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Studies of Hafnium-Carbide Wafers using a Thermogravimetric Analyzer

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Abstract

Solar thermal propulsion can improve orbital transfer and maneuvering of space payloads due to double the performance of specific impulse (Isp) over chemical propulsion systems. Solar thermal can accomplish this increased performance by absorbing concentrated solar energy with very high temperature materials which through conduction heat hydrogen (H_2). Hafnium carbide (HfC) is an excellent candidate material as a solar absorber and conductor because of its high melting temperature of 3950°C (7142°F)[1]. Several reticulated vitreous hafnium carbide wafers with varying porosities were made by a commercial vendor. Samples of these wafers were placed in a Thermogravimetric Analyzer (TGA) and heated from room temperature to 1000°C (1832°F). This would determine any weight gains or losses of the wafers during testing. Results of this analysis show that the hafnium carbide increased in weight approximately 2.5 percent .

INTRODUCTION

Solar propulsion is the unique application of solar energy to heat propellant which produces thrust in a space-based rocket with improve performance capabilities. A solar powered rocket could be capable of generating thrust from 4 to 445 newtons (1 to 100 pounds) and Isp values of 600 to 1200 seconds[2] . To achieve these performance capabilities, the solar concentrators will focus the solar energy into the thruster (a blackbody cavity), absorb the energy, raise the temperature up to 2000° to 3500°C (3632° to 6332°F), and transfer the energy to the propellant (hydrogen) which is exhausted out a propulsive nozzle to produce thrust. The thruster cavity must be able to survive temperatures from 2000° to 3500 °C (3632° to 6332°F) with hydrogen flowing. Therefore, high temperature materials are needed to withstand this environment. Refractory metals or their carbides are ideal candidates for a thruster cavity.

Hafnium carbide is an ideal candidate for this study due to its high melting point of 3950°C (7142°F). Eighteen reticulated vitreous hafnium carbide wafers were purchased from a local vendor. These wafers are to be tested in the solar laboratory in a special built calorimeter. These tests will involve using concentrated solar energy to heat the wafers in hydrogen gas flow to determine if hafnium carbide wafers are a satisfactory heat transfer medium for solar energy and hydrogen. Impurities normally found in hafnium carbide[3] would indicate that in the test environment, the wafers would experience significant amounts of outgassing and weight loss. The TGA was used to determine how much mass the wafer samples would lose when heated from room temperature to 1000°C (1832°F).

PROCESS HISTORY OF WAFERS[4]

Reticulated vitreous carbon preforms were processed in a graphite susceptor at an operating temperature of 1250°C (2282°F). The hafnium sponge feedstock used was chlorinated in situ upon reaction with flowing chlorine at 750°C (1390°F). Chemical vapor deposition was done by hydrogen reduction of hafnium tetrachloride ($HfCl_4$) in the presence of methane (CH_4) to form hafnium carbide. The reaction is shown below:

$$HfCl_4\,(g) + CH_4\,(g) \text{ ----> } HfC\,(s) + 4\,HCl\,(g)$$

The random variation in chlorination of the hafnium may alter the final deposition of the product. The reticulated vitreous carbon preforms were certified as being deposited with hafnium carbide and that the deposition was performed using furnace parameters consistent with stoichiometric deposition determined by skilled practitioners. Materials used throughout the process were of sufficient purity to keep impurities to a minimum.

BACKGROUND[1,5]

Hafnium carbide is in the class of compounds that comprises the interstitial carbides of the transition metals of Group IVB. Interstitial carbides are those transition metals where a carbon atom and even atoms of hydrogen, nitrogen or oxygen can be deposited in the octahedral interstices of the parent lattice. Carbon atoms used to complete the octahedral interstices give the metal-carbon phase, hafnium carbide. The carbide doesn't form a true stoichiometeric compound, but a solution of carbon at preferred interstitial sites in a face-centered cubic hafnium lattice. Hafnium carbide is a dark gray brittle solid.

The carbide can be prepared either through heating an intimate mixture of the elements or by reaction of hafnium tetrachloride ($HfCl_4$) with methane (CH_4) at 2100°C (3812°F). The later method was used on the sample wafers used for testing. A commonly used method for processing hafnium carbide is reaction of hafnium oxide (HfO) with lampblack in graphite crucibles in hydrogen at 1900°-2300°C (3452°-4172°F) or under vacuum at 1600°-2100°C (2912°-3812°F).

At room temperature, hafnium carbide is inert to most reagents but dissolves in hydrofluoric acid solution containing an oxidizing agent. Above 250°C (482°F), hafnium carbide reacts exothermically with halogens to form hafnium tetrahalide. Hafnium carbide reacts with oxygen above 500°C (932°F) to form hafnium dioxide. At higher temperatures with flowing hydrogen, hafnium carbide slowly loses its carbon.

PREVIOUS STUDY

A study of hafnium carbide outgassing was done by Robert L. Ammon for the Army Materials and Mechanics Research Center[3]. This study involved five powder samples of hafnium carbide heated in hydrogen, helium and vacuum environments. The results showed that hafnium carbide experienced significant weight losses at 204°C (400°F) and at 426°C (800°F). At 482°C (900°F), the samples gained weight in the hydrogen and helium environments and the tests were stopped at this point. An ultra-high purity hydrogen ($\leq$1 ppm H) was used on a sample and when heated the sample gained weight as in previous runs but stopped gaining weight at 646°C (1200°F). Above 760°C (1400°F), the sample started losing weight. In vacuum test, the sample lost weight at 204°C (400°F) and continued to lose weight with no weight gain noted. The weight gain was interpreted as a possible hydriding reaction by the elemental hafnium present in the hafnium carbide. It was concluded that the most effective method for removing absorbed gases from the surface of the fine powder was by vacuum degassing.

THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric Analysis (TGA) measures changes in sample mass as a function of time, temperature or atmosphere. The resulting thermogram can then be used to determine the thermal stability (defined as a general term indicating the ability of a substance to maintain its properties as nearly unchanged as possible during heating) and composition of the initial sample or of any intermediate compounds that may have formed or of the residue.

TGA operation involves the following steps: First, the sample is loaded onto a pre-zeroed balance boat and slid into a quartz tube which together are placed into the furnace. Next, an atmosphere is purged through the cell at a specified flow rate to create an inert or reactive environment and this gas is purged through the cell for ten minutes prior to heating. For these tests, nitrogen was used because the TGA was already setup for nitrogen and no reaction with nitrogen was expected. Then, the sample is heated at a specified heating rate, usually linearly to a high temperature end point. For the hafnium carbide samples, each sample was heated at 10°C/min (50°F/min) to 1000°C (1832°F) in a nitrogen atmosphere of 50 ml/min (0.0132 gal/min). Finally, data reduction is carried out using instrumentation software.

Data interpretation is done by finding the initial temperature (T_i) on the thermogram where the cumulative mass change reaches a magnitude that the thermobalance can detect. The final temperature (T_f) on the thermogram is the temperature at which the cumulative mass change first reaches its maximum value, corresponding to a complete reaction. At a linear heating rate, T_f must be greater than T_i and the difference is called the reaction interval.

Figure 1 shows an example of what a weight loss and weight gain thermograph would look like. The scales are not shown on the example. The scales on the graphs will have temperature on the bottom scale increasing from left to right and percent weight on the left hand side increasing or decreasing depending on weight gain or loss, respectively.

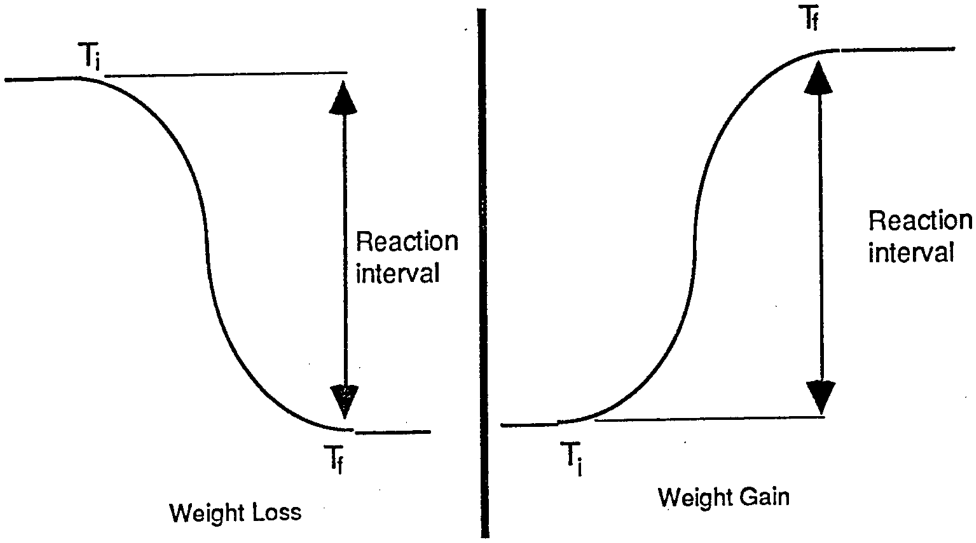


Figure 1. Sample Thermographs

RESULTS

Seven samples from different wafers were used. The samples collected consist of broken filaments from the wafers. These broken filaments resulted from normal handling of the wafers in sealed plastic bags. Thermographs were made of each sample (see following graphs). Data from the graphs is tabulated below:

Hafnium Sample	Weight, mg (lbs)	Percent weight	T_i, °C (°F)
M-2	43.4210 (0.0957)	101.42	325 (617)
M-3	21.2620 (0.0468)	102.1	500 (932)
M-6	9.3450 (0.0206)	105.16	590 (1094)
M-7	58.8240 (0.1296)	101.08	200 (392)
M-8	67.4980 (0.1488)	101.065	425 (797)
M-9	36.2020 (0.0798)	102.43	430 (806)
M-15	8.0190 (0.0177)	106	180 (356)

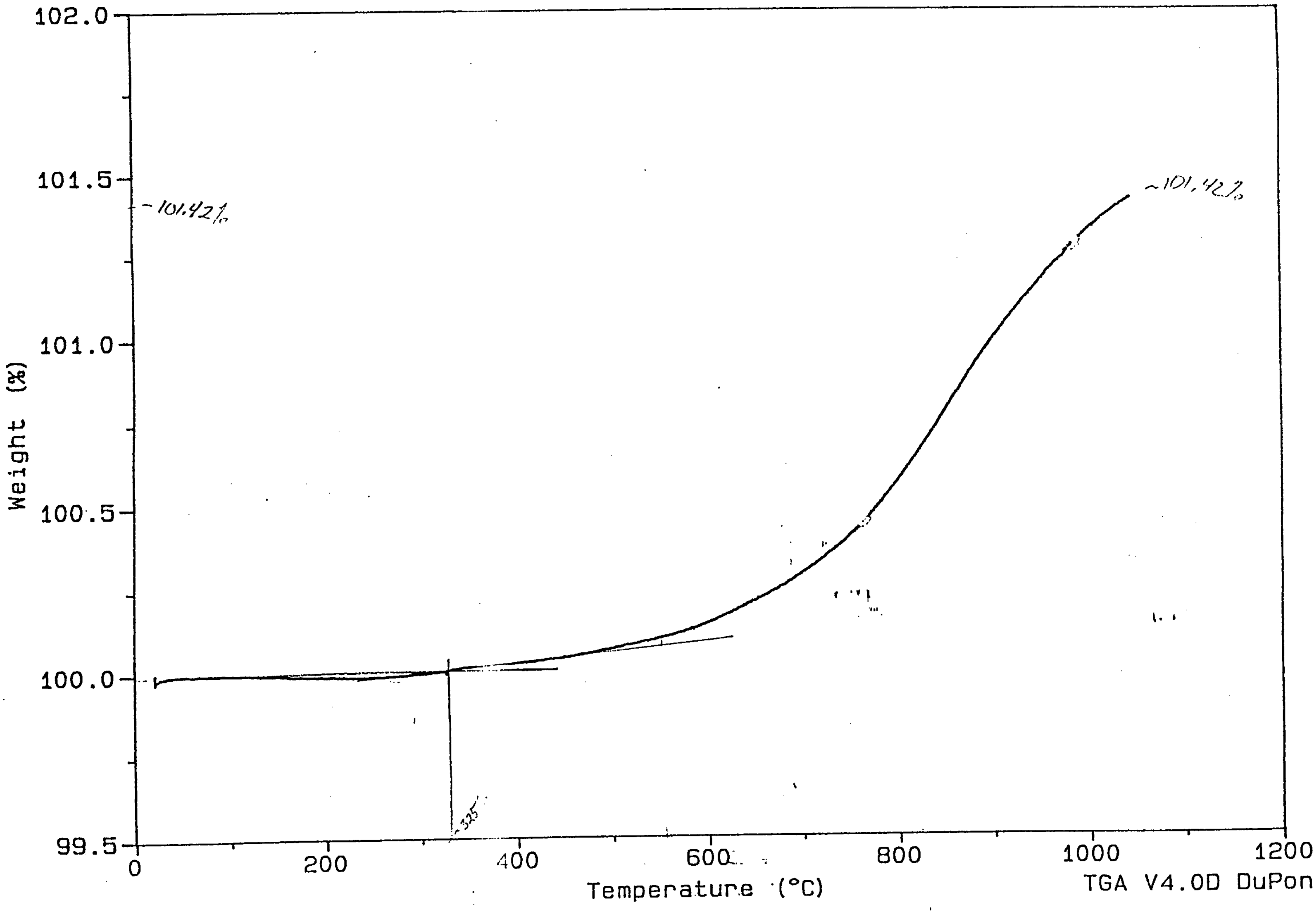
Findings from the data are:

1. Percent weight increase was higher for lighter samples (M-6, M-5) and lower for the heavier samples (M-8, M-7).
2. Excluding samples M-8 and M-15, the heavier samples start increasing weight at a lower temperature and the lighter samples at higher temperature. However, M-8 begins losing weight at about 250°C (482°F) and M-15 begins a significant weight gain at about 475°C (900°F).
3. M-8 was the only sample to show an initial weight loss.
4. Sample percent weight gains started in a temperature range from 180°C (356°F) to 590°C (1094°F).
5. All samples had most significant percent weight gains above 600°C (1112°F).

Sample: M-2 HFC
Size: 43.4210 mg
Method: POLYMERS
Comment: RATE 10°C/MIN, GN2 ATMOSPHERE 50 ML/MIN

TGA

File: A: TGASOLAR.007
Operator: PAUL JONES
Run Date: 31-May-93 21: 43

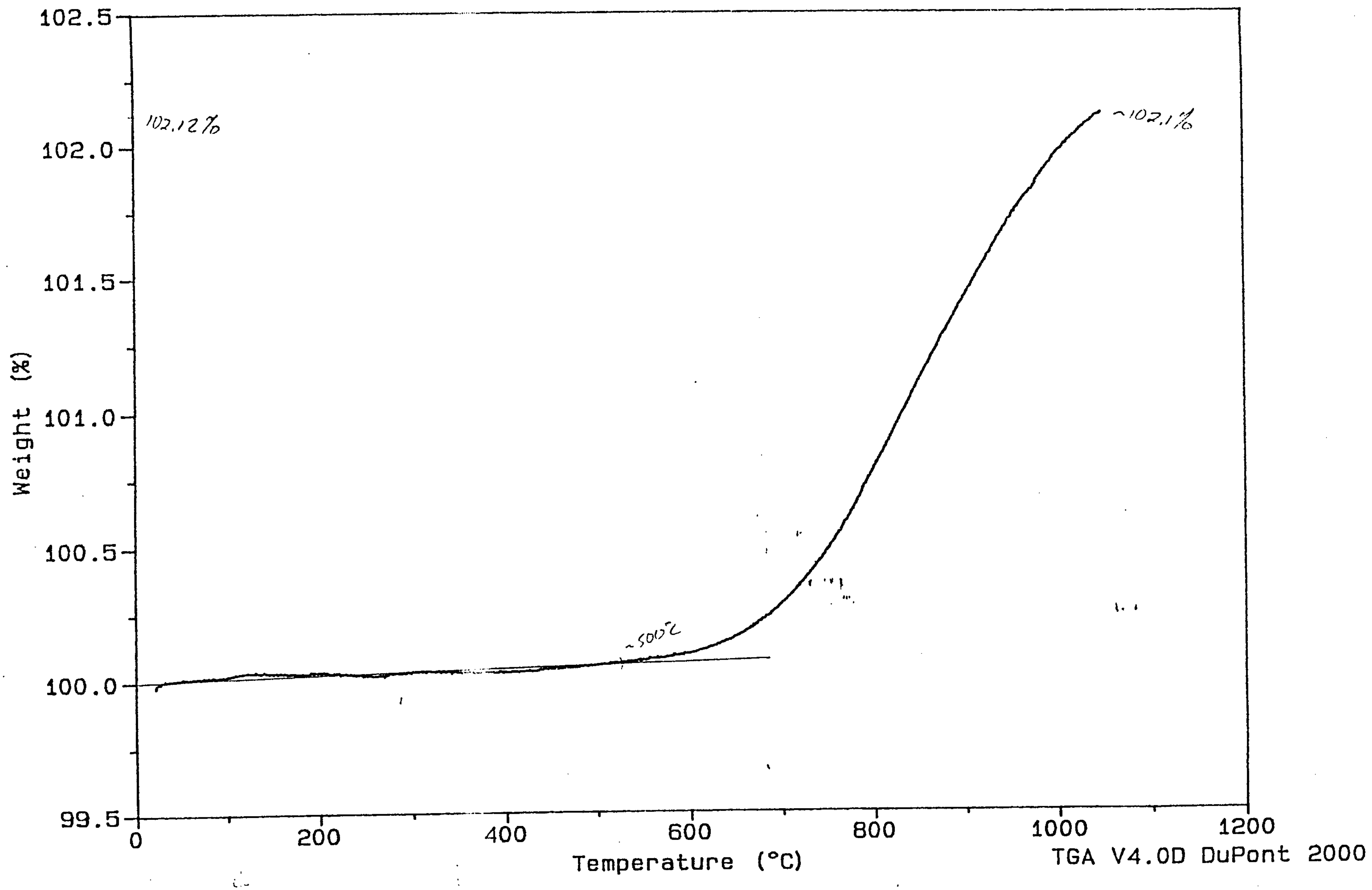


TGA V4.0D DuPont 2000

Sample: M-3 HFC
Size: 21.2620 mg
Method: POLYMERS
Comment: RATE 10°C/MIN, GN2 ATMOSPHERE 50 ML/MIN

TGA

File: A: TGASOLAR.009
Operator: PAUL JONES
Run Date: 2-Jun-93 23: 12



TGA V4.0D DuPont 2000

Sample: M-6 HFC
Size: 9.3450 mg
Method: POLYMERS
Comment: RATE 10°C/MIN. GN2 ATMOSPHERE 50 ML/MIN

TGA

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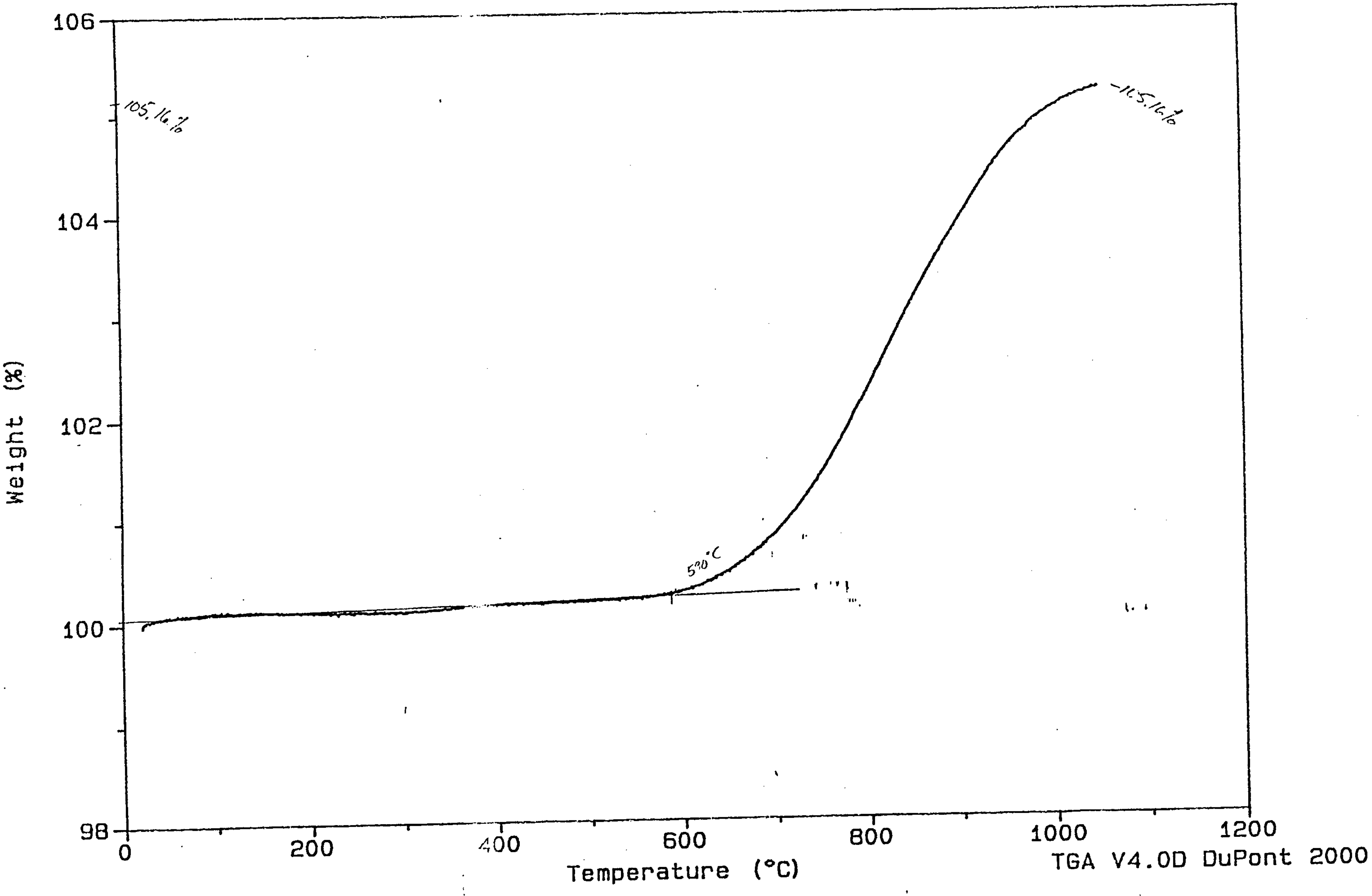
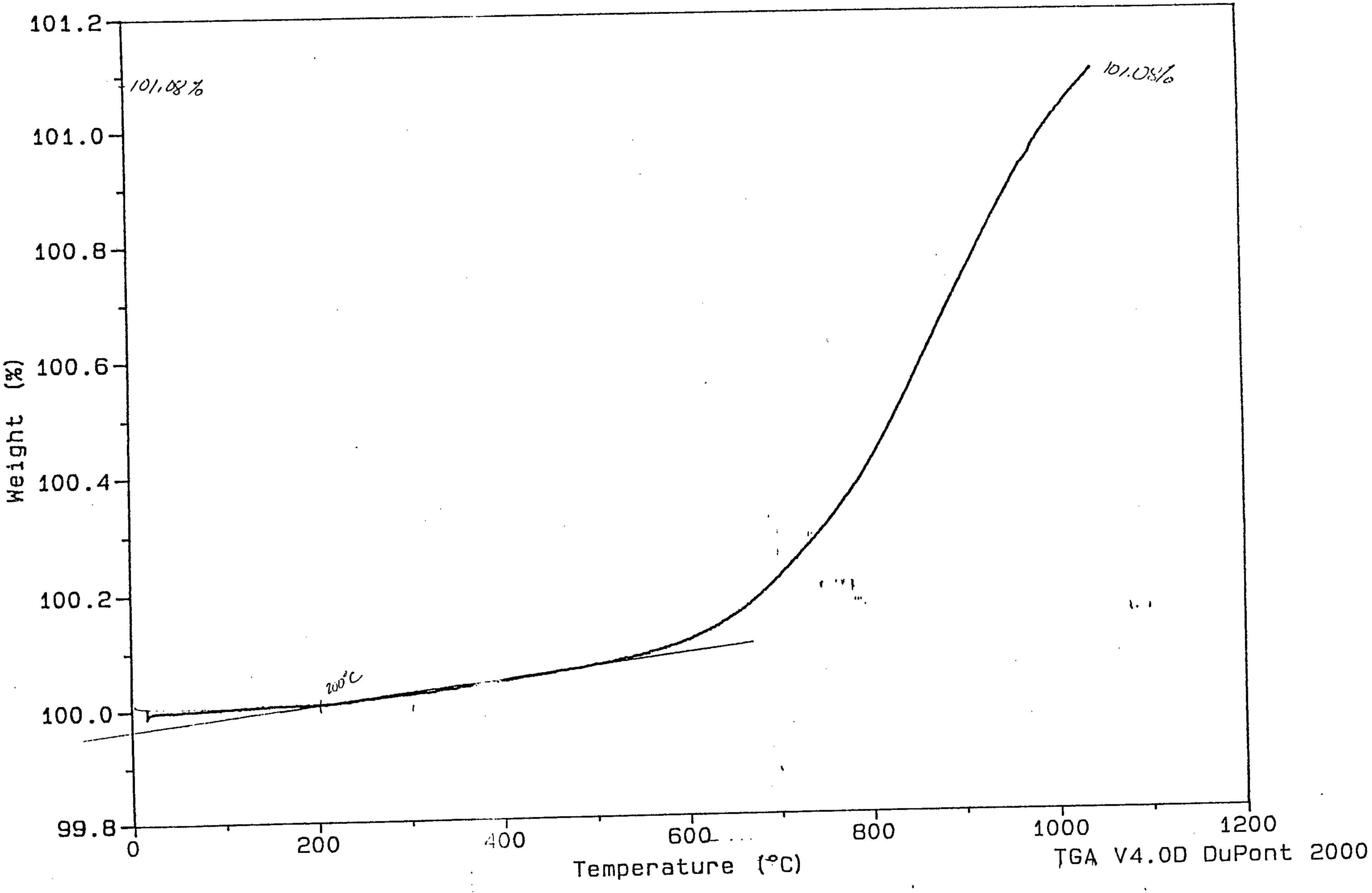


TGA V4.0D DuPont 2000

TGA

Sample: M-7 HFC
Size: 58.8240 mg
Method: POLYMERS
Comment: RATE 10°C/MIN, GN2 ATMOSPHERE 50 ML/MIN

File: A: TGASOLAR.004
Operator: PAUL JONES
Run Date: 27-May-93 16: 57



Sample: M-8 HFC
Size: 67.4980 mg
Method: POLYMERS
Comment: RATE 10°C/MIN, GN2 ATMOSPHERE 50 ML/MIN

TGA

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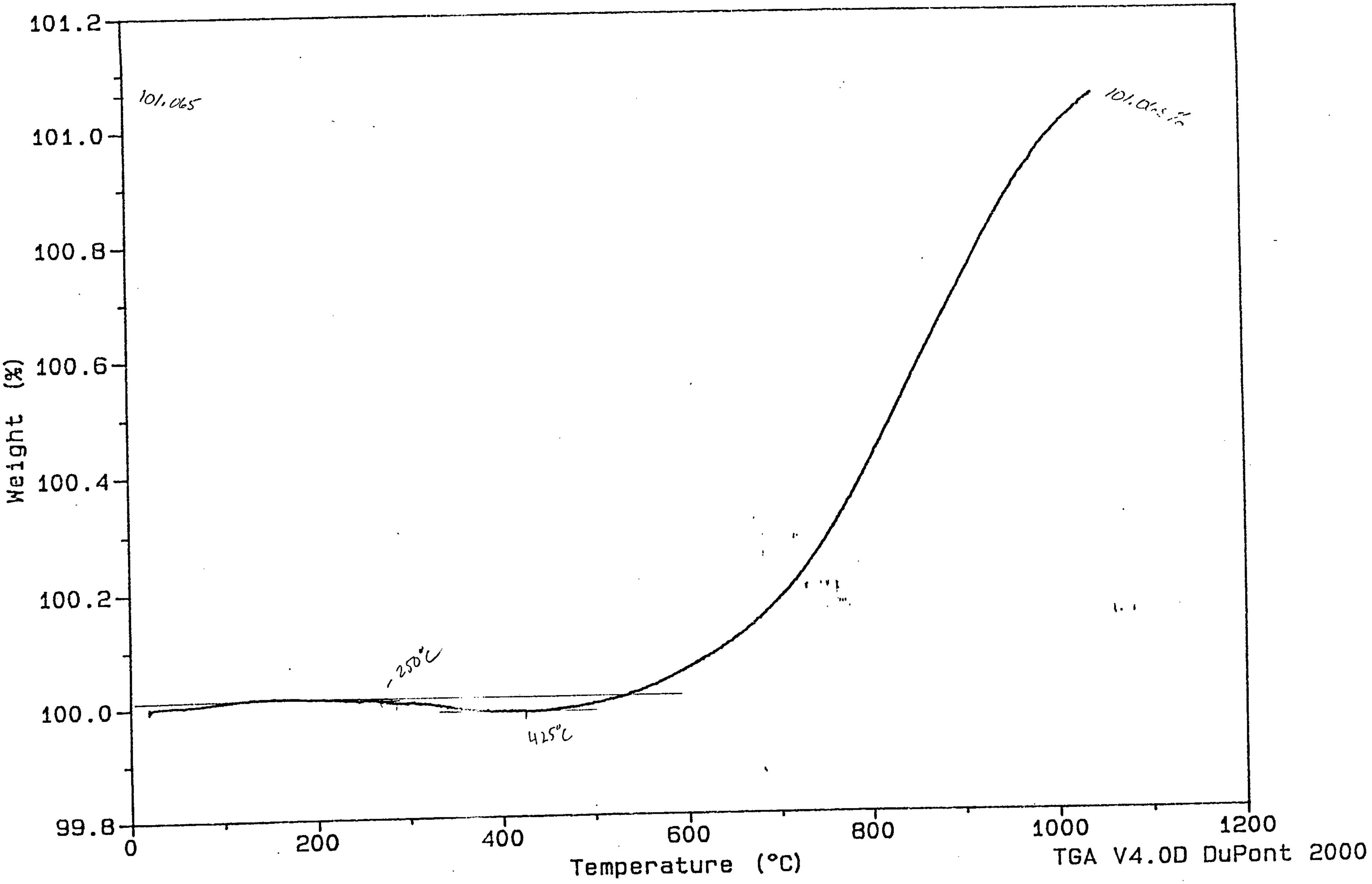
Operator: PAUL JONES
Run Date: 3-Jun-93 16: 33



Sample: M-9 HFC
Size: 36.2020 mg
Method: POLYMERS
Comment: RATE 10°C/MIN, GN2 ATMOSPHERE 50 ML/MIN

TGA

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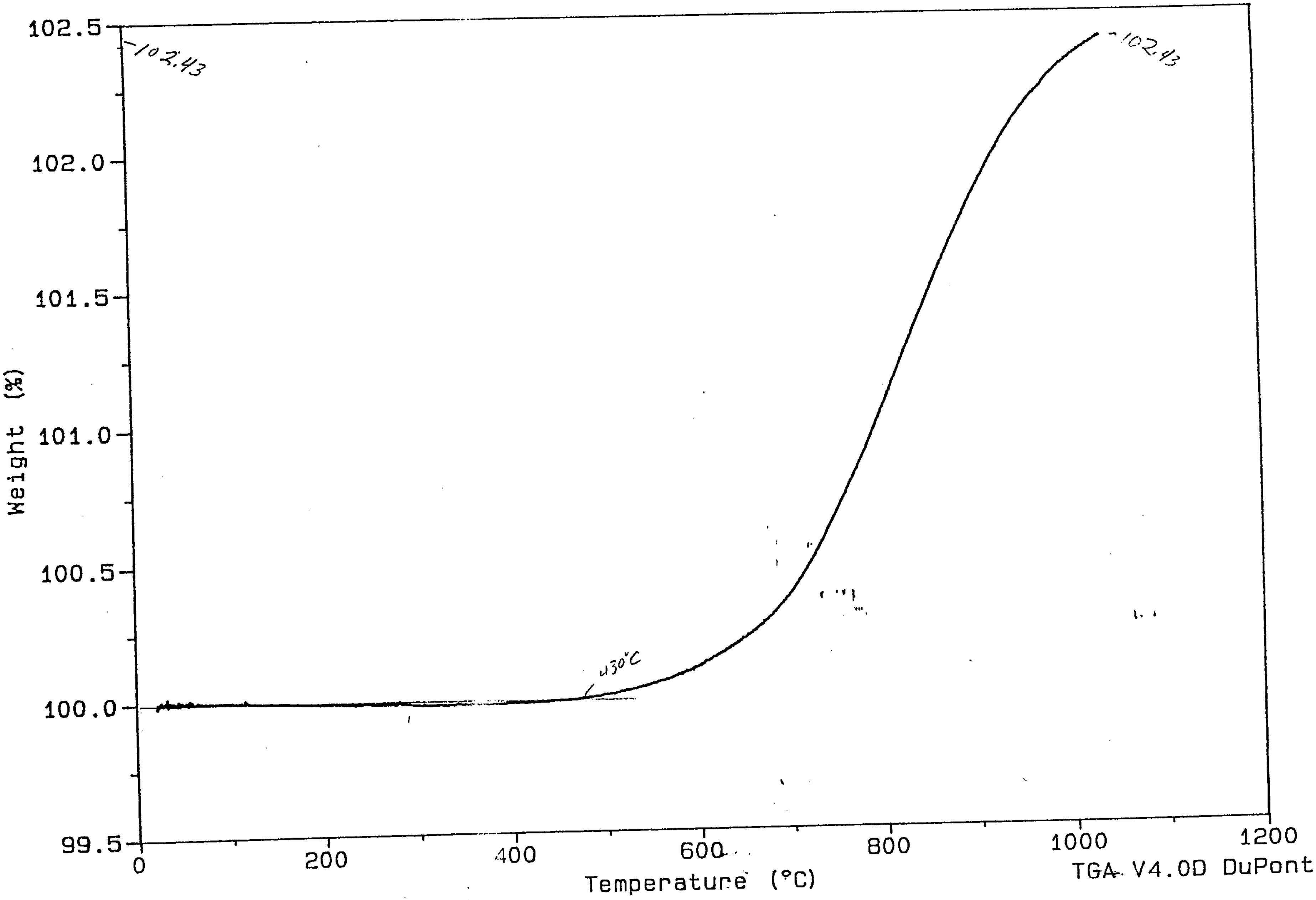

TGA V4.0D DuPont 2000

Sample: M-15 HFC
Size: 8.0190 mg
Method: POLYMERS
Comment: RATE 10°C/MIN, GN2 ATMOSPHERE 50 ML/MIN

TGA

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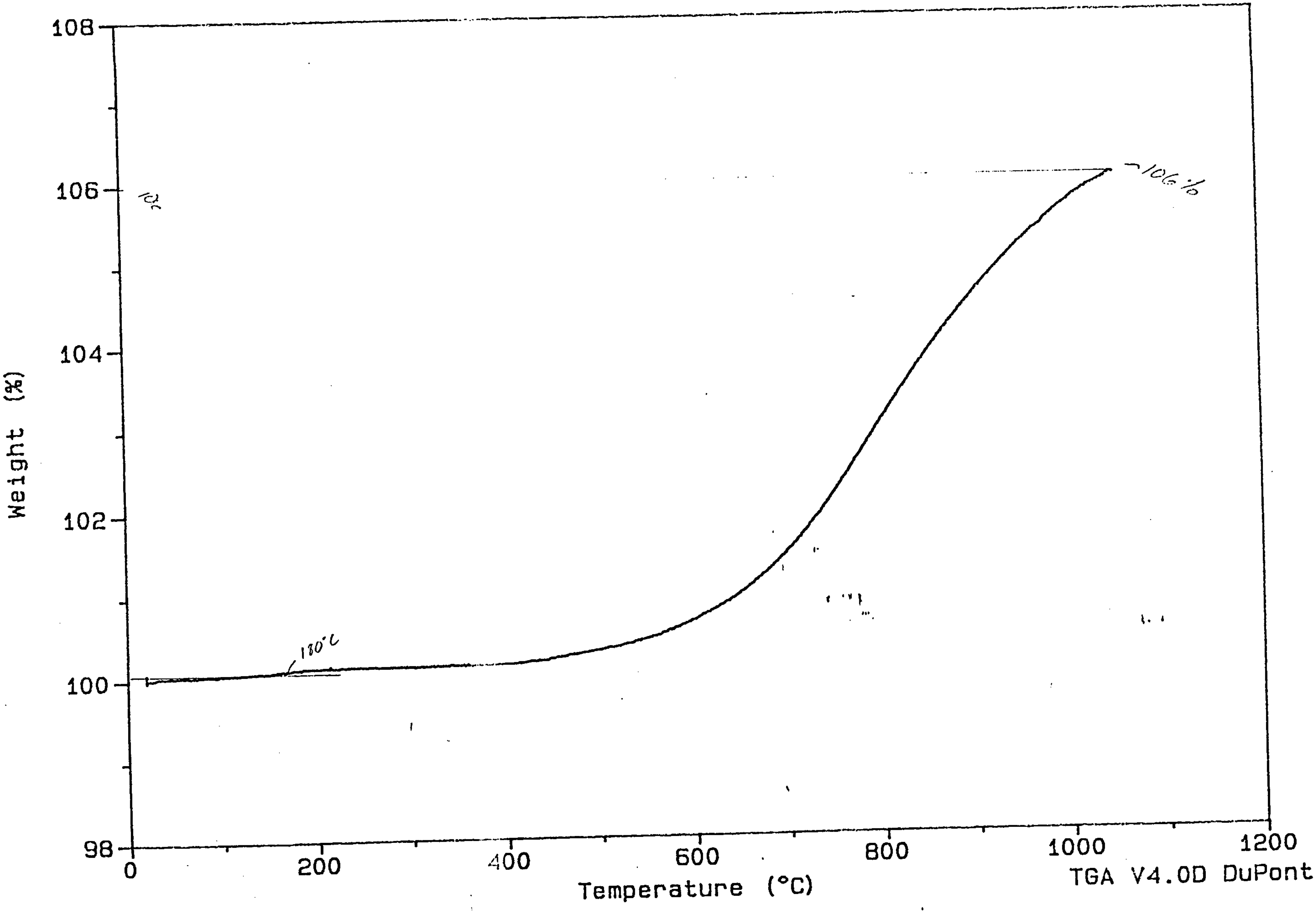

TGA V4.0D DuPont 2000

CONCLUSION

Weight gains were not expected in these tests. The possible formation of hafnium nitride (HfN) is ruled out because the temperature needed for reaction of hafnium and nitrogen is from 1000° to 1500°C (1832° - 2732°F)[1]. It is possible that the nitrogen is reacting with one or more of the impurities in the material or impurities in the nitrogen are reacting with the material. Oxygen in the material is suspected as the most likely candidate for reacting with nitrogen and causing the weight increase. However, no definite conclusion can be drawn from this study without further experimentation and analysis.

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