RESEARCH ON LOW DENSITY THERMAL INSULATION MATERIALS FOR USE ABOVE 3000°F

Fourth Quarterly Status Report

Contract NASw-884

National Beryllia Corporation
Haskell, New Jersey

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National Aeronautics and Space Administration

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for the Period October 1 through December 31, 1964

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ABSTRACT

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Experiments using ZrO_2 polycrystalline fibers as a structural reinforcement for ZrO_2 foams have demonstrated the feasibility of such a concept and indicate that substantial improvements may be shown in foam strength.

Preliminary data on Mo-containing ZrO_2 foams show considerable improvement in thermal insulation performance when compared with plain calcia stabilized ZrO_2 foams of similar density. Author

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1. INTRODUCTION

This is the fourth quarterly report of Contract NASw-884 on the subject, "Research on Low Density Thermal Insulation Materials for Use above 3000^{o}F." This program is a continuation of work performed on Contract NASr-99 which was conducted for seven quarters from April, 1962, through December, 1963.

1.1 Purpose of the Program

Low-density foamed ceramic thermal insulation rapidly loses efficiency above 2400^{o}F due to the transfer of heat through the pores by thermal radiation. The purpose of this program is to study the reduction of this radiation or photon contribution to the thermal conductivity by the incorporation of a thermal radiation barrier phase into a low-density refractory structure. Mechanisms such as absorption and re-radiation by embedded particles, scattering by incorporated phases and reflection by metallic foil radiation barriers are being investigated and evaluated.

1.2 Phases of the Program

The goals of this program are being achieved through the pursuit of the three phases described briefly below with details of the progress made during this quarter discussed in Section II

A. Phase I - Technical Review

Review of previous high temperature heat transfer work, essentially completed during the first quarter, has been continued at a sufficient level of effort to keep abreast of the rapidly changing technology.

B. Phase II - Materials Formulation

The major effort of the program is concerned with the fabrication of low-density, low thermal conductivity materials. Light weight pure oxide ceramic matrices have been developed and impregnated with various volume percentages of potential radiation shielding phases introduced by a variety of techniques. Specimens of ceramic oxides whose thermal conductivity have been previously reported have also been prepared for calibration and equipment checkout purposes.

C. Phase III - Experimental Measurements

Evaluation of the thermal radiation barrier concept is being conducted in this phase of the program. A high temperature thermal conductivity test cell, capable of maintaining under steady conditions, specimen hot face temperatures of $4500^{\circ}F$ and above has been fabricated and calibrated. Measurement of the apparent thermal conductivity of the ceramic foam composite test samples is in progress.

2. DISCUSSION

2.1 Phase 1 - Technical Review

A report dealing with theoretical and experimental thermal transfer characteristics of non-opaque oxide ceramic materials at high temperatures has been reviewed. [1] Thermal energy transfer, simplified to the two modes, (1) radiation, and (2) lattice conductivity, is considered in semi-transparent materials such as polycrystalline ceramics. It was established that radiant energy emission from these materials, when used for high temperature applications, is a volume process rather than the surface "emittance" characteristic normally considered.

The emittance of alumina, for example, was shown experimentally to be dependent upon sample thickness and also to vary by a factor of 2 between two specimens of identical composition and size but different microstructure and density in the 2 to 3 micron range. Similarly, a sample of very low porosity and high translucency alumina had a much higher emissivity than normally processed commercial aluminum oxide ceramics. These polycrystalline ceramics, and to an even greater extent the foamed ceramics considered in the present program, contain pores and grain boundaries which act as scattering centers. Radiant energy transfer and other optical characteristics will then be greatly structure dependent in these latter types of materials.

The study concludes that radiant energy scattering assumes overwhelming importance at wave lengths below 5 microns where the absorption coefficient rapidly increases. As a result of this high ratio of scattering coefficient to absorption coefficient, the emissivity is relatively low in the near infrared and very sensitive to composition and microstructure. These observations aid in the understanding of experimental apparent thermal conductivity data obtained on oxide and ceramic foam specimens, both plain and as composites with metal radiation reflecting particles obtained in the current program. The high thermal gradients observed in the experimental composite insulating systems developed are apparently due not only to an increase in thermal resistivity due to the radiation reflecting phases, but also to changes in optical characteristics due, at least in part, to the optically dense materials added.

2.2 Phase II - Materials Formulation

2.2.1 Matrix Material

Mechanical failure of ceramic foam specimens due to the extremely high temperature gradients developed in these insulating systems has become an increasing problem. A series of experiments was therefore initiated to more closely control particle size in an attempt to produce a more dense web between adjacent pores in the foamed ceramic structure. Initial trials indicate some improvement can be made through the use of this approach. Further experiments are scheduled.

An alternate means of increasing mechanical strength of zirconia foams is by reinforcement with fibrous materials. Polycrystalline stabilized zirconia fibers have been obtained and incorporated into oxide ceramic foams. Such fibrous reinforcement has been accomplished in zirconia foamed ceramics using both large mats of zirconia fibers aligned circumferentially within the specimen and by blending many small bunches of polycrystalline fibers randomely within the structure during the foaming operation. Initial experiments indicate the latter method will increase modulus of rupture strength by a factor of 2 and will significantly improve sample performance. Further experiments using this randomly oriented fibrous reinforcement are in progress.

A third approach to increasing the mechanical strength of the matrix material is by the use of alternate refractory compounds. Experiments with zirconium diboride, at the National Beryllia Corporation laboratories in an unrelated experimental program, had indicated that this material may be useful in the fabrication of strong refractory foam shapes. Necessary raw materials have been ordered and experiments will be performed toward this end when they are received.

2.2.2. Composites

Verification of the radiation attenuation effect of zirconium metal in a zirconium dioxide ceramic, as reported by the General Electric Company and described in a previous quarterly report, is in progress. Zirconia metal powder has been received and successfully incorporated within a zirconium dioxide foam sample. Specimens are being sintered in an argon atmosphere to prevent oxidation of the zirconium metal and reduction of the zirconium dioxide. Thermal conductivity data on these systems are not yet available.

The erratic test data obtained on several samples of zirconium dioxide foam, in which molybdenum disilicide is used as a potential thermal radiation barrier phase, has resulted in careful analysis of these systems. X-ray data on composites exposed to very high temperatures (greater than 4000°F) indicates that destabilization of the cubic zirconia results. Diffraction patterns show a major monoclinic phase of zirconium dioxide along with substantial quantities of zirconium silicate and molybdenum metal in addition to the molybdenum disilicide phase initially added. This is in contrast to a similar specimen in which molybdenum metal only was added to the stabilized cubic zirconium dioxide ceramic foam. After exposure to a similar thermal environment, the molybdenum-zirconia specimen remained in the cubic stabilized form with the molybdenum metal still present as such. These data explain the cracking, failure and erratic thermal conductivity values obtained on several duplicate stacks of the molybdenum disilicide composite specimens.

Preliminary experiments were conducted at the Lewis Space Flight Center of NASA in Cleveland on the stability of the zirconium dioxide matrix in a hydrogen atmosphere at elevated temperatures. These data indicate that ZrO_2 remains essentially as such up to its melting temperature of about $4700^{o}F$. X-ray diffraction data show that the slight reduction of the oxide as indicated by a discoloration to a dark gray does not affect the lattice spacing of the cubic ZrO_2 and is probably due to a small oxygen difficiency similar to that frequently observed in titanium dioxide at much lower temperatures in air.

2.3 Phase III - Experimental Measurements

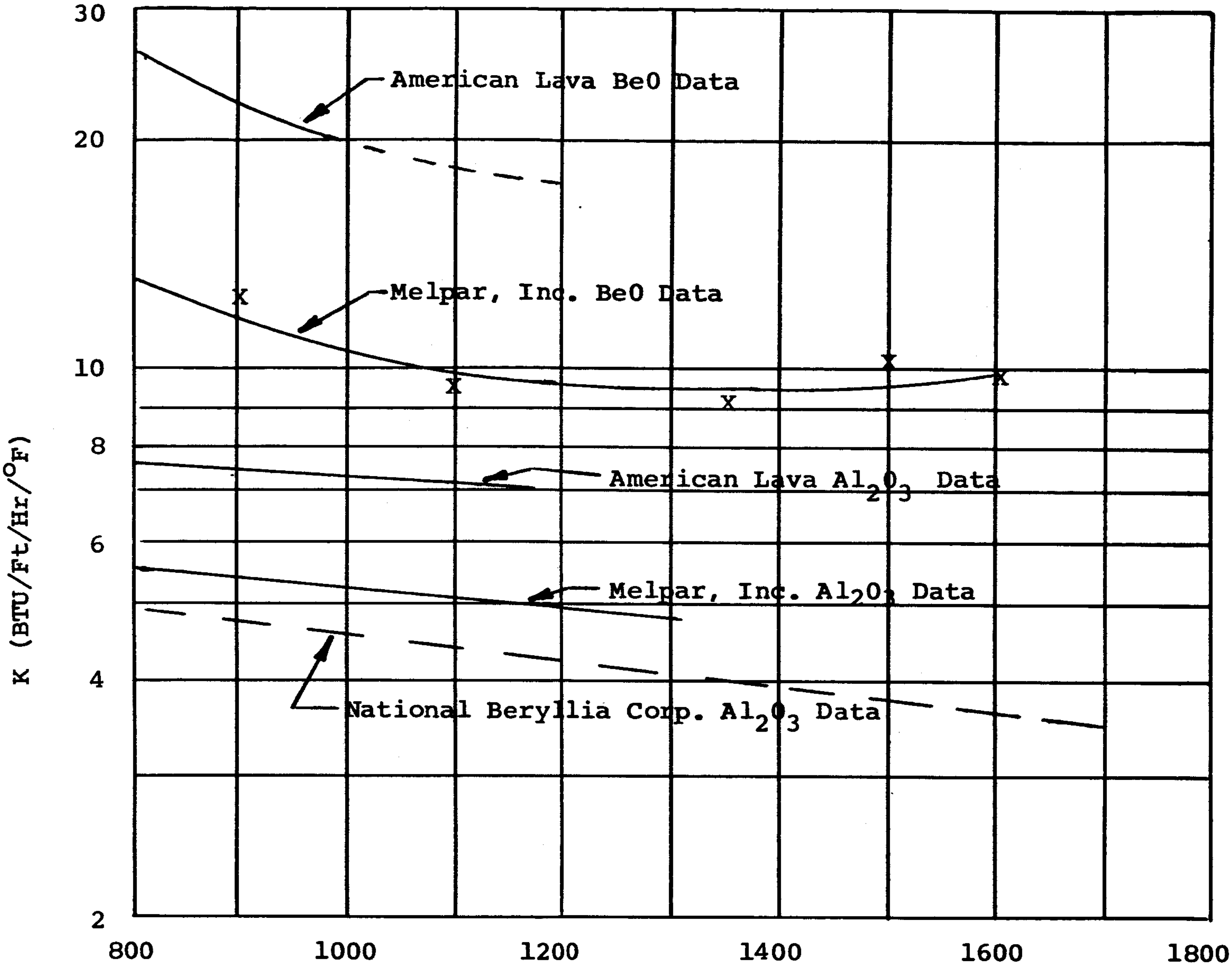
2.3.1 Verification of Test Data

Two measurement runs were conducted on a stack of aluminum oxide specimens obtained on a round-robin test series sponsored by ASTM, Committee C-25. The test conditions were non-ideal for this type of ceramic material. Several of the specimen discs were thermal shocked due either to a high thermal gradient induced in the specimens or too rapid heating by the internal graphite hairpin heater. X-ray diffraction analysis of the surface of the surface of the alumina specimens adjacent to the graphite hairpin heater indicates the formation of aluminum carbide (Al_4C_3) and aluminum oxicarbide (Al_2OC). A composite experimental curve is shown, however, in Figure 1, along with data reported by American Lava Co. and Melpar, Inc. on the same stack of specimens.[2] Data on Brush electronic grade BeO specimens, previously reported in the "Third Quarterly Report" [3] is included to correct the misprint in the K units of Figure 1 of that document.

2.3.2 Composite Measurements

Thermal conductivity test data were obtained on two specimens of foamed zirconium dioxide prepared by different processing techniques as is shown in Figure 2. Run 70 is a verification of previously reported run 68, a normally processed zirconium dioxide ceramic foam of density 0.9 g/cc. Run 71 is a similar composition processed, however, with controlled particle size distribution designed to produce a more dense web between adjacent pores in the oxide foam shape. These process conditions resulted in a density of 1.1 g/cc and an approximate 20 percent improvement in modulus of rupture strength. As indicated in Figure 2, the thermal conductivity of the more dense structure is not significantly higher than the former material.

Also shown in Figure 2 is a thermal conductivity vs. temperature curve determined in run No. 73 for a zirconia foam containing 10 wt.% molybdenum metal. This specimen, having a density of 1.2 g/cc including the molybdenum, has a thermal conductivity approximately equal to that reported in the previous quarterly report for a specimen of Zr36 zirconium dioxide containing 20 Wt.% tungsten metal. The molybdenum in the specimen of run 73 was added by the



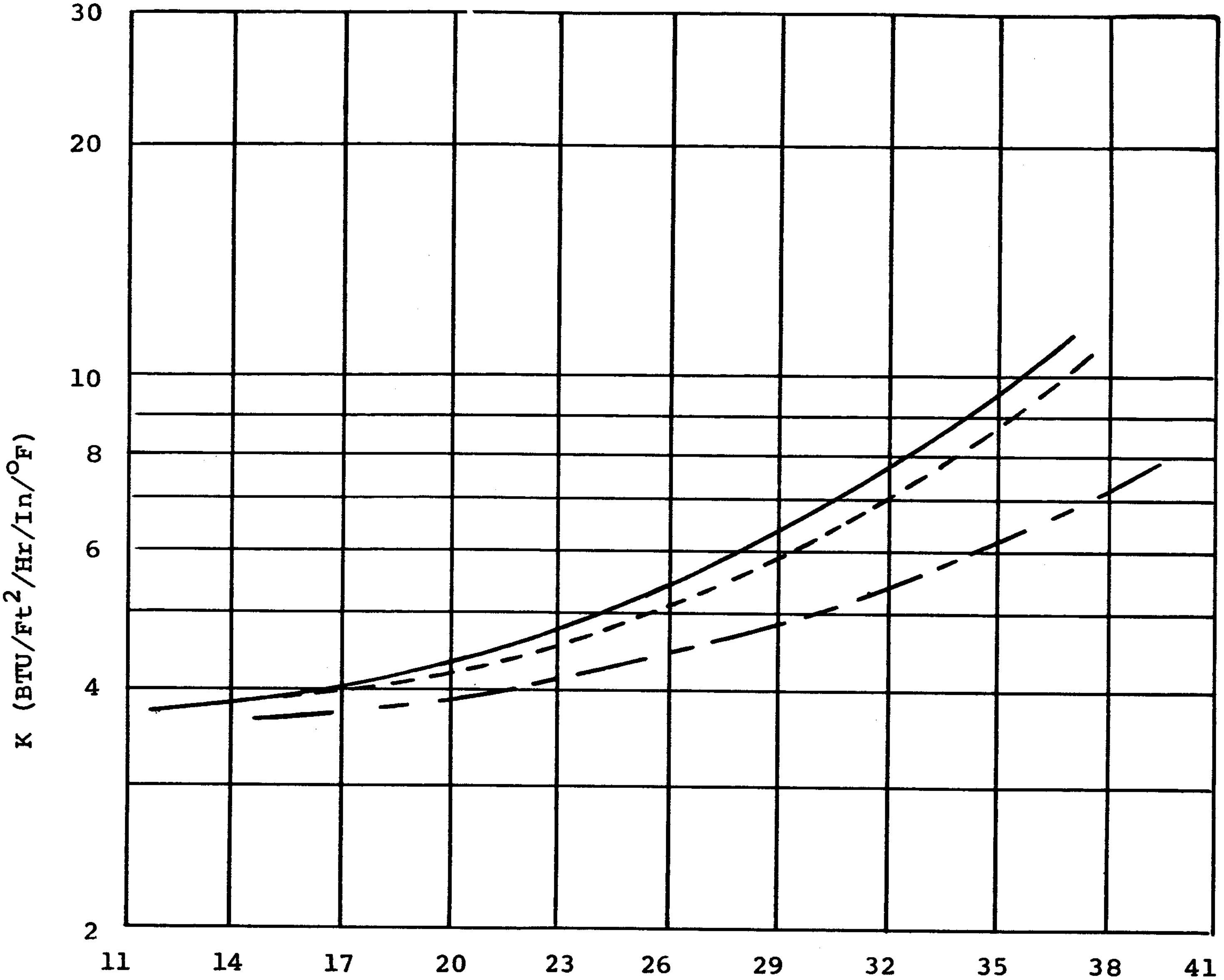
Temperature °C x 100

Results of Round Robin Test on Brush Beryllium Co. Electronic Grade BeO and Electronic Grade Al_2O_3

X - Data points from NASA/NBC radial heat flow apparatus run No. 64 on Brush electronic grade BeO.

THERMAL CONDUCTIVITY -VS- TEMPERATURE

FIGURE 1



Temperature °F x 100

———— Zr36 foam density 1.10 g/cc

- - - - Zr36 foam density 0.91 g/cc

— - — Zr36 foam with 10 Wt.% Mo metal

<u>THERMAL CONDUCTIVITY -VS- TEMPERATURE</u>

FIGURE 2

molybdate decomposition technique which tends to concentrate the added molybdenum phase near the surfaces of the specimen rather than homogeniously throughout the structure. The relative effects of the thermal reflecting mechanism, due to the added phase, and the surface emissivity changes, due to the opaque additions, have not yet been resolved.

3. PROGRAM FOR NEXT QUARTER

The development of foam structures of improved physical strength will be continued, both fiber reinforcement of zirconium dioxide foams and foams of alternate refractory compounds will be evaluated.

Specimens of zirconium dioxide reinforced with zirconia fibers and containing the more successful thermal radiation barrier phases examined to date will be prepared and measured in the thermal transfer cell. Measurements of the zirconia foam specimens containing zirconia metal powder will also be measured in the thermal conductivity test apparatus. The compatibility of zirconium diboride with zirconium dioxide with a variety of atmosphere and thermal conditions will be evaluated. Ceramic foams of pure zirconium diboride will be developed if possible and foams of zirconium dioxide containing zirconium diboride as potential thermal radiation barrier phases will be fabricated, evaluated and measured.

REFERENCES

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3. K. H. Styhr, "Research on Low Density Thermal Insulation Materials for Use Above 3000°F" Third Quarterly Report, Contract NASw-884, National Beryllia Corporation, October, 1964.