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(54) Thermally stabilized polyacrylonitrile polymers for carbon fiber manufacture.

(57) Disclosed is a process for manufacturing carbon fiber in which a polyacrylonitrile polymer in the form of a multitude of filaments is heated in an atmosphere that is substantially free of oxygen to form a thermally stabilized carbon fiber precursor in an oxygen-containing atmosphere to form a stabilized and oxidized precursor and then the thermally-stabilized precursor is heated in an oxygen-containing atmosphere to oxidize the precursor, which is then conventionally carbonized in an atmosphere substantially free of oxygen.

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THERMALLY STABILIZED POLYACRYLONITRILE POLYMERS FOR CARBON FIBER MANUFACTURE

This invention relates to a process for manufacturing carbon fiber by carbonizing a precursor comprising a polyacrylonitrile polymer, and more particularly to the stabilization of the precursor prior to carbonization.

Carbon fiber is useful in a variety of applications for which its mechanical, chemical and electrical properties are uniquely suited, particularly for making lightweight composites comprising the fiber in inorganic or organic matrices.

Although the cost of carbon fiber has been decreasing significantly even while its properties and reliability have been improved, there are still problems in some aspects of its production. In particular, the stabilization step in which polyacrylonitrile polymer, in the form of a tow comprising a multitude of filaments, is heated in air or other oxygen-containing gaseous medium prior to carbonization, adversely limits the rate at which carbon fiber can be manufactured on a commercial scale.

Such stabilization through oxidation is rate-limiting because of the risk of fusing the filaments or even causing an uncontrollable self-generating reaction (a "thermal runaway") if the precursor is heated too fast or too high during the stabilization. It is customary to use certain comonomers, such as acrylic acid, in forming the polyacrylonitrile polymer filaments in order to permit initiation of the oxidation reaction at a temperature lower than that otherwise required, e.g. between about 200 and 400 ° C. There is risk of thermal runaway even at such lower temperatures, but the risk is less and there is obviously less risk of fusion of the filaments.

However, to produce carbon fiber having uniform properties requires strict control of the amounts of the comonomer that is used to permit oxidation at lower temperatures, which presents production problems in addition to the rate limitation caused by the need to maintain a relatively low temperature.

The problems associated with the stabilization step have been extensively studied, for instance, in "Studies on Carbonization of Polyacrylonitrile Fibre - Part 5: Changes in Structure with Pyrolysis of Polyacrylonitrile Fibre: by Miyamichi, et al., Journal of Society of Fibre Science and Technology, Japan, 22, No. 12, 538 - 547 (1966).

U.S. Patent 4,104,004 suggests dividing up the stabilization step so that the precursor is heated in separate temperature zones, and U.S. Patents 3,775,520 and 3,954,950, while they suggest driving off residual solvent and producing controlled shrinkage by an initial brief heating step in an inert atmosphere prior to oxidizing the precursor, also limit the initial heating step to prevent stabilization from occurring.

There is still need for a process for manufacturing carbon fiber having uniform properties from a polyacrylonitrile polymer carbon fiber that reduces the risk of thermal runaway and fusion of the filaments while increasing the possible rates of reaction. It is also desirable to permit the use of polyacrylonitrile homopolymer, which is more economical to make than the comonomers conventionally used to reduce the temperature of oxidation.

According to the invention, a process for manufacturing carbon fiber in which a polyacrylonitrile polymer in the form of a multitude of filaments is heated in an oxygen-containing atmosphere to form a stabilized and oxidized precursor that is then carbonized in an atmosphere substantially free of oxygen, is characterized in that the polyacrylonitrile filaments are heated in an atmosphere that is substantially free of oxygen to form a thermally stabilized carbon fiber precursor prior to the step of heating the filaments in an oxygen-containing atmosphere to oxidize the thermally-stabilized precursor.

By that process, the precursor is readily and safely stabilized in a form that is capable of being oxidized for subsequent carbonization below the range of temperatures ordinarily used for oxidation, or alternatively permits the use of conventional oxidation temperatures or even higher temperatures to achieve a faster rate of oxidation. The carbonization conditions after oxidation follow the conventional procedures for making carbon fiber from polyacrylonitrile precursor.

Polyacrylonitrile polymers conventionally used as precursors for carbon fiber manufacture, and conventional procedures for the manufacture of such precursors are well known, for instance from U.S. Patents 4,001,382, 4,009,248, 4,397,831 and 4,452,860. While the same polyacrylonitrile polymers are preferred as precursors for carbon fiber manufacture according to the invention, a greater variety of polyacrylonitrile polymers may be used. For example, polyacrylonitrile homopolymer may be used as a precursor and is readily stabilized by the process of this invention.

Preferably, the atmosphere that is substantially free of oxygen consists essentially of nitrogen or other inert gas, although a vacuum may be also used. The temperature to which the precursor is heated is preferably at least about 130 ° C, more preferably at least about 230 ° C.but may be up to 500 ° C or higher without risk of thermal runaway. Typically, one or more tows each comprising a multitude of continuous

filaments traveling as a band are heated in a furnace or oven for stabilization in that inert atmosphere according to the invention. The stabilization step takes from a few minutes up to about an hour or more depending on the temperature chosen and may be conducted in a series of steps, if desired.

The duration of the stabilization step may be pre-determined by a conventional technique that measures thermal rearrangement, such as by differential scanning calorimetry (DSC). The reduction in residual heat of reaction measured by DSC in an inert atmosphere before and after the stabilization step is an appropriate measure of thermal rearrangement, and preferably is from about 10% to about 35%, more preferably by about 20%.

The diameter of filaments within the tow preferably ranges between 1 and 10 microns, although the magnitude of such diameter is not critical in accordance with this invention. Moreover, each tow may comprise between 500 and 20,000 filaments per tow. The conventional use of surface treatments on the filaments within the tow does not detract from the benefits of this invention.

After being thermally stabilized, the tows are may be oxidized at temperatures ranging surprisingly as low as room temperature or even lower, but it is preferred that oxidation take place in a gaseous medium containing oxygen such as air at temperatures ranging between 150 ° C and 300 ° C for a time sufficient to allow these thermally stabilized tows to be self supporting (i.e. to retain dimensional integrity) during carbonization. Too high a temperature during oxidation is undesirable unless such heating takes place in apparatus for carrying away thermal decomposition products of the fiber being oxidized.

While undergoing stabilization in the non-oxidizing atmosphere or oxidation, the band of filaments may be stretched to a length longer than its original length, held constant in length or allowed to shrink as desired.

After oxidation, the thermally stabilized and oxidized precursor tows are carbonized using conventional techniques for making carbon fibers. For example, the stabilized and oxidized precursor tow is heated in an inert atmosphere or vacuum at a temperature between about 500 ° C and 800 ° C for tar removal followed by heating at higher temperatures, also in nitrogen or other non-oxidizing atmosphere, to yield a carbonized fiber suitable for use with or without surface treatment according to conventional practice.

The following examples illustrate the invention, and Figures 1 - 14 graphically display the results of tests made according to the examples. The DSC apparatus used was a DuPont 910 DSC Module with a Model 1090 or like controller. The X-axis in Figures 1 through 11C is temperature in degrees centigrade. The Y-axis is heat flow in milliwatts. Figures 12, 13 and 14 show load (tension) in grams per denier versus degree of reaction in percent. The degree of reaction is determined using density.

The sample size in Figure 1 was 1.136 milligrams. The rate of temperature increase was 10 degrees centigrade per minute and was in air. The sample size in Figure 2 was 1.110 milligrams and the rate of temperature increase was 10 degrees centigrade per minute in nitrogen. The sample type and rate of temperature increase are set forth below for the data in Figures 3 - 11C.

Figure	Sample Size	Type	Rate
3	1.332 mg	AB	10
4	1.396 mg	CE	10
5	1.369 mg	AB	10
6	1.320 mg	CE	10
7	0.243 mg	AB	10
8	0.791 mg	CE	10
9	1.246 mg	DUP	10
10	8.826 mg	DUP	10
11	4.624 mg	DUP	10
11A	1.332 mg	DUP	10
11B	1.327 mg	DUP	10
11C	3.178 mg	DUP	10

In Figures 1 and 2 DSC was respectively in air and nitrogen. DSC of Figures 3 and 4 was in nitrogen. DSC was in air for Figures 5, 6 (both purge) and 7 and 8 (second heating). Figure 9 of the DSC was in air (purge) and DSC was in nitrogen (Figure 10) and then in air in Figure 11. Figure 11A was run in nitrogen; Figure 11B run in air; and Figure 11C is rerun in air after initial heating in nitrogen.

Examples

In the work described below "AB Precursor" and "CE Precursor, are standard carbon fiber precursors made from acrylonitrile and methacrylic acid (2 weight %) in the case of the AB precursor and acrylonitrile, methylacrylate and itaconic acid in case of the CE precursor.

Several experiments were initially run with varying degrees of nitrogen (N_2) pretreatment and then analyzed thermally. As seen in Figures 1 and 2, the amount of change in heats of decomposition (H_D) between precursor heated in air and heated in nitrogen (N_2) were different. These differences are typical for acrylic polymers heated in oxygen containing and oxygen free atmospheres with the low H_D (in N_2) due to thermal rearrangement reactions and the large H_D in air due to thermal rearrangement and oxidation reactions. Table 1 shows the results of two experiments where precursor was first pretreated in N_2 at elevated temperatures.

TABLE 1

HEATS OF DECOMPOSITION IN AIR AND N_2			
	Air	H_D cal/gm	N_2
AB Precursor (Baseline)	1121		165
Pretreatment: 235° C, 55 min in N_2	943		116
Pretreatment: 235° C, 116 min in N_2	844		90.8

The change in H_D was 178 cal/g when heated in air after pretreatment in N_2 but only 49 cal/g when heated in N_2 after the same nitrogen pretreatment for the first sample and 277 cal/g when heated in air after pretreatment and only 74 cal/g when heated in N_2 after pretreatment for the second. Since the pretreatment heating was carried out in N_2, it might be expected that the change in H_D would be the same in both air and N_2. However, from this data at least part of the oxidation reaction is not involved with or linked to the rearrangement reaction. If the sample 1 pretreatment (235° C/55 min) had been run in air instead of N_2, the residual H_D, air would be 740 cal/g. The N_2 preheat generated only 49 cal/g, but lowered the H_D, air by 178 cal/g, so it appears that 129 cal/g of reaction with oxygen was by-passed by the N_2 preheat. The N_2 preheat for 116 min at 235° C generated 74 cal/g and lowered the H_D, air by 277 cal/g so it by-passed 203 cal/g of the expected reaction with oxygen. It is evident that the chemical structure of the fiber is different when preheated in N_2 prior to air oxidation.

Samples of four different polyacrylonitrile polymers were thermally analyzed in nitrogen and air to better define the mechanisms that were occurring. As part of the analysis, ground precursor fiber was first analyzed in nitrogen, up to about 430° C. The results are shown in Figure 3 (AB Precursor) and 4 (CE Precursor). The results were not unusual; an exponentially-increasing heat evolution peaking at about 285-290° C, followed by a rapid heat decrease to give about 100-135 cal/g evolved heat. The resultant thermally-stabilized powder was then reweighed and reanalyzed, this time in air. Normally the air oxidation curve will follow the route shown in Figure 5 (AB Precursor) and Figure 6 (CE Precursor). Instead, the curve shape was markedly changed. The area under the curve was significantly reduced, from about 1000-1100 cal/g to about 250 cal/g for AB Precursor and 335 cal/g for CE Precursor. In addition, the oxidation-initiation temperature was reduced about 20° C, indicating that the oxidation would be more rapid than non-prestabilized fiber (Figures 7 and 8). Additionally, the position of the two major thermal peaks shifted. For the AB Precursor the shift was more dramatic, with the lower peak dropping from a typical 228° C to 212° C. The position of the higher-temperature peak increased from 326° C to 360° C for AB Precursor while it decreased for CE Precursor from 330° C to 315° C.

These results suggest a major change in the oxidation reactions. There appear to be more oxidatively-active sites after the nitrogen pretreatment as evidenced by the decrease in initiation temperature. There also appears to be less overall oxidation, or possibly less dehydrogenation, as evidenced by the higher temperature which may imply more oxidative stability or may simply mean that the influence of the lower-temperature reactions is dissipated leaving only the higher-temperature part of the response.

The thermal analysis of DuPont T-42 polymer, a commercial grade polyacrylonitrile polymer fiber, in air (Figure 9) indicates that it would be a less suitable precursor than AB Precursor due to its high initiation

temperature and rapid heat evolution rate. If the precursor is first prestabilized in N_2 (Figure 10) and then reheated in air (Figure 11), the thermal response changes dramatically, similar to what has been seen with the other acrylic polymers. The reaction initiation temperature has decreased substantially, the single peak has split into two very distinct peaks, and the total heat of reaction is only 34 cal/gm.

PAN homopolymer, which is typically avoided at present as a carbon fiber precursor in commercial practice because of its slow reaction rate, high rate of that evolution once it begins to react, and high initiation temperature was also found to undergo dramatic changes in thermal characteristics once it was prestabillzed. Figure 11A shows the typical DSC curve for this polymer in nitrogen with a heat of decomposition of 124 cal/gm, while Figure 11B shows the thermal curve in air. The heat of reaction in air (1103 cal/gm) is typical of other acrylic polymers, but the homopolymer is characterized by a high initiation temperature (250 ° C) and rapid heat evolution rate (steep slope). When the polymer is prestabilized by running the DSC in nitrogen and then rerun in air, the changes are dramatic (Figure 11C). The initiation temperature drops to 155 ° C with the single peak splitting into two distinct peaks, the rate of heat evolution drops significantly as evidenced by a change in initial slope (note change in y-axis range between Figures 11B and 11C), and the overall heat of reaction has dropped to 237 cal/gm. Those results indicate the polymer may make a much more suitable carbon fiber precursor from the standpoint of ease of processability, safety, and potentially, economics.

These data also suggest that the fiber will be more easily oxidized after prestabilization. As such, a fiber that has been prestabilized and oxidized for a given time at temperature will have a higher density than a fiber that is only oxidized for the same time at temperature. A set of experiments was run to determine if this is true; the results are shown in Table 2 below.

TABLE 2

DU PONT T-42 PRESTABILIZATION AND OXIDATION DENSITIES	
Conditions	Density (g/cc)
235 ° C, 2 hr, air	1.2688
235 ° C, 1 hr, N_2; then 235 ° C, 1 hr, air	1.2904
235 ° C, 1 hr, air 235 ° C, 1 hr, N_2	1.2101

The fiber that has been prestabilized and oxidized does exhibit a higher density than the fiber that has just been oxidized at the same temperature for the same amount of time. This is believed due to the increase in reactivity after prestabilization since prestabilization alone results in a rate of density increase that is less than that due to oxidation in air (Table 2 and Figure 12). Looking at the density difference between the oxidized and prestabilized/oxidized fibers and assuming kinetics similar to the reaction kinetics of the AB Precursor for comparison purposes, the increase in oxidized fiber density due to prestabilization corresponds to a time savings of 40 minutes at 235 ° C. That is, in order to reach the same oxidized density as the prestabilized/oxidized fiber, the precursor fiber would have to be oxidized for 160 minutes at 235 ° C instead of stabilized/oxidized for a total of 120 minutes at 235 ° C.

Another way to monitor the reaction characteristics of an acrylic based precursor is to follow the tension that is generated as the fiber rearranges and oxidizes at elevated temperatures. Tension vs time data were generated for AB and DuPont precursors and prestabilized fibers to further clarify changes in oxidation reaction characteristics that are caused by prestabilization in an inert atmosphere.

Figure 13 shows load/time data for AB precursor in air at 235 ° C, N_2 at 235 ° C, and for AB prestabilized for varying amounts of time and then run in air at 235 ° C. Comparing the samples run in air and N_2 (no stabilization), both samples shorn the characteristic drop in tension initially followed by a tension increase as the fiber begins to react. The tension increase due to the shrinkage of the sample run in N_2 is significantly less than in air, the difference presumably being due to the added shrinkage of the oxidation reactions occurring in air.

The prestabilized fibers show a sudden increase in tension when run in air possibly indicating an initial

increase in the degree of reactivity. The load build up quickly levels out for the 60 minute prestabilized fiber, followed by 30 minute, and 5 minute which has a final load after 60 minutes, similar to AB Precursor. These lower oxidation loads could be due to a lower overall oxidation reactivity for the prestabilized fibers that would agree with DTA results showing lower than expected residual heats of reaction in air after prestabilization.

The results for the DuPont T-42 type fiber are shown in Figure 14. This fiber is characteristically slower to react than AB as evidenced by the slow load buildup for the AB 10 Precursor. After prestabilization, the shrinkage characteristics of the fiber are greatly altered. The tension increase with time, while not as great as for AB Precursor, is similar in shape, indicating the fiber may oxidize more readily after prestabilization. As with the prestabilized AB Precursor samples, the T-42 type fibers show a rapid initial increase in tension (the greater the degree of prestabilization, the greater the rate of tension buildup). After 60 minutes, the more highly prestabilized fiber has a lower load buildup than the other prestabilized fiber (similar to AB results) but both samples are significantly higher than the baseline indicating the prestabilization (even after as little as five minutes) results in an increase in oxidation reaction rate, but may reduce the number of sites available for reaction. These results indicate that prestabilization can be used to make certain precursor fibers more reactive while also increasing the safety of the process by reducing the oxidation exotherm.

Another interesting finding from these experiments is that prestabilization changes fiber reactively sufficiently to cause a subsequent reaction in air at room temperature.

A set of AB fibers were stabilized in N_2 at 250 ° C for times ranging from 5 minutes to 6 hours. In each case, the sample was then divided in half, with half placed in an inert atmosphere and the other half stored in air, both at room temperature. In all cases, the sample in air continued to change color and slowly darken while the sample in N_2 remained golden brown. It was found that this reaction could be suspended by placing the partially darkened sample in N_2 and then reinitiated by exposing again to air. The fibers exposed to air after prestabilization were able to oxidize at room temperature. If oxidation type reactions were indeed occurring, it would be expected that the residual heat of reaction would decrease with increasing time of exposure to air at room temperature. A series of experiments was per-formed to determine if this was indeed the case. In one set of experiments, a length of AB Precursor was stabilized in N_2 for 2 hours at 250 ° C; the fiber was divided in half with half exposed to room-temperature air for 3 hours and the other half exposed to air for 24 hours. The samples were then restored in N_2 and submitted for thermal analysis. In all cases, the thermal lab was careful to run the samples as quickly as possible after the N_2 seal was broken. In the second experiment, a sample of AB Precursor was stabilized for 16 hours at 250 ° C in N_2 and then divided with parts exposed for 0 hours, 1 hour, 3 hours, and 24 hours in air. Samples were then restored in N_2 and thermally analyzed. The results are shown in Table 3 below:

TABLE 3

CHANGE IN H_{air} OF STABILIZED FIBERS AFTER VARYING AMOUNTS OF EXPOSURE TIME IN AIR

Stabilization Conditions in N_2	Air Exposure Time at Room Temperature (hr)	H_{air}
2 hours at 250 ° C	3	684
2 hours at 250 ° C	24	624
16 hours at 250 ° C	0	678
16 hours at 250 ° C	1	652
16 hours at 250 ° C	3	605
16 hours at 250 ° C	24	548

For both sets of these experiments, the heat of reaction decreased with time of exposure in air, indicating a reaction occurring at room temperature which is responsible for the color change we had noted. A stabilized fiber was also run to determine if free radicals are present, which might be initiating the reaction at room temperature in air. The results indicated the presence of some free radical activity, which is as yet unidentified.

Claims

1. A process for manufacturing carbon fiber in which a polyacrylonitrile polymer in the form of a multitude of filaments is heated in an oxygen-containing atmosphere to form a stabilized and oxidized precursor that is then carbonized in an atmosphere substantially free of oxygen, is characterized in that the polyacrylonitrile filaments are heated in an atmosphere that is substantially free of oxygen to form a thermally stabilized carbon fiber precursor prior to the step of heating the filaments in an oxygen-containing atmosphere to oxidize the thermally-stabilized precursor.

2. A process for manufacturing carbon fiber as claimed in claim 1, further characterized in that the temperature to which the polyacrylonitrile filaments are heated in an atmosphere that is substantially free of oxygen is heated is preferably at least about 230°.

3. A process for manufacturing carbon fiber as claimed in claim 1, further characterized in that the atmosphere that is substantially free of oxygen is nitrogen.

4. A process for manufacturing carbon fiber as claimed in claim 1, 2, or 3, further characterized in that the polyacrylonitrile filaments are heated in an atmosphere that is substantially free of oxygen until the reduction in residual heat of reaction as measured by differential scanning calorimetry is from about 10% to about 35%.

5. A process for manufacturing carbon fiber as claimed in claim 4, further characterized in that the filaments are heated until the reduction in residual heat of reaction is about 20%.

6. A process for manufacturing carbon fiber as claimed in any of the preceding claims, further characterized in that the thermally stabilized carbon fiber precursor in the form of a tow is heated in an oxygen-containing atmosphere at a temperature from 150° C to 300° C for a time sufficient to allow the tow to be self supporting.

7. A process for manufacturing carbon fiber as claimed in any of the preceding claims, further characterized in that the polyacrylonitrile filaments in the form of a band of closely spaced tows are moved in an atmosphere that is substantially free of oxygen through an oven maintained at a first range of temperatures to heat the filaments to form a thermally stabilized carbon fiber precursor and then are moved at a higher line speed in an oxygen-containing atmosphere through an oven maintained at a second range of temperatures to oxidize the thermally-stabilized precursor.

Fig.1

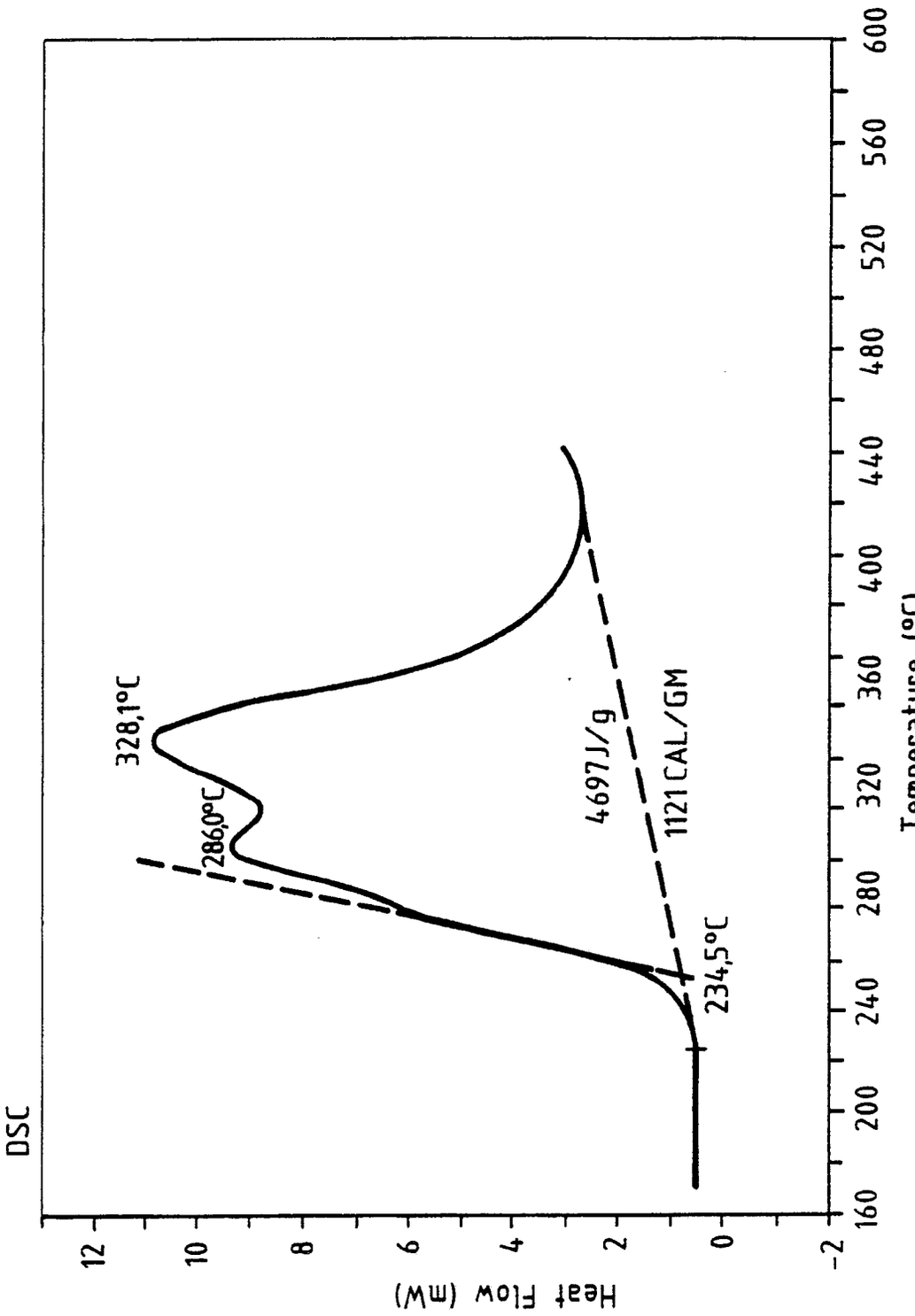

DSC
328,1°C
286,0°C
4697J/g
1121CAL/GM
234,5°C
Heat Flow (mW)
Temperature (°C)
12
10
8
6
4
2
0
-2
160
200
240
280
320
360
400
440
480
520
560
600

Fig. 2

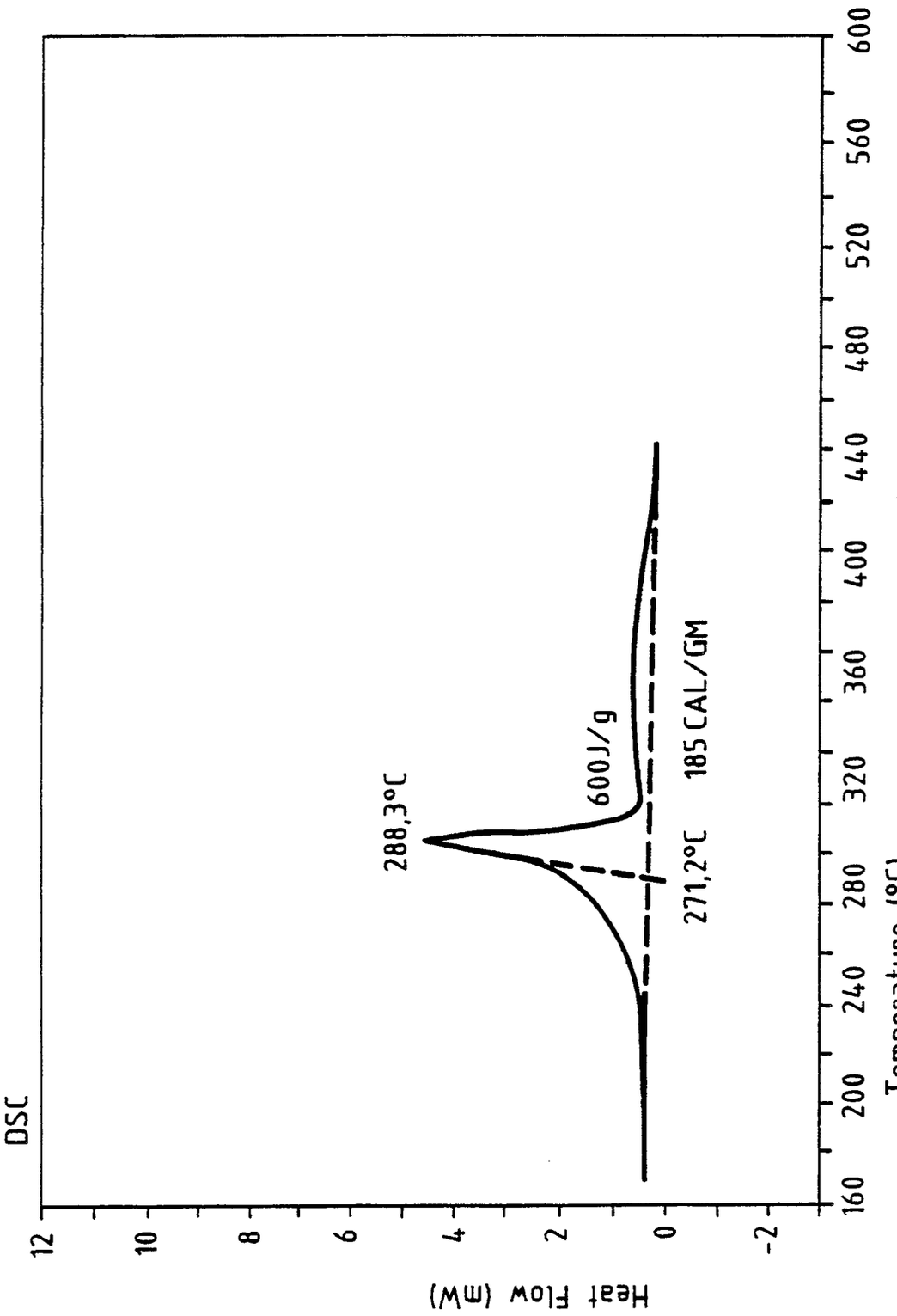
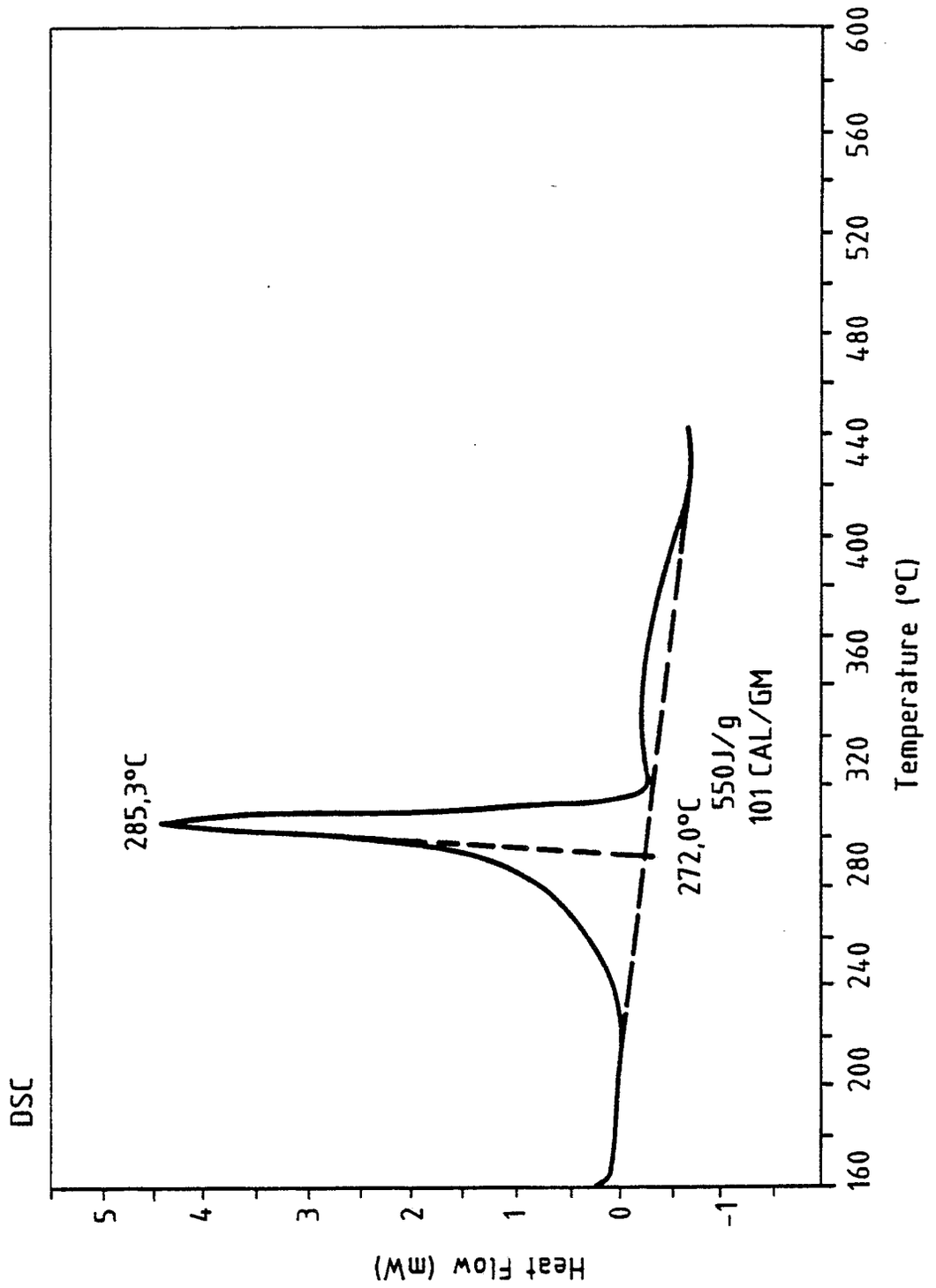

DSC
Heat Flow (mW)
12
10
8
6
4
2
0
-2
160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)
288,3°C
600J/g
271,2°C
185 CAL/GM

Fig.3


DSC
285,3°C
272,0°C
550J/g
101 CAL/GM
Heat Flow (mW)
5
4
3
2
1
0
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160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)

Fig.4

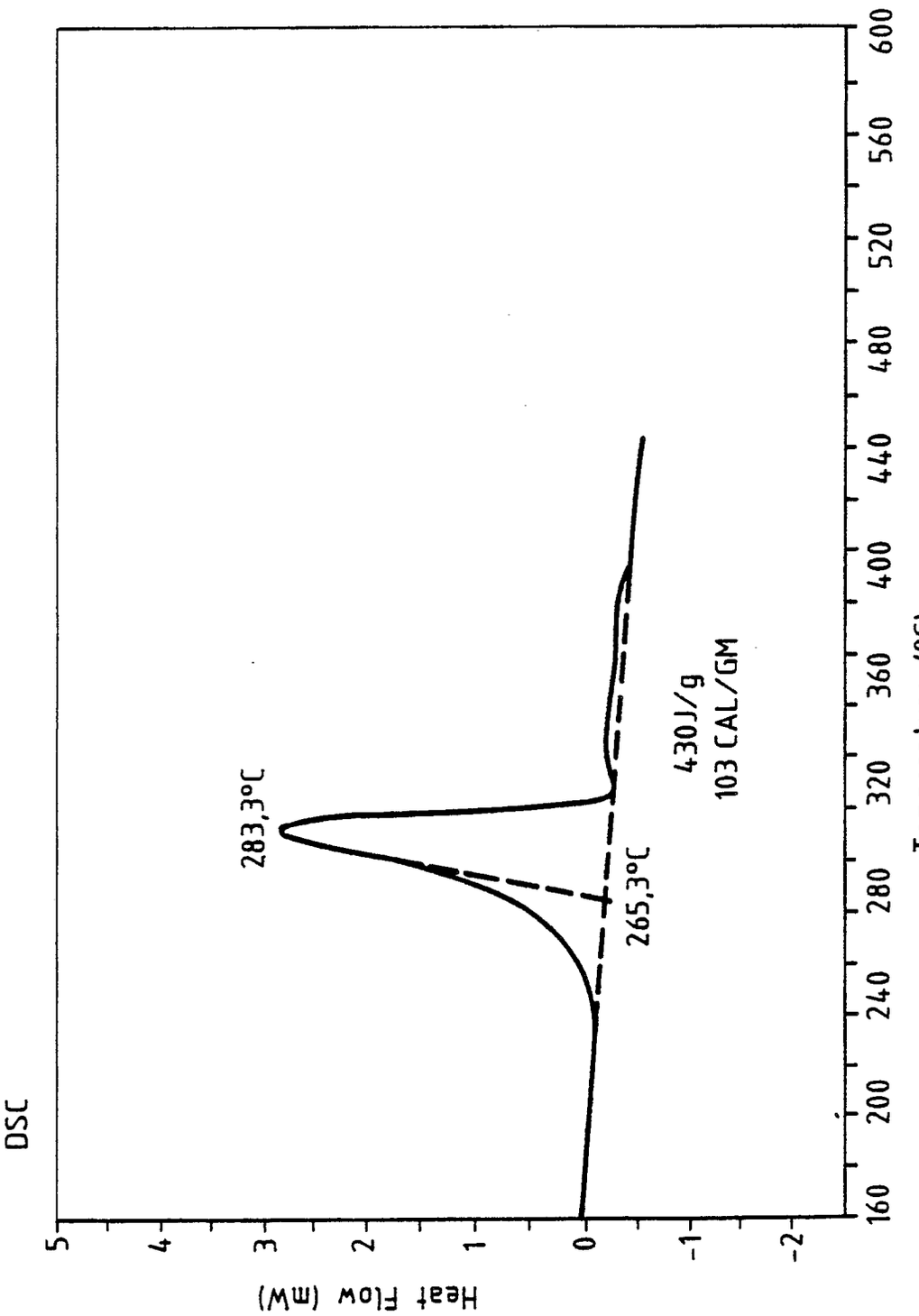

DSC
Heat Flow (mW)
5
4
3
2
1
0
-1
-2
160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)
283,3°C
265,3°C
430J/g
103 CAL/GM

Fig.5

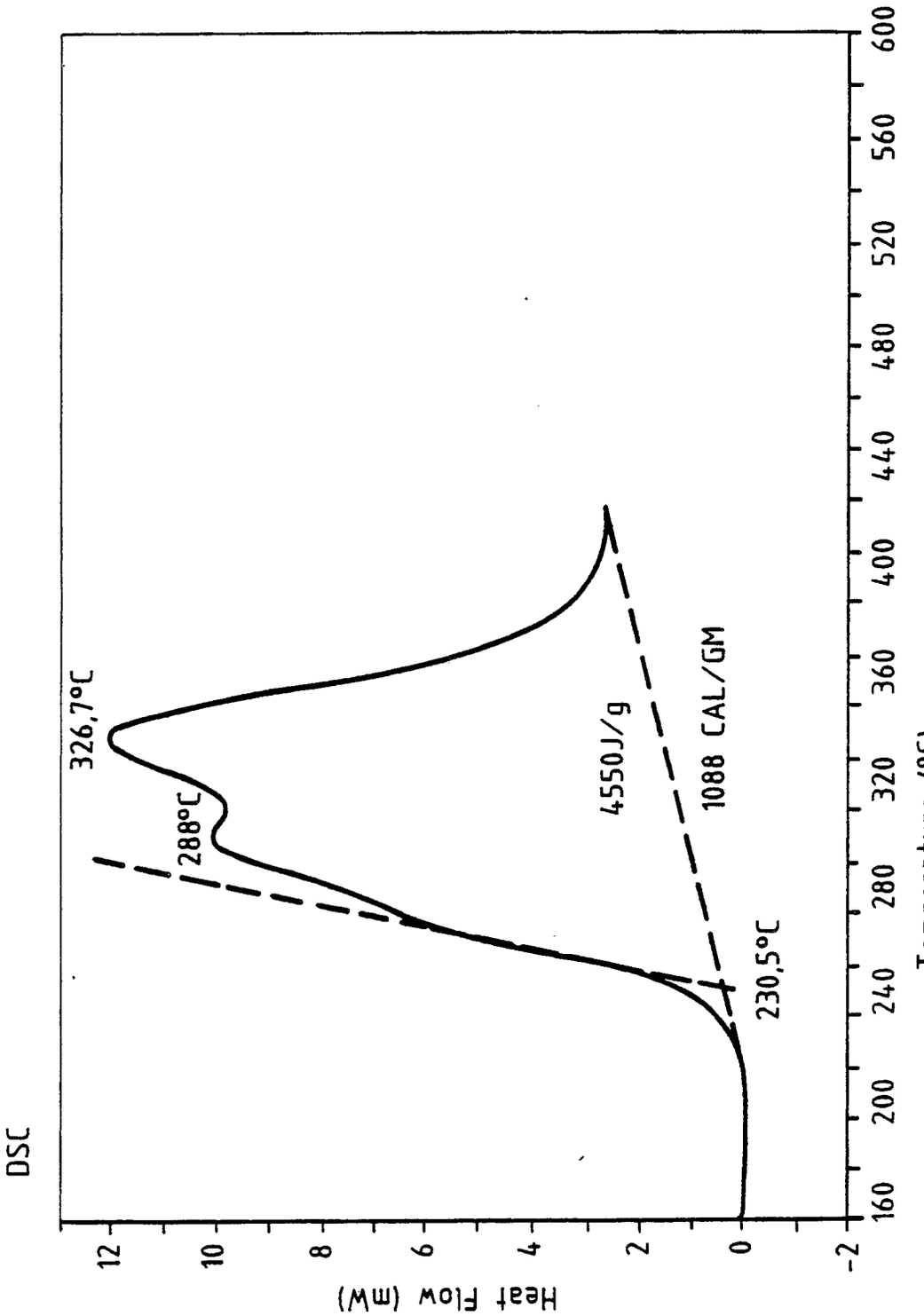

DSC
Heat Flow (mW)
12
10
8
6
4
2
0
-2
160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)
326,7°C
288°C
230,5°C
455OJ/g
1088 CAL/GM

Fig.6

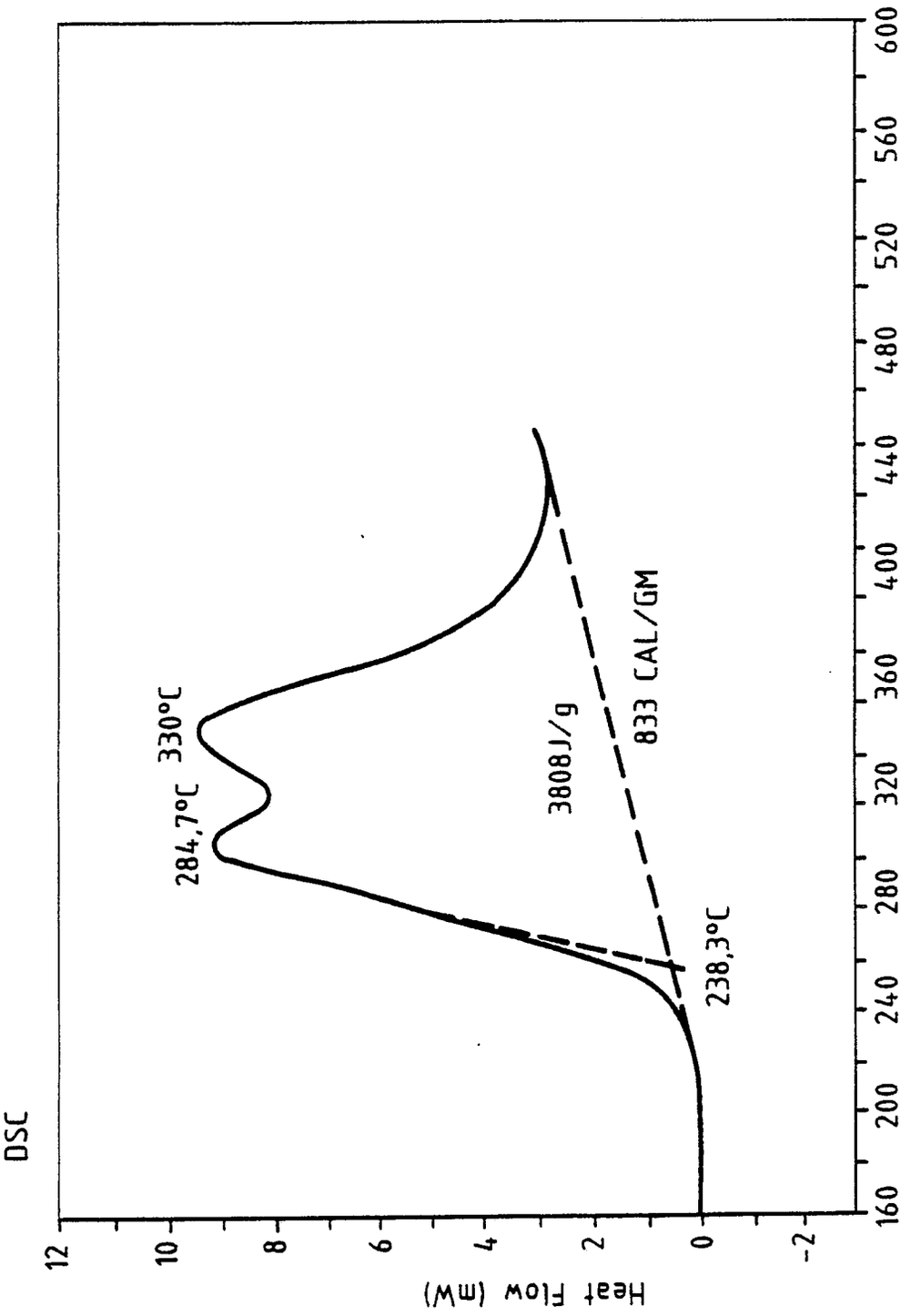
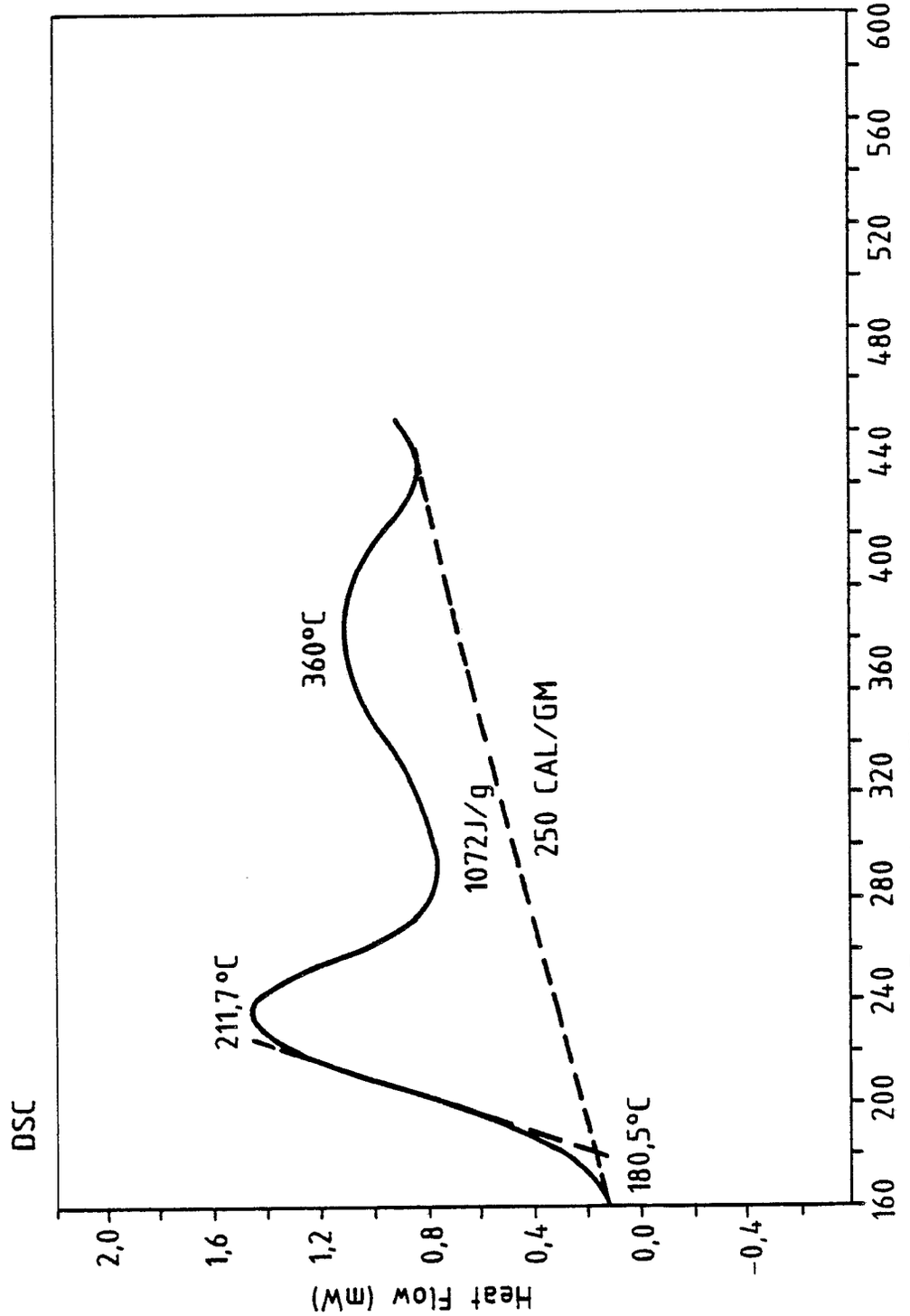

DSC
Heat Flow (mW)
12
10
8
6
4
2
0
-2
160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)
284,7°C
330°C
238,3°C
3808J/g
833 CAL/GM

Fig.7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360°C
1072J/g
250 CAL/GM
180,5°C
Heat Flow (mW)
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1,6
1,2
0,8
0,4
0,0
-0,4
160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)

Fig.8

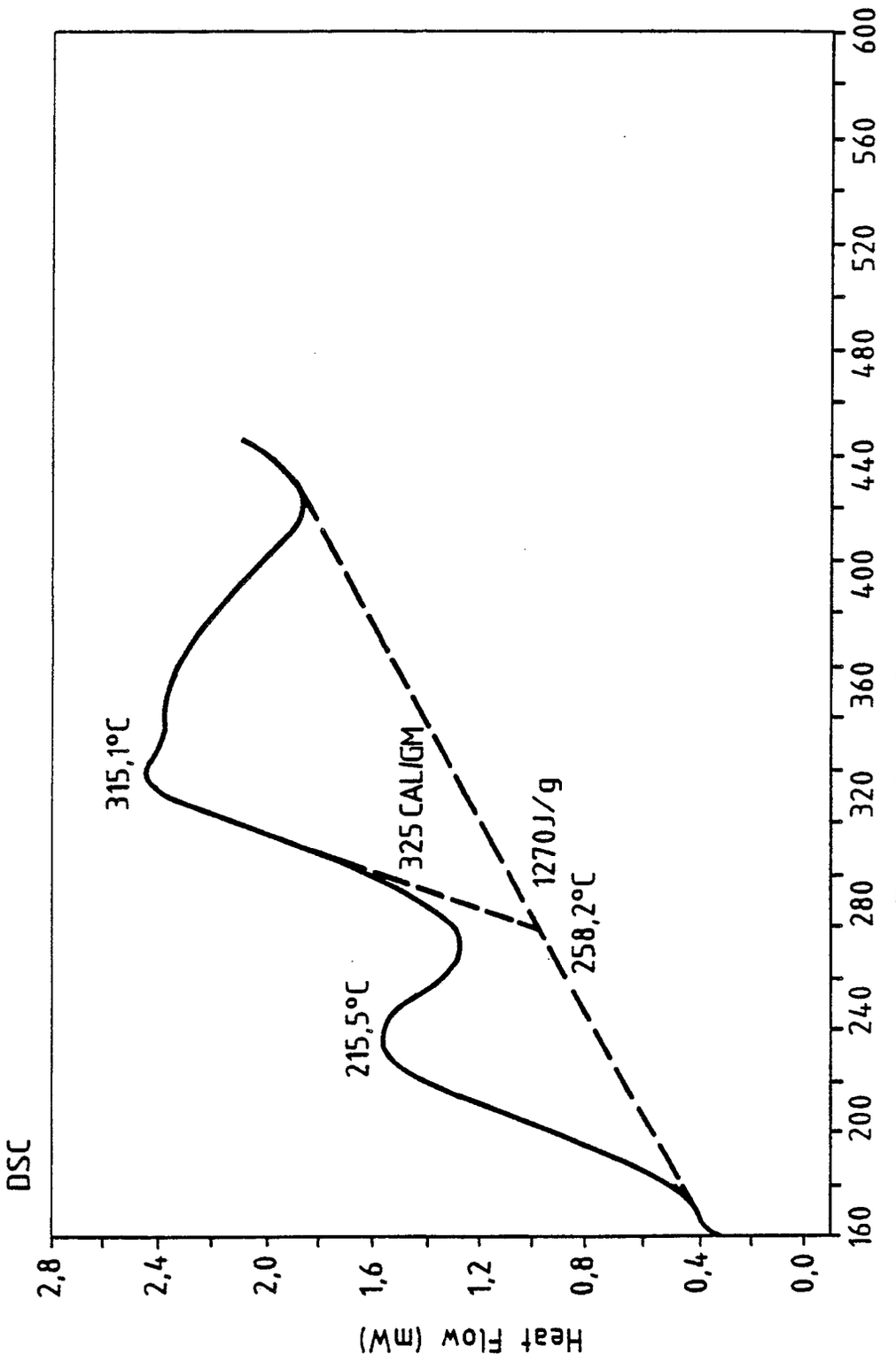

DSC
315,1°C
215,5°C
325 CAL/GM
1270J/g
258,2°C
Heat Flow (mW)
2,8
2,4
2,0
1,6
1,2
0,8
0,4
0,0
160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)

Fig.9

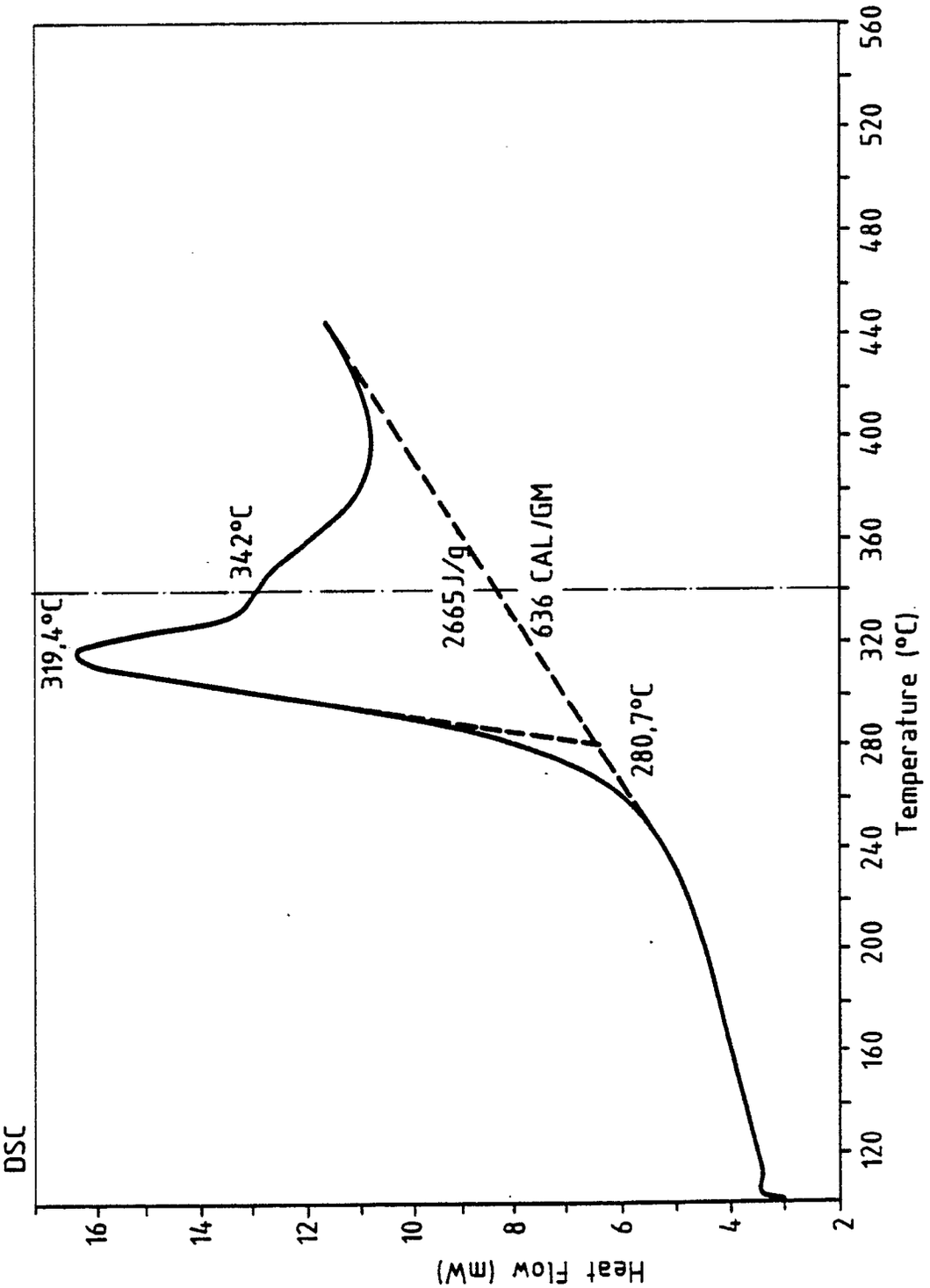

DSC
Heat Flow (mW)
16
14
12
10
8
6
4
2
120
160
200
240
280
320
360
400
440
480
520
560
Temperature (°C)
319,4°C
342°C
280,7°C
2665J/g
636 CAL/GM

Fig.10

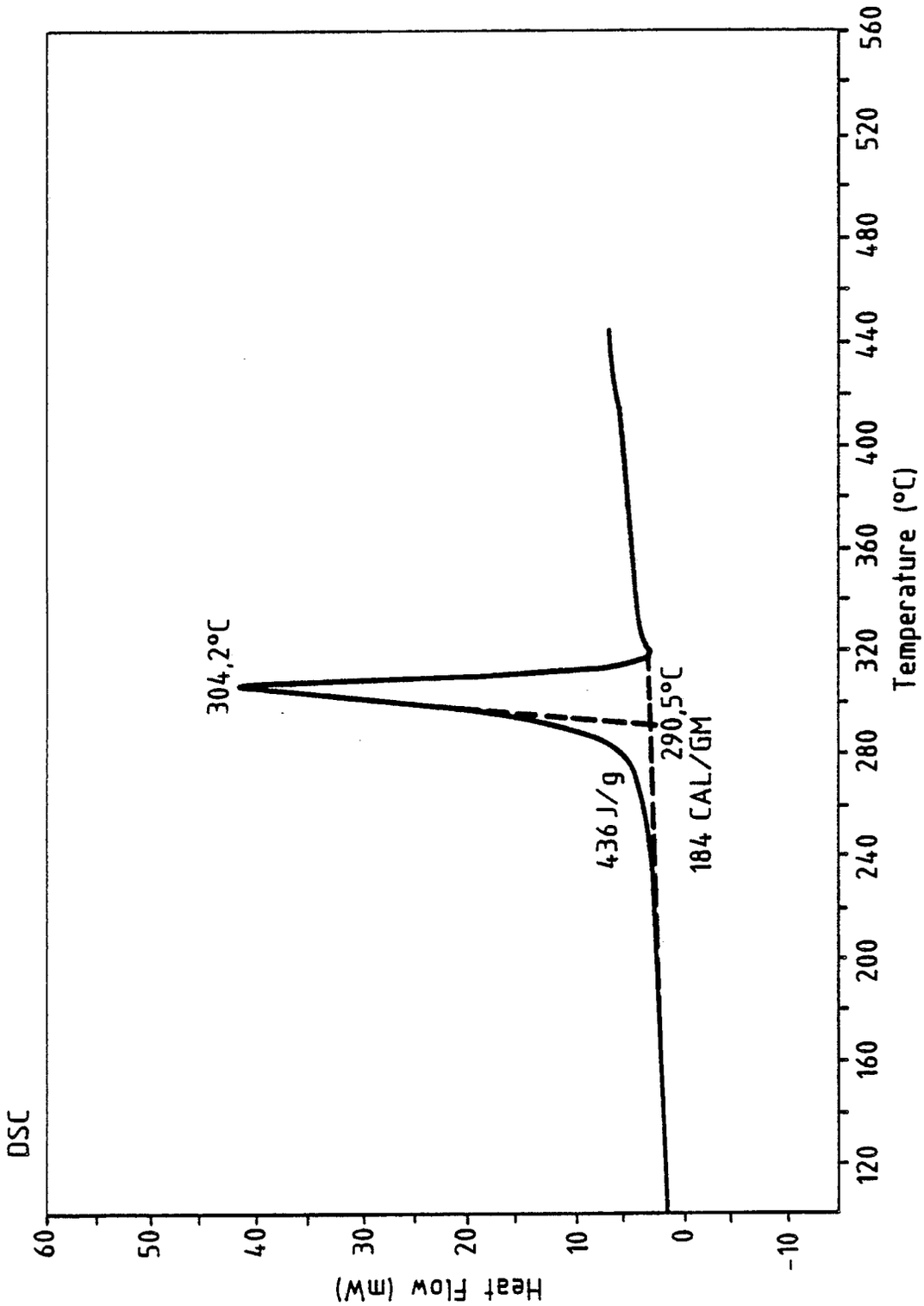

DSC
Heat Flow (mW)
60
50
40
30
20
10
0
-10
120
160
200
240
280
320
360
400
440
480
520
560
Temperature (°C)
304,2°C
290,5°C
436 J/g
184 CAL/GM

Fig.11

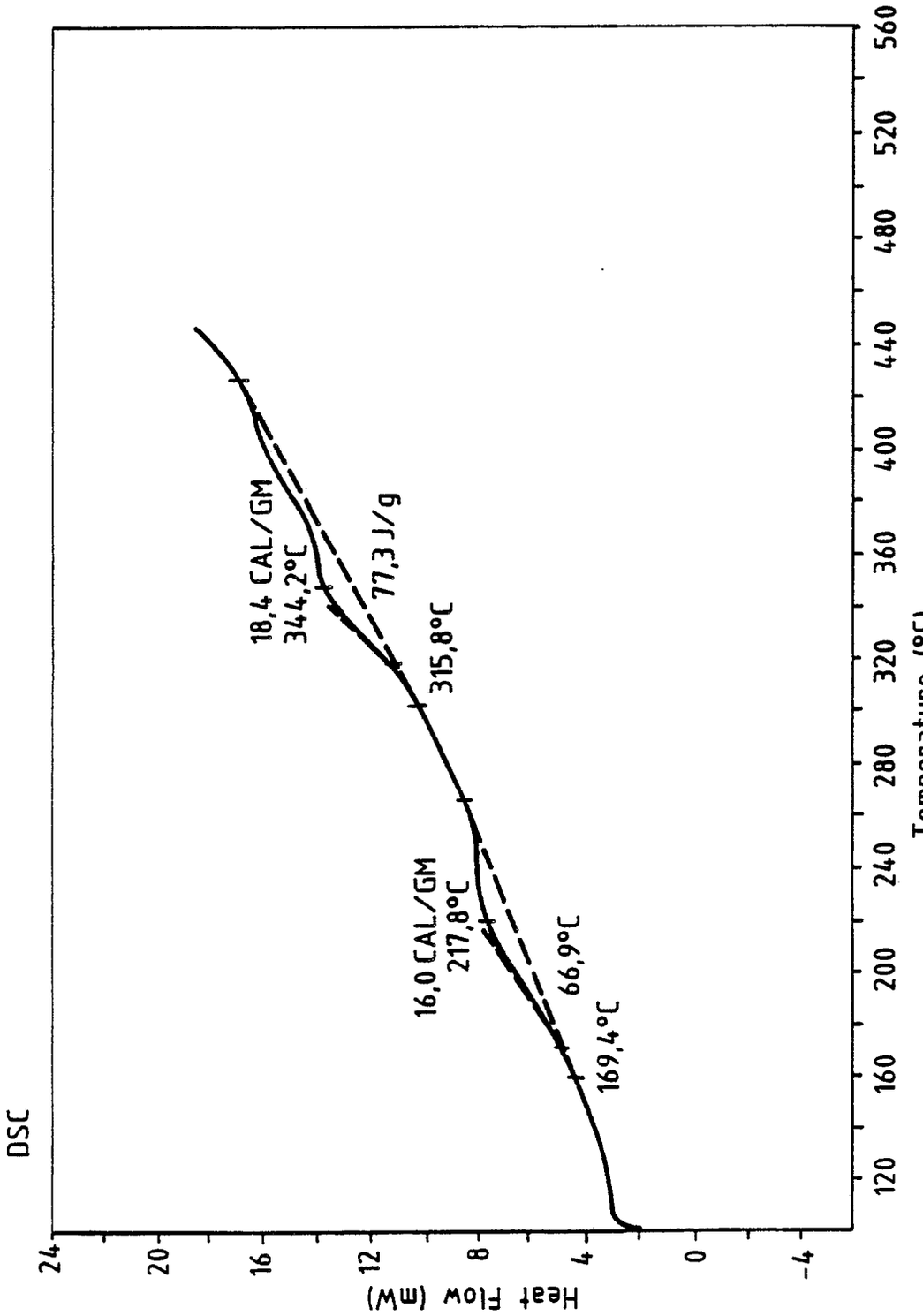

DSC
Heat Flow (mW)
24
20
16
12
8
4
0
-4
120
160
200
240
280
320
360
400
440
480
520
560
Temperature (°C)
18,4 CAL/GM
344,2°C
77,3 J/g
315,8°C
16,0 CAL/GM
217,8°C
66,9°C
169,4°C

Fig.11A

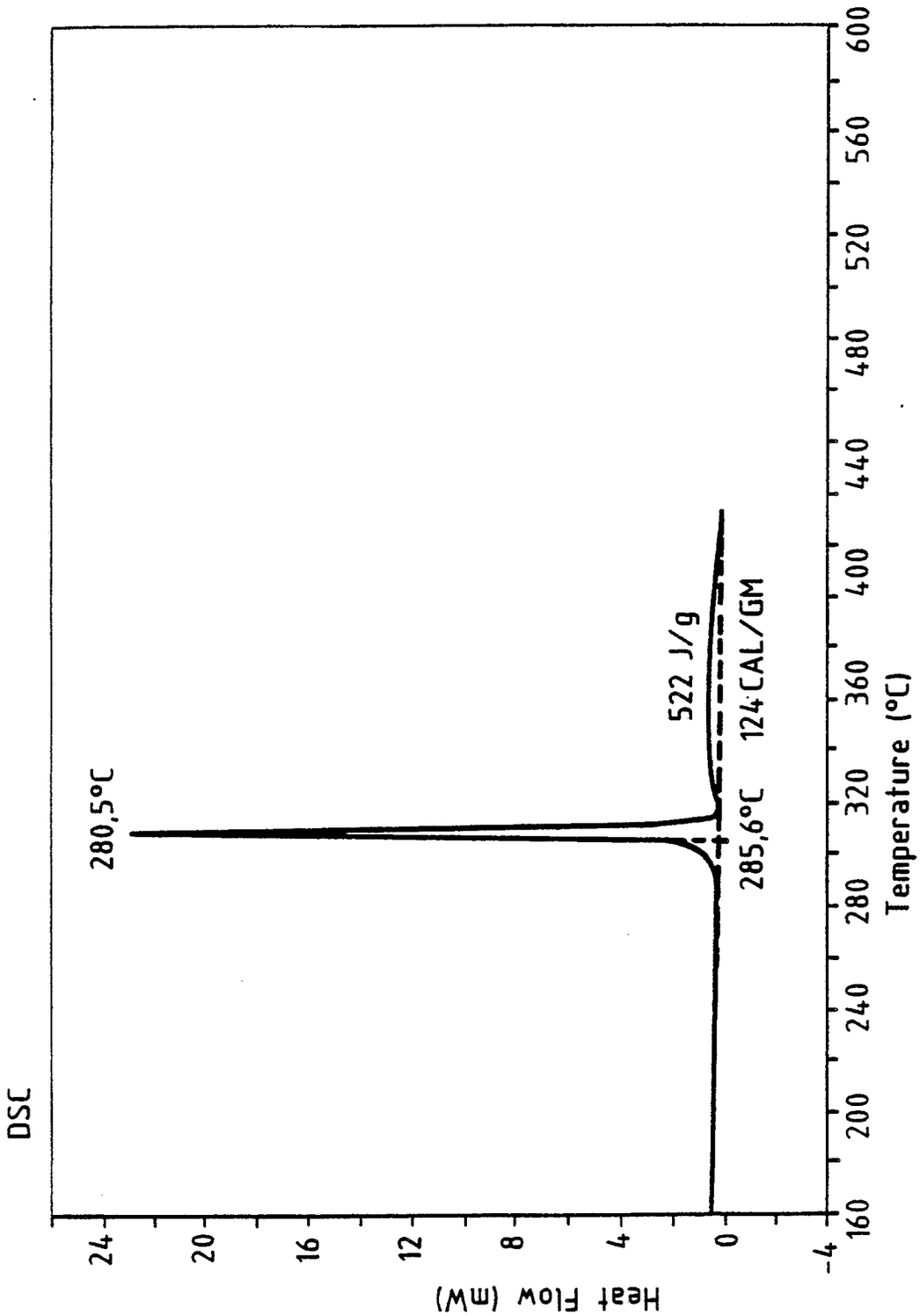

DSC
280,5°C
285,6°C
522 J/g
124 CAL/GM
Heat Flow (mW)
Temperature (°C)
24
20
16
12
8
4
0
-4
160
200
240
280
320
360
400
440
480
520
560
600

Fig.11B

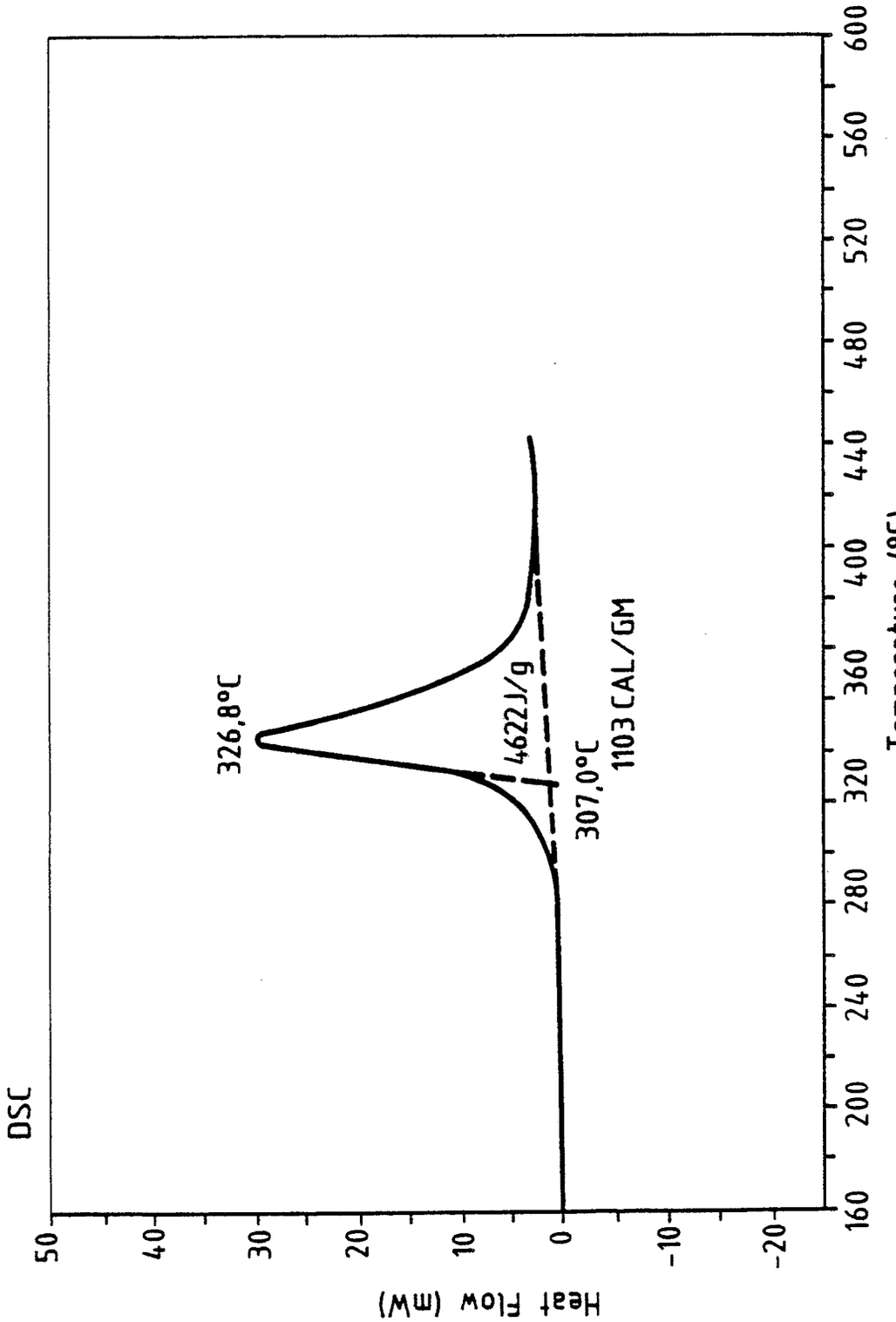
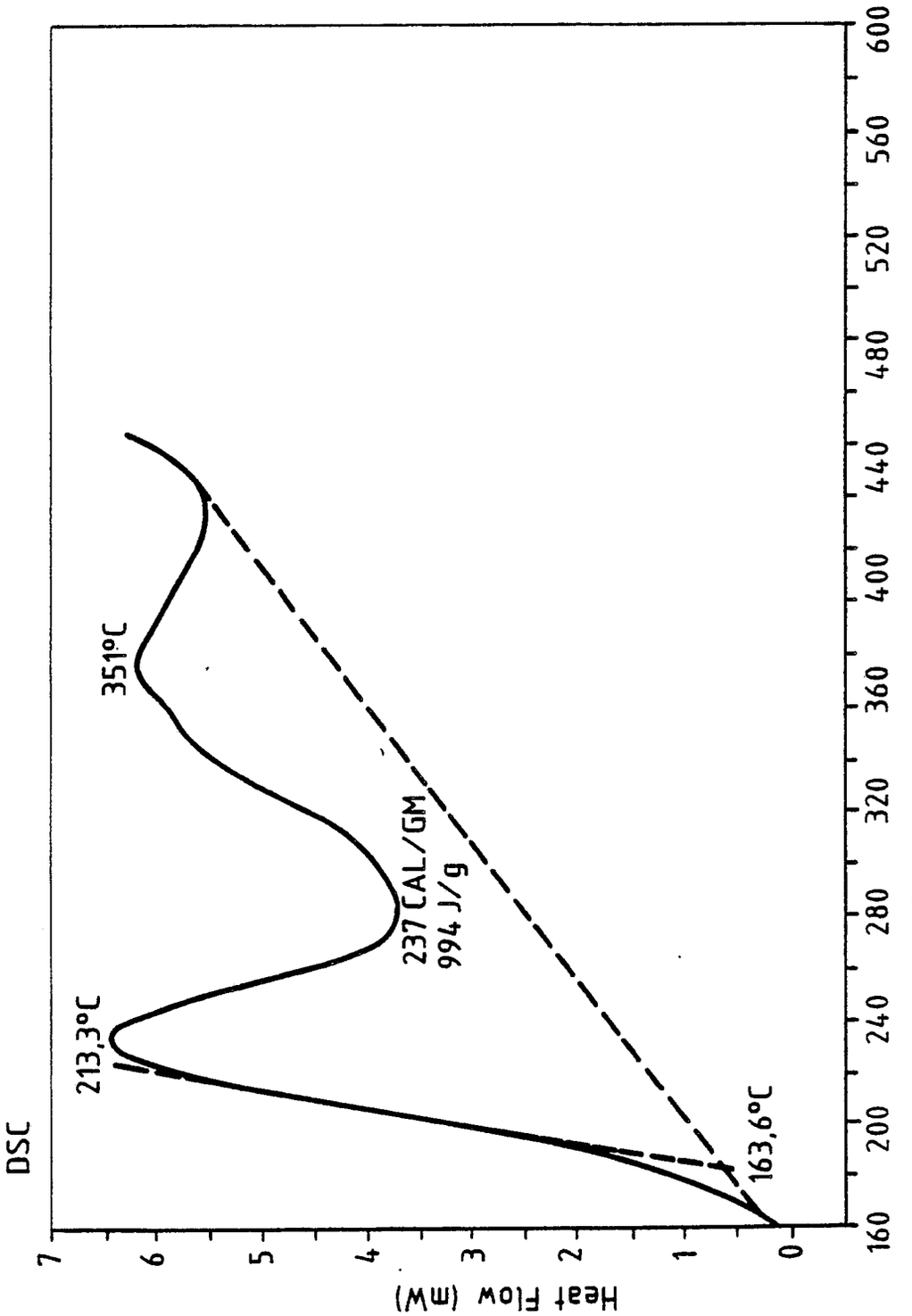

DSC
326,8°C
4622J/g
307,0°C
1103 CAL/GM
Heat Flow (mW)
50
40
30
20
10
0
-10
-20
160
200
240
280
320
360
400
440
480
520
560
600
Temperature (°C)

Fig.11C


DSC
213,3°C
351°C
237 CAL/GM
994 J/g
163,6°C
Heat Flow (mW)
Temperature (°C)
0
1
2
3
4
5
6
7
160
200
240
280
320
360
400
440
480
520
560
600

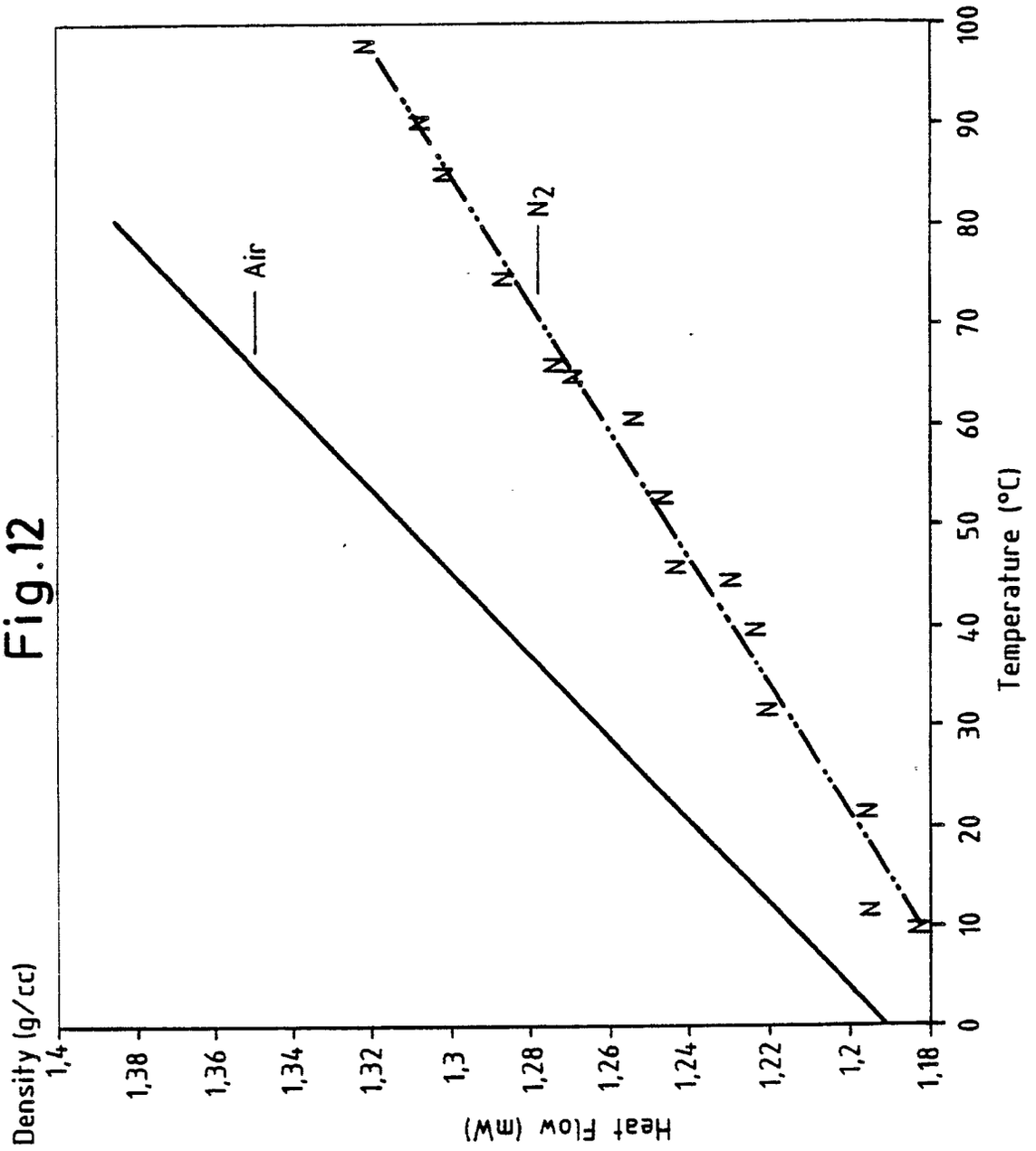
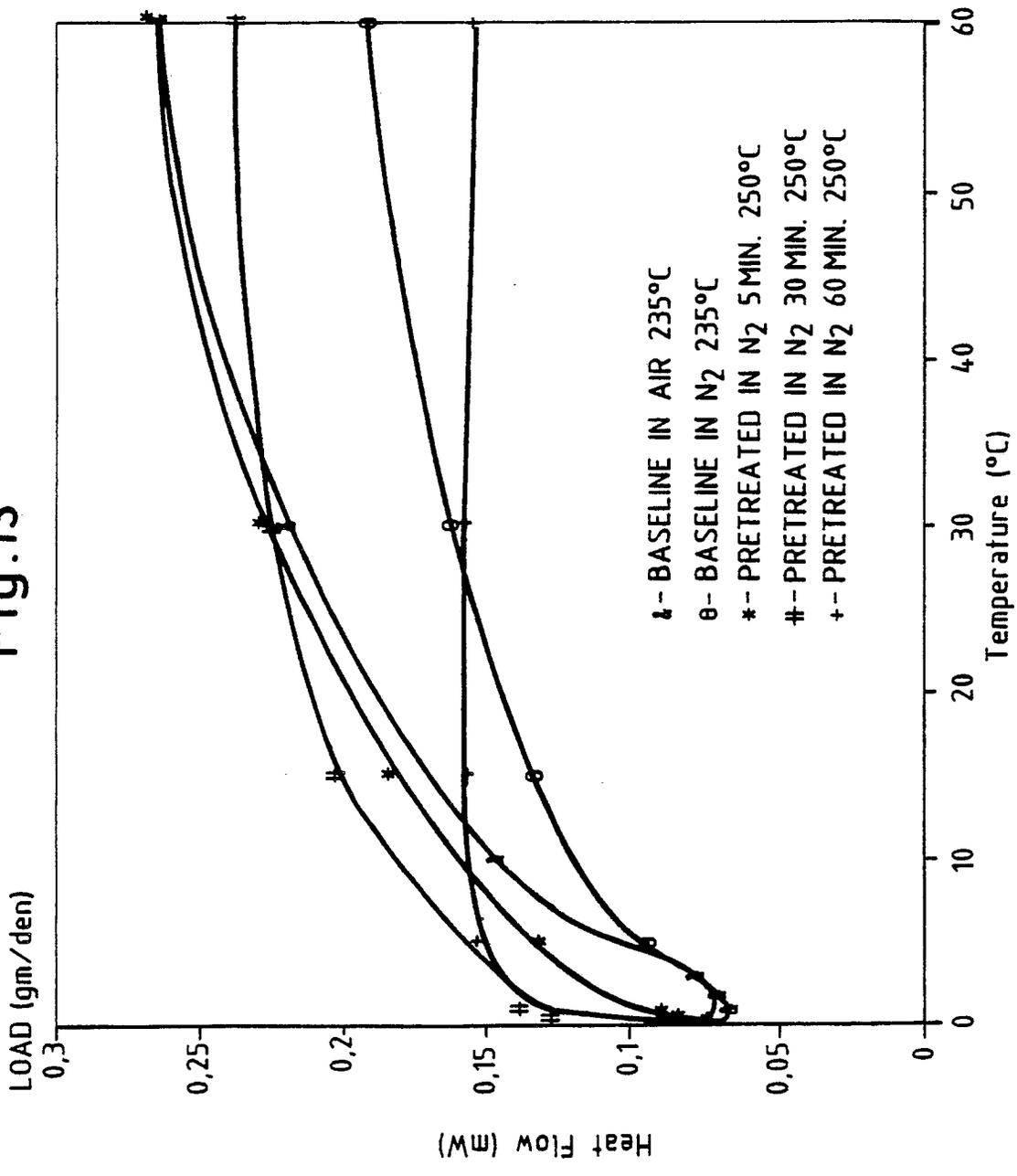

Density (g/cc)
1,4
1,38
1,36
1,34
1,32
1,3
1,28
1,26
1,24
1,22
1,2
1,18
Heat Flow (mW)
0
10
20
30
40
50
60
70
80
90
100
Temperature (°C)
Air
N2

Fig.12

Fig.13


LOAD (gm/den)
0,3
0,25
0,2
0,15
0,1
0,05
0
Heat Flow (mW)
0
10
20
30
40
50
60
Temperature (°C)
4- BASELINE IN AIR 235°C
8- BASELINE IN N2 235°C
*- PRETREATED IN N2 5 MIN. 250°C
#- PRETREATED IN N2 30 MIN. 250°C
+- PRETREATED IN N2 60 MIN. 250°C

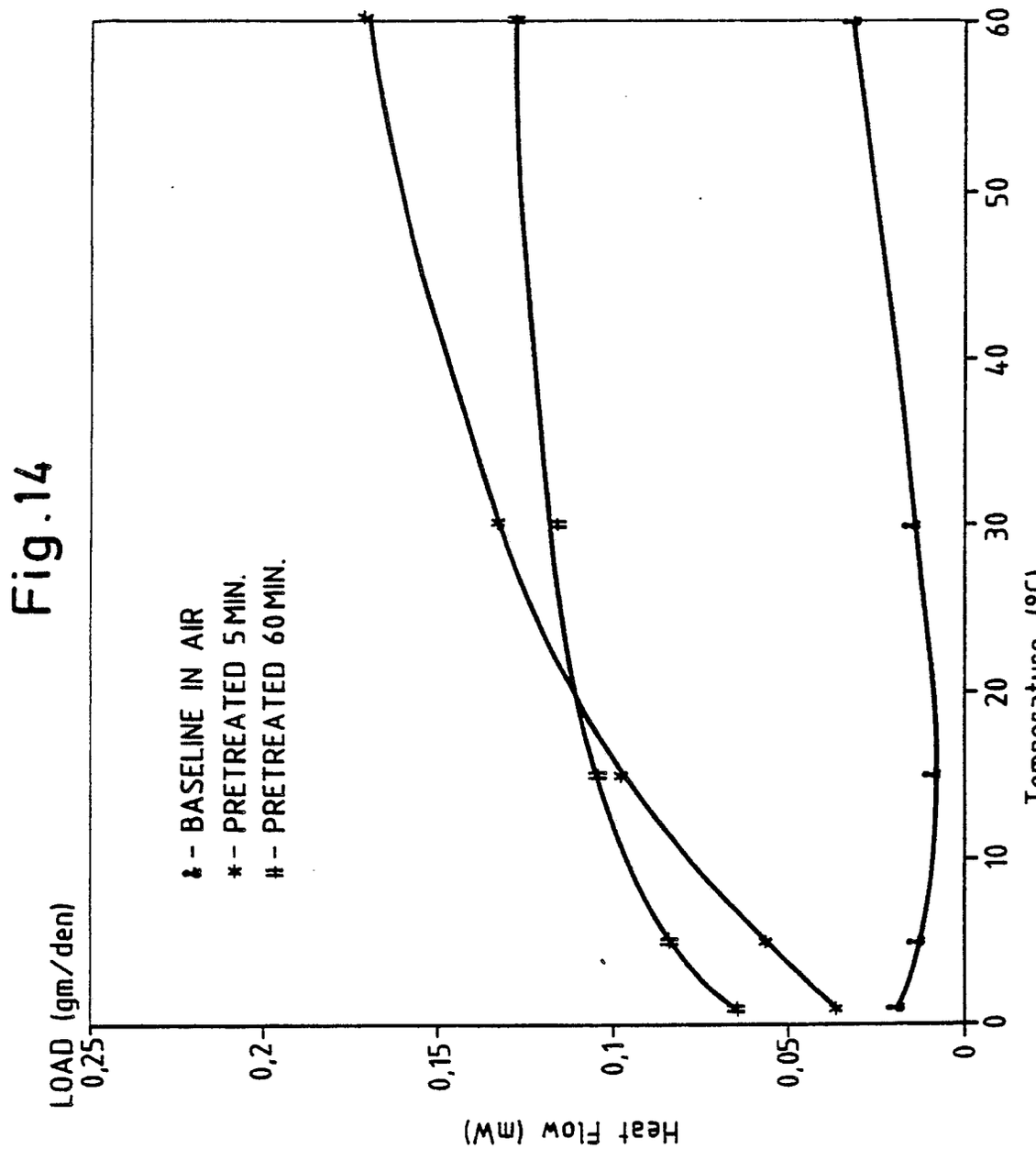

LOAD (gm/den)
0,25
0,2
0,15
0,1
0,05
0
Heat Flow (mW)
0
10
20
30
40
50
60
Temperature (°C)
& - BASELINE IN AIR
* - PRETREATED 5 MIN.
# - PRETREATED 60 MIN.

Fig.14