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EFFECTS OF HEAT STERILIZATION
AND VACUUM EXPOSURE ON SOME
LOW-DENSITY HEAT-SHIELD MATERIALS

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16. Abstract

The effects of dry heat sterilization for 92 hours at 135° C in flowing nitrogen and 200 hours of exposure at 66° C to pressures in the 10^{-5}-N/m^2 range upon the thermochemical properties of five blown-foamed and five molded composite heat-shield materials have been determined. Differential thermal analysis (DTA) was employed to follow the changes which occurred in each material as a result of sterilization and vacuum exposure. The results show that, on the whole, the composite materials have greater sterilization mass losses than the foamed materials and that the high-vacuum losses of both types of material are approximately equal. During high-vacuum exposure, the mass loss was approximately 1 percent after 200 hours of exposure, and at 200 hours the rate of mass loss ranged between 2.5×10^{-4} and 11.1×10^{-4} percent per hour for most of the materials.

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EFFECTS OF HEAT STERILIZATION AND VACUUM EXPOSURE ON

SOME LOW-DENSITY HEAT-SHIELD MATERIALS

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SUMMARY

The effects of dry heat sterilization for 92 hours at 135° C in flowing nitrogen and 200 hours of vacuum exposure at 66° C to pressures in the 10^{-5}-N/m^2 range upon five blown-foamed and five molded composite heat-shield materials have been determined. Differential thermal analysis (DTA) was employed to follow the changes which occurred in each material as a result of sterilization and exposure to vacuum. Nine of the 10 materials tested contained a silicone polymer as the base resin system, and one was a nitrile rubber.

The results show that, on the whole, the composite materials have greater sterilization mass losses than the foamed materials and that the high-vacuum losses of both types of material are approximately equal. During high-vacuum exposure, the mass loss was approximately 1 percent after 200 hours of exposure, and at 200 hours the rate of mass loss ranged between 2.5×10^{-4} and 11.1×10^{-4} percent per hour for most of the materials. DTA results showed several materials to have changes in their thermochemical properties after sterilization and exposure to vacuum.

INTRODUCTION

The heat-shield materials which are currently in use (ref. 1) and those planned for future interplanetary use (ref. 2) are generally composed of combinations of several polymeric materials. As noted in references 3 and 4, these materials frequently undergo changes when exposed to a space environment. One of the changes which can occur at extremely low pressure is the removal of volatile products which can change the chemical and physical properties of the material. In addition, condensation of volatized products on spacecraft components may have a detrimental effect on the function of that component. In addition to the interactions of the material with the vacuum of space, all materials which may impact another planet must be capable of withstanding sterilization procedures prior to use. (See ref. 5.) These procedures can also produce undesirable effects on the heat-shield material. The sterilization procedure and vacuum-exposure conditions may vary for each mission. For a typical Mars mission, the prelaunch sterilization is

accomplished through as many as 6 cycles, each at 135° C in flowing dry nitrogen for 92 hours. The vacuum exposure would consist of about 9 months at -38° to -73° C in a vacuum of 10^{-10} to 10^{-14} N/m^2. (See ref. 5.)

The effect of sterilization and long-term vacuum exposure upon spacecraft polymers has been studied by many investigators, and some results from these studies are presented in references 6 and 7. These studies were performed on relatively pure organic materials, which differ widely from the multicomponent heat-shield materials currently in use. Some useful information can be obtained from these data on the interaction of heat-shield components with space conditions but, in order to evaluate the effects upon the actual material and its thermal properties, each material should be evaluated in its final form. Therefore, investigations have been initiated to study the response of candidate heat-shield materials to sterilization and high-vacuum environments.

Results from one of these investigations are presented in reference 8 where the effects of sterilization and vacuum exposure upon the mechanical properties of several candidate materials are given. The present report gives additional data on several new candidate materials and describes the experimental techniques used in this investigation. These techniques differ from those of reference 8 in that in this investigation the materials were subjected to an accelerated test program designed to evaluate, over a short test period, the possible effects of dry heat sterilization followed by vacuum exposure upon each material. The sterilization procedure consisted of a single cycle of 92 hours at 135° C in flowing dry nitrogen whereas the vacuum exposure consisted of 200 hours at a pressure of 10^{-5} N/m^2 and a constant temperature of 66° C. Each candidate heat-shield material was analyzed by differential thermal analysis (DTA) in the as-received condition and after sterilization and vacuum exposure to determine the effects of these procedures upon the thermochemical properties (chemical and physical changes occurring in the material that absorb or evolve heat) of each material.

The units used for the physical quantities in this paper are given in the International System of Units (SI). Reference 9 presents factors relating the International System with other frequently used systems of units.

MATERIALS

Table 1 lists the 10 materials studied in the present investigation. As shown in this table, all the materials tested were relatively low-density materials. The bulk density of the as-received heat-shield materials ranged between 230 and 320 kg/m^3. The first five materials (designated A, B, C, D, and E) were foam-type materials which were foamed by the addition of blowing agents to the material before curing. The second five materials (designated F, G, H, J, and K) were molded composites formed by the

addition of low-density fillers to a liquid resin system. In addition, nine of the 10 materials contained a silicone polymer. Material D was a foamed nitrile rubber composition.

Eight of the materials tested were obtained from commercial sources, and their exact compositions are proprietary. The composition of these materials, as listed in table 1, shows the major ingredients as determined from visual observation and manufacturers' literature and therefore does not list ingredients, such as plasticizers, which may be present in small quantities in each material. Materials F and G, however, were fabricated at the Langley Research Center, and their compositions are as shown.

Materials A, B, and C were spongelike foamed silicone polymers with small quantities of various fillers. Material A, for example, in addition to containing ferric oxide (Fe_2O_3) also contained 12 percent inorganic fiber. Reference 10 indicates that this is aluminum silicate. Materials B and C also contained the aluminum silicate fiber; however, material C, which was an epoxy silicone, contained only 2 percent fibers. The bulk density of each of the three materials was about 240 kg/m^3. Material E was also a foamed silicone; however, this material also contained an inorganic sublimer. No information on the type of sublimer was available. After exposure to the atmosphere, large drops of liquid that was corrosive to metals was found on the surface of this material. The final foamed material (material D) was a nitrile rubber with a density of 320 kg/m^3.

All the composite materials (materials F, G, H, J, and K) were combinations of a silicone polymer with various types of fillers. In general, the filler material served to lower the bulk density of the prospective ablation material. Materials F, G, H, and K employed various quantities of phenolic microspheres (described in ref. 11). These spheres are derived from a resole resin and are filled with inert gas, primarily nitrogen. Material H had, in addition to the phenolic microspheres, a large quantity of cork particles. Material J employed silica microspheres as filler.

EXPERIMENTAL PROCEDURE

The experimental procedure employed throughout this investigation was as follows: A sample of each specimen material, in the as-received condition, was characterized by differential thermal analysis (DTA). A second sample of this material was subjected to dry heat sterilization. After the sterilization procedure, the sterilized specimen was removed from the nitrogen environment and taken to an analytical balance where the mass loss during sterilization was determined. During this time the specimen was exposed to ambient conditions (25° C in air). Immediately after the mass loss determination, the sample was placed in a vacuum balance where the pressure was lowered to the 10^{-5}-N/m^2 range and maintained at a constant temperature for 200 hours. Approximately 5 minutes were involved in transfer from the sterilization canister to the

10^{-5}-N/m^2 pressure in the vacuum system. Immediately after vacuum exposure, the heat-shield specimen was removed from the vacuum system and placed in a moisture-proof container, and this container, in turn, was placed in a desiccator. The transfer time from vacuum-system backfill (explained in a subsequent section) to sealing in the moisture-proof container was about 2 minutes. During this time the sample was exposed to dry air. After vacuum exposure, DTA was employed to characterize each material and thus to determine any thermochemical differences that may exist between the as-received specimens and the specimens subjected to sterilization and vacuum exposure. The DTA specimen was prepared from the exposed specimen, and about 5 minutes were involved in preparation. During this period the specimen was exposed to the atmosphere. Each technique employed during the test procedure is described in the subsequent sections.

Differential Thermal Analysis

Differential thermal analysis (DTA) is a technique used for the determination of thermal changes which occur in a material as the material is heated under controlled conditions. The endothermic and exothermic reactions which occur are determined by measuring the temperature difference between the sample and an inert reference material while both are exposed to the same heating conditions in an inert atmosphere (helium).

Figure 1 shows a drawing of the arrangement of the DTA sample holder. In the investigation solid chips of sample weighing 5 to 15 mg were placed in a 1-gram inconel cup. An empty cup of equal mass was used as reference. The inconel sample cup and inconel reference cup were supported directly on the differential thermocouples which passed through alumina posts. The beads of the differential thermocouples were situated well inside the sample and reference cups. (See inset of fig. 1.)

In each DTA test, the sample holder assembly was evacuated to approximately 130 N/m^2 and backfilled with helium to atmospheric pressure. A flow of helium (1 to 1.2 cm^3/s) was then maintained around both the sample and reference cups throughout the test by means of gas injection tubes at the base of the sample holder (shown in fig. 1).

The thermogram obtained from each run is a plot of differential temperature ΔT between sample and reference cups as a function of the temperature of the sample holder. The endothermic reactions are shown as downward peaks from the line $\Delta T = 0$ whereas the exothermic peaks are shown as upward peaks from the line $\Delta T = 0$. All thermograms shown in this report are actual tracings of the experimental test data. A more complete discussion of the DTA technique employed may be found in reference 12.

Dry Heat Sterilization

Individual solid samples of the as-received material cut in cubes approximately 1 cm^3 in size were placed in a preheated ($800°$ C in air), dried, porcelain crucible which

was then placed in an airtight canister, as shown in figure 2. The samples remained in flowing dry nitrogen for approximately 30 minutes before the entire canister was placed into an insulated heater. The materials were sterilized by heating them to a temperature of 135° C and maintaining this temperature for 92 hours $\pm$ 10 minutes. At the end of the sterilization period, the materials were cooled to 25° C while in the flowing-nitrogen atmosphere. After cool down, the mass loss of each sample was determined by weighing the sample and crucible on an analytical balance.

Vacuum Exposure

Immediately after the mass loss from dry heat sterilization was determined, the sample and crucible were placed inside the high-vacuum system. A photograph of the apparatus is shown in figure 3. Basically, the system consisted of pumping, balance, and furnace sections. The pumping section consisted of a forepump and a 10.2-cm diffusion pump. The foreline was trapped with a molecular sieve to reduce backstreaming of fore-pump oil into the test chamber. Vacuum-system pressure was measured by an ionization gage located in the T-shaped block directly above the furnace section and immediately below the balance pan. The balance had a capacity of 100 grams and a sensitivity of 0.1 mg. The furnace section was located approximately 45 cm below the sample pan of the balance. A resistance furnace (shown in fig. 4) was employed to heat the specimen to 66° C and maintain the specimen at this temperature throughout the exposure period. Surrounding the furnace was a water-cooled copper shroud, and both the furnace and shroud were located within the vacuum system. The furnace and specimen temperatures were controlled by thermocouples located in the lower portion of the furnace. The beads of the thermocouples were located approximately 1 cm from the base of the sample cru-cible and were coated with a small mass of high-temperature cement. (See fig. 4.) A glass suspension was employed to connect the sample crucible to the sample pan of the balance. The approximate size of the crucibles is shown in figure 4.

After the sample was placed into the vacuum system, the pressure was lowered into the 10^{-4}-N/m^2 range before the furnace temperature was increased to 66° C. Approxi-mately 10 minutes was required to lower the pressure to the 10^{-4}-N/m^2 range. When the furnace temperature was raised to 66° C, specimen outgassing caused the pressure to increase to the 10^{-3}-N/m^2 range and, depending upon the level of outgassing, the sys-tem pressure would lower to the 10^{-4}-N/m^2 range in approximately 3 hours and into the 10^{-5}-N/m^2 range within 6 hours. Each specimen was allowed to remain in the vacuum environment for approximately 200 hours, and the mass loss was continuously determined during this time. At the end of the 200-hour exposure period, the furnace was allowed to cool to ambient temperature before the pressure in the vacuum chamber was brought to atmospheric pressure by allowing dry air to enter the system.

RESULTS AND DISCUSSION

Foamed Materials

Dry heat sterilization.- Table 2 summarizes the results of dry heat sterilization upon the five foamed heat-shield materials (materials A, B, C, D, and E). The mass losses for materials A, B, and C were less than 1 percent in every case. Materials D and E, however, exhibited higher losses. The nitrile rubber specimen (material D) lost 8.1 percent of its mass during sterilization, and the sublimer-filled silicone (material E) lost approximately 16.6 percent of its original mass. In addition to the large mass loss, material D was observed to turn darker as sterilization progressed. The high mass loss during sterilization for material E is attributed to the presence of a corrosive liquid on the as-received material.

Vacuum exposure.- Figure 5 presents high-vacuum mass-loss data as a function of vacuum exposure time for the five foamed heat-shield materials. Table 2 presents, for comparison purposes, the percent mass loss at 200 hours of exposure and the mass-loss rate for each material at this exposure time. As figure 5 indicates, all the materials show high mass-loss rates initially. With increasing exposure time, however, the rate of mass loss decreases. During vacuum exposure, materials A, B, and C exhibited mass losses of 0.69 percent, 0.50 percent, and 0.45 percent, respectively, in addition to their sterilization losses. The mass-loss rates of materials A and B appear to be similar after 30 hours of exposure and at 200 hours were approximately 8×10^{-4} percent per hour. Of all the foamed materials tested, material C (epoxy silicone) exhibited the lowest mass-loss rate, as shown in figure 5. The actual vacuum loss was also lower than that observed for materials A and B. The nitrile rubber specimen (material D) lost approximately 1.82 percent of its mass during vacuum exposure and at the end of the exposure period had a mass-loss rate of 11.1×10^{-4} percent per hour. Material E shows mass-loss characteristics similar to those observed for materials A and B throughout the 200 hours of exposure. The mass loss of 0.67 percent for this material and the mass-loss rate of 8.7×10^{-4} percent per hour are in the same range as those found for materials A and B.

Differential thermal analysis.- In figure 6 are the results of differential thermal analysis of the as-received sample and the vacuum-exposed sample of material A. As can be seen from these data, no significant differences exist to indicate whether material A was affected by sterilization and vacuum exposure. The sharp endothermic reaction at 400° C is not typical of silicone polymer degradation. Silicone polymers degrade gradually over a wide temperature range as will be shown in data from other materials in subsequent sections. Material A is composed of a methyl-phenyl siloxane which is reinforced by 12 percent aluminum silicate fibers. The sharp endothermic reaction is

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attributed to a loss of chemically bound water attached to the silicate. Additional DTA tests of pure aluminum silicate resulted in a similar strong endothermic reaction in this temperature range. The differences shown between the reaction peak temperatures is believed to be an effect of differences between sample packing (packing of the DTA sample cup) from test to test. In several tests of the same specimen materials, this endothermic peak could be made to shift between the limits shown by the two tests of figure 6.

Figure 7 shows the DTA results of material B. For this material, just as for material A, no significant differences were observed on the DTA thermogram to indicate whether its thermochemical properties were affected by sterilization and exposure to vacuum. A difference is observed, as in material A, between the 400° C endothermic reactions of both thermograms. The difference, as for material A, is attributed to sample packing. Both materials, A and B, appear to be quite similar through 500° C. The thermogram of material B, however, exhibits a high-temperature reaction between 550° and 700° C, which again is not typical of silicone polymer degradation. Since this high-temperature reaction was not observed in material A, the base resin system for material B was examined by DTA. The thermogram obtained for the base resin showed a high-temperature reaction of the same shape and at the same temperature as that observed for material B.

In figure 8, the DTA results of material C are given. The thermograms of this material are more typical of siloxane degradation as a result of the lower percentage (2 percent) of aluminum silicate fibers. The endothermic peak at approximately 400° C is, however, still observable. A comparison of the two thermograms of figure 8 shows that there is a difference between the two samples. For the as-received sample, no reaction is seen before 270° C. However, for the vacuum-exposed sample, the thermogram appears to indicate an endothermic nature after 125° C which continued as the temperature was increased. The thermogram of the vacuum-exposed material is also different from the thermogram of the as-received material between 250° and 300° C. From these results, it is concluded that sterilization and high-vacuum exposure had an effect upon the thermochemical properties of this material.

Figure 9 shows the DTA thermograms of the two specimens of material D. The as-received sample exhibits a broad endothermic reaction zone between 50° and 150° C. A portion of this endothermic area is most likely associated with elimination of adsorbed moisture. Comparing the thermograms of the vacuum-exposed specimen and the as-received specimen shows that the endothermic area around 100° C has been reduced and that the portion after 100° C of the broad endothermic reaction has been eliminated. The large exothermic reaction between 300° and 400° C followed by the endothermic reaction after 400° C is attributed to specimen decomposition. No differences appear to exist between the DTA thermograms of figure 9 through this temperature range. An

unexplained difference is observed after 600° C where the thermogram of the vacuum-exposed specimen appears exothermic.

Figure 10 shows the results of analysis of the as-received and the vacuum-exposed specimens of material E. The as-received material exhibits an endothermic reaction at approximately 150° C that is assumed to be associated with the sublimer originally present in the material. Degradation of the silicone is initiated at the end of this endothermic reaction (175° C). A comparison of this thermogram with that obtained for the vacuum-exposed sample shows that the 150° C endothermic reaction was completely eliminated. Material degradation, however, is still observed to begin at approximately 175° C and continue through 550° C. The shape of the degradation endothermic reaction especially between 300° and 500° C and the peak temperature have been altered due to sterilization and high-vacuum exposure. After sterilization and exposure to the vacuum environment, the degradation occurs at a slightly higher temperature. The peak of the reaction was moved to a point approximately 50° C higher. From these results, it is concluded that the presence of the sublimer in the ablation material tends to shift the degradation reaction to a lower temperature.

General trends.- An overall look at the results of tests of foamed materials indicates certain general trends. For materials C, D, and E, the sterilization procedure produced greater mass losses than the vacuum exposure. With the exception of material D, the foamed materials had mass losses during vacuum exposure of about 1 percent and mass-loss rates at 200 hours of exposure of 8.7×10^{-4} percent per hour or less. The low quantity of mass loss of most of the materials during vacuum exposure indicates that most of the candidate ablative materials were fully cured and contained minimum quantities of highly volatile products as evaluated under the conditions of this investigation. Only material E was significantly affected by sterilization and vacuum exposure. Slight differences in the thermochemical properties of several other materials were noted. However, most of the materials tested exhibited no change in their thermochemical properties, and, therefore, their ablative properties are expected to be unchanged after longer sterilization and vacuum exposure. No attempts were made to determine changes in other material properties.

Molded Composite Materials

Dry heat sterilization.- The results obtained from dry heat sterilization of the five composite materials (materials F, G, H, J, and K) are presented in table 2. As shown, the mass loss observed for these materials ranged from 1.2 percent for material J to 7.4 percent for material G. In general, the mass losses for these composite materials were larger than those observed for the majority of the foamed materials. Materials F and G, which were similar in composition (table 1), had mass losses of 6.4 percent and

7.4 percent, respectively. The higher mass loss during sterilization for material G is attributed to the 5-percent higher content of phenolic microspheres which are extremely hygroscopic. Composite material H which contained a variation of fillers, including cork and phenolic microspheres, lost only 2.9 percent of its mass during sterilization. Material J, a silicone polymer highly filled with silica microspheres, lost only 1.2 percent of its mass during sterilization. The relatively low total mass loss observed for this material results from the type of fillers present. The sterilization mass loss of 6.9 percent for material K was on the order of that observed for materials F and G.

Vacuum exposure.- The results of vacuum exposure following the sterilization cycle of each composite material are shown in figure 11 and are summarized in table 2. For materials F and G, vacuum exposure resulted in nearly identically shaped mass-loss curves as shown in figure 11. After 200 hours, material F had a mass loss of 0.69 percent and material G had a mass loss of 0.56 percent. Mass-loss rates for materials F and G were 3.4×10^{-4} and 2.5×10^{-4} percent per hour, respectively. The mass losses for both of these materials fall within the same range as those observed for the unfilled, foamed silicone polymers (materials A, B, and C).

The mass-loss data for material H shows that the highly filled material lost 1.37 percent of its mass after 200 hours of vacuum exposure and had a rate of mass loss of 17.0×10^{-4} percent per hour at 200 hours. This material had the highest mass-loss rate at 200 hours of all materials studied.

Vacuum exposure of material J resulted in only a 0.12-percent mass loss after 200 hours. The rate of mass loss at this time was 3.7×10^{-4} percent per hour.

Exposure of material K to vacuum conditions after sterilization resulted in a large mass loss of 3.18 percent. This loss is in addition to the 6.9-percent loss observed during sterilization and was the largest material loss found during the investigation of vacuum exposure. The rate of mass loss at 200 hours was, however, only 7.0×10^{-4} percent per hour and was comparable to that observed for most of the foamed and other molded materials. The vacuum mass-loss curve of figure 11 for this material indicates that a large percentage of the observed vacuum loss occurred in the initial hours of exposure. Since the sterilization conditions are expected to remove adsorbed moisture, the initial mass loss indicates the presence of components with low vapor pressure. Reference 13 has shown that the vacuum mass loss of silicones is a function of the amount of constituents with low molecular weights that were retained during fabrication of the material. Further, by using preconditioning, such as effective thermal curing, the mass loss in high vacuum could be maintained at a low level (less than 0.5 percent). The large mass loss observed for material K (3.18 percent at 200 hours) thus indicates that the silicone resin employed was composed of a large quantity of species with low molecular weights or was insufficiently cured.

Differential thermal analysis.- Data from differential thermal analysis for the five molded materials are given in figures 12 to 16. Figure 12 shows the DTA thermograms of the as-received and the vacuum-exposed specimens of material F. A comparison of these two thermograms shows only small differences and thus indicates that sterilization and vacuum exposure had little effect upon the thermochemical properties of this material. Both thermograms show endothermic areas beginning at approximately 175° to 200° C and continuing through 700° C. At approximately 260° C, the melting of the nylon portion of the composite can be seen. The large endothermic area surrounding 400° C results from nylon degradation. (See ref. 14.) Phenolic degradation occurs over the entire temperature range shown; the relatively strong peak at 500° C is the principal degradation reaction. (See ref. 12.) No significant differences exist between the degradation reactions of the two samples of this material, as shown in figure 12.

The analysis of the as-received and the vacuum-exposed specimens of material G are shown in figure 13. The melting of nylon at 260° C and its endothermic decomposition around 400° C is again easily seen. For this material, just as for material F, there are no significant changes in the degradation area or low-temperature portion of the thermograms to indicate that sterilization or vacuum exposure had an effect upon the material. The small endothermic area before 100° C on the thermogram of the as-received sample corresponds to elimination of absorbed moisture. This endothermic area was also larger than that observed for material F because of the larger quantity of phenolic microspheres in the material.

Figure 14 shows the DTA thermograms of the as-received and the exposed specimens for material H. Both thermograms show the lack of reaction zones, an indication that a large percentage of the heat-shield material is relatively nonreactive. No significent differences exist between the two samples of material as determined by DTA.

DTA thermograms of the as-received and the vacuum-exposed specimens of material J are shown in figure 15. The thermograms of this material exhibit typical characteristics of silicone polymer degradation. (See ref. 15.) This degradation begins near 200° C and continues through 650° C; the principal degradation peak occurs at approximately 525° C. These thermograms are typical of those that would be obtained for the silicones of all the materials of this investigation if the fillers were removed. As the thermograms of this material show, no differences were noted between the vacuum-exposed and the as-received specimen of this material.

Figure 16 shows the DTA thermograms of the as-received and the exposed specimens of material K. A small endothermic area between ambient temperature and 100° C on the thermogram of the as-received material marked the elimination of moisture. A small endothermic area between 200° and 275° C on the thermogram of the

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vacuum-exposed sample indicates that the sterilization and vacuum exposure had an effect upon the material. No other significant differences exist between the two thermograms.

General trends.- An overall look at the results from tests on composite materials indicates certain general trends. For all composite materials, the sterilization procedure produced greater mass losses than the vacuum exposure. With the exception of one material, the composite materials had mass losses during vacuum exposure of about 1 percent and mass-loss rates at 200 hours of exposure of 7×10^{-4} percent per hour or less. The low quantity of mass loss of most of the materials during vacuum exposure indicates that most of the candidate ablative materials were fully cured and contained minimum quantities of highly volatile products as evaluated under the conditions of this investigation. Only material K was significantly affected by sterilization and vacuum exposure. Slight differences in the thermochemical properties of several other materials were noted. However, most of the materials tested exhibited no change in their thermochemical properties, and, therefore, their ablative properties are expected to be unchanged after longer sterilization and vacuum exposure. No attempts were made to determine changes in other material properties.

CONCLUSIONS

The effects of dry heat sterilization and vacuum exposure upon the thermochemical properties (chemical and physical changes that absorb or evolve heat) of 10 candidate heat-shield materials have been determined by differential thermal analysis (DTA) and mass loss. The sterilization procedure consisted of about 92 hours at 135° C in flowing dry nitrogen while the vacuum exposure lasted for 200 hours at 66° C at pressures in the 10^{-5}-N/m^2 range. The 10 candidate heat-shield materials consisted of five foamed and five molded composite materials. Four foamed and all molded materials contained a silicone polymer as the base resin system. One foamed material was a nitrile rubber. The results of analysis of these materials have led to the following conclusions:

1. The molded composite materials show a greater mass loss than the foamed materials during dry heat sterilization.

2. For most of the materials, the sterilization procedure produced greater mass losses than did the vacuum exposure.

3. With the exception of one molded and one foamed material, both types exhibited mass losses of approximately 1 percent during exposure to 200 hours at 10^{-5} N/m^2 and 66° C. The rate of mass loss at 200 hours of exposure ranged between 2.5×10^{-4} and 11.1×10^{-4} percent per hour for most of the materials.

4. The low quantity of mass loss observed during vacuum exposure indicates that most of the candidate ablative materials were fully cured and contained minimum quantities of highly volatile products as evaluated under the conditions of this investigation.

5. Only one material, a silicone polymer with an added sublimer was significantly affected (as determined by DTA) by sterilization and vacuum exposure. However, slight differences were noted in the thermochemical properties of several other materials. No attempts were made to determine changes in other material properties.

6. Most of the materials tested exhibited no change in their thermochemical properties under the conditions which they were tested; therefore, their ablative properties are expected to be unchanged after longer sterilization and vacuum exposure.

Langley Research Center,
    National Aeronautics and Space Administration,
        Langley Station, Hampton, Va., December 22, 1969.

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TABLE 1.- SUMMARY OF MATERIALS TESTED

Material designation	Material and/or source	Composition or principal ingredients (a)	Bulk density (as-received material), kg/m^3
Blown-foamed material			
A	General Electric ESM 1004-X	Silicone, 12% inorganic fibers, ferric oxide (red)	240
B	General Electric ESM 1004-XW	Silicone, inorganic fibers (white)	240
C	General Electric ESM 1030-1	Epoxy silicone, 2% inorganic fibers (beige)	230
D	Boeing Company	Nitrile rubber (tan)	320
E	Grumman Aircraft	Silicone, subliming salt (beige)	280
Molded composite material			
F	Langley MG 64	25% silicone, 56% phenolic microspheres, 15% nylon, 4% SiO_2 fibers (brown)	310
G	Langley MG 65	25% silicone, 61% phenolic microspheres, 10% nylon, 4% SiO_2 fibers (brown)	310
H	Martin Marietta SLA-561	Silicone, phenolic microspheres, cork	240
J	Martin Marietta SLA-220	Silicone, silica microspheres (white)	240
K	AVCO 480-2	Silicone, phenolic microspheres, fibers (brown)	240

[a]In most cases, principal ingredients have been determined by visual observation and manufacturers' literature; therefore, the materials may contain small quantities of additional components. All materials except F and G have proprietary compositions.

TABLE 2.- MASS LOSSES OF FOAMED AND COMPOSITE MATERIALS

DURING STERILIZATION AND VACUUM EXPOSURE

Material	Principal ingredients	Mass loss, percent		Mass-loss rate in vacuum at 200 hours, percent per hour
		Sterilization	Vacuum	
Blown-foamed material				
A	Silicone	0.35	0.69	8.0×10^{-4}
B	Silicone	.32	.50	6.0
C	Epoxy silicone	.60	.45	3.7
D	Nitrile rubber	8.1	1.82	11.1
E	Silicone and sublimer	16.6	.67	8.7
Molded composite material				
F	Silicone and phenolic	6.4	0.69	3.4×10^{-4}
G	Silicone and phenolic	7.4	.56	2.5
H	Silicone and cork	2.9	1.37	17.0
J	Silicone and silica	1.2	.12	3.7
K	Silicone and phenolic	6.9	3.18	7.0

Cover plate

Sample-holder block

Differential—
thermocouple beads

Cup

Sample

Post

Cross section showing cup on
differential—thermocouple post

Block thermocouple

Gas inlet

1 cm

Gas injection tubes
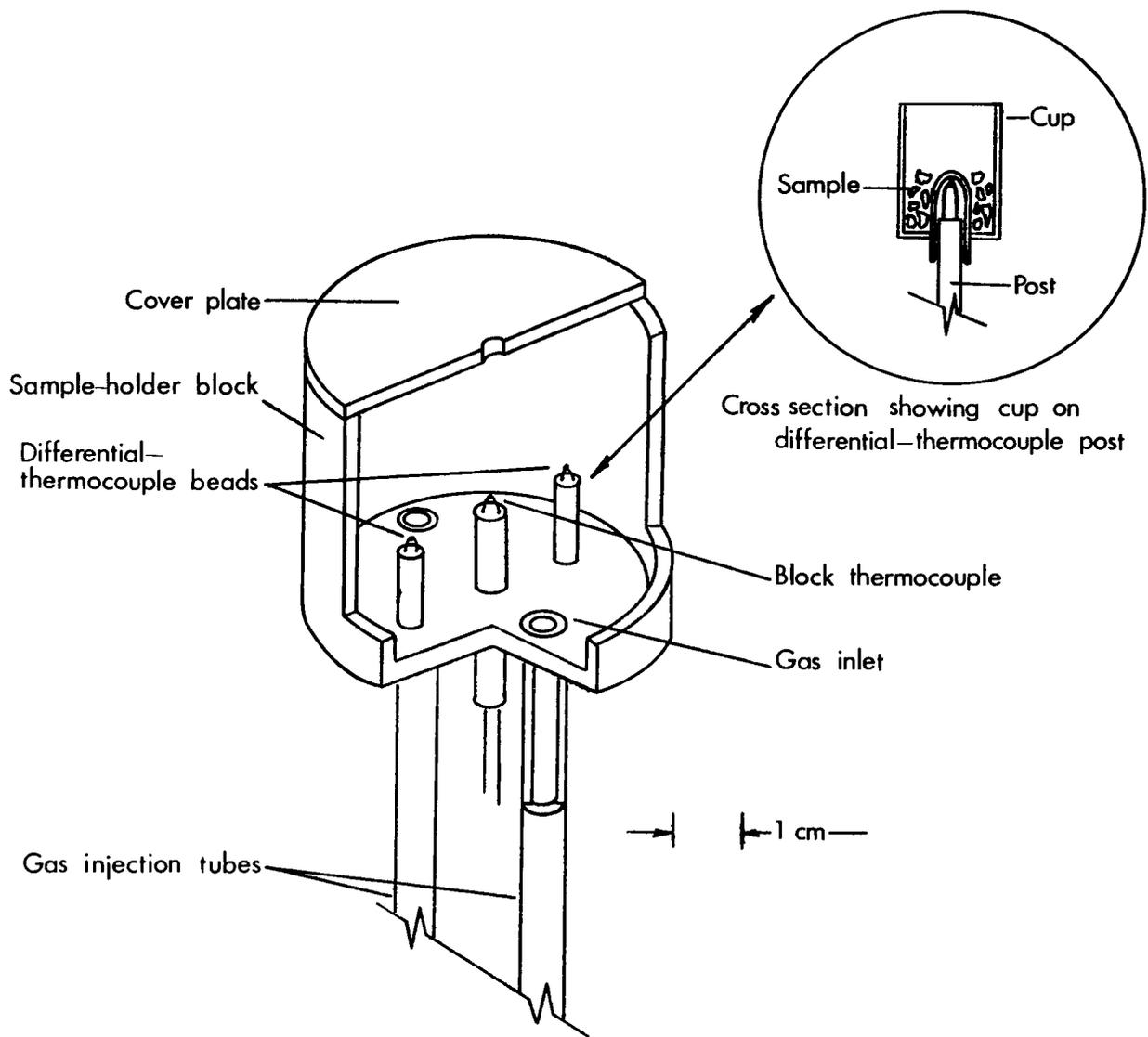
Figure 1.- Sample holder for differential thermal analysis.
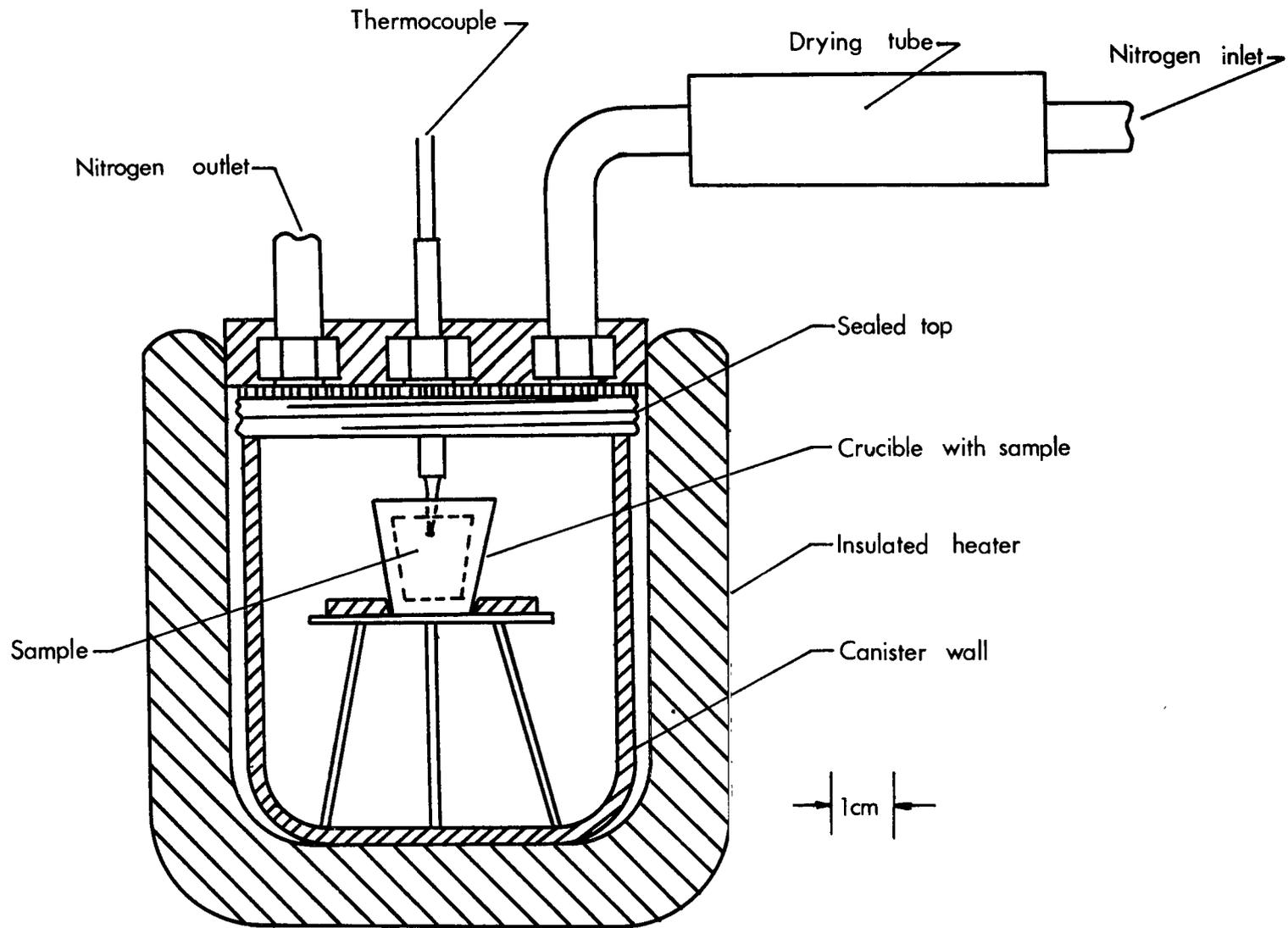
Figure 2.- Apparatus for dry heat sterilization.
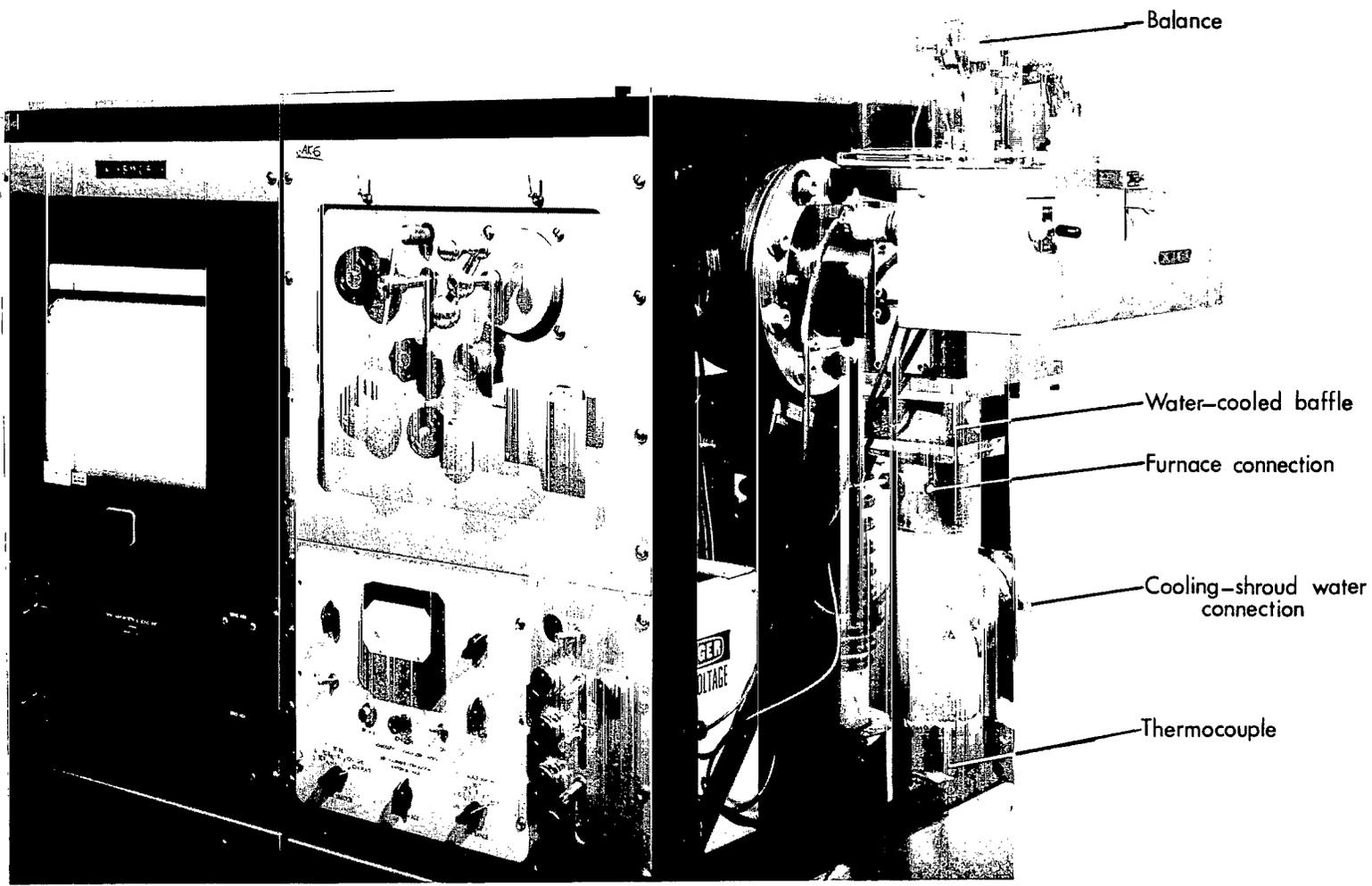
Figure 3.- Vacuum balance apparatus used for mass-loss studies.

Balance

Water-cooled baffle

Furnace connection

Cooling-shroud water connection

Thermocouple

L-69-5146

Glass suspension

Crucible

Thermocouple

Furnace connections

Furnace elements

Water-cooled shroud

1.0 cm
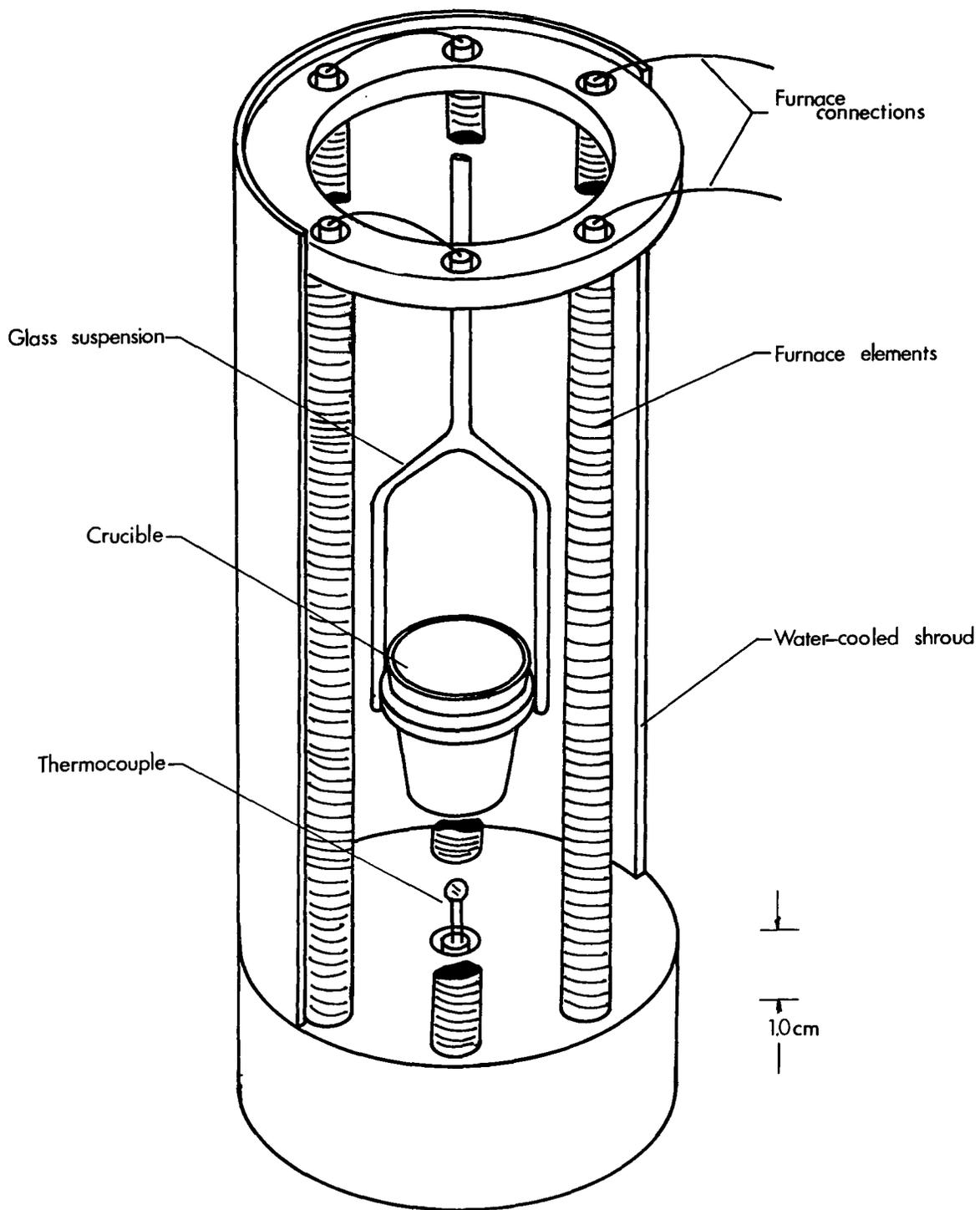
Figure 4.- High-vacuum furnace assembly.
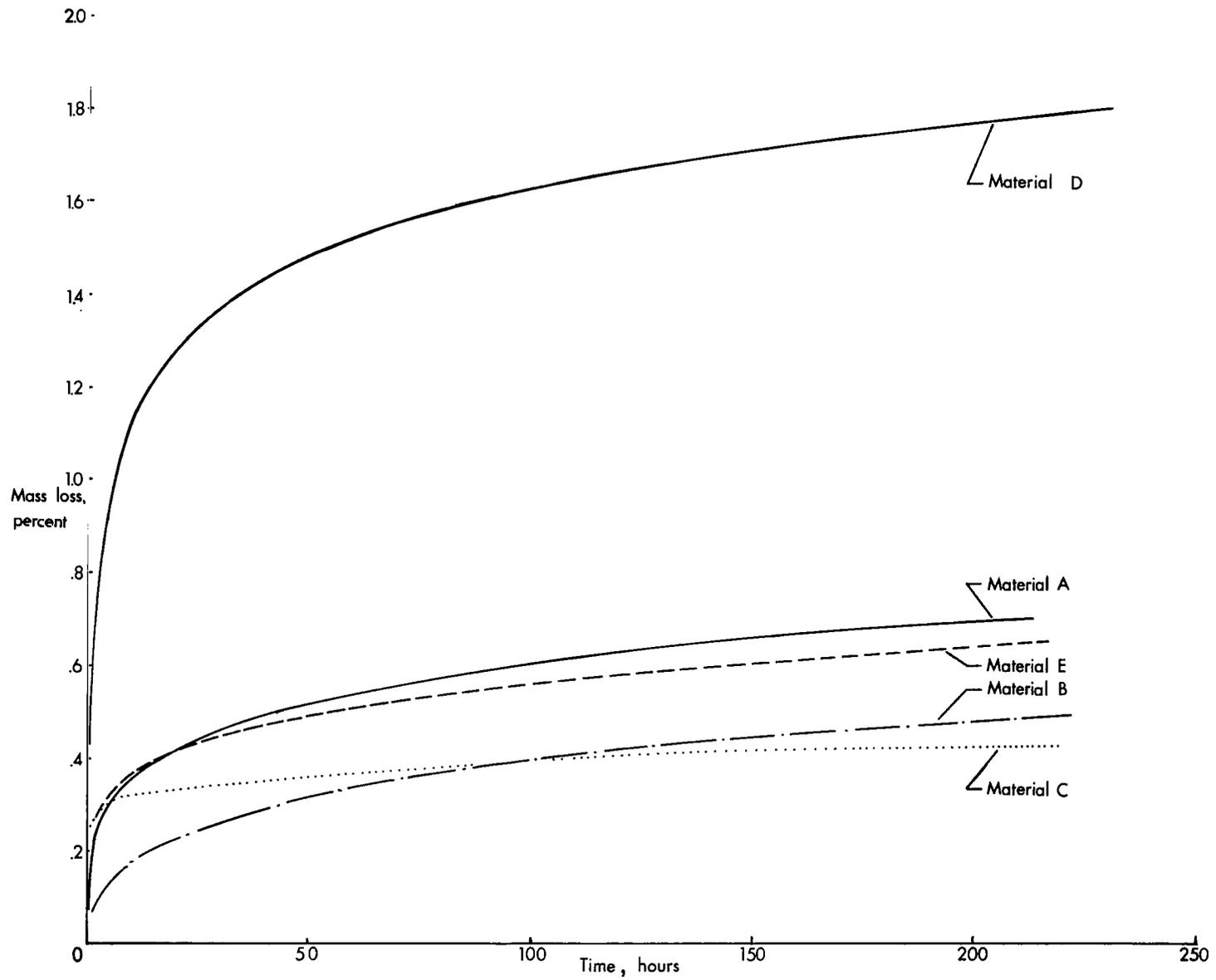
Figure 5.- High-vacuum mass losses of foamed materials at 10^{-5} N/m^2 and 66^0 C.
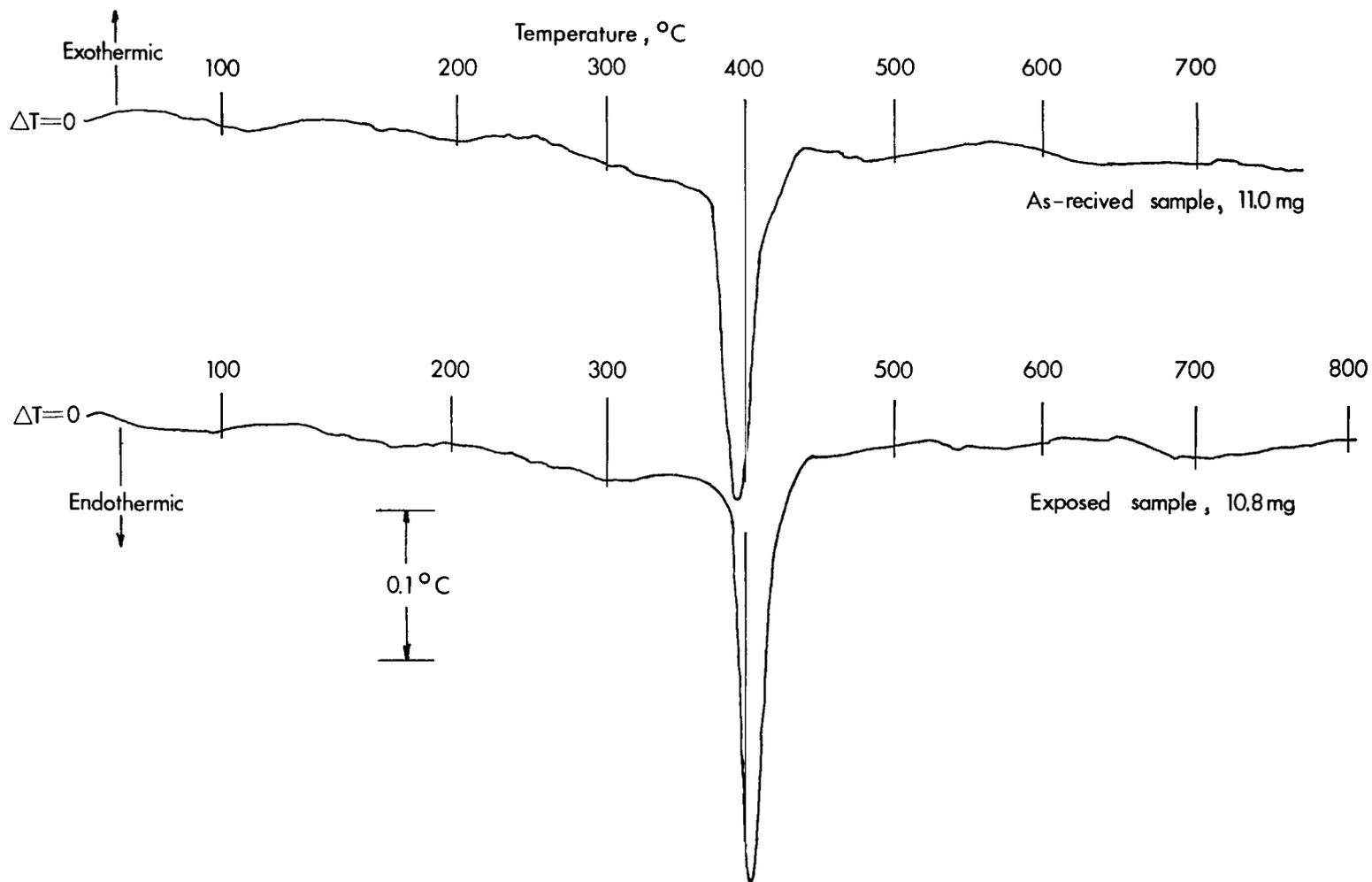
Figure 6.- DTA thermograms of material A.
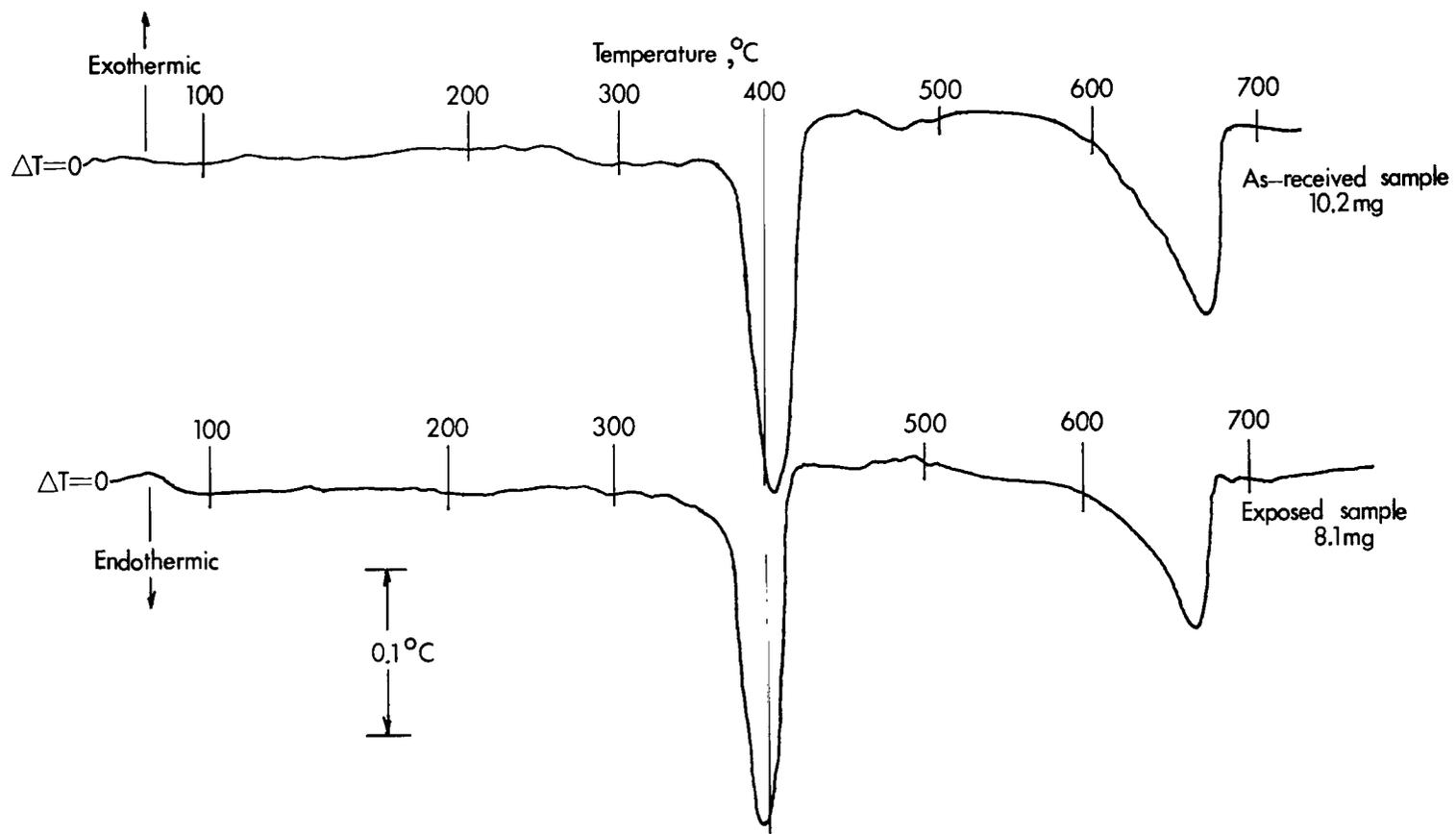
Figure 7.- DTA thermograms of material B.
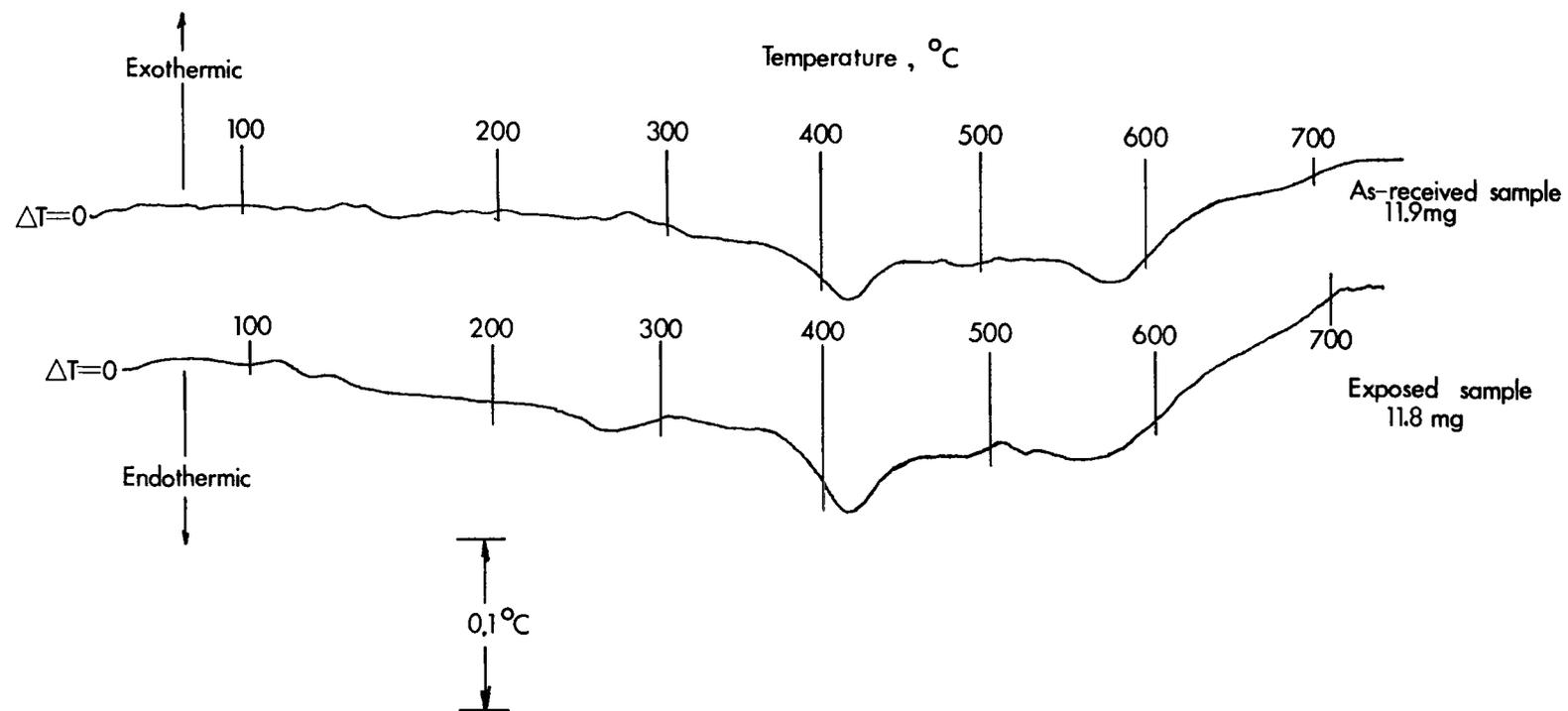
Figure 8.- DTA thermograms of material C.
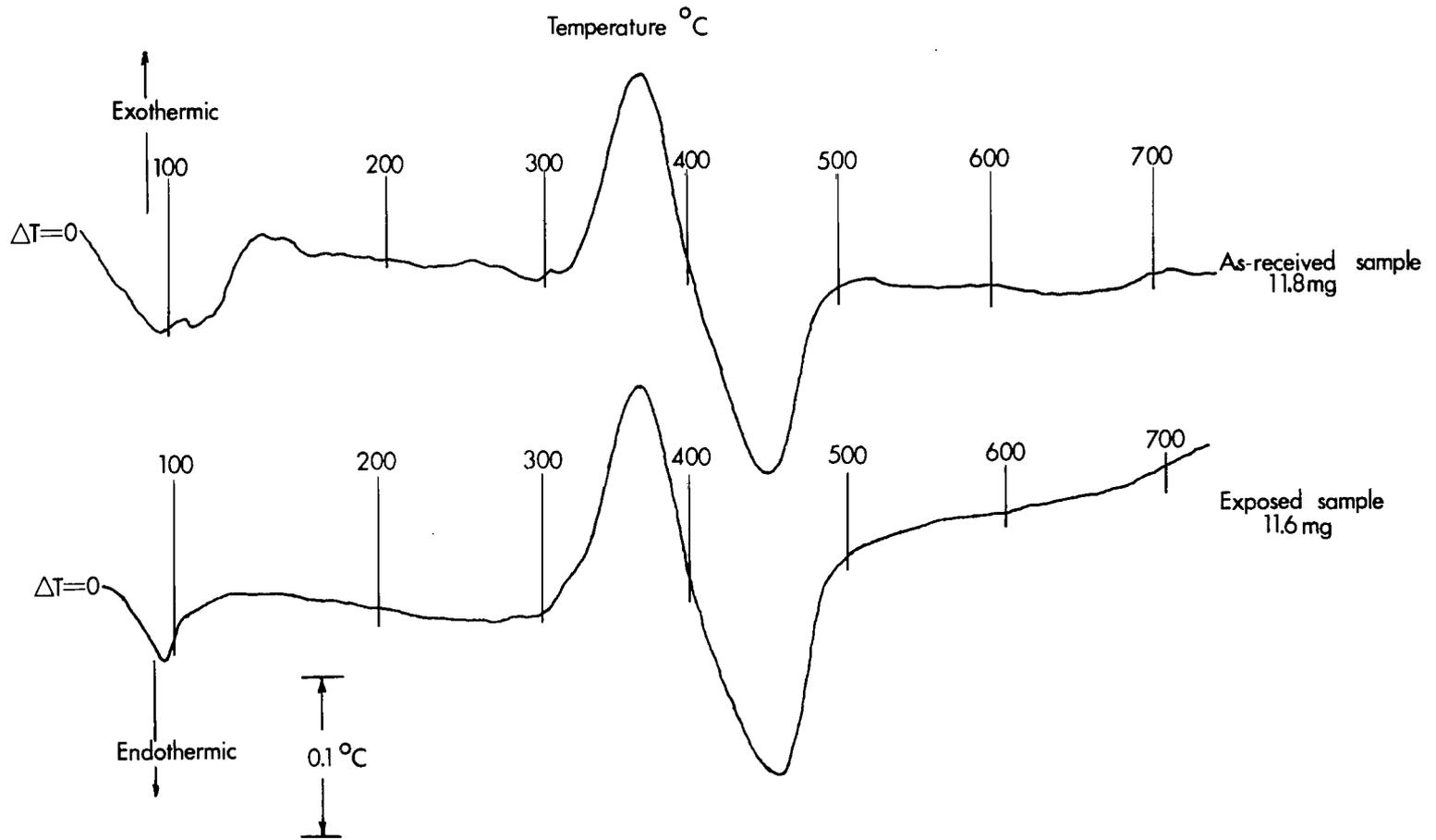
Figure 9.- DTA thermograms of material D.
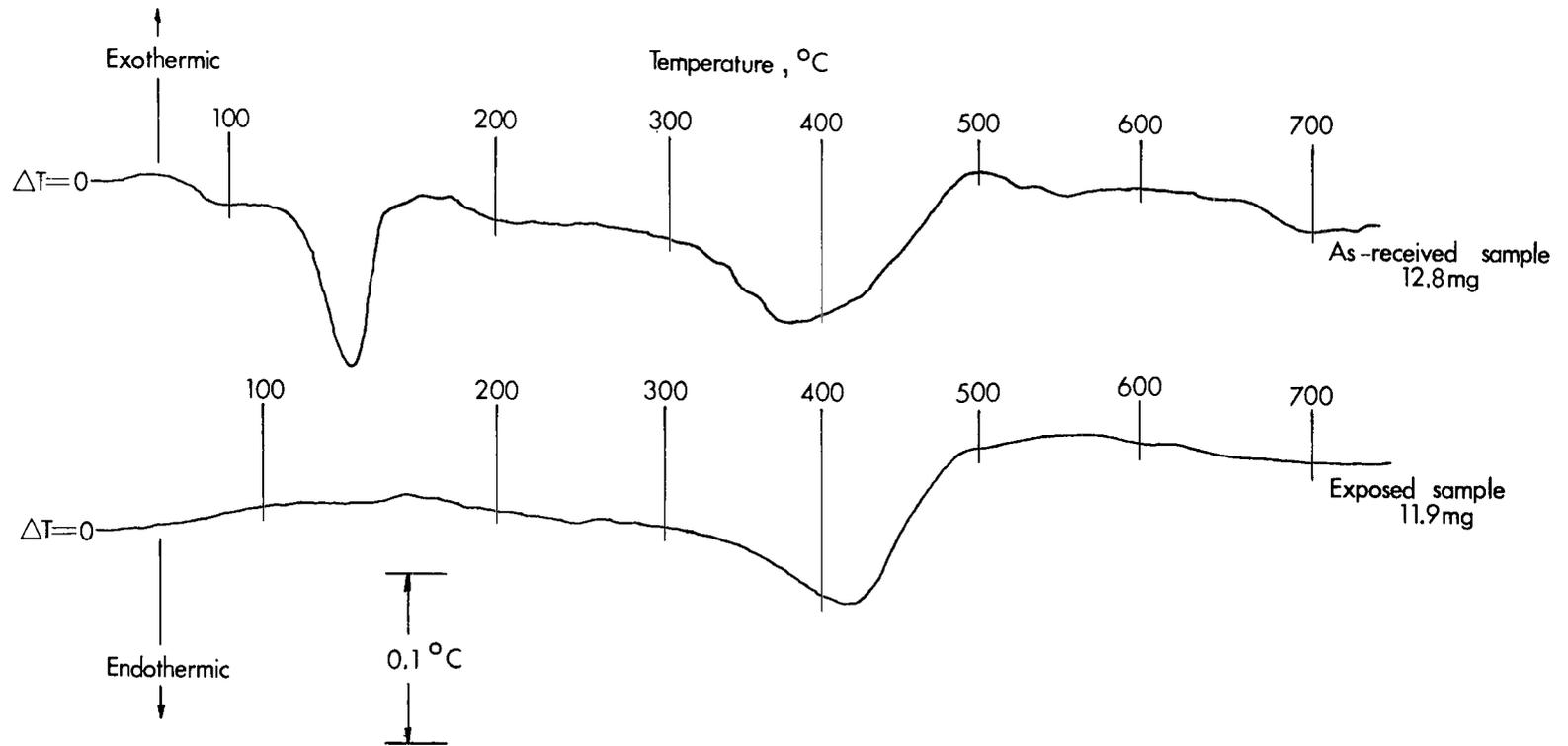
Figure 10.- DTA thermograms of material E.
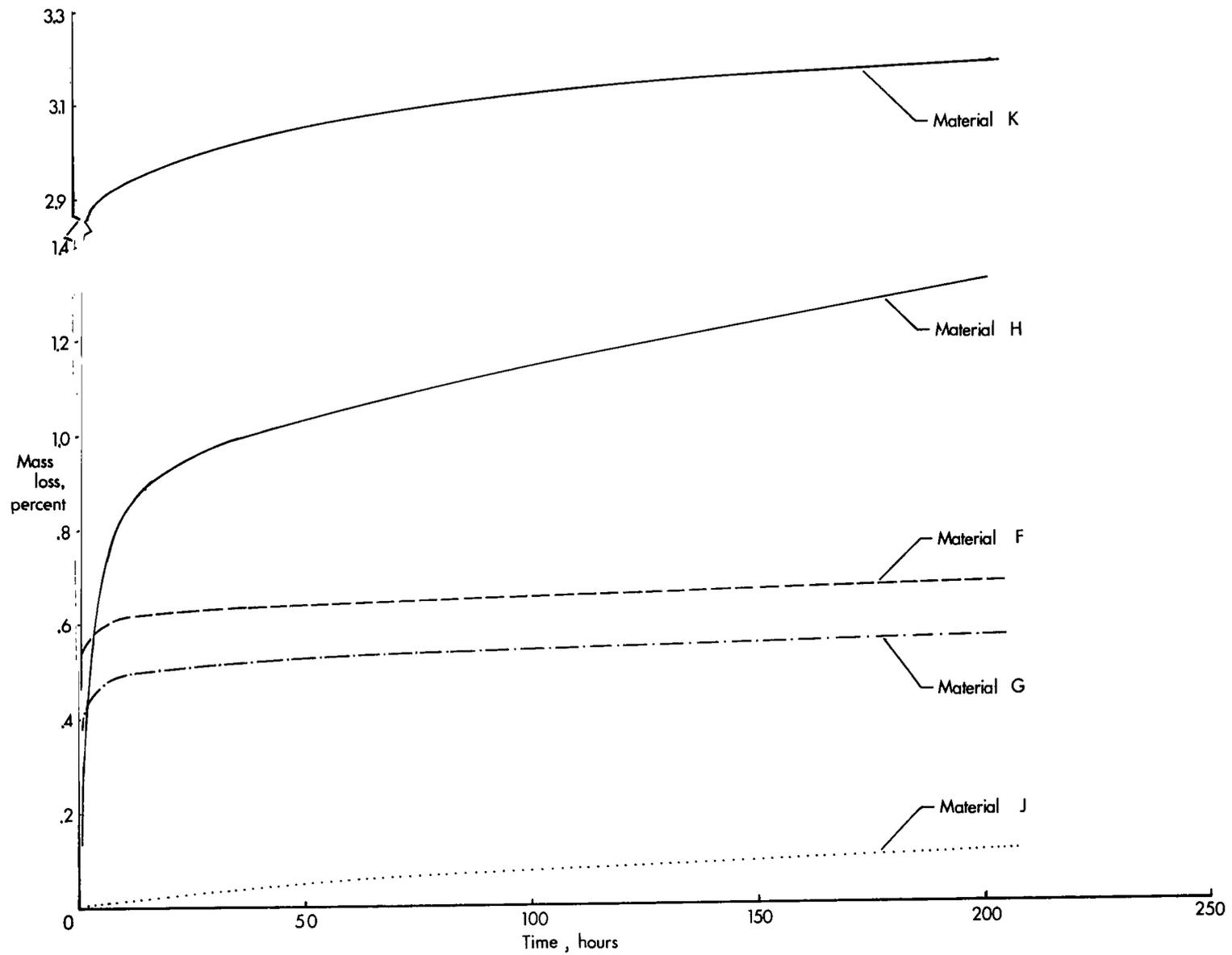
Figure 11.- High-vacuum mass losses of molded composite materials at 10^{-5} N/m^2 and 66° C.
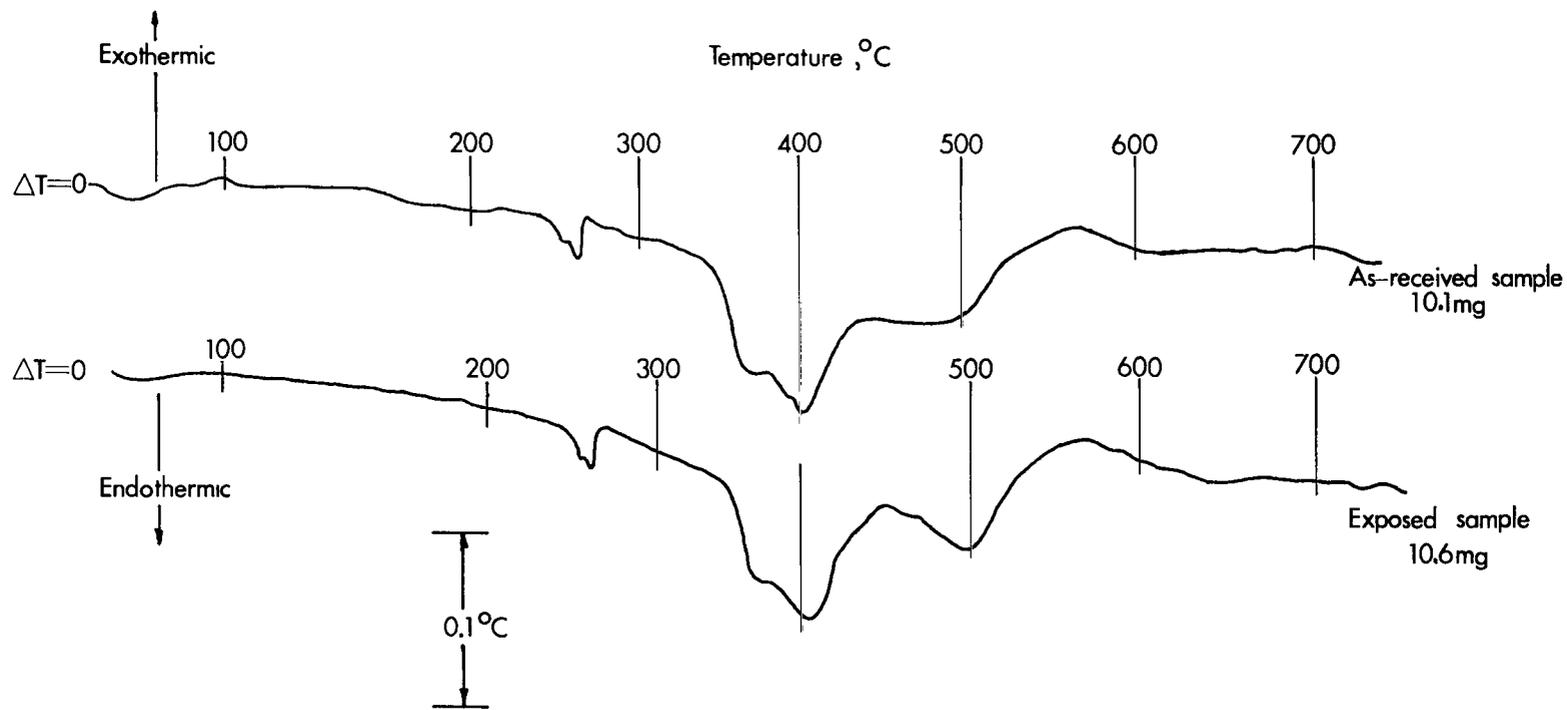
Figure 12.- DTA thermograms of material F.
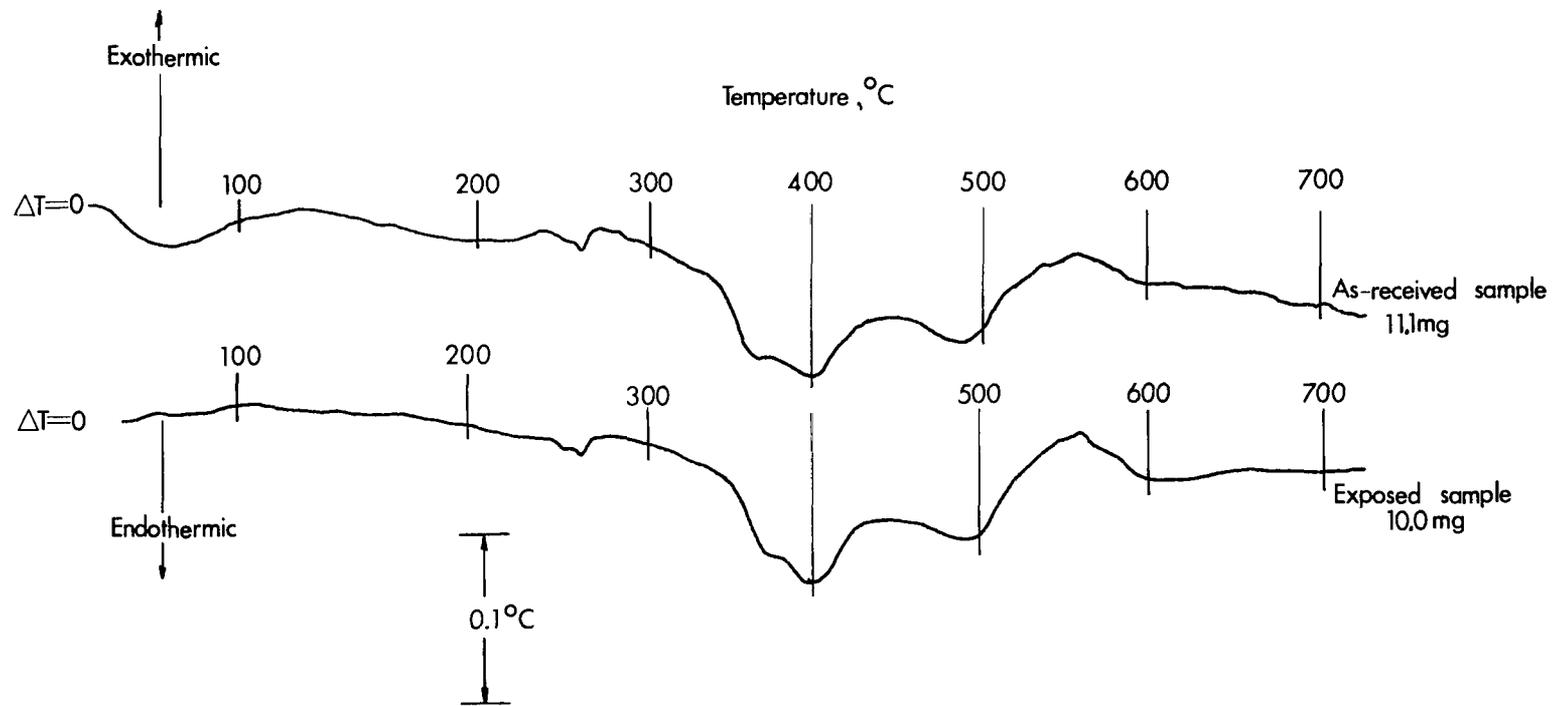
Figure 13.- DTA thermograms of material G.
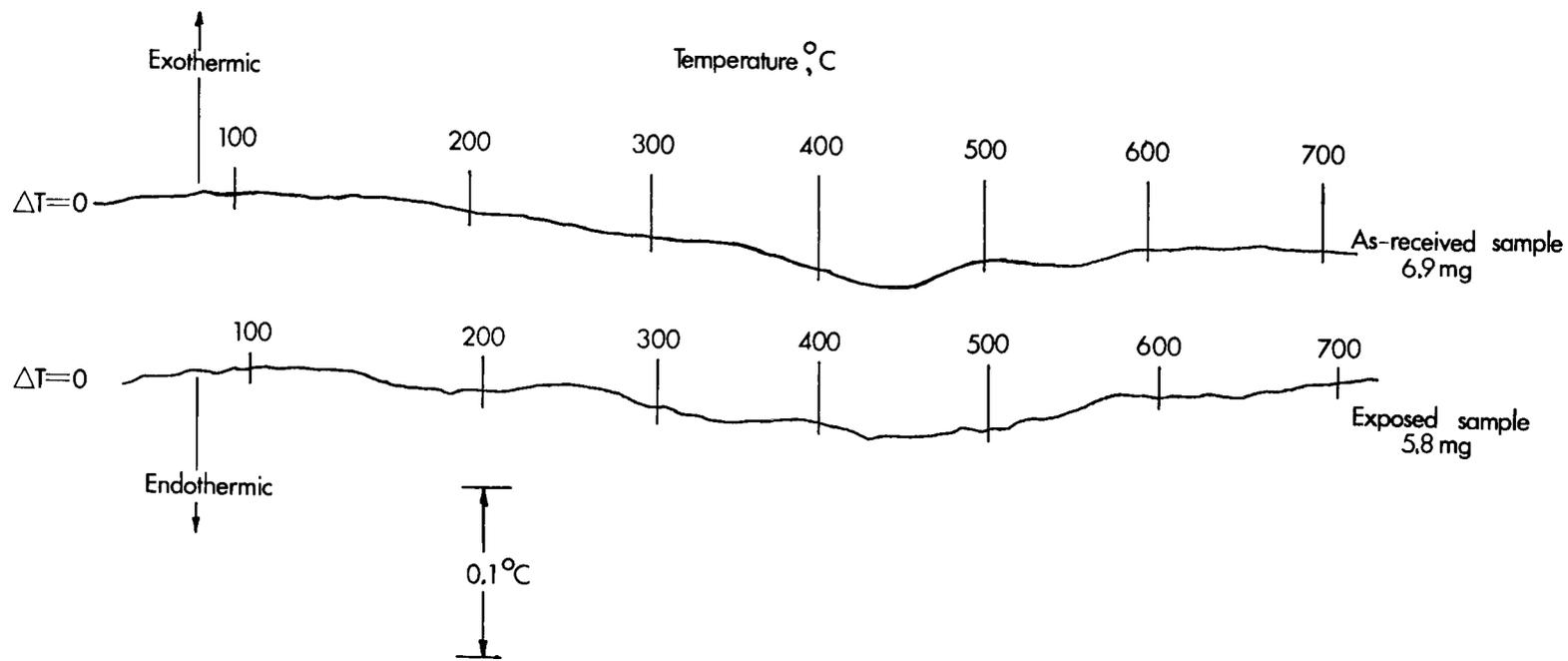
Figure 14.- DTA thermograms of material H.
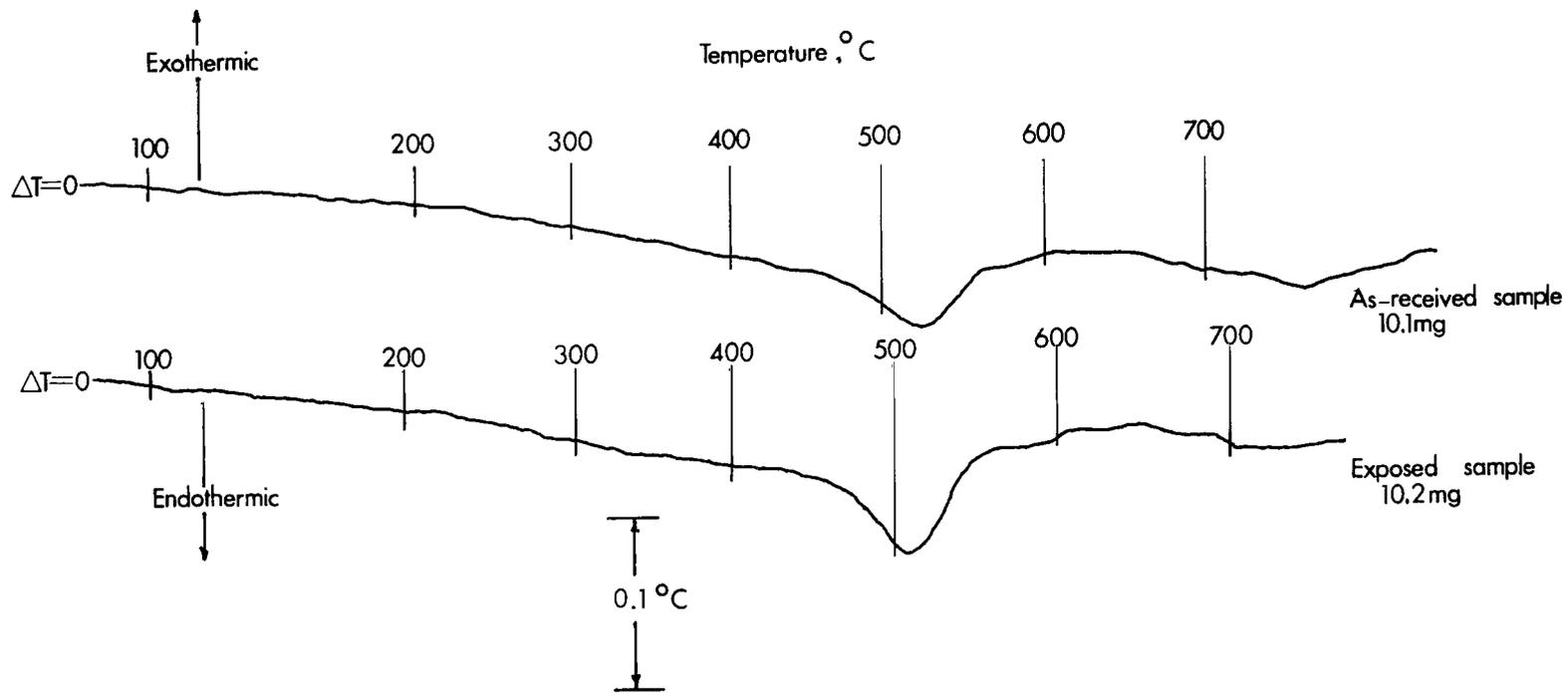
Figure 15.- DTA thermograms of material J.

Exothermic

Temperature , °C

ΔT=0

100   200   300   400   500   600

As-received sample
10.3mg

ΔT=0

100   200   300   400   500   600

Endothermic

0.1 °C

Exposed sample
9.9mg
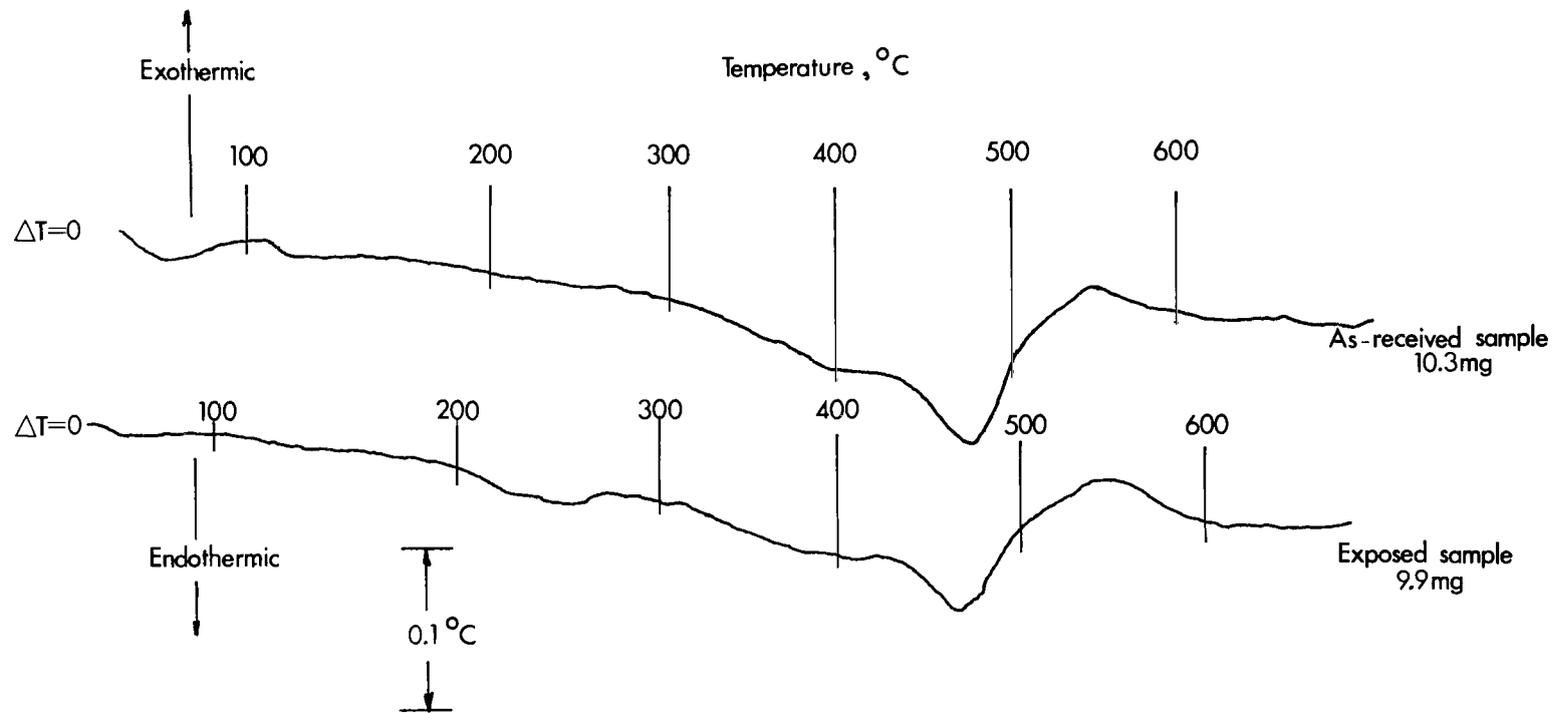
Figure 16.- DTA thermograms of material K.

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— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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