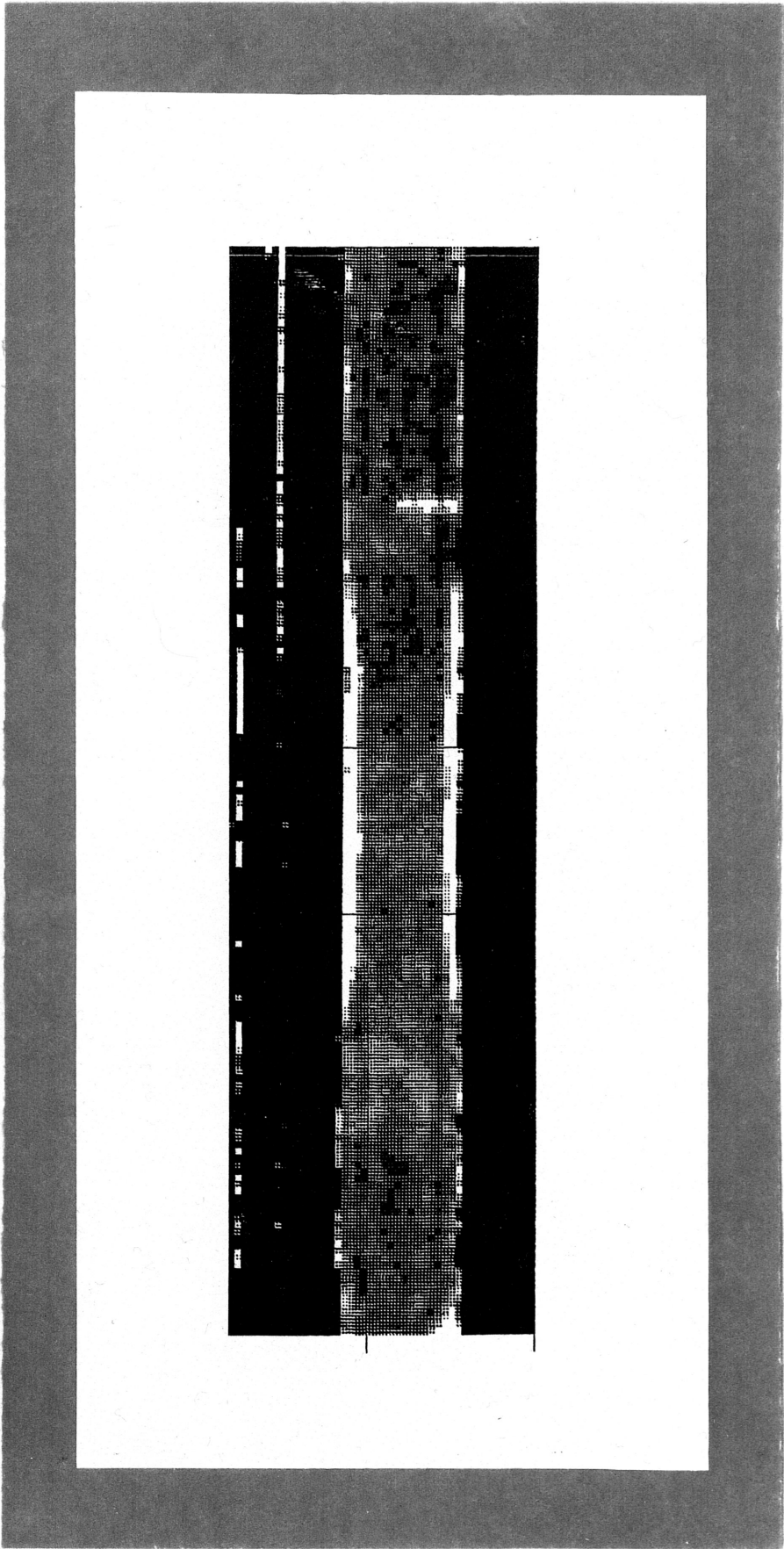


Figure 23: C-scan of a carbon-carbon composite, oxidized in the middle gage section at high temperature.

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