NASA CR-66874

SOLAR REFLECTIVE THERMAL CONTROL COATINGS FOR A METEOROID DETECTOR SPACECRAFT

FINAL SUMMARY REPORT
VOLUME II

By James A. Cooley

Prepared under Contract No. NAS1-7043 by
MARTIN MARIETTA CORPORATION
Denver, Colorado

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FOREWORD

This document is submitted in accordance with the requirements of paragraph 5.8 of NAS1-7043, Contract Statement of Work L-7138A, Exhibit A.

The work pertaining to development of meteoroid detectors is included in Volume I (NASA CR-66840). This volume comprises the investigation performed on thermal control coatings for the MPPD program.

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INTRODUCTION

The objective of this portion of the Meteoroid Penetration Detector Development (MPDD) program was to formulate and evaluate solar reflective thermal control coatings for a micrometeoroid spacecraft. This included principally an investigation of selected white, crystalline materials as candidate pigments for thermal control coatings. The intent was that the investigation would ultimately lead to the development of one or more thermal control coatings having optical and radiative properties which remain stable in the radiation environments of space.

Spacecraft temperature control is accomplished by regulation of the radiative interchange of thermal energy between the vehicle and its low density environment. In order to maintain the temperature of spacecraft subsystems within operation limits passive thermal control coatings are frequently applied to vehicle surfaces. In cases where a net transfer of energy to the environment is necessary, white thermal control paints having low ratios of solar absorptance to infrared emittance are used.

A requirement of a thermal control system is that its optical and radiative properties must remain stable during long periods of exposure to the space environment. Unfortunately, many white thermal control coatings are so affected by exposure to solar ultraviolet radiation and/or space indigenous charged particles that their optical properties change and they can no longer control temperatures within desired or even tolerable limits. The primary cause of optical property changes of the coatings is the damage induced in the pigments by the radiations. No white thermal control coating yet formulated is really optically stable in both electromagnetic and charged particle space radiation environments.

Because of an indicated need for thermal control coatings related to the MPDD Program, Dr. John Buckley of NASA Langley Research Center (LRC) proposed the investigation of a number of refractory materials as pigment candidates. The study was initiated in August, 1968 under modification 15 to the MPDD contract.

The program continued under that modification and subsequent modifications 17 and 19. The effort under the first two modifications resulted in the isolation of a sintered disc of hafnium oxide, containing 5 percent calcia by weight in solid solution, as demonstrating stability to space radiations. Modification 19 was then approved and permitted a more comprehensive investigation of undoped and calcia doped hafnia and possible methods of preparing these materials aside from sintering.

SUMMARY

The portion of the Meteoroid Penetration Development (MPDD) program devoted to a study of thermal control coatings was organized into five phases. Phase A was concerned with the formulation of coatings using calcia (CaO), boron nitride (BN), hafnia (HfO_2) zirconia (ZrO_2) and thoria (ThO_2) as pigments. The pigment materials were supplied by NASA. Calcia was found to be incompatible with a potassium silicate binder and to have poor hiding power in silicone binders. Boron nitride was supplied only in a solid sample so could not be used as a pigment. Hafnia, zirconia and thoria all formed satisfactory to excellent coatings with potassium silicate.

In Phase B samples of the coatings or pigments prepared in Phase A were exposed to simulated solar electromagnetic radiation to evaluate the stability of their optical properties to near ultraviolet (2000 to 4000 Å) radiation. None of the materials tested were very stable.

In Phase C some effects of doping, heat treating and cryochemical synthesis of some materials were examined.

Specimens of hafnia doped with various weight percents of yttria and calcia and sintered at high temperature were tested. During this phase it was found that one of these specimens containing 5 percent calcia exhibited no change in solar absorptance after 240 equivalent sun hours (ESH) of ultraviolet exposure. This appeared to be the most stable material yet found for a thermal control pigment.

In Phase D the same 5 percent calcia doped specimen was exposed to 1200 eV hydrogen ions in a fluence equal to a year in a solar wind environment. The stability in this environment was almost as good as in the ultraviolet environment. An undoped specimen and a 2 percent doped specimen exhibited similar stability.

Two efforts were carried on during Phase E. After some initial difficulties, NASA personnel under Dr. John Buckley's direction began to routinely produce specimens of 5 percent CaO doped HfO_2 sintered at 1700°C for about 24 hours. These were generally quite stable to ultraviolet radiation but two samples exposed to 1200 eV hydrogen ions incurred greater than expected changes in solar absorptance.

Some of the specimens were reduced to pigment-sized powders at Denver Research Institute. Samples of the powders were subjected to ultraviolet exposure in vacuum resulting in substantial increases in solar absorptance. Reasons for lack of stability of the powders have not been defined but impurities introduced during preparation from the sintered pellets are probably partly at fault.

Attempts by personnel of the Martin Marietta Corporation Thermophysics Laboratory to synthesize doped and undoped hafnia by cryochemical techniques were unsuccessful. However, information about a modification of the method developed at Bell Telephone Laboratories would appear to make synthesis by cryochemical methods quite possible. A brief investigation of a co-precipitation technique for doping hafnia also looks promising.

The possibility of ultimately producing a very stable thermal control coating through the techniques pursued at Langley Research Center and Martin Marietta Corporation under this study seems highly promising. Refinements in the preparation of materials and in their processing should lead to solutions of the problems that presently exist.

TECHNICAL DISCUSSION

The technical effort was divided into five phases through modifications 15, 17 and 19 of Contract NAS1-7043.

Phase A and B

In Phase A of the thermal control study attempts were to be made to formulate five coatings using refractory pigment materials supplied by NASA. In Phase B the experimental coatings were to be exposed to simulated solar electromagnetic radiation in vacuum with solar absorptance evaluated by means of in situ spectral reflectance measurements to determine the damage induced by the radiation.

Calcia (CaO)-Calcia was found to be incompatible with a potassium silicate binder. An aqueous suspension of CaO was filtered and added to the silicate solution. A white precipitate formed, probably some form of $CaSiO_3$. CaO has poor hiding power in silicone binders and a large amount of the oxide was observed to limit the shelf-life of a one-component silicone. A compressed powder specimen, when subjected to approximately 130 equivalent sun hours (ESH) of near ultraviolet (2000 to 4000 Å) radiation, exhibited an increase in solar absorptance from 0.12 to 0.19. No further work was done with this material.

Boron nitride (BN).- No coating was formulated from this material since no powdered pigment was available. The BN used in the solar simulation evaluation was tooled from a solid bar. About 310 ESH of ultraviolet irradiation increased the solar absorptance from 0.24 to 0.29.

Zirconia (ZrO_2).- Zirconia forms an excellent coating with potassium silicate. A pigment to binder ratio study was carried out using an impure oxide to conserve the high purity (99.9+%) ZrO_2. With reflectance of primary importance in a practical coating, a maximum of 4 grams of ZrO_2 (325 mesh) to 1 mil PS-7 silicate (Sylvania) and water, used as a diluent to spray consistency, appears to be an optimum ratio. A specimen prepared in this ratio had a measured normal emittance of 0.84. Attempts to prepare a ZrO_2/silicone coating indicate that the ZrO_2 may require other agents to maintain suspension. The addition of such agents would have complicated interpretation of the damage data.

An estimated 110 ESH of ultraviolet irradiation increased the solar absorptance of a ZrO_2/K_2SiO_3 specimen from 0.14 to 0.18.

Hafnia (HfO_2).- Two different hafnia-silicate formulas were prepared and irradiated separately with approximately 75 ESH of ultraviolet. A coating with a low pigment content had a relatively high solar absorptance (0.27) and suffered an increase in solar absorptance of 0.01. A coating with higher pigment content had a solar absorptance of 0.21 which increased to 0.24 during exposure. The best HfO_2/K_2SiO_3 coating made had a solar absorptance of 0.14 and a normal emittance of 0.93.

Thoria (ThO_2).- ThO_2/K_2SiO_3 coatings were formulated and a sample exposed to an estimated 80 ESH of ultraviolet exhibited an increase in solar absorptance from 0.12 to 0.16.

Phase C

Some of the work during this phase of the study was directed toward evaluation of a possible relationship between hydroxyl ion absorption bands in pigment materials and their stability in the space radiation environments. No conclusive data were obtained during the study which would establish whether or not such a correlation existed. A definitive study would entail a much more comprehensive investigation than was available here.

Several metal oxides were heat treated to 1650°C in an unsuccessful effort to eliminate, from spectral reflectance scans, the near infrared absorption bands indicative of the presence of hydroxyl ions in the material. Unfortunately, the fact that some such ions remained does not prove that they were present in the crystal structure.

Cryochemically prepared MgO which was subsequently heated to 1700°C exhibited no such absorption bands but damaged substantially during ultraviolet exposure.

Spectral reflectance curves were run on six samples of hafnia doped with various percentages of yttria. These specimens which were in the form of small sintered discs were prepared by Dr. John Buckley of Langley Research Center. It was noted that the strength of the infrared absorption bands due to the presence of hydroxyl ions become less as the percentage of yttria dopant increased and also as the sintering temperature increased. One specimen doped with 7 percent yttria and sintered at 2000°C showed no trace of the absorption bands.

One specimen of hafnia doped with 5 percent yttria and sintered at 1800°C exhibited a change in solar absorptance of 0.06 after exposure to an estimated 192 ESH of ultraviolet.

A sample of hafnia doped with 5 percent calcia and sintered at 1800°C was investigated next. The introduction of 5 weight percent of calcia in complete solid solution results in stabilizing the phase transformations in hafnia and results in a face centered cubic crystal structure. This specimen exhibited no trace of the infrared absorption bands in question.

The 5 percent calcia doped HfO_2 sample was exposed to simulated solar radiation in vacuum. After total of approximately 240 ESH of ultraviolet exposure, the solar absorptance of the sample remained unchanged at 0.17 as determined from in situ spectral reflectance measurements. The spectrum, as were all others tested, was attached to a water-cooled metallic heat sink maintained at a temperature near 298°K.

Phase D

During this phase of the study three sintered hafnia specimens prepared by Dr. Buckley were exposed in a vacuum environment to a beam of 1200 eV hydrogen ions. The three specimens included one of undoped hafnia, one of 2 percent calcia doped hafnia and one of 5 percent calcia doped hafnia. The latter specimen was the identical one described under Phase C which had exhibited remarkable stability in an ultraviolet environment. It is not known whether the sample face that was exposed to the ion beam was the same one that had been exposed to the electromagnetic radiation.

No attempt was made to achieve a pure proton beam by mass separation. Based on a previous analysis of the beam it probably consisted of about 25 percent protons and 75 percent molecular and triatomic hydrogen ions. The undoped HfO_2 and 5 percent CaO doped HfO_2 were exposed to a particle flux density estimated at about $2x10^{11}$ p/cm^2/sec (about 1000 X solar wind levels) to a resultant fluence of approximately $5x10^{15}$ p/cm^2 (about 1 year at solar wind levels at 1 AU) corresponding values for the HfO_2 with 2% CaO were about 0.6 of the above. Pre and post spectral reflectance measurements of the specimens were made in an integrating sphere at atmospheric conditions rather than in situ, because the vacuum sphere was not attached to the test chamber, so that some recovery from damage may have occurred. There was some indication of a slight increase in absorptance of all three specimens in the wavelength range from 0.4 to 0.6 micron with approximately the same change for all three. The measured change was scarcely greater than the error of measurement and was much less than the measured increase in absorptance of a ZnO/K_2SiO_3 sample tested under similar conditions. The test must not be regarded as definitive because of lack of optimum test conditions, but it is indicative of good stability in a low energy proton environment. Figure 1 shows the changes in spectral absorptance which occurred for the 5 percent doped specimen.

Phase E

This phase provided for a further study of sintered specimens of undoped and calcia doped hafnium oxide specimens furnished by NASA. It further provided for the cryochemical synthesis of undoped and calcia doped hafnia followed by high temperature treatment. Heat treatment in the case of doping would be required for the calcia to go into solid solution.

Sintered Specimen Study.- Early efforts in this part of the study were marked by problems of NASA personnel in producing good specimens principally because of problems with high temperature furnaces. The first batch of freshly prepared, doped hafnia specimens consisting of three specimens with 3 percent calcia and three with 5 percent calcia was received on 15 April. A second batch, all 5 percent calcia, arrived on 28 April. All of the specimens were somewhat yellowed about the edges probably from contaminants picked up in the furnace. Some of the specimens had gray areas indicating possible non-stoichiometry with an excess of hafnium or a substantial amount of metallic impurity. Three samples selected from these batches were exposed in vacuum to simulated solar electromagnetic radiation from a xenon compact arc lamp at an irradiance of three solar ultraviolet equivalents. Total exposure varied from 50 to 200 ESH of ultraviolet radiation. All three samples, including one cleaned with ethyl alcohol in an attempt to remove possible surface contamination, exhibited changes in solar absorptance of 10 percent or more.

Ultraviolet exposure tests were conducted on two sintered hafnia specimens received during Phase C of the study. One was an undoped specimen and the other doped with 5 percent calcia. Comparison of the results indicated that doping definitely increased ultraviolet stability of hafnia.

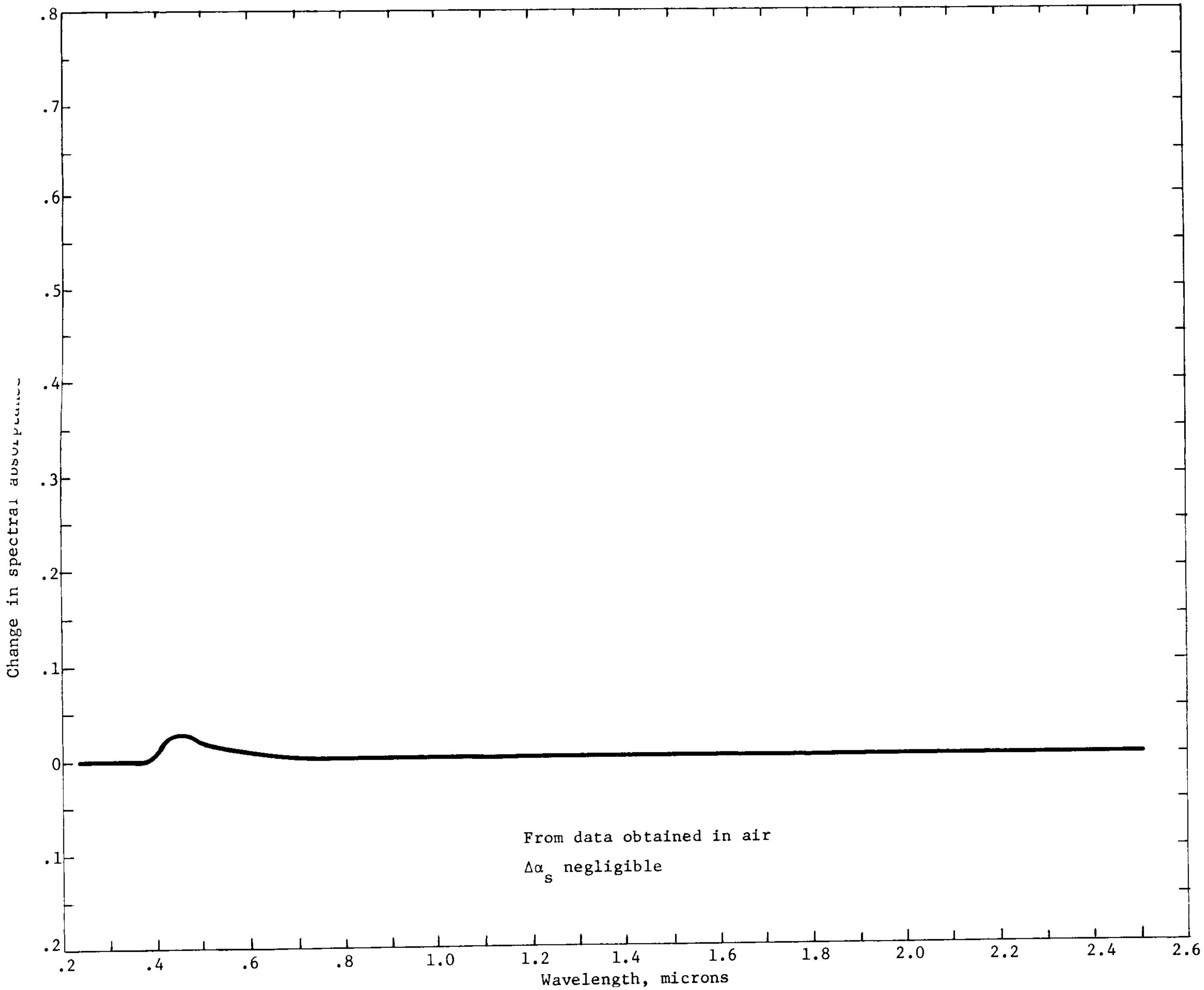

Figure 1.- Effect of 1.2 keV Hydrogen Ions (>5 x 10^{15} p/cm^2 at 2 x 10^{11} p/cm^2/sec) on the First Sintered Sample of 95% HfO_2, 5% CaO Received

Sintered specimens of 100% hafnia prepared by sintering for 3 hours in vacuum at 2000°C followed by sintering for 13 hours at 1700°C in air to reoxidize were observed to be contaminated. Spectral reflectance curves of these specimens differed substantially from each other. Calcia stabilized specimens prepared by sintering for 3 hours at 2000°C in vacuum followed by 7 hours at 1700°C in air did not exhibit visible contamination. The specimens did lose calcia during the vacuum sintering and were not fully stabilized.

Specimens of 5% calcia doped hafnia which had been sintered for 6 hours at 1700°C exhibited an increase in absorptance in the visible region (fig. 2) but no net change in solar absorptance because of an increased reflectance in the infrared spectral region when exposed to 207 equivalent sun hours of ultraviolet radiation. Spectral reflectance data for these determinations was taken in the range 0.25 to 2.5 microns. Similarly doped specimens which were sintered at 1700°C for 22 (fig. 3) to 24 (fig. 4) hours, i.e. a longer period, exhibited less damage in the visible spectrum than the specimen just described after up to 340 equivalent sun hours of ultraviolet, and no net change in solar absorptance.

A specimen of 100% hafnia sintered at 1700°C for 6 hours incurred substantial damage during approximately 140 equivalent sun hours of ultraviolet exposure. The specimen, however, even before exposure, exhibited an anomalous absorption band in the wavelength range from 0.45 to 0.8 microns. There may have been a correlation between this band and the susceptibility of the specimen to ultraviolet radiation. The major cation impurity found in the specimen was copper (1000 ppm). Copper was also found at 700 ppm in a calcia doped specimen which did not have the anomalous absorption band and was stable in ultraviolet radiation. The spectrographic grade (Wah Chang) powder from which the specimens were made exhibited the same impurity content as the sintered 100% hafnia pellet, without the absorption band.

Preparation of specimens sintered at 1700°C for approximately 24 hours in a platinum basket hanging from the top of the alumina muffle tube in the furnace was being accomplished rather routinely by NASA personnel at this stage of the program. The resultant specimens varied somewhat in their stability to ultraviolet radiation but were generally good. Spectral reflectance curves were made for both faces of 18 of the sintered discs and no anomalies were noted. Spectrochemical analyses of representative samples indicated no anomalous impurities.

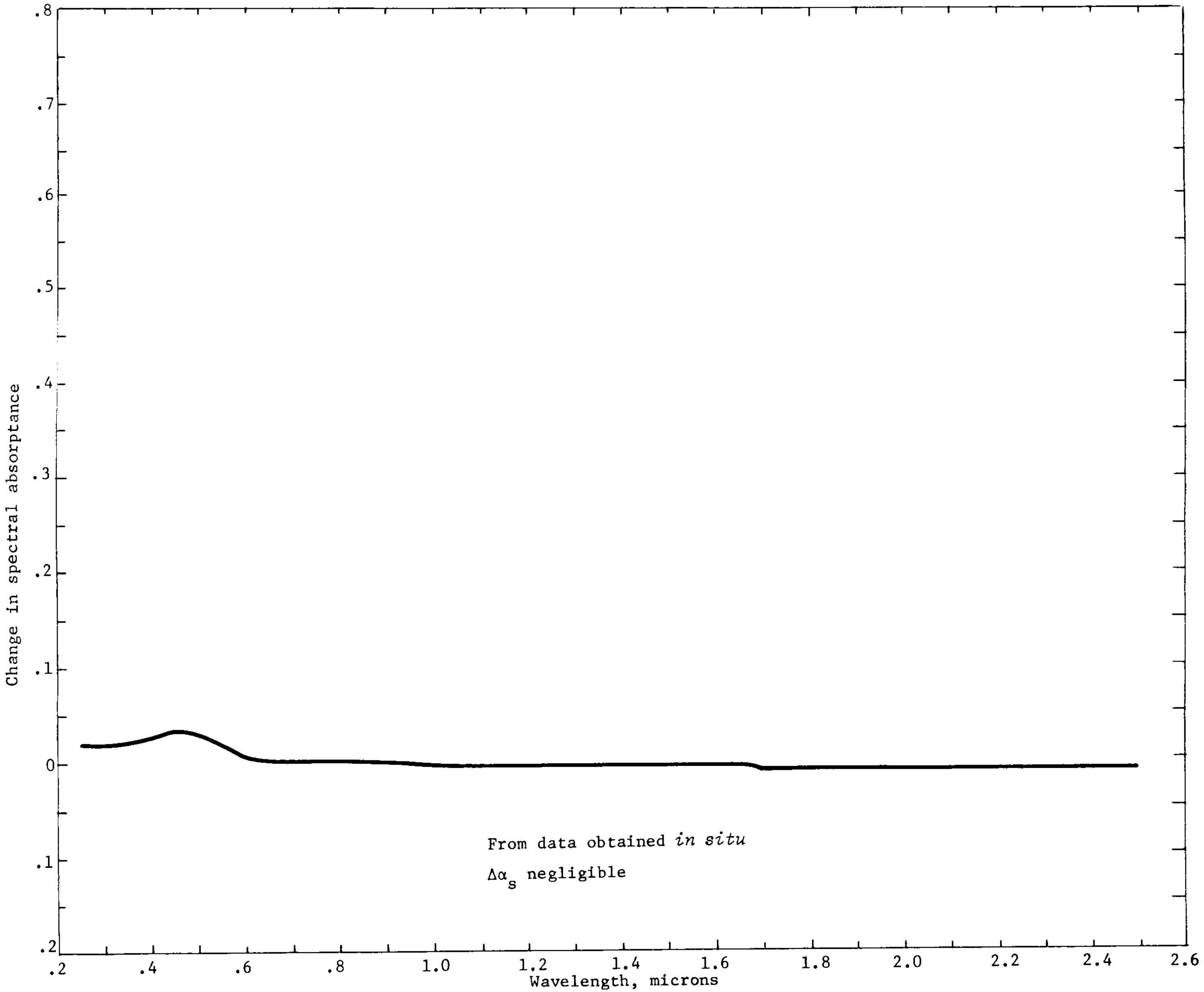

Figure 2.- Effect of 207 ESH of Ultraviolet Radiation on a 95% HfO_2, 5% CaO Sample Sintered at 1700°C for 6 Hours (Batch of 7/28/69)

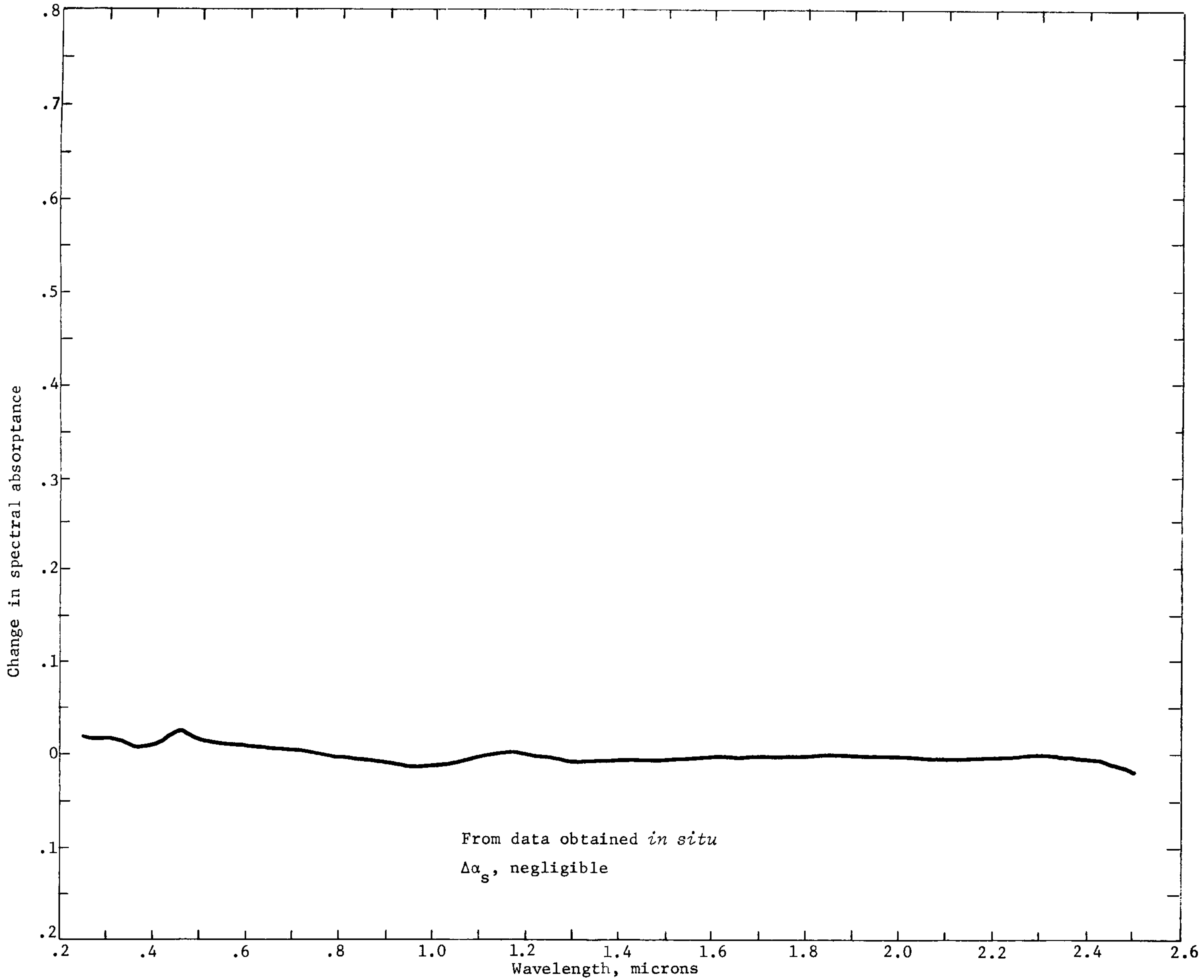

Figure 3.- Effect of 340 ESH of Ultraviolet Radiation on a 95% HfO_2, 5% CaO Sample Sintered at 1700°C for 22 Hours (Batch of 7-28-69)

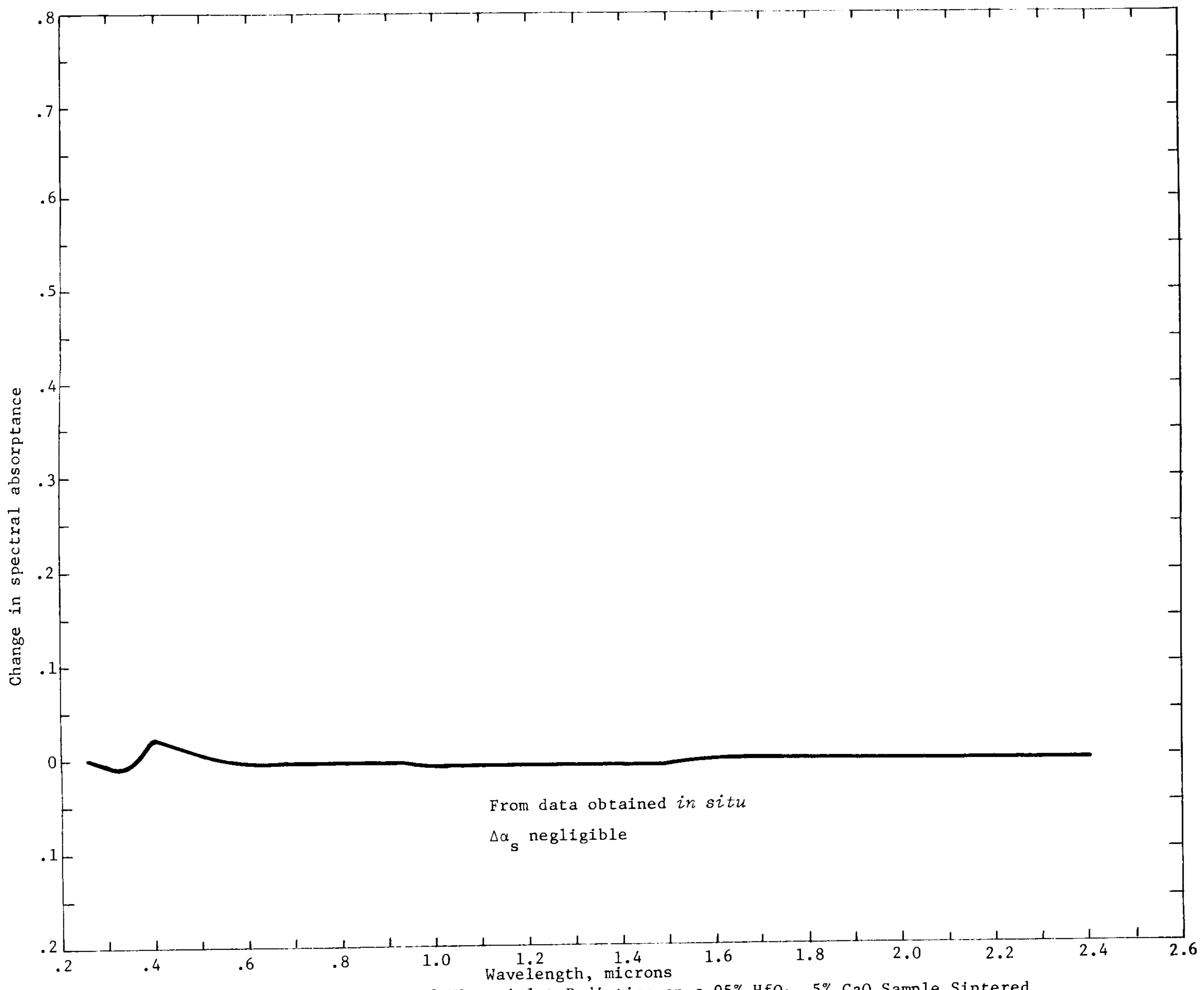

Figure 4.- Effect of 270 ESH of Ultraviolet Radiation on a 95% HfO_2, 5% CaO Sample Sintered at 1700°C for 24 Hours (Batch of 8/18/69)

Two of the sintered 5 percent calcia doped specimens were exposed to 1200 eV hydrogen ions in the combined environments test chamber. These included a specimen sintered at 1700°C for 12 hours which came from a batch picked up at Langley Research Center on 23 September and a specimen sintered for greater than 24 hours at 1700°C from a batch received on 2 September. Again there was no attempted made to mass separate the ion beam which probably consisted of 25 percent protrons and 75 percent heavier hydrogen ions. The former sample was exposed to a fluence of 8×10^{15} p/cm^2 at a flux density of 5×10^{10} p/cm^2/sec. Figure 5 shows pre and post exposure spectral reflectance curves for this sample from data that was obtained in situ. The change in solar absorptance was 0.02. The other specimen was exposed to a fluence of 5.6×10^{15} p/cm^2 at a flux density of 3.5×10^{10} p/cm^2/sec and its solar absorptance change was 0.015. While these specimens did damage more than the first specimens subjected to hydrogen ion bombardment, these changes are not large by comparison with changes for ZnO and some other commonly used pigments.

Twenty of the 5 percent calcia doped sintered hafnia specimens were taken to Denver Research Institute to be converted into powders of a size useful as pigments for thermal control coatings. Work there was accomplished under the direction of Dwight Moore. Two different methods were used to reduce the sintered pellets to powder form. Table 1 lists the processing data for the powders developed by the two methods.

Samples of both powders designated DRI H-1 and DRI H-2 were exposed to 52 equivalent sun hours (ESH) of ultraviolet radiation in vacuum and pre and post exposure spectral reflectance data were obtained in situ. Figures 6 and 7 present changes in spectral absorptance curves for the two specimens. Samples H-1 and H-2 had solar absorptance increases of 0.06 and 0.05, respectively. It is notable (fig. 8) that the initial absorptance of these powdered specimens which were prepared by pressing into a sample cup, is much lower than that of the sintered pellets from which they were made. The reasons for this require further analysis.

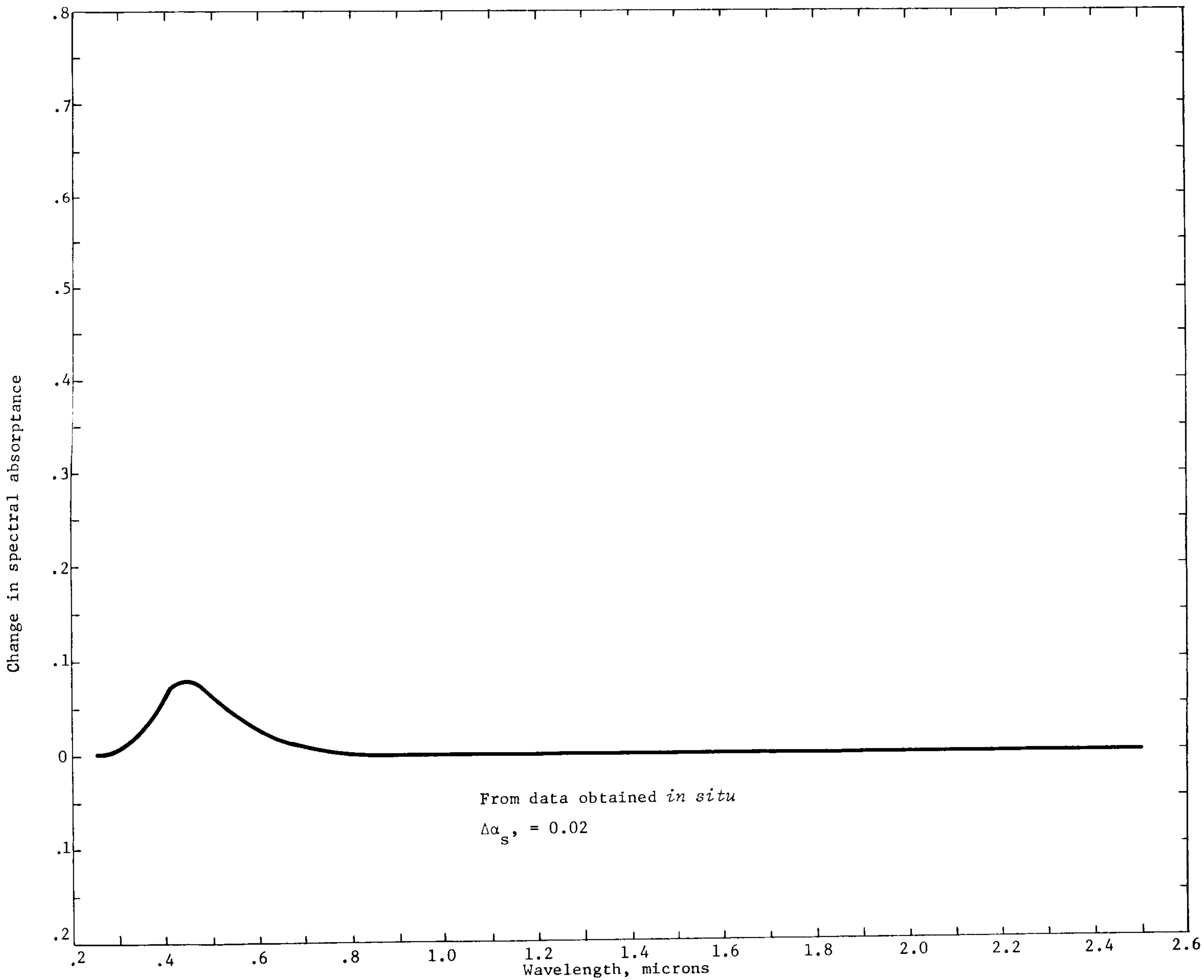

Figure 5.- Effect of 1.2 keV Hydrogen Ions (8 x 10^{15} p/cm^2 at 5 x 10^{10} p/cm^2/sec) on a 95% HfO_2, 5% CaO Sample Sintered at 1700°C for 12 Hours (Batch of 9-23-69)

TABLE 1.- PROCESSING DATA FOR HAFNIUM OXIDE PIGMENTS

	Sample H-1		Sample H-2	
(A) Processing	(1) Pellets crushed with sintered alumina mortar and pestle to approx. -60 mesh. (2) Unscreened material passed through fluid energy mill lined with polyurethane. (3) Resulting pigment heated at 800°C for one hr. in air in zirconia boat.		(1) Pellets crushed in steel motar to pass a 60 mesh brass screen. (2) Screened material leached in 10% HCl for one hr. at 85°C. (3) Washed and dried -60 mesh material passed through fluid energy mill. (4) Resulting pigment heated at 800°C for one hr. in zirconia boat.	
(B) Yield				
Wt. of Pellets	37.6 gms		37.6 gms	
Wt. of Samples for Analyses	2.0		2.0	
Wt. of Pigment sent to MMC	27.3		26.0	
Processing Loss	8.3		9.6	
(C) Particle Size of Pigment				
Estimated Ave. Part. Diam.	2		2	
Diam. of Largest Particle	15		4	
% of Particles 5	99.94		100.	
D Spectro Chemical Analyses in ppm	H-1A Coarse Mtl.	H-1B Pigment	H-2A Coarse Mtl.*	H-2B Pigment
Fe	26	27	350	25
Cu	10	14	140	10
Al	1100	1000	120	140
Si	60	95	110	95
Mg	100	125	120	150

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*Sample for analysis taken before acid leaching operation.

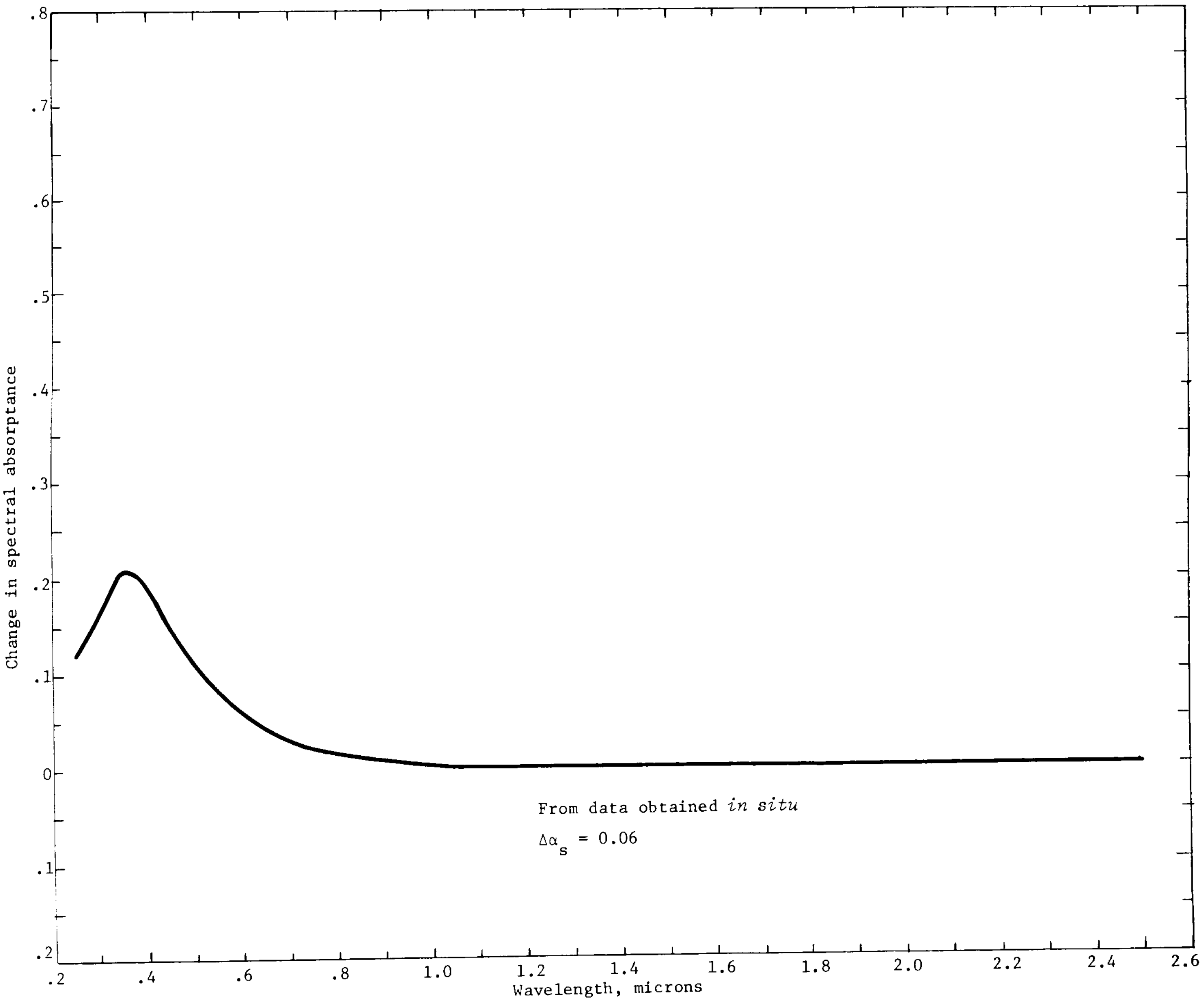

Figure 6.- Effect of 52 ESH of Ultraviolet Radiation on DRI H-1 Powdered 95% HfO_2, 5% CaO

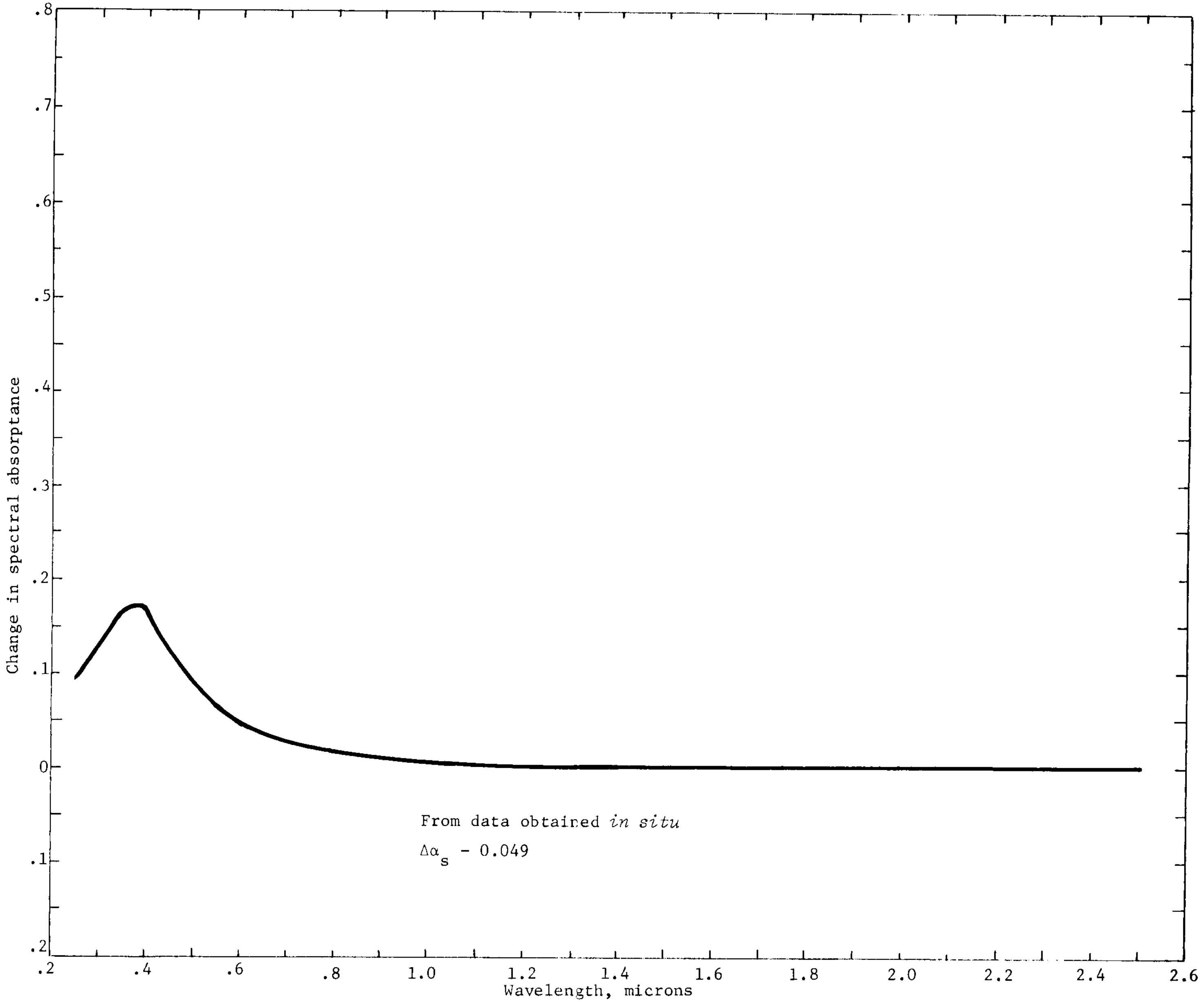

Figure 7.- Effect of 52 ESH of Ultraviolet Radiation on DRI H-2 Powdered 95% HfO_2, 5% CaO

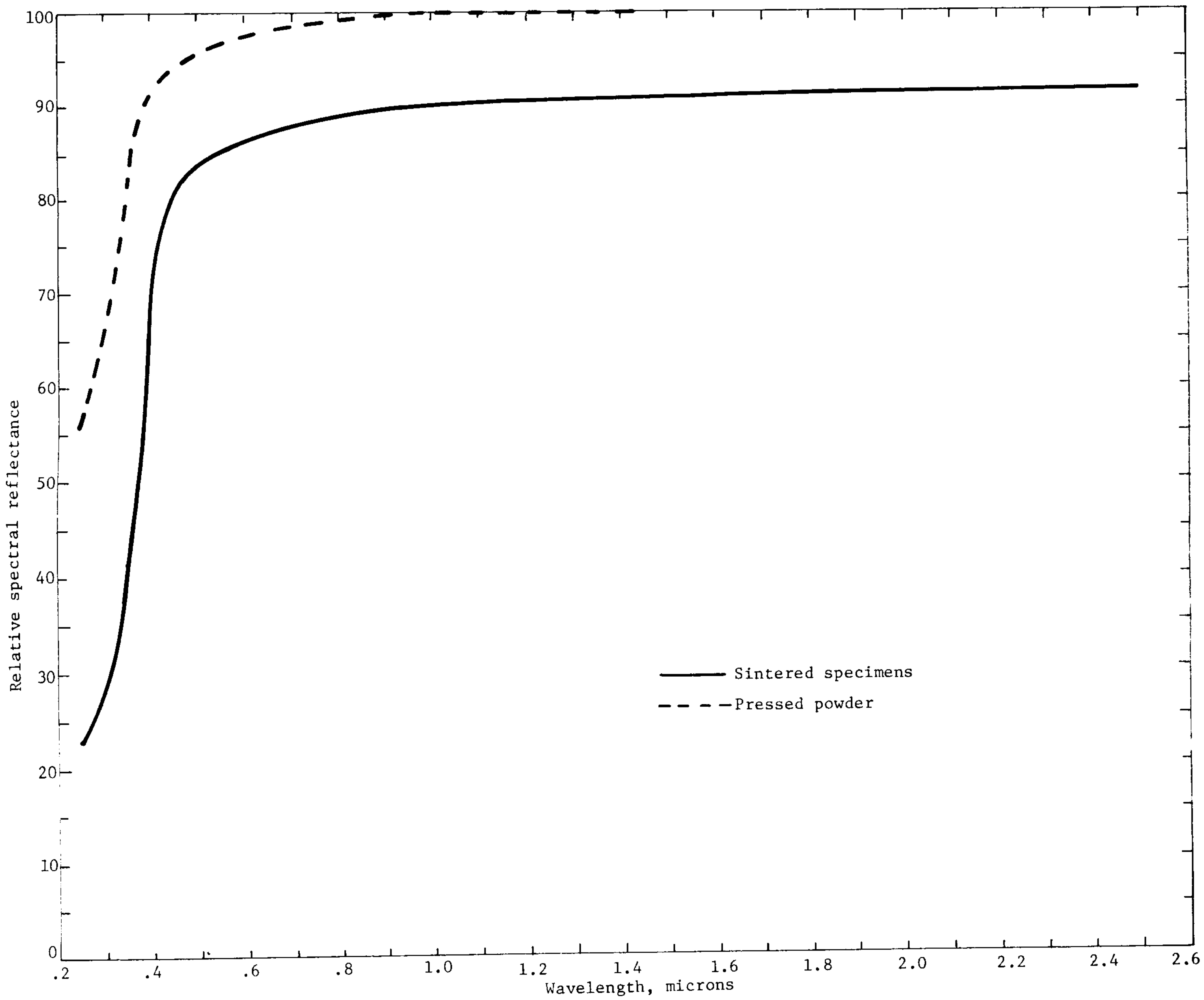

Figure 8.- Typical Spectral Reflectance Curves for a Sintered 90% HfO_2, 5% CaO Specimen and for a Pressed Powder Specimen Made from It

The reason for the considerable optical damage to the powdered samples from ultraviolet exposure is not immediately available. In part it may be due to impurities added in the processing. Aluminum is the only impurity, however, which appears to be present in abnormal quantity in both of the finished powders. Its level in the H-2 powder is surprising. The impurities which are gained in the processing would have no way of getting into the hafnia structure but would exist as separate oxides mixed with the hafnia. Defects introduced in the crystal structure and the large increase in surface area may in part account for the damage. X-ray diffraction analysis confirmed the cubic structure of the powders. Further investigation is necessary in order to analyze the problem.

More recent specimens which were hung in a basket made of irridium-rhodium wire in the alumina muffle tube in the furnace have a tan surface discoloration which is very evident as an absorption band in spectral reflectance curves. A sample exposed to ultraviolet radiation suffered quite a bit of damage.

Cryochemical synthesis of fine-particle HfO_2 and calcia-doped HfO_2.- The cryochemical method for preparation of fine-particle materials was developed by personnel at the Bell Telephone Laboratories and is characterized by an unsual amount of control over the properties of the final product (ref 1). The product is controlled with respect to composition, particle size and size range, and chemical homogeneity.

The process requires four basic operations: (1) mixing; (2) freezing; (3) sublimation; and (4) decomposition. In the first operation analyzed stock solutions of suitable salts of the various metal components are apportioned either by weight or volume to give the desired composition. The starting solution prepared in this way is quick-frozen by injection as a fine stream into a bath of hexane chilled to a low temperature in a mixture of dry ice and acetone. On freezing, the tiny droplets retain their spherical form. After all of the solution is frozen, the mass of frozen spheres is separated from the hexane by screening. The frozen product is then transferred to a prechilled tray which is placed in the refrigerated chamber of a freeze-drier apparatus. After the chamber is evacuated heat is supplied to effect the sublimation of the water in the product. The free-flowing, dust-free spheres of anhydrous salt which are the result of the freeze-dry process are then transferred to a furnace for the final step-thermal decomposition of the salt or mixture of salts.

The chief advantage of the method for the preparation of a pure oxide such as HfO_2 is the fine-particle state of the product. This eliminates the need for grinding which may cause strain or surface defects and also contamination of the material. For the case of calcia-doped HfO_2 an additional advantage is the assurance of uniform distribution of the dopant. Since the two components are mixed as solutions, mixing takes place at the atomic level.

Since a solution of a salt of hafnium is the required starting material for the preparation of HfO_2 cryochemically, the high purity oxide available had to be first converted to a soluble compound. Acid and alkali fusion methods are standard techniques for the extraction or separation of titanium, zirconium, and hafnium from their ores and seemed suitable for this conversion. Acid fusions are usually carried out with either the bisulfate or pyrosulfate of potassium ($KHSO_4$ or $K_2S_2O_7$) and the titanium, zirconium, or hafnium eventually obtained in solution as the oxysulfate or sulfate. In alkali fusions, either the hydroxide, e.g., KOH, or the carbonate, e.g., K_2CO_3 is the reagent and the product is an alkali titanate, zirconate, or hafnate. These compounds are decomposed by sulfuric acid to form solutions of oxysulfates or sulfates.

For converting the spectrographic grade HfO_2 (99.9+%, Wah Chang) to the sulfate, both acid and alkali fusion methods were examined. When a 20 gram portion of oxide was fused with an excess of potassium pyrosulfate in a quartz crucible, problems were encountered in processing the hard fused product for the desired hafnium sulfate. Turning to the examination of alkali fusion methods using 10 gram portions of HfO_2, problems of a somewhat different nature were encountered. When the oxide was fused with KOH in a nickel crucible, attack on the crucible by the alkali was so severe that contamination by nickel seemed a certainty. With the use of K_2CO_3 in a platinum crucible, the likelihood of contamination was minimized, but the reaction appeared far from complete. A relatively large quantity of insoluble residue remained after an attempt was made to dissolve the fusion product in dilute H_2SO_4.

Although considerable difficulty was encountered in extracting the hafnium sulfate formed in the pyrosulfate fusion from the hard fused mass of by-product potassium sulfate and excess pyrosulfate, it was eventually accomplished and results indicated that nearly all of the oxide had been converted. The hafnium sulfate was recovered by the break-up and grinding of the fused mass with a mortar and pestle followed by extraction with dilute sulfuric acid and filtering. The residue from extraction was subjected repeatedly to the process of grinding, extraction, and filtering until only a small amount of finely divided insoluble residue (presumably unreacted oxide) remained.

When the problems were encountered in the conversion of the high-purity hafnium oxide to the sulfate, a 100 gram sample of hafnium sulfate (anhydrous) was purchased from K & K Laboratories (Plainview, N. Y.)

A 35 gram portion of this material was used in the preparation of the starting solution for the first attempt to prepare HfO_2 cryochemically. In the preparation of this solution it was found that the material contained some insoluble solids. This was presumably either unreacted oxide or oxide produced by decomposition of some sulfate in the heating required to drive off excess H_2SO_4 in the final step of the sulfate preparation. The insoluble material was removed by filtration and the clear filtrate brought to a volume of 75 ml by the addition of water.

The sulfate solution was injected into the cold hexane bath, the hexane drained off, and the flask containing the frozen product transferred to a freezer for overnight storage. The next morning the product was transferred to a prechilled Petri dish and placed in the refrigerated chamber of a commercial freeze-drier unit. Efforts to remove more than a little water from the frozen ice-sulfate mixture, however, were unsuccessful and the material showed signs of melting despite the low system pressure as soon as the chamber was allowed to start warming to ambient temperature. Apparently the sulfate had not crystallized in the freezing step but had formed a glass from which the water could not be removed by sublimation.

Proceeding on the assumption that the cause of failure was impurities in the hafnium sulfate, possibly free sulfuric acid not removed in the final heating of the sulfate during its preparation, a second attempt was made to prepare the oxide cryochemically this time using sulfate which had been purified by recrystallization. A thirty-five gram portion of K & K hafnium sulfate was dissolved in water, the insolubles filtered off, and the hafnium sulfate tetrahydrate, $Hf(SO_4)_2.4H_2O$, crystallized by the addition of 1 part concd. sulfuric acid to 2 parts sulfate solution. The heavy crystalline precipitate was filtered, the adhering sulfuric acid removed by washing with acetone, and dried in air.

The white crystalline material (23.5 grams) recovered was dissolved in 50 ml of water and the solution used as starting material for the second attempt to prepare HfO_2 cyrochemically. The procedure was essentially the same as that used in the earlier attempt with the exception that the frozen product was transferred to a freeze-drying apparatus immediately after it was prepared and drained of excess hexane. There was no overnight storage of the frozen product in a freezer before attempting the freeze-dry operation.

Results in this second effort, however, were much the same as in the earlier experiment. The frozen material could not be freeze-dried, again behaving as a glassy substance rather than a well-crystallized mixture of ice and sulfate.

In a conversation with Dr. Schnettler of Bell Labs, it was learned that he had experienced similar difficulties in attempts to prepare Y_2O_3 from yttrium sulfate solution and in the use of certain nitrate starting solutions (ref 2). These solutions apparently resist rapid freezing and tend to become viscous supercooled liquids or glasses. In the case of single component systems, e.g., the preparation of Y_2O_3 from yttrium sulfate, the difficulty was readily by-passed by the slow freezing of the bulk solution in the refrigerated chamber of the freeze-drier prior to freeze-drying. Thus, the quicker freeze injection step is eliminated but the freeze-dried product was still obtained in a fine-particle state. This approach is also applicable to multi-component systems, if care is taken to avoid the possibility of precipitation of one or more of the salts because of reduced solubility at temperatures between ambient and freezing. This means that the starting solution would have to be sufficiently dilute to minimize the possibility of any of the salts separating out before freezing as the solution is cooled from ambient temperature.

Coprecipitation synthesis methods.- In view of the difficulties encountered in attempting to prepare even the pure hafnium oxide cryochemically, it seemed advisable to explore another possible route to fine-particle calcia-doped hafnium oxide. The method selected for study was that of coprecipitation of the hydroxides of hafnium and calcium.

To a hot solution (70-75°C) of hafnium oxycholoride containing the appropriate amount of calcium chloride, an excess of potassium hydroxide solution was added dropwise with continuous stirring to coprecipitate the hydroxides of hafnium and calcium. Unfortunately, there was not enough time to complete the processing of this material and evaluate it before the end of the program.

<u>Heat treatment</u>.- The possibility of improving the radiation stability of spectrographic grade hafnium oxide by heat treatment was investigated. A 10 gram sample was placed in a platinum crucible with a platinum lid. The cruicible was positioned in the alumina muffle tube in the Centorr laboratory furnace and heated at 1700°C for 15 hours, then cooled. The material tended to sinter into a semi-hard mass and had to be pulverized in an alumina mortar and pestle. No impurity analysis has been made but it is possible that the material may contain some platinum since condensed crystals of platinum were found in the muffle tube.

A sample of the powder after heat treatment was subjected to 51 ESH of ultraviolet radiation from the Spectrolab X25L solar simulator to compare its stability with that of a sample of powder from the same lot but not heat treated. The change in solar absorptance for the untreated sample was 0.11 and for the heat treated sample was 0.08. These results should not be considered as conclusive evidence that heat treatment is advantageous.

RECOMMENDATIONS

The most important result of the study reported here was the determination that hafnia can be made stable, in its optical properties, to space radiations by the addition in solid solution of a sufficient amount of calcia to stabilize the phase transformations. This section of the report discusses recommendations for a continual study effort designed to produce a stable thermal control pigment based upon that discovery.

Several other techniques for reducing sintered pellets of doped hafnia to powders should be investigated in an effort to find a method which will not affect the space radiation stability. The reasons for change in stability, e.g., addition of impurities or defect production due to grinding should be determined.

Other methods of synthesizing the doped hafnia should be fully investigated such as cryochemical and coprecipitation techniques followed by heat treatment. The intimate mixture of hafnium and calcium compounds attained in each particle prior to heat treatment should eliminate the need for high pressure forming to obtain intimate contact between particles as required in the method now being used. Although some sintering normally occurs during heat treatment even without pressure less energy should be required to break up the resultant mass.

Doping of the hafnia with yttria should be more thoroughly investigated to see if there is any advantage to use of yttria versus calcia as the stabilizer.

Zirconia should be investigated with both calcia and yttria as dopants to establish if it can be made radiation stable by the same techniques as those applied to the hafnia. Zirconia is chemically similar to hafnia, is also a polymorph and has the advantages of being cheaper and lighter.

The compatability of the stabilized hafnia and zirconia with available binder materials, both organic and inorganic, should be thoroughly investigated both from the standpoint of formulation and possible interactions affecting radiation stability.

Characterization of materials as to cation and/or anion impurities, crystal structure, crystal defects, defects stoichiometry and particle size should be accomplished wherever this will add to an understanding of results of the study.

FACILITIES

Ultraviolet Test Facility

The ultraviolet test chamber is a small vacuum chamber pumped by an Ultek 25 liter/sec DI ion pump. Rough pumping is accomplished with cryo-sorption pumps. A single test specimen can be mounted against a metal heat sink through which fluids can be forced to establish the temperature of the sample. Water at approximately 298°K was used as the coolant for this program. The heat sink can be moved vertically and positioned behind an ultraviolet grade quartz window for exposure to solar simulation. It can also be lowered to position the test sample in a quartz tube which is part of the vacuum system. A standard Gier-Dunkle integrating sphere attached to a Beckman DK-2 spectrophotometer can be positioned over the quartz tube so the sample is centered in the sphere. In this way spectral reflectance data can be obtained in situ. There are two such chambers in the laboratory.

During the early phases of the study a solar simulator was used which utilized a 2.5 kilowatt xenon compact-arc lamp and a mirror and lens system to focus the radiation from the lamp on the chamber window. During most of the Phase E tests a Spectrolab X25L solar simulator was used in order to enhance the quality of the tests.

Combined Environment Test Facility

The vacuum system of this facility consists of the test chamber, an ion source - mass separator unit, and a mass spectrometer. The latter is usually used to evaluate the effectiveness of the mass separator in producing a pure proton beam. The vacuum system is pumped by an Ultek 500 liter-sec ion pump and rough pumped by sorption pumps. It is a very clean system. A Faraday cup is available for measuring ion beam currents. Four samples can be exposed to the ion beam while being maintained at a fixed temperature by circulating a fluid through individual heat sinks. Two of the samples can be exposed to solar simulation. The specimens can be removed from the heat sinks and transferred in situ to a vacuum integrating sphere, which is optically coupled to a Beckman DK-2 spectrophotometer, for spectral reflectance measurements.

Other Facilities

Other facilities used during the course of the study included a Centorr laboratory furnace, a freeze drier and other equipment for material synthesis, and apparatus for formulating and applying coatings.

REFERENCES

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