RESEARCH ON THERMAL TRANSFER PHENOMENA

Final Report

for the period January 1 to December 31, 1965

Contract NASw-1197

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Haskell, New Jersey

To:

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National Aeronautics and Space Administration
Washington, D. C. 20546

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ABSTRACT

This report summarizes previous research under Contracts NASr-99 and NASw-884, and constitutes the final report on Contract NASw-1197. These contracts covered a continuing four-year program with the object of developing low density thermal insulation for use at temperatures above 3000°F. The initial proposals included the investigation of various means of reducing the radiation component of heat transfer at high temperatures, such as by the incorporation of thermal radiation barrier phases into the pores of foamed ceramic structures. These latter attempts were in general unsuccessful.

The methods proposed in the present contract for improving the strength of calcia-stabilized zirconia foams by zirconia fiber reinforcement, metallic additions, changes in particle size distribution and other strengtheners did not result in any significant increase. Change to magnesium oxychloride or oxysulfate bonds enabled foams to be made and sintered at 1550°C which exhibited room temperature strength of more than twice the former system and which retained their strength up to 2500°C hot face temperatures. Strength is directly affected by bulk density, and both properties can be varied by proper control of compositional and processing variables.

Reconsideration of all raw thermal conductivity data led to the conclusion that gradients which included the heater temperature are subject to temperature dependent errors which decrease at higher temperatures. Use of longer thermal gradients and an averaging technique permitted the construction of smooth average thermal conductivity curves for both calcia- and magnesia-stabilized foams. The use of mean temperatures through a gradient did not permit direct determinations for temperatures higher than 3700°F, but all curves converge above 4000°F as errors in using heater temperature approach zero. Average co-efficients are given for 500°F intervals, which in individual specimens are often subject to variation by a factor of two, sometimes because of structural failure within the specimen.

During the first three years of this program, K. H. Styhr served as Project Engineer under the direction of P. S. Hessinger,

ABSTRACT (CONT'D)

Vice President and then Manager of Research and Development and E. Ryshkewitch, Director of Research. For most of the final year, W. C. Allen served as Project Engineer assisted by D. Werner and H. Greenwood, under the direction of Dr. W. A. Taebel, Manager of Research.

Report prepared by Walter C. Allen
Dr. W. C. Allen

Report approved by
Dr. W. A. Taebel

K. H. Styhr

P. S. Hessinger, Vice President
Manager of Technical Operations

bj

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1. INTRODUCTION

This is the final report on Contract NASw-1197, an extension of previous contracts NASr-99 and NASw-884. The present contract, awarded for the year 1965, has two stated objectives:

1) Research on composite insulation leading to increased reliability in thermal measurements. In practice, this has meant developing increased strength so that integrity was maintained up to the highest possible temperatures.

2) Final determination of thermal conductivity of these materials up to 4500°F.

2. TECHNICAL REVIEW

2.1 Contract NASr-99: Research on Low Density Thermal Insulating Materials for Use Above 3000°F.

This contract and an extension ran from April 1, 1962 through December 31, 1963. Seven quarterly reports were issued (Ref. 1.) Its program consisted of three phases:

1) Technical review of heat transfer mechanisms and measurement;

2) Fabrication of low density, low thermal conductivity materials for use in space vehicles at temperatures above 3000°F, with investigation of barrier phases to reduce the radiation component of heat transfer; and

3) Measurement of heat transfer and other properties of these composites.

The technical review resulted in a bibliography of heat transfer phenomena; a presentation of the theory of thermal conductivity, with equations; a summary of measurement methods and apparatus; and a discussion of the properties of materials, and the effects of impurities, defects, and pores. Subsequent references have been reviewed as they appeared.

Of the initial list of candidate materials, ThO_2, MgO, ZrO_2 and BeO have the highest temperature capabilities in that order. However, thoria is radioactive, and has a high specific gravity; beryllia, as a foam, could be hazardous because dust would easily be created; and magnesia is susceptible to hydration and is not stable in reducing atmospheres or in vacuum at high temperatures. Zirconia, which must be stabilized to prevent disruption at phase transformation temperatures, remains as the most attractive candidate material. Some work was done on MgO, thoria, and multiple oxides, in the preliminary evaluation stage, but most of the work has been carried out on zirconia-base composites.

A procedure was developed to produce foam structures using organic lathering agents of the glucoside type. A fast-setting calcium sulfate-base plaster was incorporated to rigidize the zirconia foam structure at room temperature, and to provide CaO as a stabilizer at high temperature.

Several methods of incorporating a barrier phase were investigated: vacuum impregnation of a carbon-containing material into the pores; pyrolytic deposition of carbon or metal onto the pore surfaces; incorporation of aromatic hydrocarbon particles into the slip to yield carbonaceous particles after firing; incorporation of flake graphite in the slip; and impregnation of the foam with solutions yielding W or Mo on firing.

The measurement phase was largely devoted to the successful design of a thermal conductivity apparatus, based on the radial heat flow principle, using a central hairpin heater capable of temperatures to at least 4500°F.

Zirconia foams were found to have densities in the range 0.7 to 1.3 g/cc, or about 12 to 23% of theoretical. Thermal conductivity curves showed an upward slope from 3-5 BTU/ft^2/hr/in/°F at 2000°F to 10-15 at 4000°F, for zirconia foams with no barrier phase, as compared to 10-12 and 15-18 respectively for 85% dense zirconia.

Barrier phases, added to scatter and re-radiate thermal energy and reduce the radiative component of heat transfer, were only of limited success. Carbonaceous barriers tended to oxidize during firing or testing, and it was impossible to form a "cloud" of particles which would stay in suspension within the pores. Metallic additions provided a different structure than was originally desired, and although slight improvements in heat transfer coefficient were noted in some cases, the same range of conductivity values was obtained as with the plain zirconia foam.

Strength of the foams at high temperature was the limiting factor in obtaining heat transfer measurements. Few reliable data points could be obtained higher than 4000°F because of cracks opening through the sight holes.

2.2 Contract NASw-884: Research on Low Density Thermal Insulation Materials for Use above 3000°F.

This contract ran for the calendar year 1964. Four quarterly reports were issued (Ref. 2.) Its objective was to continue to develop and evaluate fabrication techniques for special ceramic composite insulating materials, capable to the 4500°F range. Emphasis was to be placed on methods of developing porosity and introducing radiation barrier phases, and on determining effects of pressure, atmosphere, temperature and time on heat transfer characteristics.

Varying properties of the zirconia raw materials, from batch to batch and supplier to supplier, prevented reproducible foam properties. A reliable source of high-purity, reactor grade zirconia was finally established, and allowed foams to be made reproducibly.

Work continued on developing means of incorporating barrier phases: adding tungsten flake or tungsten-coated hollow spheres of zirconia; reduction of Mo or W from molybdates or tungstates impregnated into the pores; addition of molybdenum disilicide; and deposition of tungsten into the pores from a reducible halide gas. Strength was improved by adding zirconia fibers to the composite.

To assess our method and apparatus for measuring thermal conductivity, dense specimens of electronic grade BeO and Al_2O_3 ceramics were also tested by two other organizations. Our data showed excellent fit with one of the other curves.

Thermal conductivity curves were similar in shape and range of values as before, with barrier phase additions providing in some cases slightly reduced heat transfer values.

Molybdenum disilicide additions were detrimental in destabilizing the zirconia and the forming zirconium silicate, causing cracks to form during testing. Low resistance to thermal stresses during conductivity measurements continued to be a major obstacle in obtaining values above 4000°F.

Four technical papers were presented at various conferences as a result of the aforementioned work (Ref. 3.)

2.3 Literature Survey: Progress reports on the current contract were issued for the first three quarters of 1965 (Ref. 4.)

A report prepared under Contract AF 33(657)-11286 by Ipsen Industries, Inc., Rockford, Illinois (Ref. 5,) described methods for the reproducible manufacture of zirconia and other foams, with densities in the range 18-45% of theoretical and good resistance to thermal shock. Their foams were substantially more dense than our foams, and suffered from very low strength in relation to density (160-200 PSI modulus of rupture, for 18-27% dense foam.) The thermal conductivity coefficient was 6 to 7 BTU/ft^2/hr/in/°F at 2600°F, the maximum temperature reached.

Pirogov (Ref. 6) produced a zirconia foam, stabilized with 15% gypsum, in the relative density range 35-41%. However, these pieces cracked badly on firing and were crushed and re-cemented into useful articles by a zirconium sulfate chemical bond.

Long and Barr (Ref. 7) developed a lightweight composite for radomes, from hollow alumina spheres bonded by liquid phase sintering using a magnesium pyrophosphate-alumina entectic. Densities were in the range 0.9 to 1.4 g/cc, or about 22-35% of theoretical.

Sklarew (Ref. 8) described a zirconia-base refractory coating bonded with ammonium di-hydrogen phosphate and fluorophosphoric acid.

Weber (Ref. 9) reviewed the literature on zirconia; the wide variation in compositions and properties of commercial grades is emphasized; for example, Hf content ranges from less than 100 ppm to 2.4%. Prefiring zirconia to 2000°C in vacuum will "boil off" a large proportion of certain common impurities such as Al, Ca, Fe and Mg.

Weber also reviews the stabilization of zirconia which is pertinent to this program. Pure ZrO_2 is monoclinic in crystal structure at room temperature, transforming to tetragonal in the range 1000-1200°C on heating. On cooling, the transformation is reversible but shows a hysteresis (700-1050°C.) In a polycrystalline body, this transformation is accompanied by a volume change of about 9% causing fracture and failure. It can be effectively prevented by solid solution with other oxides which form a cubic crystal structure that does remain stable with changing temperature. Among the many different oxides which stabilize ZrO_2, CaO, MgO, and Y_2O_3 are the most widely used. The phase diagrams show that about 8 wt percent CaO, or 4 wt percent MgO is required for complete stabilization.

Smoot and Ryan (Ref. 10) determined the limits of initial detection of the cubic phase in zirconia-base systems. With 6% MgO addition, cubic zirconia is first detected at 900°F; with CaO and MgO together, at 1000°F, but with 3% CaO alone, at 1500°F. Other additives require higher percentages and/or higher reaction temperatures; it is desirable to keep the percentage low to minimize lowering the liquidus temperature.

Ryshkewitch (Ref. 11) has patented an alternative method of stabilizing zirconia, using fluorides; this is claimed to retain stability over a wide temperature range.

Smoot and Ryan also indicate that solid solution is greater at higher temperatures, with exsolution of the transformable phase on cooling. This is consistent with phase equilibrium considerations, and suggests that de-stabilization can occur. De-stabilization has in fact been observed (Refs. 12, 13, 14.) Duwez et al (Ref. 12) noted that zirconia stabilized with more than 16 mol % MgO reverted to the monoclinic form with exsolution of free MgO, after thermal cycling, but that zirconia stabilized with similar amounts of CaO remained as the cubic form in the same circumstances. The impurity level of the zirconia starting material was stated to be "less than 1%;" but the identity of the particular impurities is not disclosed and it is suspected that this one percent does not include hafnium oxide.

Buckley and Wilson (Ref. 13) noted destabilization of zirconia refractories, 80% cubic and containing 4% CaO, in a heat exchanger at Langley Field, in a zone subject to thermal cycling between 1600-2000°F. When the original refractory had been 100% cubic, presumably because of higher CaO content, it was not affected by thermal cycling. The authors postulate that volume changes during inversion cause mechanical pressure on neighboring grains, favoring expulsion of the large Ca ions from solid solution in the lattice.

Smoot and Whittemore (Ref. 14) confirm that zirconia which is not wholly stabilized will partially revert to additional monoclinic phase on thermal cycling, whereas fully stabilized zirconia remains wholly cubic. They conclude that this is not due to expulsion of Ca ions by mechanical pressure, but that impurities having a greater affinity for CaO than for ZrO_2 will react to form Ca-compounds and removes Ca from the lattice. This has been confirmed by Hayashi and co-workers in Japan (Ref. 15;) they reported that silica, alumina and titania retard the formation of cubic Ca-Zirconia, and that SiO_2 will destabilize cubic zirconia by combining with the CaO.

The stability of "stabilized" zirconia can, therefore, be affected by the amount and identity of the stabilizing agents and other non-stabilizing impurities, and the temperature levels through which it must be cycled.

3. EXPERIMENTAL WORK

3.1 Research Toward Increased Reliability

Four approaches were suggested in the work statement as a means of increasing the strength of zirconia foams to allow greater reliability in heat transfer measurements:

1) Reinforcement of the composite with polycrystalline stabilized zirconia fibers;

2) Incorporation of metallic zirconium;

3) Optimization of particle size distribution;

4) Development of metallic coatings and strengtheners.

3.1.1 Reinforcement with Zirconia Fibers

The concept of fiber reinforcement has been most successfully applied to plastics, where fiber-glass-reinforced laminates find even household use. Extensions to metal and ceramic matrices with capability for higher use temperatures have also been explored, but commercial applications have been limited.

Fibrous materials have an inherent advantage as reinforcing media because of their high strength. This is due to their surface perfection and freedom from flaws (Ref. 16,) so that the tensile strength of a fiber ideally approaches the theoretical or chemical bond strength of the material.

Accordingly it was felt that fiber reinforcement of foam structures should be investigated. However, the microstructure of a ceramic foam makes this inherently a different problem than that encountered in reinforcing a dense body, where a strong bond occurs between fiber and matrix. Whereas dense fiber-reinforced composites are generally systems of two contrasting phases, a foam for refractory insulation should be single-phase for maximum temperature capability in oxidizing atmospheres. Metallic or carbon fibers might provide excellent reinforcement but would oxidize and be destroyed as useful fibers. Fibers of oxides would survive oxidation, but would react with the matrix oxide, if different, to form intermediate compounds or eutectic liquids and either destroy the foam structure or limit its maximum useful temperature. Zirconia fibers are therefore the only logical choice to reinforce a zirconia foam for increased strength at high temperature.

Zirconia fibers are available from the H. I. Thompson Fiber Glass Company and have been described (Ref. 17.) A supply of "A" grade, stabilized with 5 % CaO, was obtained for this study. A spectrochemical analysis is given in Ref. 17 (page 9,) and is reproduced as Table I, since it is believed to be representative of the material purchased.

Figure 1 is a photomicrograph of these fibers. Diameters are in the range 2-10 microns; according to the manufacturer, these fibers are polycrystalline. Length-to-diameter ratio is generally very high. Many fibers are more than 1000 microns long and they are very flexible. No tensile strength data were given in Ref. 17.

The meaningful data obtained in this phase of the investigation are summarized in Table II. Small additions of zirconia fibers have no significant effect on strength; however, a 5% fiber addition apparently does bring about a significant increase.

Other simultaneous effects are also noted. In series 16-269, those with 2% dextrin generally have higher strengths than those with only 1% dextrin. Firing to 1800°C produces a stronger, but also denser, foam than firing to 1550°C. Thermal conductivities of the two samples measured show slight but perhaps non-significant differences (Ref. 4.)

Although this method of strengthening gave a positive effect at the 5% level, results were not sufficiently encouraging to allow thermal conductivity measurements much above 4100°F. As a high-temperature strengthener, therefore, this method did not satisfy the requirements of this program.

TABLE I

SPECTROCHEMICAL ANALYSIS OF ZIRCONIA "A" FIBERS

SiO_2	0.15%
Al_2O_3	0.04
TiO_2	0.06
B_2O_3	Nil
CaO	4-6
CuO	Trace
HfO_2	1.4
FeO	0.07
MgO	0.08
NiO	0.04
ZrO_2	92-94

Lattice Parameter: 5.156 a.u.

(Source: Reference 17)

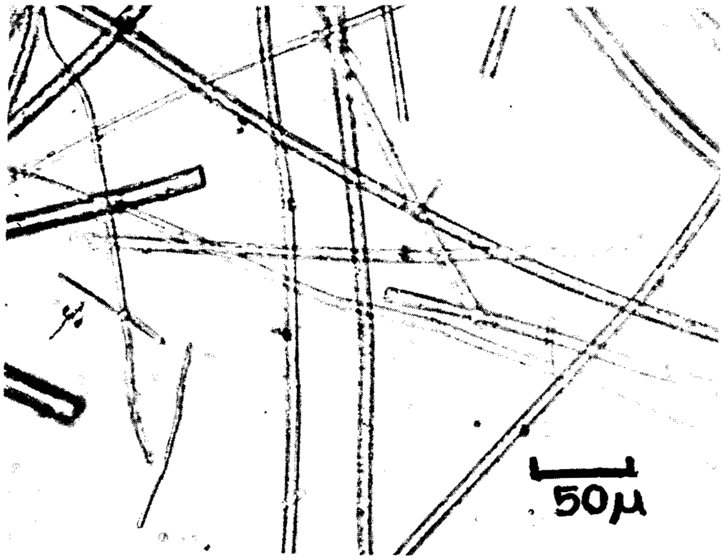

Figure 1. Photomicrograph of

Zirconia "A" Fibers

(Transmitted Light, 260X)

TABLE II

Properties of Zirconia Foams Reinforced with Zirconia Fibers

Code No. 16 --	256	266	267-1	267-2	267-3	269-1	269-2	269-3	269-4	270
Batch Composition, grams per 100 g ZrO_2 powder										
Plaster	15	15	15	15	15	15	15	15	15	15
Dextrin	1	2	2	2	2	1	2	1	2	2
Zirconia fibers	1.7	2	0	3.3	5.3	0	0	5	5	5.3
Batch Composition, cc liquid per 100 g. ZrO_2 powder										
Foaming Agent	6	6	6	6	6	6	6	6	6	6
PVA	2	2	2	2	2	2	2	2	2	2
Water	100	100	100	100	100	100	100	100	100	100
Fired in Air, SiC elements										
Temp. °C	1500	1500	1500	1500	1500	1550	1550	1550	1550	--
Bulk density, g/cc	0.73	0.80	--	--	--	0.61	0.63	0.77	0.71	--
Modulus of Rupture, psi.	53	23	32	32	55	65	89	81	124	--
Gas Fired in Air										
Temp. °C	--	--	--	--	--	1800	1800	1800	1800	1800
Bulk density, g/cc	--	--	--	--	--	0.83	0.81	0.92	0.98	1.30
Modulus of Rupture, psi.	--	--	--	--	--	101	182	254	221	286

3.1.2 Incorporation of Metallic Zirconium

Zirconium metal incorporated into a zirconia foam would be oxidized during firing to produce more zirconium dioxide. Two alternative mechanisms are suggested for increasing the strength of such a foam: 1) the zirconia so formed would grow as needles or fibers, effectively causing a reinforcement according to the preceding discussion; or, 2) oxidation would form in a more "active" zirconia sintering more readily to the pre-existing particles, forming a stronger ceramic bond.

A supply of zirconium metal powder was treated by the gradual introduction of air to form a thin oxide layer on its surface, protecting it against pyrophoric oxidation during handling at room temperature.

Compositions made according to the "standard" formula (16-269-1, Table II) but with 10 parts by weight of treated zirconium metal powder added, did not foam or fire well. Only one sample (16-268, with 10 parts Zr metal and 3 parts ZrO_2 fibers) was processed far enough for testing; its density was 1.01 g/cc, and its modulus of rupture only 63 psi. These values show no improvement in properties, and because of the high cost of zirconium metal, further work on this method was abandoned.

3.1.3 Optimization of Particle Size Distribution

A third possible means of increasing the strength of a foam structure is to vary the particle size distribution of the matrix material. This may be done by milling the raw materials and varying the proportions of as-received and milled powder. Variations in milling as well as in raw material source, are outlined in Table III. The results do not indicate any particular effect which can be attributed to lot-to-lot variation of the "A" brand zirconia, although the use of 50 parts milled powder resulted in an apparent strength increase. This strength, however, is within the range of variation for foams made at different times and is not considered a significant improvement.

The effects of particle size variation are not necessarily the same in a foam structure as in the sintering of a dense body.

With the latter, each particle is surrounded on all sides by other particles, and the increased number and surface area of contacts between particles due to a reduced average particle size may improve strength. In a foam, however, each particle may have only a few points of contact with other particles, and because real sintering is not achieved or desired, the contact area between particles does not appreciably increase. Since strength of a porous body is related primarily to the number and area of individual bonds, it is not surprising that a major improvement in strength of a foamed ceramic does not take place by partial substitution of a finer powder.

Thermal conductivity measurements were limited to 3900-4100°F, because of low resistance to thermal stress at these high temperatures. The coefficients at 3500°F are in the same range as before (Ref. 4).

3.1.4 Addition of Strengtheners

3.1.4.1 Organic Binder Systems: These zirconia foams were formulated using 1 to 2% dextrin and 2% polyvinyl alcohol solution as the organic binder system (Tables II - III). Dextrin is a generic name given to a family of water-soluble colloidal starch or vegetable gum powders of uncertain formula. Various brands are commercially available; NADEX 791 was used in this program. Polyvinyl alcohol (PVA) is a water-soluble synthetic resin made by the hydrolysis of polyvinyl acetate. Again, no specific chemical formula can be assigned, since these are polymers with widely varying characteristics; the specific brand used here was DuPont No. 70-005 as a 17% solution in water.

In an initial series of trials, Table IV, the proportions of dextrin, PVA and plaster were varied and the effects noted in a qualitative way by judging the "hardness" of the foam structure after firing. In a general way it might be concluded that 2% dextrin is better than 1%, that 4% PVA is too much, and that 20% plaster is too much.

The results of a more systematic investigation of the effects of varying the levels of dextrin and PVA are given in Table V. On the basis of smallest pore size, Nos. 3, 7, 8 and 9 are the

TABLE III

Effects of Raw Material Source and Milling Time

Code No. 16 --	257-1	257-2	257-3	260-1	260-2	260-3	271-1	271-2	274-1	274-2	275
Supplier, ZrO_2*	A3	A3	A3	A1	A2	A3	A3	A4	B2	B2	A4
ZrO_2 as rec'd#	100	67	50	100	100	100	100	100	100	100	50
ZrO_2 milled (2 hrs. in wtr.)	0	33	50	0	0	0	0	0	0	0	50
Plaster	15	15	15	15	15	15	15	15	15	15	15
Dextrin	2	2	2	1.3	1.3	1.3	2	2	1.3	2	2
Foaming Agent	6	6	6	6	6	6	6	6	4	6	6
PVA	2	2	2	2	2	2	2	2	2	2	2
Water	100	100	100	100	100	100	100	100	80	100	100
Powder density	--	--	--	0.58	0.55	0.53	--	--	--	--	--
Firing Temp. °C	1500	1500	1500	1500	1500	1500	1550	1550	1550	1550	--
Density, g/cc	0.64	0.59	0.54	0.73	0.69	0.64	0.70	0.68	Poor	foams	--
Modulus of rupture, psi.	48	44	115	45	60	61	78	135	--	--	--

* A - Pittsburgh Plate Glass Co., Reactor grade; numerals indicate lots 1, 2, 3, or 4.

B - Carborundum Metal Climax, Inc., nuclear grade.

\# Numbers indicate parts by weight of powders, and cc of liquids, per 100 g. ZrO_2.

TABLE IV

Qualitative Estimation of Binder System

Code 16--	253-1	253-2	253-3	253-4	253-5
Plaster, g*	15	15	15	15	20
Dextrin, g*	1	0	1	2	1
Foaming Agent, cc *	6	6	6	6	6
PVA, cc*	2	4	4	2	2
Water, cc*	100	100	100	100	100
"Hardness"	Fair	Good	Very Good	Best	Good

Firing Temp. °C	1550	1800
Density, g/cc	0.79	0.93
Strength, psi	123	292

*per 100 grams of ZrO_2 powder

best; on the basis of lowest fired density, Nos. 2, 3, 4, 5 and 9 are the best; and on the basis of strength, Nos. 1, 3, 9 and 10 are the best. No. 3 and No. 9 are excellent in all three respects. PVA inhibits moisture removal during air drying at room temperature, as noted from high moisture loss in oven drying; it also tends to increase green and fired density. It can be eliminated with no adverse effects; in fact, from No. 1, the absence of any binders has not resulted in any loss of fired strength.

3.1.4.2 Zirconium Diboride: Of the refractory carbides, borides, and nitrides, ZrB_2 has the best oxidation resistance. Work on another contract (Ref. 18) showed that ZrB_2 will resist oxidation for as much as ten to twenty minutes while heating to 1900°C.

Foam structures were made from ZrO_2 modified with 10% ZrB_2 addition, and from zirconium diboride alone (Table VI). Specimens of both were fired at 1100° and 1700°C, and in all cases oxidation was almost complete. This oxidation produced primarily monoclinic ZrO_2 at 1100° which became largely cubic at 1700°C, either by reaction with CaO from the plaster and/or by solution of B_2O_3 in the lattice. All four foams were structurally weak, indicating that this type of oxidation does not improve strength.

The low resistance to oxidation of the ZrB_2 in these foams is attributed to the porous structure and large surface area. In a dense specimen of ZrB_2, the formation of an outer coating of oxide would be expected to inhibit oxidation of the interior, but in a foam all particles are equally accessible to the air.

3.1.4.3 Metallic Coatings: A continuous metallic coating throughout the foam structure may conceivably offer a strengthening effect because of the ductility of the metallic phase. The possible added benefits as regards its radiation-scattering characteristics have been discussed in previous contract reports (Refs. 1, 2).

Three specimens (Table VII) were coated with molybdenum by the decomposition and reduction of a deposit of ammonium molybdate solution.

Thermal conductivity readings were obtained only to hot face temperatures in the range 3400-3800°F (Ref. 4). Again these structures did not have sufficient resistance to thermal stress to allow measurements to the desired level of 4500°F.

TABLE V

Experiments to Optimize Organic Binder Content

Code 34-1-	1	2	3	4	5	6	7	8	9	10
Dextrin, g*	0	1	2	4	0	0	0	1	2	4
PVA, cc*	0	0	0	0	1	2	4	1	2	4
Green Density, g/cc (dried 4 hrs. 70°C)	0.30	0.27	0.28	0.27	0.30	0.36	0.45	0.37	0.34	0.27
Moisture Loss, % (oven dried)	37	23	30	31	31	41	46	40	43	39
Pore Size Range, Microns	1400 300	1400 400	800 200	1000 600	1500 500	1700 800	800 400	400 100	800 100	1100 160
Fired Density, g/cc (1500°C, 4 hrs.)	0.79	0.63	0.60	0.62	0.64	0.69	0.71	0.71	0.66	0.68
Modulus of Rupture psi (average)	99	62	95	70	74	73	70	72	100	95

*per 100 grams of ZrO_2 powder

TABLE VI

Experiments with Zirconium Diboride

Code No.-	16-261-1	16-261-2
ZrO_2, g	100	0
ZrB_2, -325 mesh	10	100
Plaster, g	15	15
Dextrin, g	2	2
Foaming Agent, cc	6	6
PVA, cc	2	2
Water, cc	100	100
Firing Temps., °C	1100 1700	1100 1700

TABLE VII

MOLYBDENUM COATINGS
(Decomposition of Ammonium Molybdate)

Code No. -	16-264-1	16-264-2	16-266
Reinforcement	-- 10% Zr Metal --		2% ZrO_2 fibers
Coating method	Suspension painted onto outer surface	Solution soaked into pores	Solution soaked into pores
Estimated Molybdenum Content	0.05	1.0	1.0
Coated density, g/cc	0.83	0.73	0.81

TABLE VIII

Colloidal Silica Bonding Experiments

Code No. -	34-4-1	34-4-2	34-10-1	34-10-2	34-11-1
Ethyl silicate, %[#]	3.5	7.0	--	--	--
pH	5-6	5-6	--	--	--
Silica sol, %*	--	--	3.5	3.5	3.5
NH_4HCO_3,%	--	--	2	2	4
(as wt.% SiO_2)	1.0	2.0	1.0	1.0	1.0
Dried Strength	very fragile	very fragile	--	--	--
Green density	--	--	0.86	1.2	1.0

[#] Tetraethyl Orthosilicate: Matheson, Coleman & Bell, No. TX-275

*Syton brand: Monsanto Chemical Co., No. P-50

3.1.4.4 Colloidal Silica Bond Systems: Colloidal silica bonding systems are well known in the investment casting industry, providing a hard, strong ceramic mold after a room-temperature cure of a few hours. Various proprietary colloidal silica sols are available, such as Monsanto's SYTON brand (Ref. 19); these are suspensions of amorphous silica particles, in the size range 100-400 Angstrom units, dispersed in water at typical concentrations of the order of 30-40% SiO_2. Used in a ceramic bonding system, it forms a silica gel on drying which acts as a room-temperature adhesive.

The other type of colloidal silica bond is derived from tetraethyl orthosilicate ("ethyl silicate" $(C_2H_5)_4 SiO_4$). Soluble in alcohol, it is hydrolyzed with addition of water to form a colloidal silica which bonds adhesively on drying as above. This setting action is accelerated by ammonia and by carbon dioxide.

A series of attempts was made to form a colloidal silica air-setting bond in zirconia foam. The results are tabulated in Table VIII. Ammonium bicarbonate was tried as an accelerating agent because it generates both ammonia and CO_2. The results were not encouraging. Those with ethyl silicate were very fragile, and the foams collapsed on firing. The three using silica sol bond did not foam well and were lumpy in texture.

Since this method also introduces into the system significant quantities of silica which forms a liquid phase at 1775°C with zirconia, no further work was warranted.

3.1.4.5 Bonding and Stabilization by Magnesium Compounds: Since the general levels of strength, density and thermal conductivity of zirconia foams stabilized by calcium oxide had been thoroughly explored with little prospect of major improvement, it was necessary to study other bond systems which would also stabilize the zirconia. Calcia had been added as plaster of Paris (calcium sulfate hemihydrate) forming a hydraulic bond and then decomposing on firing to yield CaO which formed a solid solution with zirconia. The hardening is relatively rapid, however, so that proper mixing times for the formation of a fine, rather than coarse, bubble structure could not be attained.

Other oxides, such as MgO and Y_2O_3, also stabilize zirconia in the cubic form. Since MgO forms complex oxychloride and oxysulfate cements in combination with $MgCl_2$ or $MgSO_4$(the former being the so-called "Sorel cements"), this suggested a means of achieving a foam structure which would not set as rapidly as the plaster and which would form a magnesia-stabilized zirconia phase.

Initial experiments (Table IX) showed that density and strength levels comparable to those of the lime-stabilized foams could easily be produced with MgO and $MgCl_2$. Some experimentation to determine proper ratio of MgO to $MgCl_2$ and the best type of MgO, were then undertaken (Table X). United Mineral and Chemical Corp. MgO (No. 6) was selected for trials because it hardened reasonably slowly, and because of its high purity. Other sources of MgO might work just as well. For every gram of MgO powder, 1 cc of 1.23 specific gravity $MgCl_2$ solution (20% $MgCl_2$) was added to the batch.

The results are listed in Table XI. Foaming action was excellent and mixing could be continued as long as necessary to eliminate large bubbles. Dextrin was added to most batches as an aid in retaining maximum foam volume during the initial stages of hardening. In mix No. 34-14-1, only 67 cc. of water was added for 100 g. of ZrO_2, resulting in a thick batter and a very weak fired structure. In the more dense mixes, however, using a ratio of 100 cc. water to 100 g. ZrO_2, the strength was much improved, by factors of 4 to 12 over the plaster-bonded foams.

Figure 2 shows that density of Mg-stabilized foams is definitely related to strength. Nos. 34-21 and 34-23 were poured into larger horizontal molds from which fired pieces approaching the size of a brick were recovered (Fig. 3). This demonstrates the feasibility of casting larger shapes.

A single foam has so far been made using the oxysulfate bond (Table XII) with equally promising results.

A further series of foams has been made since the last quarterly report (Table XIII) to investigate the effects of changing the amount of water, the amount of foaming agent, the amount and proportions of MgO and $MgCl_2$, and the rate of drying. A duplication of part of this series (Table XIV) was identical except that a different lot of the ZrO_2 powder was substituted; the corresponding strengths and densities were much lower.

Several conclusions can be drawn from these series of experiments (see Table XV):

1) Raw material variation is still a source of uncertainty in

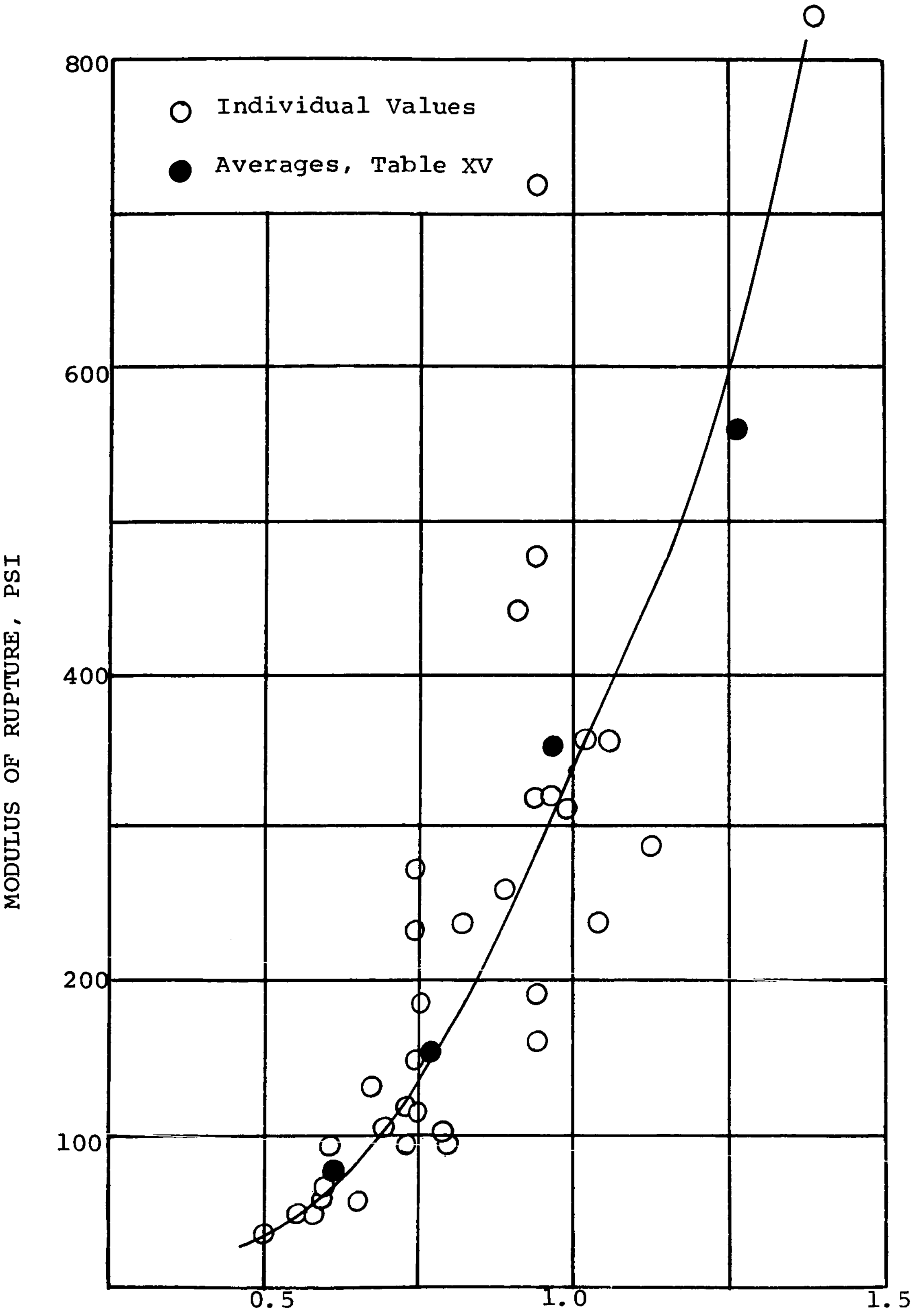

Figure 2. Strength vs. Density of MgO-stabilized Zirconia Foams

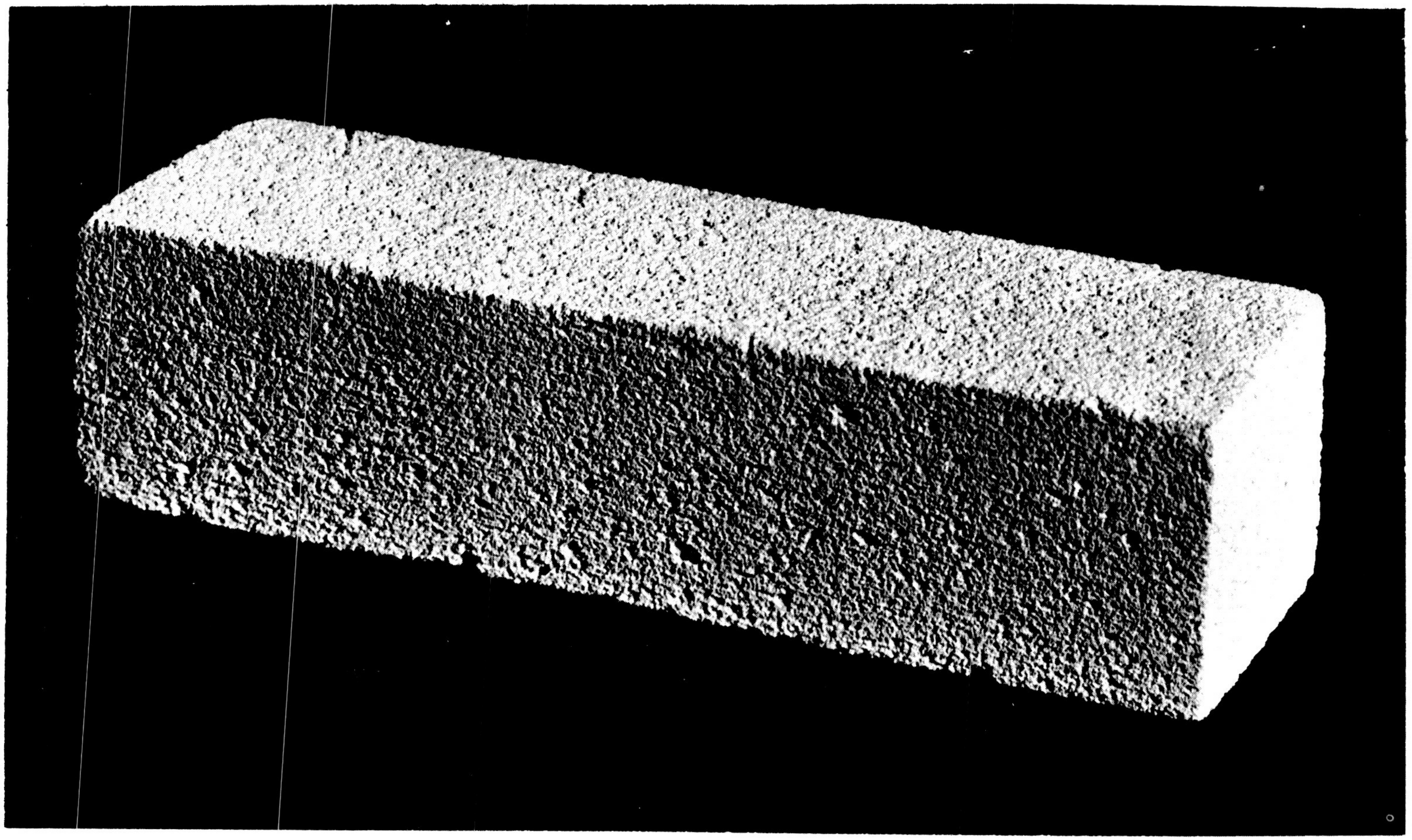

Figure 3. "Brick" of ZrO_2 Foam

TABLE IX

Magnesium Oxychloride Bonding Experiments

Code #	34-4-3	34-4-4	34-4-5	34-4-6
Mol Ratio $\frac{MgO}{MgCl_2}$	2.35	4.6	2.35	4.6
% Equivalent MgO	2.1	2.4	4.3	4.8
% Foaming Agent	6	6	6	6
% Moisture Loss	18	26	25	24
Density, g/cc				
Air-dried	0.30	0.30	0.30	0.30
Oven-dried	0.28	0.28	0.27	0.26
Fired 1550°C	0.87	0.77	Distorted	Distorted
Modulus of Rupture, PSI (Fired 1550°C)	76	79		

NOTE: Zirconia-base composition
MgO: Whittaker, Clark and Daniels, #310, Heavy, U.S.P.

TABLE X

MAGNESIUM OXYCHLORIDE SETTING TIMES

Source of MgO (see Note)	Mol Ratio $MgO/MgCl_2$	Hardening Time
1. Fisher, electronic grade, boiled in water 18 hrs. to form hydioxide	5.1	Plastic after 24 hrs.
2. Mg. Nitrate, MCB #CB488	1.15	Liquid after 24 hrs.
3. WCD, #H222	7.4	Hardened 24 hrs.,but liquid layer on top
4. WCD, #1323	7.4	Hardened 24 hrs., initially tacky
5. WCD, USP Heavy	7.4	Same as 4
6. UMC, 99.96% pure	7.4	Same as 4
7. Fisher, electronic grade, #M-300	3.7	Hardened 24 hrs.
8. Mallinckrodt, fired 1000°C	6.3	Hardened 4-5 hrs.
9. Mallinckrodt,as rec'd	6.3	Hardened 18 hrs.
10. Fisher, electronic grade, fired 850°C	2.0	Dried 4-5 hrs.

Note: MCB = Matheson, Coleman and Bell
WCD = Whittaker, Clark and Daniels, Inc.
UMC = United Mineral and Chemical Corp.

TABLE XI

MAGNESIUM OXYCHLORIDE FOAMS

Code #	34-13-1	34-13-2	34-14-1	34-16-1	34-16-2	34-21	34-23
Dextrin, wt.%	0	1.0	1.0	0	1.0	1.0	1.0
Foaming Agent	6	6	6	6	6	6	6
Mol ratio $\frac{MgO}{MgCl_2}$	7.4	7.4	7.4	7.4	7.4	7.4	7.4
% Equivalent MgO	3.4	3.4	3.4	3.4	2.3	3.4	3.4
Max. pore size, mm.	1.0	0.4	0.7	0.5	0.5	2.0	2.0
% Drying Loss, 24 hr. @ 85°C	4.0	2.0	1.7	22.8	21.9	--	--
Density, g/cc, as fired 1550°C	0.92	1.07	--	1.40	0.96	0.94	0.76
Modulus of rupture PSI (fired) avg.	437	350	(weak)	823	719	472	182

Basic formulation consists of ZrO_2 powder (lot 4), water, and foaming agent. Percent additives above based on 100% ZrO_2. Only 2/3 amount of water used in 34-16-1. MgO was UMC, 99.96% pure.

TABLE XII

MAGNESIUM OXYSULFATE FOAM

Code #	34-18-1
Dextrin, %	1.0
Mol Ratio, $\frac{MgO}{MgSO_4}$	0.104
% Equivalent MgO	3.3
Max. pore size, mm.	0.5
Density, as fired, 1550°C, g/cc	0.86
Modulus of rupture, PSI, avg. (fired)	376

Basic formulation same as in Table XI.

TABLE XIII

Magnesium Oxychloride Bonding Series

Code No. 34-	24-1,2	26-4,5	27-6,7	28-8,9	29-10,11	30-12,13	31-14,15	34-16,17	35-18,19
Dextrin, wt%	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Foaming Agent, cc*	6.0	6.0	6.0	6.0	6.0	6.0	6.0	4.0	8.0
Mol Ratio $\frac{MgO}{MgCl_2}$	7.4	7.4	7.4	7.4	7.4	3.7	14.8	7.4	7.4
% Equivalent MgO	3.4	3.4	3.4	2.3	4.6	2.6	4.3	3.4	3.4
Water, cc*	100	90	80	100	100	100	100	100	100
Fired at 1550°C									
Density, g/cc(1)	0.75	0.73	1.14	0.94	0.83	0.99	0.97	0.95	0.94
M/R, PSI (1)	266	113	282	186	232	306	314	157	314
Density, g/cc (2)	0.68	0.73	1.04	0.75	0.69	0.80	0.79	0.59	0.61
M/R,PSI (2)	129	90	233	110	101	weak	99	55	90

*per 100 g. ZrO_2

(1) Air-dried overnight, then into oven at 80-90°C until dried.

(2) Into oven at 80-90°C immediately.

TABLE XIV

MAGNESIUM OXYCHLORIDE BONDING SERIES (New Lot)

Code No. 34-37-	14A 15A	16A 17A	18A 19A
Dextrin, wt %	1.0	1.0	1.0
Foaming Agent, cc	6.0	4.0	8.0
Mol Ratio $\frac{MgO}{MgCl_2}$	14.8	7.4	7.4
% Equivalent MgO	4.3	3.4	3.4
Water, cc	100	100	100
Fired at 1550°C			
Density, g/cc (1)	0.66	0.89	0.60
M/R, PSI (1)	55	258	63
Density, g/cc (2)	0.56	0.80	0.50
M/R, PSI (2)	47	90	32

See Footnotes, Table XIII.

TABLE XV

SUMMARY OF MAJOR EFFECTS IN OXYCHLORIDE BONDING

I. **Density vs. Strength** (Tables XI, XIII, XIV; Fig. 2)

Density Range	0.50-0.69	0.70-0.89	0.90-1.09	1.10+
Strength Range	32-129	90-266	157-719	282-823
No. of samples	8	9	10	2
Avg. density	0.61	0.78	0.97	1.27
Avg. Strength	72	149	349	553

2. **Equivalent MgO Content** (Table XIII)

Code No.	34-24-1,2	34-28-8,9	34-39-10,11
Equivalent MgO	3.4	2.3	4.6
Avg. density	0.72	0.85	0.76
Avg. strength	197	148	167

3. **Mol Ratio, $MgO/MgCl_2$** (Table XIII)

Code No.	34-28-8,9	34-30-12,13	34-29-10,11	34-31-14,15
Mol Ratio	7.4	3.7	7.4	14.8
(Equivalent MgO)	2.3	2.6	4.6	4.3
Avg. density	0.85	0.90	0.76	0.88
Avg. strength	148	160	167	207
Avg. density	0.88		0.82	
Avg. strength	154		187	

4. **Amount of Foaming Agent** (Tables XIII, XIV)

Code No.	34-24-1,2	34-37-16A,17A	34-37-18A,19A
Foaming Agent	6.0	4.0	8.0
Avg. density	0.72	0.84	0.55
Avg. strength	197	174	48

5. **Rate of Drying** (Tables XIII, XIV)

Series (see Footnotes to above Tables)	(1)	(2)
Avg. density	0.87	0.71
Avg. strength	212	91

making foams with reproducible characteristics;

2) Strength is directly related to bulk density of the fired foam (Fig. 2; Table XV);

3) The total amount of equivalent MgO, over the range 2-5%, as well as the relative proportions of MgO and $MgCl_2$, has little effect on density or strength (Table XV);

4) Reducing the water content from 100 or 90 to 80 cc per 100 g ZrO_2 significantly increases density and strength (Table XIII);

5) Density can be increased by reducing the amount of foaming agent, and vice versa; the more foaming agent added, the greater the volume of foam which is formed (Table XIV);

6) Drying the foam by placing it into the oven immediately after casting causes a significant decrease in both density and strength (Table XV) as compared to curing overnight at room temperature before placing into an oven.

Foam texture may vary considerably as seen by the naked eye or at low magnification. Most foams have a few scattered pores of the order of 1 to 3 mm. diameter. In the best foams the average pore size is of the order of 1/2 mm. apparent diameter with sufficient strength and freedom from laminations that it can be cut and ground to a rectangular shape retaining its sharp edges. A weak foam, on the other hand, may have a fine pore structure but will not retain sharp edges or plane faces and will have a rough or coarse appearance.

The mineralogical constitution of a typical oxychloride-bonded zirconia foam (No. 34-21) was determined by X-ray diffraction. It was found to consist of approximately 50-60% monoclinic (unstabilized) zirconia, and 40-50% cubic (stabilized) zirconia with a cell size of 5.07 a.u. (Table XVI). No free magnesia was detected. These results are consistent with data for zirconia containing 3 1/2% MgO in solid solution. A higher percentage of MgO addition would be needed for complete stabilization.

TABLE XVI

X-RAY DIFFRACTION PATTERN OF MgO-stabilized ZIRCONIA FOAM

d value, a.u.	Intensity	Identification
5.04	5	M (5) *
3.675	15	M (15)
3.62	12	M (12)
3.15	100	M (100)
2.93	80	C (100) *
2.83	65	M (65)
2.61	20	M (20)
2.60	15	M (12)
2.53	25	C (60), M (15)
2.325	5	M (5)
2.21	10	M (10)
2.19	5	M (5)
2.01	5	M (7)
1.99	5	M (7)
1.84	15	M (15)
1.816	25	M (20)
1.796	30	C (100)
1.691	10	M (10)
1.654	10	M (12)
1.600	5	M (5)
1.540	10	M (10)
1.531	15	C (30)
1.495	3	M (5)
1.476	5	C (30), M (10)
1.418	5	M (7)
1.320	2	M (5)
1.27	3	C (30)
1.165	3	C (30)

* M: Monoclinic ZrO_2, ASTM Card No. 7-343

C: Cubic ZrO_2, stabilized with MgO; ASTM Card No. 7-337

Numbers in parentheses are the relative intensities given on the ASTM Cards.

3.2 Reliable Measurement of Thermal Conductivity to 4500°F:

Two objectives are implicit in this second major goal of the contract. One is to extend the measurements higher than the maximum hot face temperature in antecedent contracts of about 4100°F; the second is to plot a single curve and eliminate the scatter of individual data points which sometimes rendered estimation of a coefficient at any one temperature next to impossible.

3.2.1 Attainment of Temperatures to 4500°F:

The first objective was achieved by successfully producing strong zirconia foams. Previously, the modulus of rupture values associated with calcia-stabilized foams fired to 1550°C were generally less than 100 PSI (Refs. 1,2,4). Foams of higher density and with strengths up to 300 PSI could be made only by firing to 1800°C. However, by bonding with magnesium oxychloride or oxysulfate cements, instead of plaster of Paris, it is possible to produce strong foams by firing at only 1550°C. Table XV shows that even in the density range 0.70-0.89 g/cc (12-16% of theoretical) the average modulus of rupture was about 150 PSI. This average more than doubled when the density exceeded 0.90 g/cc; two very high values of 719 and 823 PSI were attained in one series. These latter values may represent strength levels attainable on a routine basis if the formulation process can be reduced to reproducible practice.

These high strength levels allow higher levels of thermal stress to be absorbed without fracture or excessive deformation of the test specimen during high temperature steady state conditions of the thermal conductivity measurement procedure. Maximum hot face temperatures of 2500°C (4532°F) have been successfully attained with these high-strength zirconia foams, without rupture of the specimen through the sight holes, although slight deformation did occur due to differential shrinkage at the hot face.

3.2.2 Selection of Best Method of Plotting Data:

The second objective was achieved by considering alternative methods of plotting data, and on the basis of possible errors in each, selecting one method providing the most reliable thermal conductivity curves.

3.2.2.1 Alternative Methods:

The temperature readings taken at various steady state conditions constitute some of the raw data fed into the thermal conductivity equation. The typical specimen has five sight holes drilled to increasing depts within the concentric thermal gradient, and at the steady state condition a temperature is read by optical pyrometer at the base of each hole. The five temperatures in increasing order are identified as T_1, at the outermost hole nearest the cold face, through T_5, at the deepest hole. Temperature T_5 is actually the heater temperature, since the fifth hole is drilled through.

In the equation, various gradients (the difference in temperature at two sight holes divided by the radial distance between them) can be used. For convenience, each gradient is designated by the two temperature values; for instance, "T_5-T_2" indicates that the gradient is determined from the difference in temperature between the fifth and second sight holes, divided by the difference in depth between them, at several different heater temperatures.

In past reports, gradients $T_2 - T_1$, $T_3 - T_2$, $T_4 - T_3$ and $T_5 - T_4$ have been used to determine thermal conductivity, which was then plotted against the higher of the two temperatures. A number of data points were obtained in each run, but frequently the points were widely scattered so that a single meaningful curve could not be constructed. It was also noted that a curve drawn through points corresponding to the $T_5 - T_4$ gradients had a significantly lower level of conductivity.

In re-examining the raw data, it was thought that much of the scatter could be eliminated by establishing a longer thermal gradient: in essence, calculating fewer, but more accurate, data points. Also, to conform with standard practice, the temperature should be reported as the mean within the gradient, rather than the higher of the two. Gradients $T_5 - T_4$ and $T_4 - T_3$ were retained for consideration, and new calculations were made for gradients $T_5 - T_2$ and $T_4 - T_1$.

These recalculated coefficients are plotted on Figs. 4 through 14; each figure shows curves derived for the four different gradients. In some cases, the short gradients ($T_5 - T_4$ and $T4 - T_3$) show a fair amount of scatter. However, by lengthening the gradient ($T_5 - T_2$ and $T_4 - T_1$), it is seen that the scatter is generally greatly reduced so that a smooth curve can be drawn through the points. The only disadvantage is that by using a mean temperature between two points, a greater distance apart, the reporting temperature is much lower, and it is not possible to determine thermal conductivity directly at temperatures close to 4500°F.

3.2.2.2 Assessment of Errors: The curves of Figs. 4-14 using gradients in which T_5 is a factor are seen to be at a significantly lower level of conductivity values than those using T_4. The heater temperature (T_5) is hotter than the

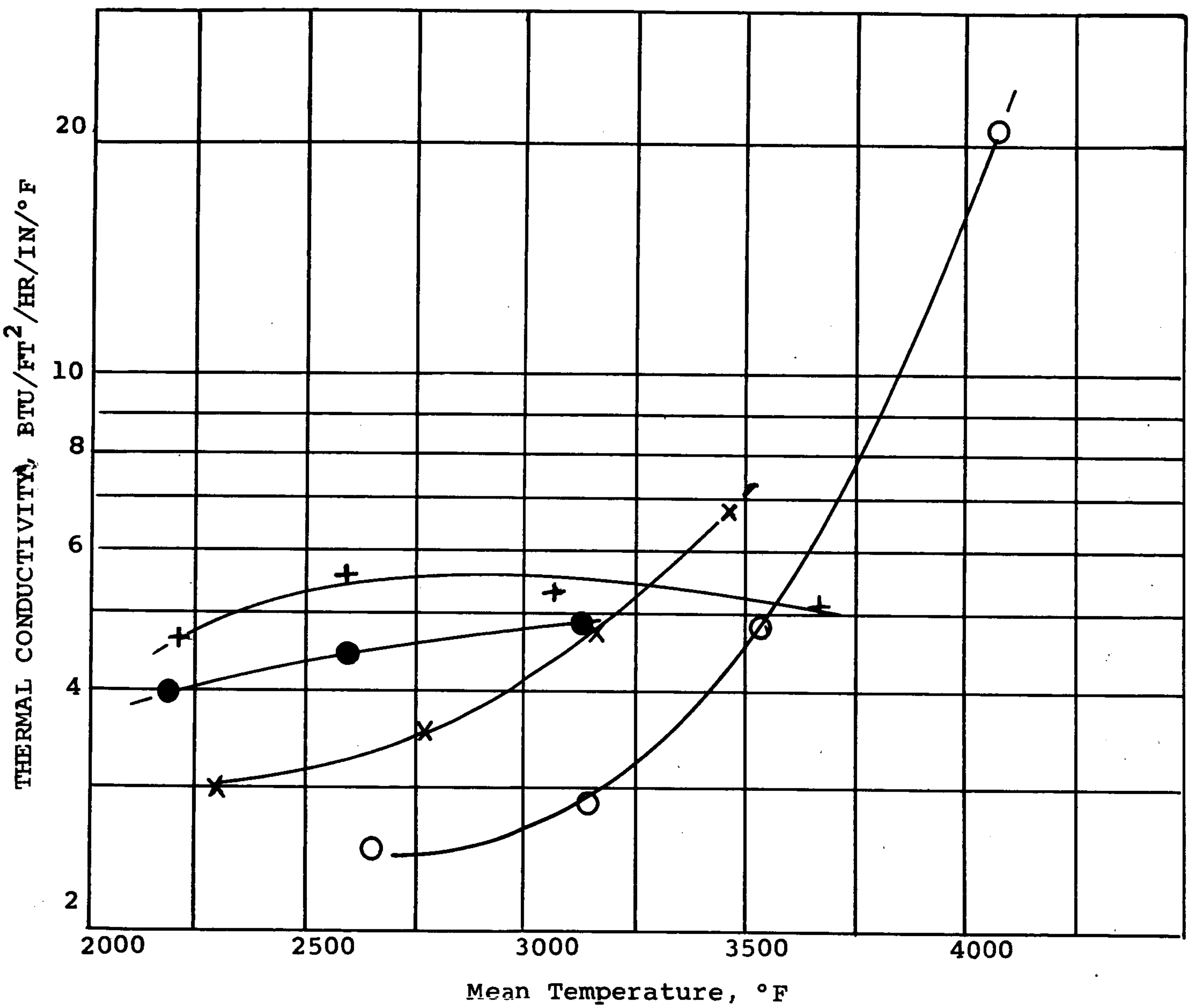

Figure 4. Thermal Conductivity vs. Temperature, Run #76 (Code 16-260-1, See Table III)

○ Gradient $T_5 - T_4$

× Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

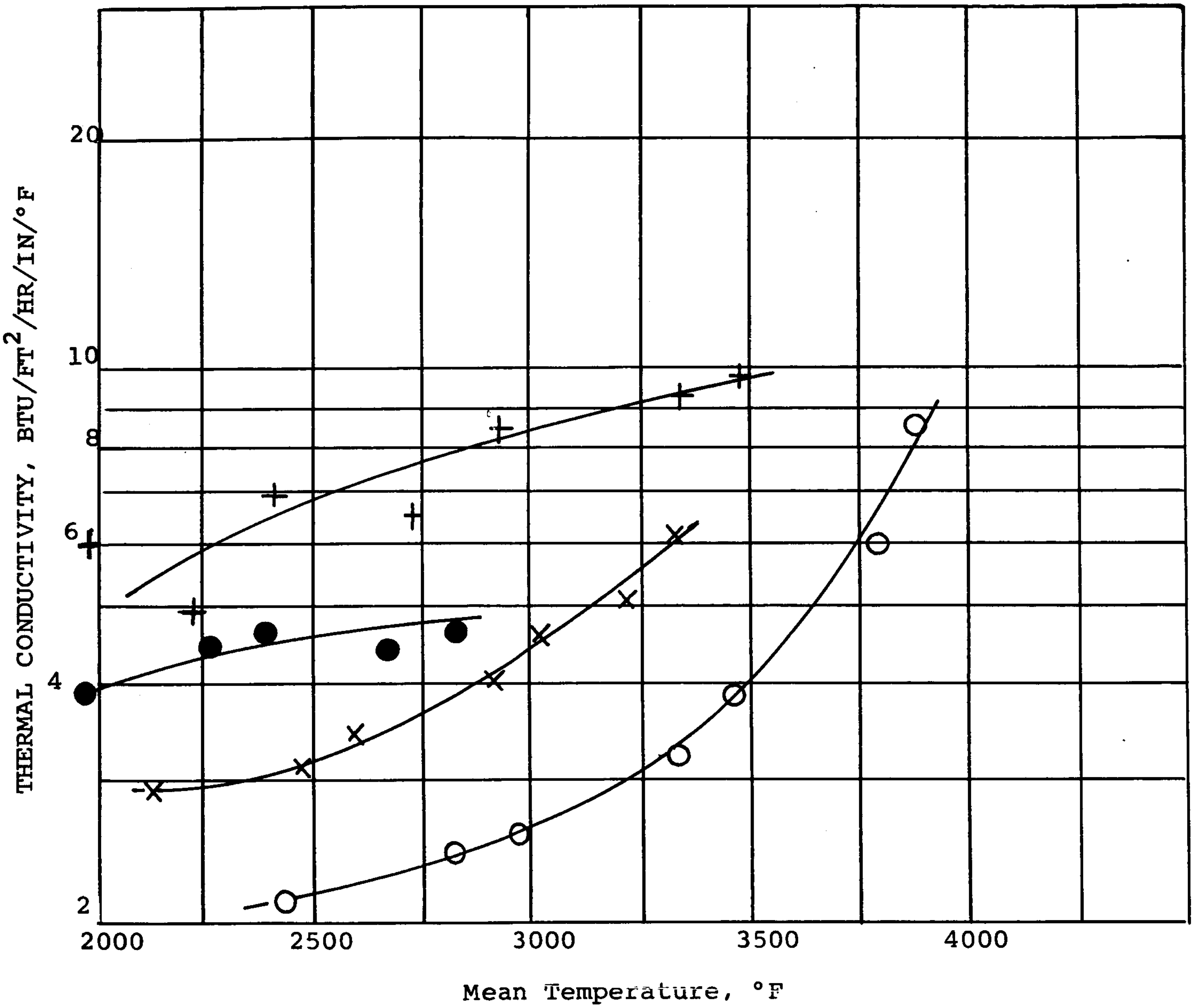

Figure 5. Thermal Conductivity vs. Temperature, Run #77
(Code 16-260-2, See Table III)

○ Gradient $T_5 - T_4$

× Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

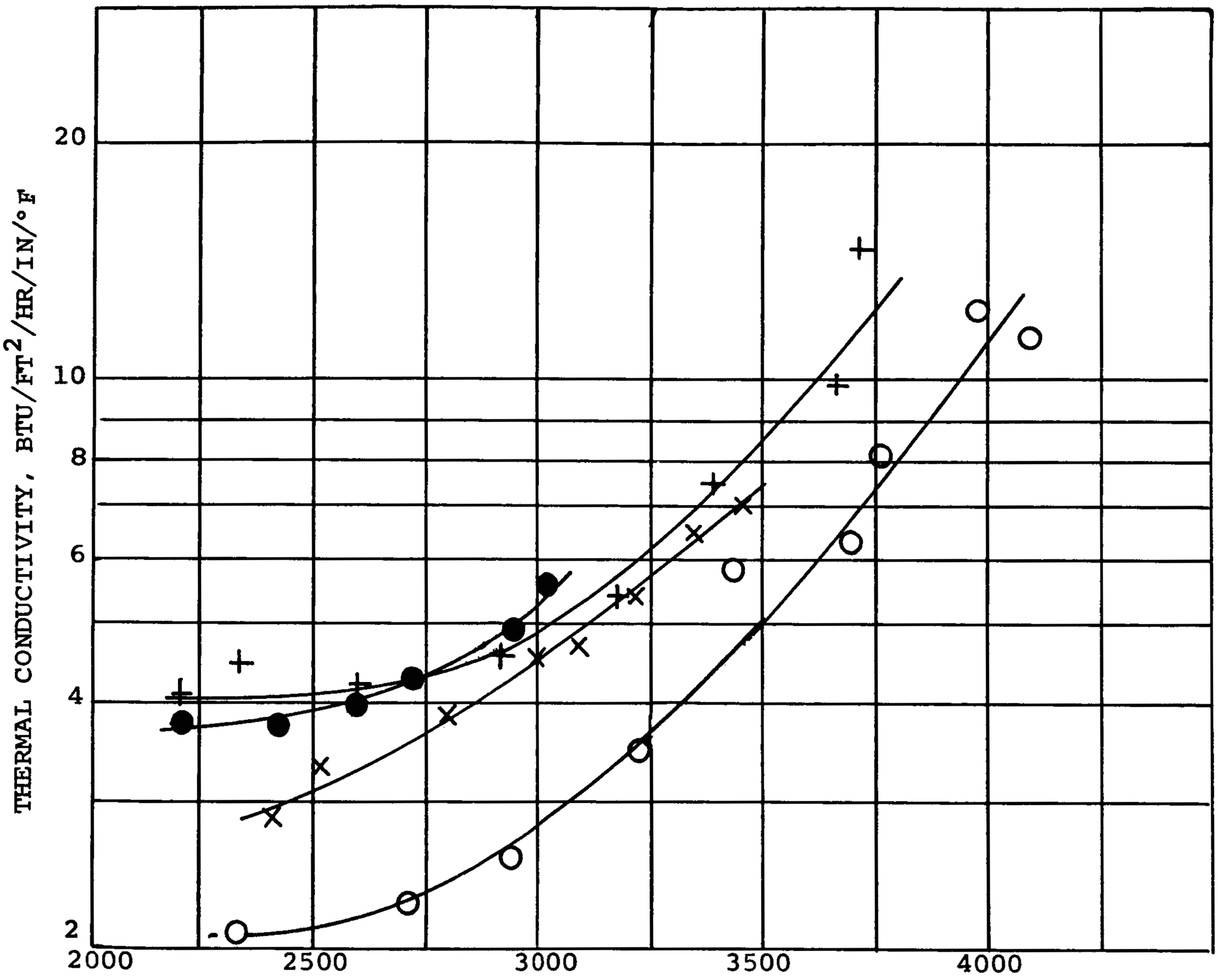

Figure 6. Thermal Conductivity vs. Temperature, Run #78 (Code 16-260-3, See Table III)

○ Gradient $T_5 - T_4$

X Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

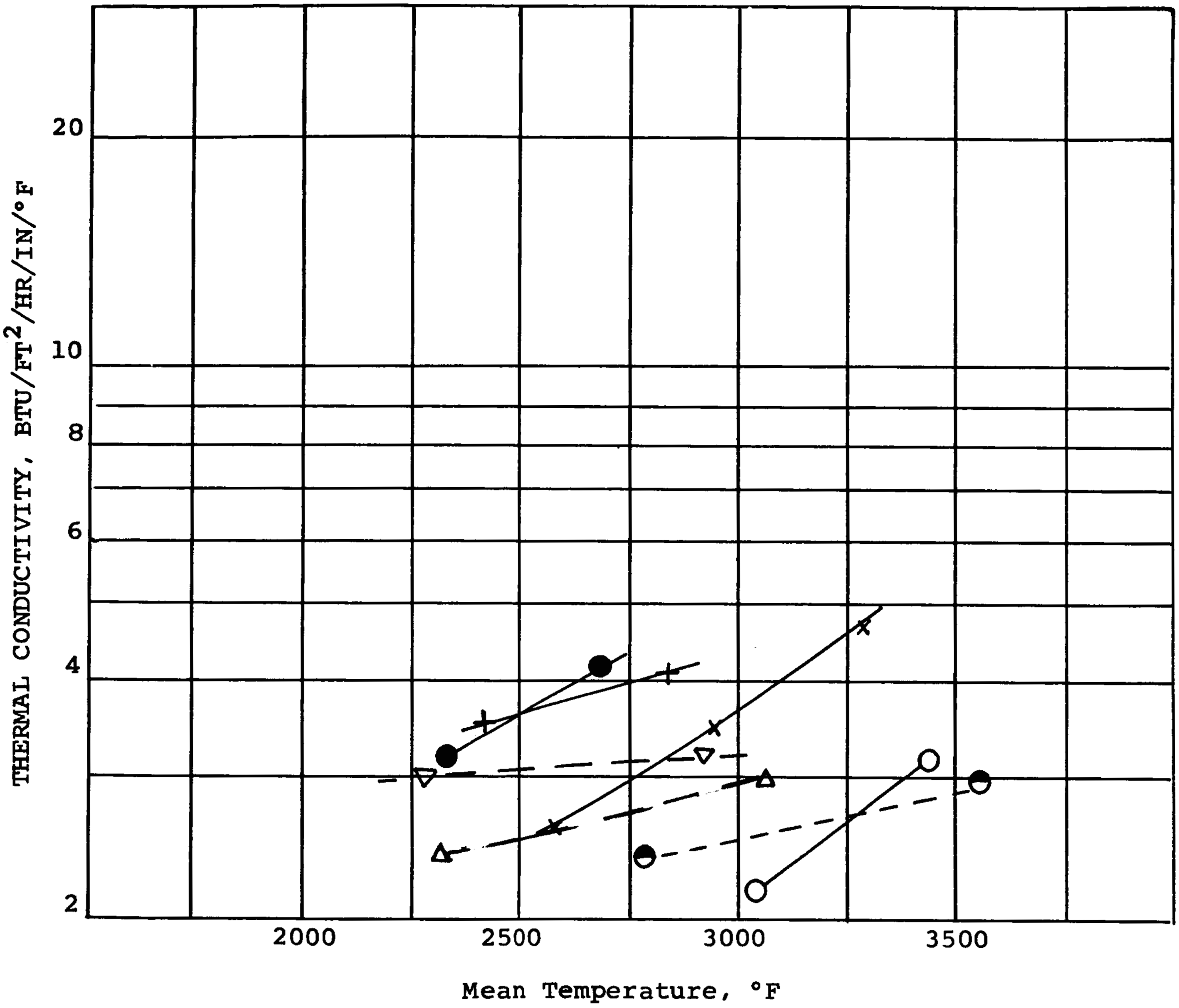

Figure 7. Thermal Conductivity vs. Temperature, Runs #83,#84
(Code 16-264-1,2, See Table VII)

83	84	
○	◓	Gradient $T_5 - T_4$
×	△	Gradient $T_5 - T_2$
+	▽	Gradient $T_4 - T_3$
●		Gradient $T_4 - T_1$

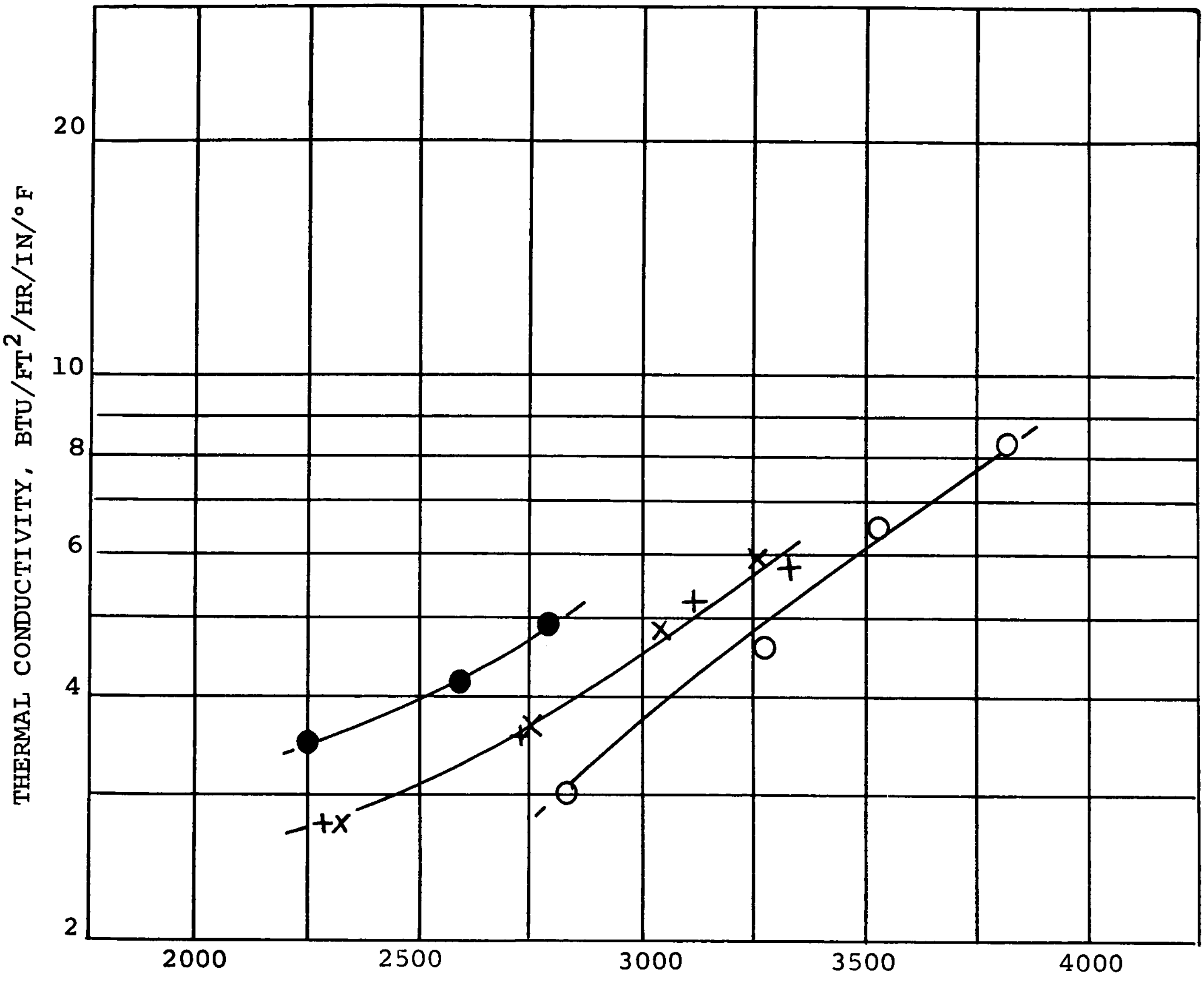

Figure 8. Thermal Conductivity vs. Temperature, Run #85 (Code 16-266-1, See Table VII)

○	Gradient $T_5 - T_4$
X	Gradient $T_5 - T_2$
+	Gradient $T_4 - T_3$
●	Gradient $T_4 - T_1$

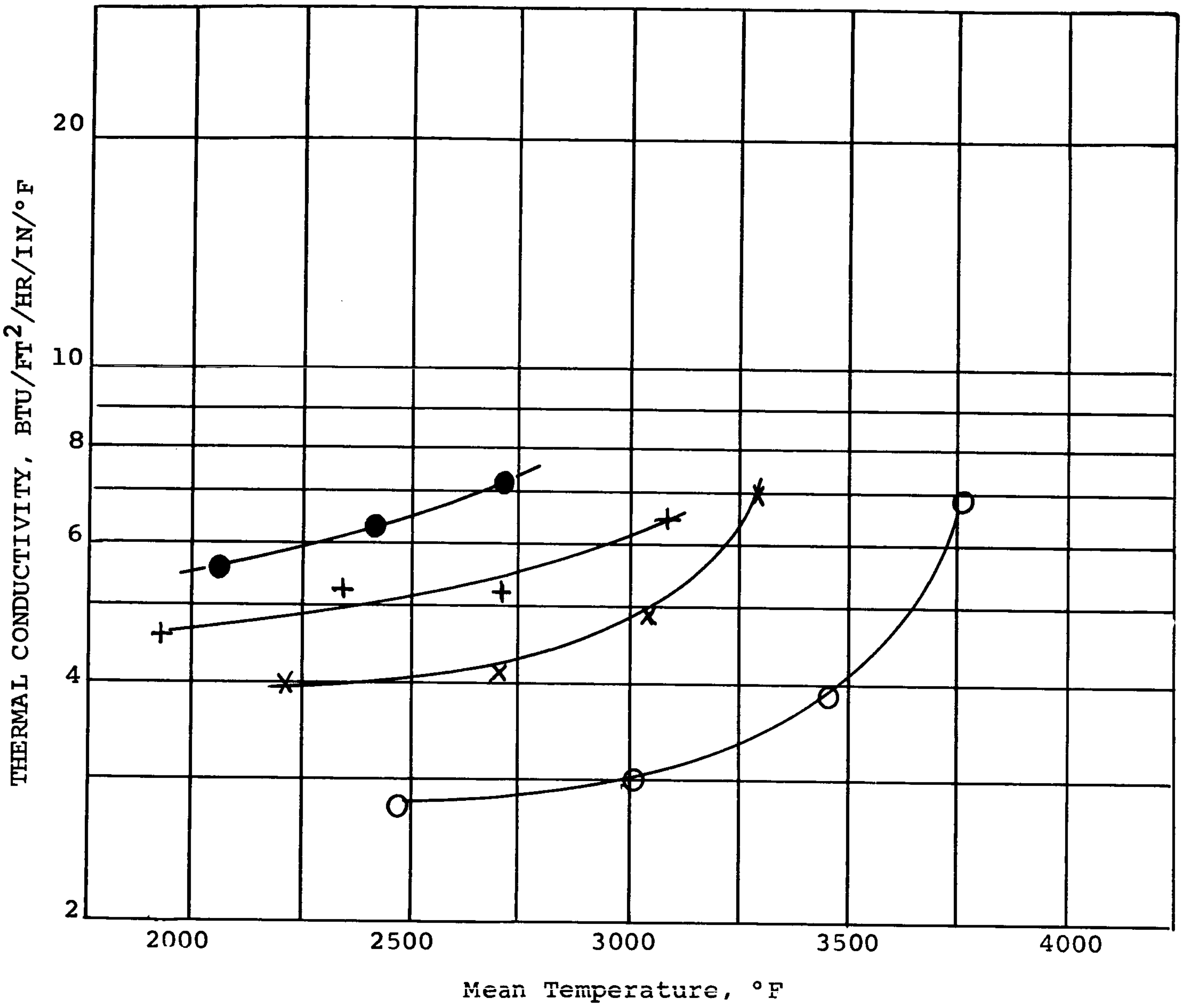

Figure 9. Thermal Conductivity vs. Temperature, Run #86 (Code 16-270-1, See Table II)

○ Gradient $T_5 - T_4$

× Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

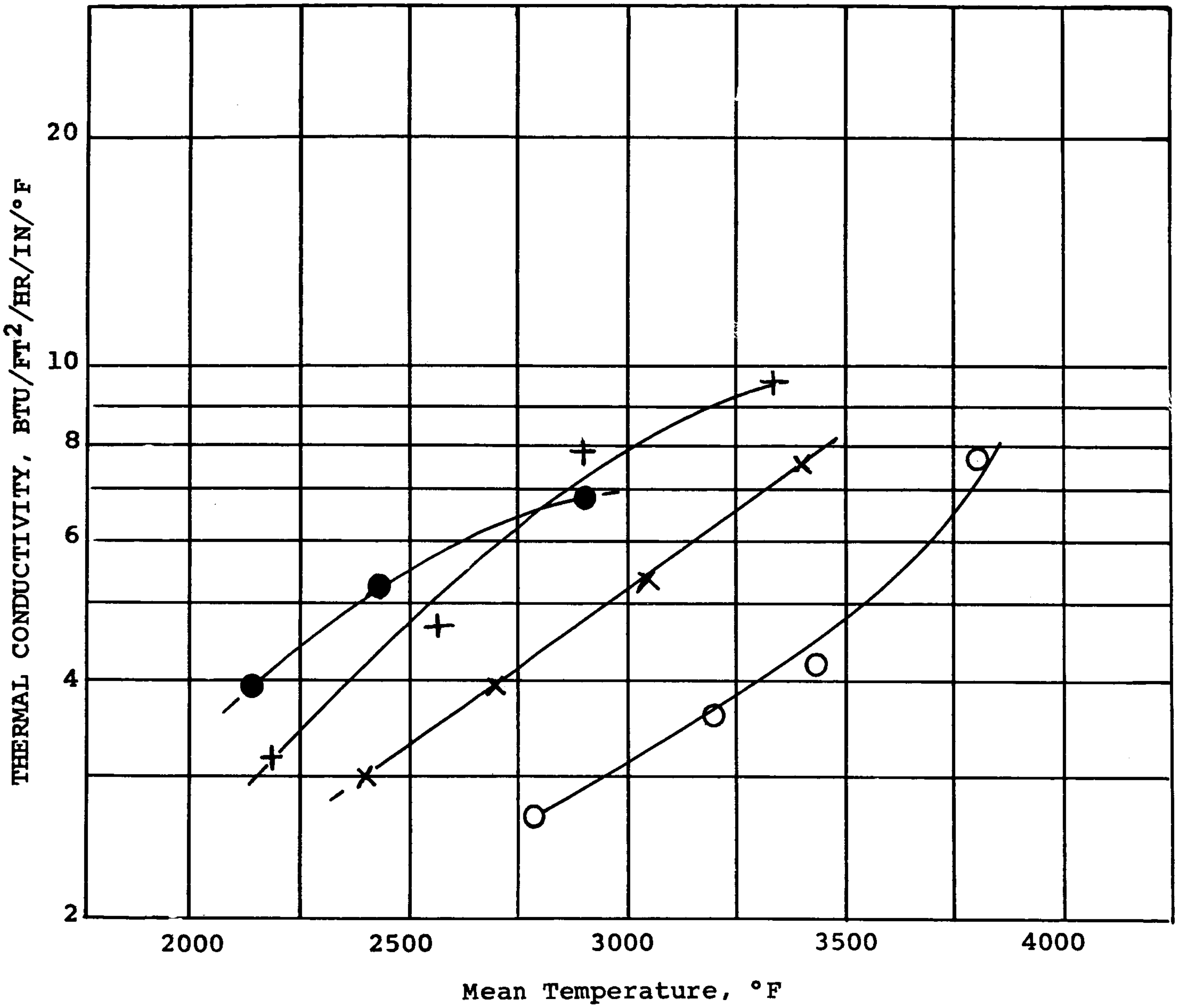

Figure 10. Thermal Conductivity vs. Temperature, Run #87 (Code 16-271-2, See Table III)

○ Gradient $T_5 - T_4$

× Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

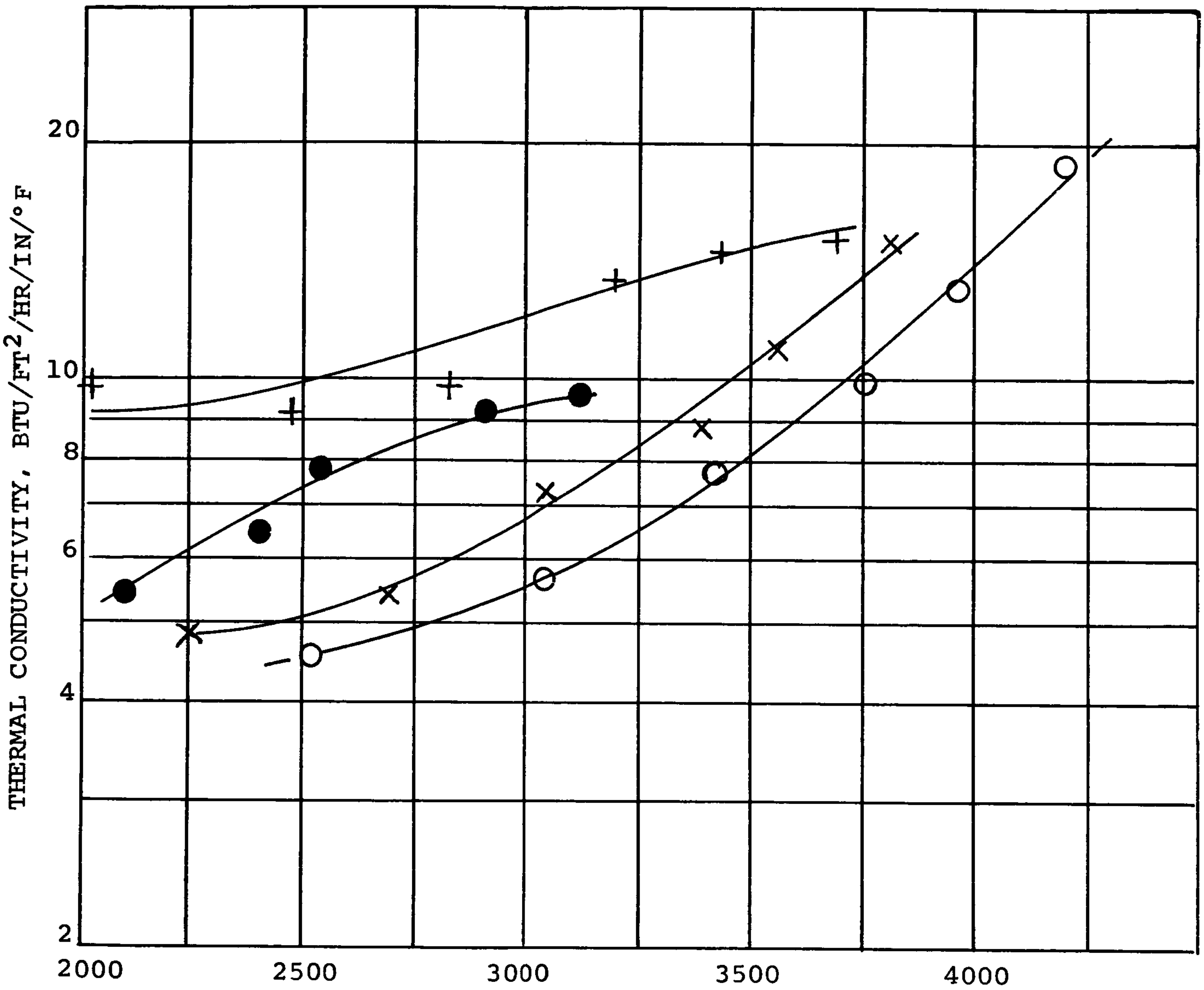

Figure 11. Thermal Conductivity vs. Temperature, Run #90 (Code 34-16-1. See Table XI)

○ Gradient $T_5 - T_4$

X Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

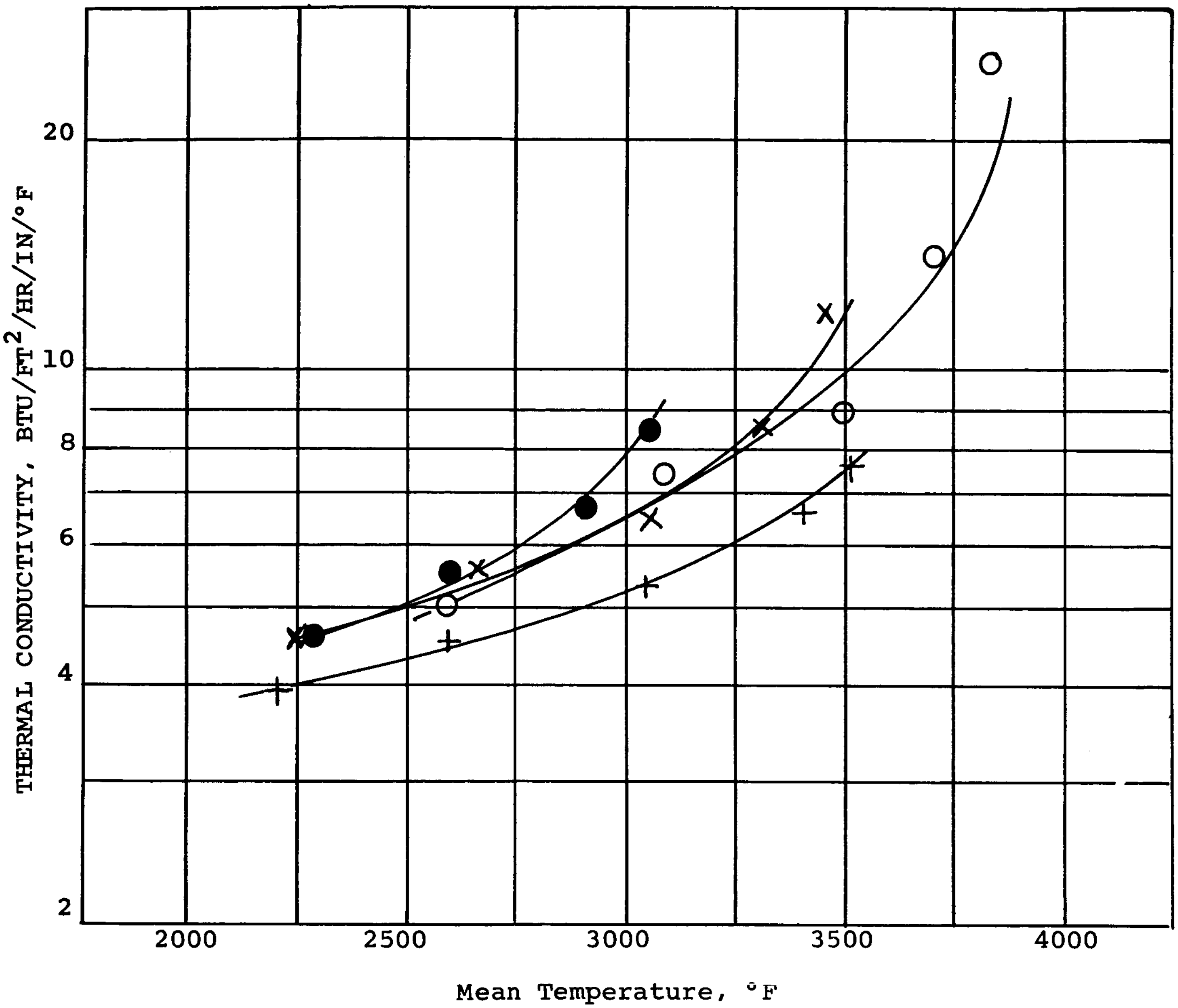

Figure 12. Thermal Conductivity vs. Temperature, Run #91 (Code 34-16-2, See Table XI)

○	Gradient $T_5 - T_4$
X	Gradient $T_5 - T_2$
+	Gradient $T_4 - T_3$
●	Gradient $T_4 - T_1$

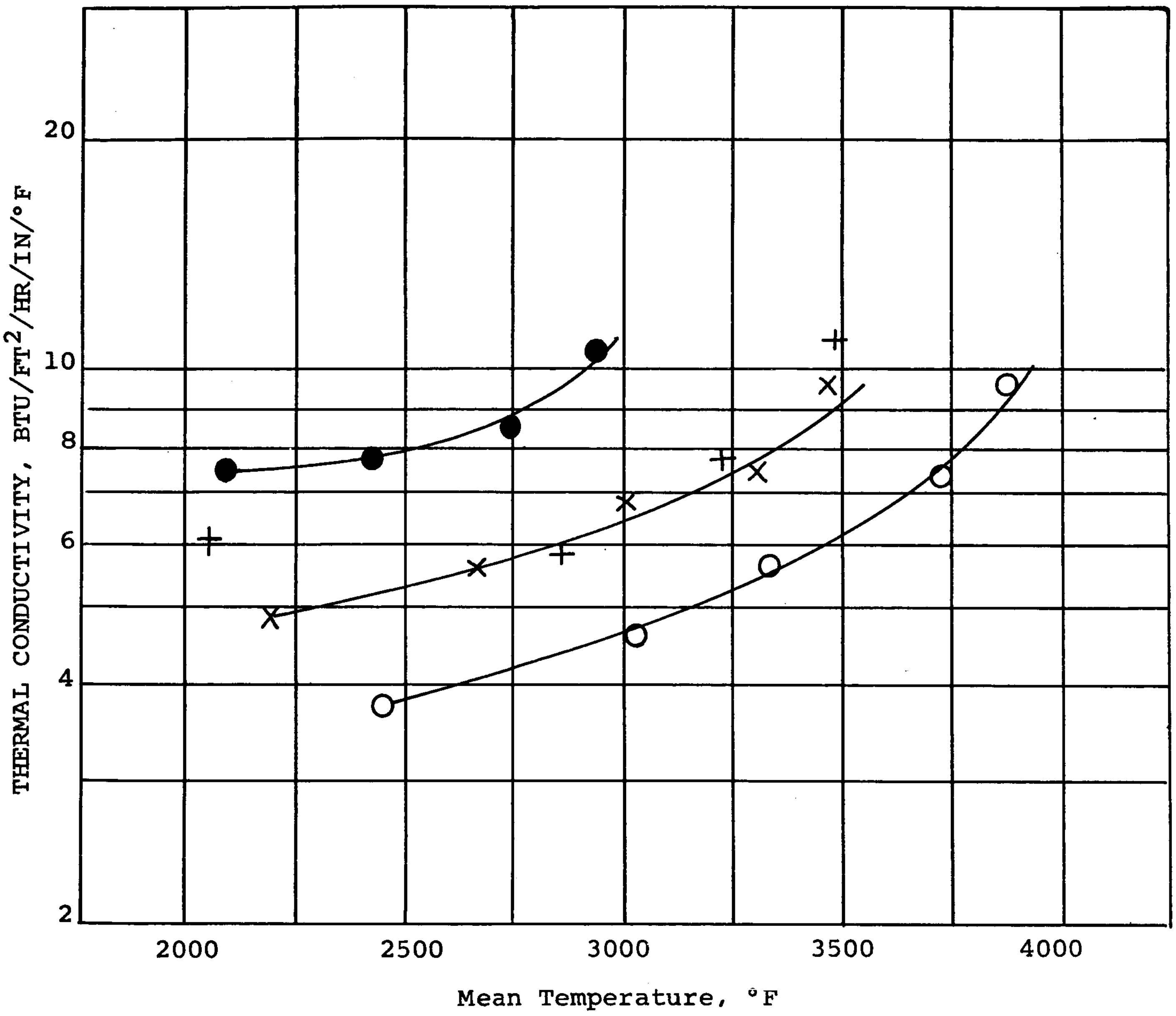

Figure 13. Thermal Conductivity vs. Temperature, Run #93 (Code 34-18-1, See Table XII)

○ Gradient $T_5 - T_4$

× Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

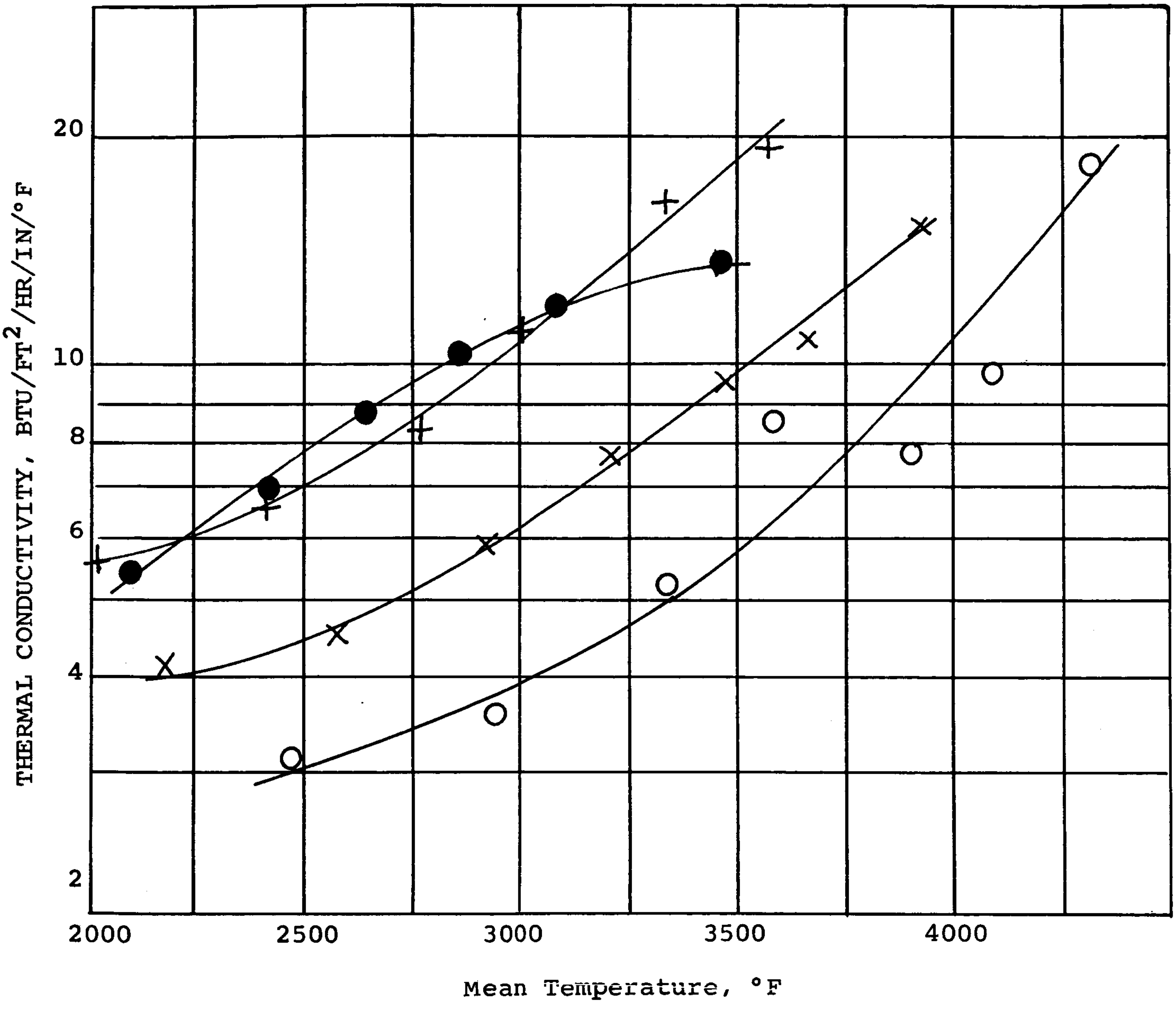

Figure 14. Thermal Conductivity vs. Temperature, Run #94 (Code 34-36-1, Mg. Oxychloride bond, density = 0.88 g/cc)

○ Gradient $T_5 - T_4$

× Gradient $T_5 - T_2$

+ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

adjacent hot face of the concentric test specimen, and since the temperature term is in the denominator of the thermal conductivity equation, delta-T is too large and reduces the apparent conductivity coefficient. This error is somewhat reduced by using the longer gradient $T_5 - T_2$, as is seen by the higher coefficients obtained with these curves.

Other errors, such as the actual depth of the holes at the temperature of measurement (i.e., in a thermally-expanded state), and temperature losses out the ends of the heater, are assumed to vary little between different specimens or runs and are, therefore, not detected in the various sets of curves.

3.2.2.3 Average Conductivity Curves: The various conductivity curves were divided into two groups: zirconia foams stabilized with calcia, and those stabilized with magnesia. The basis for this classification will be discussed below. Each curve was read at intervals of 500°F; extrapolations were limited to about 300°F at either end of the curve, these values being given in parentheses. These readings, for the four gradients, are listed in Tables XVII through XX. Runs 76 through 87 were on calcia-stabilized material, and Runs 90-94 were on magnesia-stabilized zirconia.

Averages for each group are given in these tables. These group coefficients for each gradient have been plotted on Figs. 15 and 16, and provide very smooth curves of conductivity vs. temperature. In both figures, the curves for the T_4-T_1 and T_4-T_3 gradients are consistent with each other, indicating that these coefficients can be regarded as characteristic of the material itself. These latter curves are, therefore, presumed to provide the "true" thermal conductivity of the two basic materials.

On Fig. 16 is a curve for the equation

$$\text{(Heat transfer by Radiation)} = k\ (\text{Abs.Temp.})^3$$

such that k yields a coefficient of 4 at 2000°F (1366° K). Doubling the absolute temperature to 2372° K (4458°F) multiplies the coefficient by eight. This equation incorporates the effect of radiation as a component of heat transfer. On log/log paper, this curve would be a straight line with a slope of 3; observed slopes are closer to 2.

TABLE XVII

Summary of Thermal Conductivity Coefficients for Gradient T_5-T_4

Run No.	Coefficient at Temp. °F				
	2500	3000	3500	4000	4500
76	(2.4)	2.6	4.6	16	--
77	2.2	2.6	4.0	(11)	--
78	2.2	2.6	5.0	12	--
83	--	2.2	3.4	--	--
84	--	2.6	2.9	--	--
85	--	3.4	5.5	8	--
86	2.7	2.9	4.0	--	--
87	(2.4)	2.9	4.7	(9.5)	--
Average	2.4	2.7	4.3	11.1	--
90	4.4	5.4	8.0	13	(30)
91	(5.0)	6.5	9.5	(19)	--
93	3.7	4.5	6.2	(11)	--
94	3.2	3.9	6.0	10	(20)
Average	4.1	5.1	7.4	13.3	(25)

TABLE XVIII

Summary of Thermal Conductivity Coefficients for Gradient T_5-T_2

	Coefficient at Temp. °F				
Run No.	2000	2500	3000	3500	4000
76	(2.9)	3.1	4.1	7.0	--
77	(2.9)	3.1	4.3	(7.2)	--
78	--	3.1	4.5	7.5	--
83	--	(2.5)	3.4	(6.0)	--
84	--	2.5	2.9	--	--
85	--	3.0	4.5	(7.3)	--
86	(3.8)	4.0	4.8	(8.5)	--
87	--	3.1	5.1	(8.3)	--
Average	(3.2)	3.1	4.2	7.4	--
90	(4.8)	5.0	6.8	10	(20)
91	(4.7)	5.2	6.5	10	--
93	(4.8)	5.3	6.8	10	--
94	(4.1)	4.5	6.2	10	(18)
Average	(4.6)	5.0	6.6	10	(19)

TABLE XIX

Summary of Thermal Conductivity Coefficients for Gradient T_4-T_1

Run No.	Coefficient at Temp. °F				
	2000	2500	3000	3500	4000
76	(3.7)	4.3	4.8	(5.2)	--
77	4.0	4.7	--	--	--
78	---	3.9	5.3	--	--
83	---	3.7	--	--	--
84	---	--	--	--	--
85	---	4.0	(5.5)	--	--
86	5.5	6.5	(8.3)	--	--
87	(3.4)	5.6	7.0	--	--
Average	4.1	4.7	6.2	(5.2)	--
90	(5.1)	7.5	9.4	--	--
91	(4.4)	5.1	7.6	--	--
93	(7.4)	7.9	(12)	--	--
94	(5.0)	7.9	11.2	13.6	--
Average	(5.5	7.1	10.0	(13.6)	--

TABLE XX

Summary of Thermal Conductivity Coefficients for Gradient T_4-T_3

Run No.	Coefficient at Temp. °F 2000	2500	3000	3500	4000
76	(4.0)	5.3	5.4	5.2	--
77	5.0	6.9	8.5	9.7	--
78	4.1	4.2	4.9	8.4	(20)
83	--	3.7	--	--	--
84	--	3.1	(3.3)	--	--
85	--	3.1	4.3	(6.7)	--
86	4.7	5.3	6.3	--	--
87	(2.4)	4.8	8.2	(10.3)	--
Average	4.0	4.6	5.8	8.1	(20)
90	9.0	10.3	12.2	14.5	(16)
91	(3.9)	4.2	5.3	7.4	--
93	6.0	6.5	7.9	10.5	--
94	5.5	7.1	10.4	15.0	(19)
Average	6.1	7.0	9.0	11.8	(17.5)

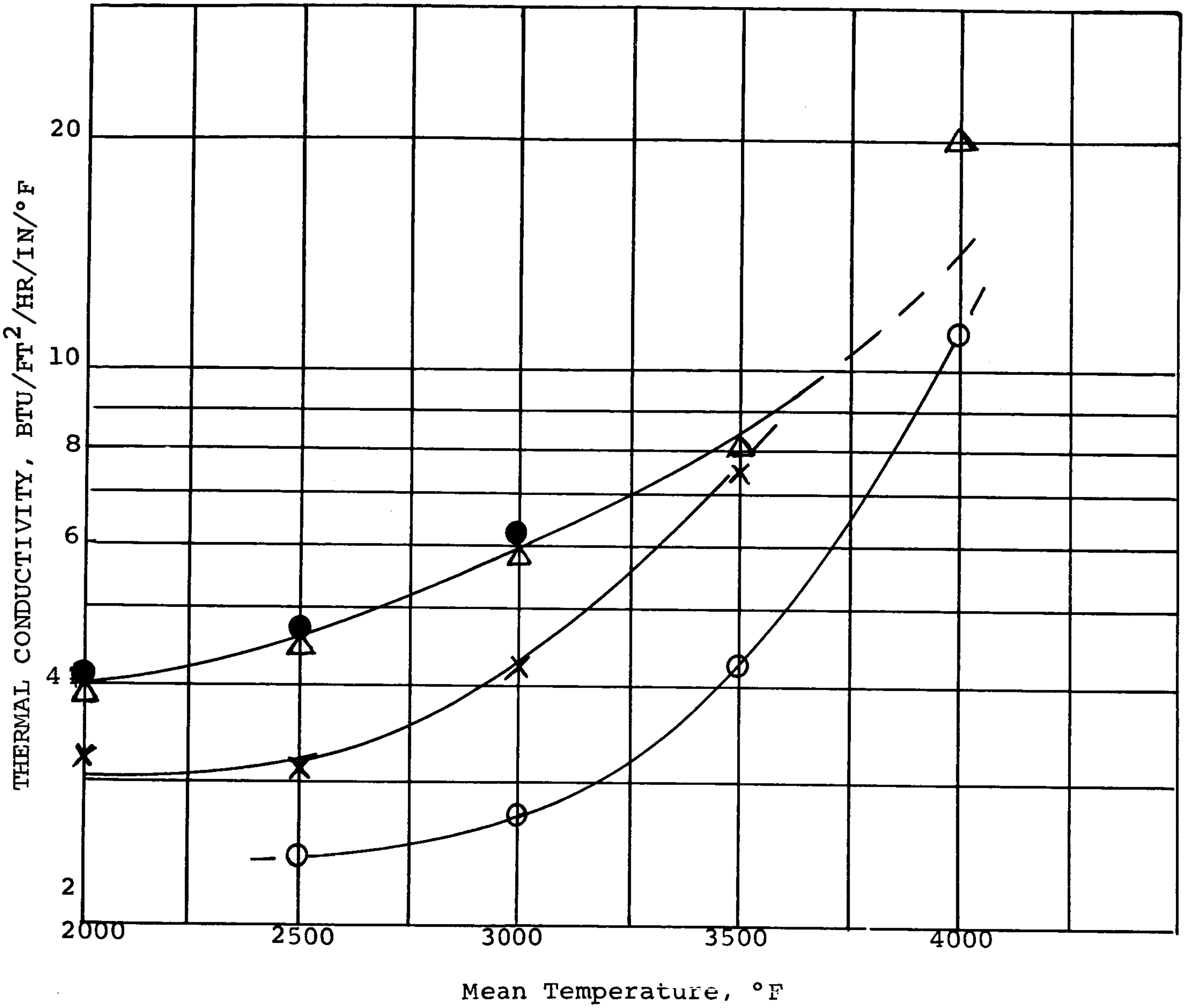

Figure 15. Average Thermal Conductivity Curves for CaO-stabilized Foams

○ Gradient $T_5 - T_4$

× Gradient $T_5 - T_2$

△ Gradient $T_4 - T_3$

● Gradient $T_4 - T_1$

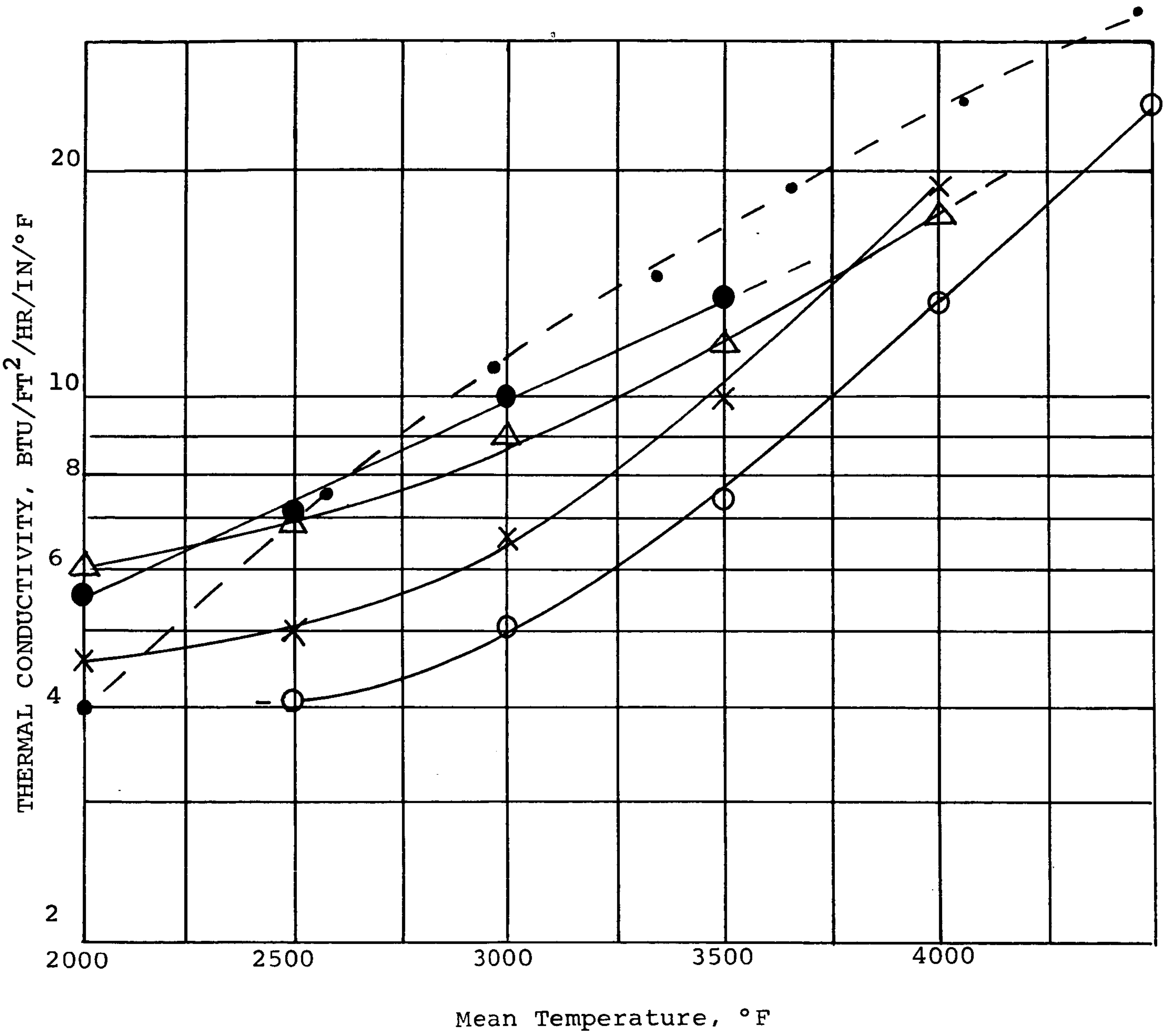

Figure 16. Average Thermal Conductivity Curves for MgO-stabilized Foams

○	Gradient $T_5 - T_4$
×	Gradient $T_5 - T_2$
△	Gradient $T_4 - T_3$
●	Gradient $T4 - T_1$
—•—	Typical Curve for kT^3

A thermal conductivity curve with this shape could be presumed to indicate that radiation was the sole mode of heat transfer. The fact that these curves show increasing "conductivity" with increasing temperature, and that they converge at the highest testing temperatures, do indicate that radiation is a significant component of heat transfer in these foams, although differences in shape and slope indicate that the conduction component is still finite. Radiation is also probably scattered and reflected by particle surfaces and pore walls.

3.2.3 Relationships of Material Properties to Conductivity:

Differences in conductivity would reasonably be considered to be associated with differences in density of the material. Figure 17 is a plot of thermal conductivity coefficients at 2500°F (from Table XIX, supplemented by data in Ref. 2) against bulk density of the foam. Foams with densities in the range 0.80-0.89 show coefficients which vary from 3.7 to 7.9, and the three highest-density foams have coefficients which are neither very high nor very low. At the high level of porosity characteristic of foams, the effects of density do not seem to be as noticeable as would have been predicted.

Since no effects are definitely attributable to density alone, the data of Tables XVII - XX were grouped on the basis of composition differences (Sec. 3.2.2.3). A density effect cannot be ruled out, but is masked by compositional and other variables.

The upper curve for the calcia-stabilized zirconia (Fig. 15) shows an average conductivity about one-third lower than for the magnesia-stabilized foam (Fig. 16), but the latter curves extend reliably to higher temperature levels because of the higher strength of these foams.

Some of the coefficients for three foams in which Mo metal was deposited by decomposition of ammonium molybdate (Runs 83-85, Tables XVII-XX) have a slightly lower level than those without metal. However, these foams were not strong and did not permit a sufficient number of readings to allow good curves to be constructed and the scatter is sufficient to cast doubt on the efficacy of Mo additions to scatter radiation.

The reason for the difference in conductivity level between zirconias stabilized by different additives is not clear. This

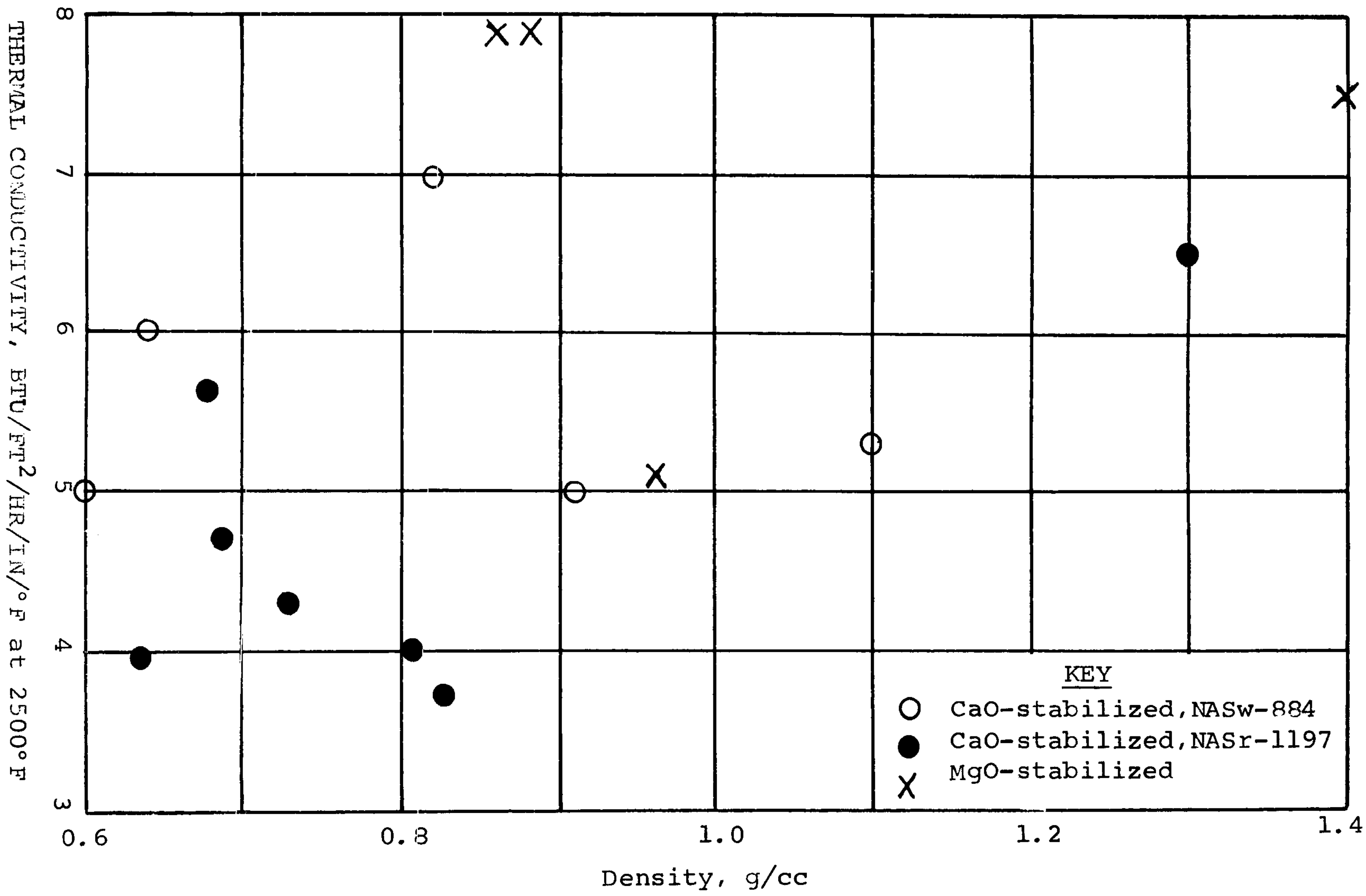

Figure 17. Density vs. Thermal Conductivity at 2500°F

difference might be attributable either to the nature of the additive, or to the amount added, or to the effect of the additive on the zirconia structure, or to any combination of these. The level of CaO addition was about 5.8 parts by weight per 100 parts ZrO_2, and X-ray diffraction analyses (Ref. 2) showed almost complete transformation to the cubic structure. The level of MgO addition was 2.3 to 3.4 parts, and X-ray diffraction (Sec. 3.1.4.5) showed that stabilization was only about 50-60% complete.

Ryshkewitch (Ref. 20) points out that calcium forms an intermediate compound with zirconia, namely the zirconate $CaZrO_3$, whereas magnesium does not. Calcia may form a solid solution with zirconia by a different mechanism, affecting its thermal properties.

3.2.4 Reliable Conductivity Coefficients:

The uppermost curves of Figs. 15 and 16 represent in the author's judgment the "best" average values of thermal conductivity for the two different zirconia foam compositions. A typical zirconia foam stabilized with about 6% of added CaO would be expected to have the following coefficients:

Temperature, °F	$BTU/ft^2/hr/in/°F$
2000	4
2500	4 1/2
3000	6
3500	8 1/2
3750	11
4000	15

A single extrapolated value of 20 at 4000°F was obtained, but this is of dubious accuracy. The low strength of these foams did not permit reliable readings at the desired high temperatures.

A typical zirconia foam stabilized with about 2 to 3 1/2% of added MgO would be expected to have the following coefficients:

Temperature, °F	$BTU/ft^2/hr/in/°F$
2000	6
2500	7
3000	9-10
3500	12-14
4000	18-20

The coefficient at 2500°F is similar to that reported in Ref. 5 (See Sec. 2.3).

It is interesting to note that both sets of curves seem to converge at temperatures in the range 4000-4500°F. It is difficult to conceive how a coefficient obtained from a $T_5 - T_2$ gradient could be significantly greater at 4500°F or above than one obtained from a $T_4 - T_1$ gradient. It is more likely that at 4500°F and above, the radiative heat transfer is so rapid that the hot face of the specimen is at almost the identical temperature as the heater, and that errors in using T_5 readings would approach zero.

Accordingly, a coefficient in the range 25-30 seems reasonable for a typical Mg-stabilized zirconia foam at 4500°F, based on this extrapolation and convergence of curves.

It should be emphasized that variations between individual specimens will still occur, because of differences in density. These variations may change the coefficient by a factor of two.

For comparison, the coefficients of other oxide materials at temperatures above 2500°F are given in Table XXI. These were determined at Southern Research Institute (Ref. 21), and pertain to comparatively dense ceramics with porosity levels of 10% or less. Because they are dense, the radiative component is small, and the curves do not rise sharply at high temperatures as do the zirconia foams. Zirconia foam is, therefore, a better thermal insulator than dense zirconia at temperatures below 3500°F, but above 4000°F its conductivity is greater but not more than double. The savings in weight, and the lower conductivity at low temperatures, render these foams attractive materials for high temperature thermal insulation.

TABLE XXI

Thermal Conductivity of Dense Refractory Oxides (Ref. 21)

Material	Conductivity, BTU/ft^2/hr/in/°F, at Temp. °F				
	2500	3000	3500	4000	4500
BeO	50-70	35-70	30-60	--	--
CeO_2	6	6	7	--	--
HfO_2	18	18	18	18	--
MgO	45	35	35	40	--
ThO_2	11	10	10	--	--
ZrO_2	10	11	12	13	15

4. SUMMARY and CONCLUSIONS

Previous contracts on this program are reviewed; an apparatus for the measurement of thermal conductivity by a radial heat-flow method, and a method of formulating zirconia foam with up to 90% porosity were developed. The foams had low conductivity but failed when measurements above 3500-4000°F were attempted because of their low strength. Attempts to reduce the heat transfer coefficients by incorporating radiation barrier phases had only limited success.

The objectives of the present contract are two-fold: improve the high-temperature strength of these foams, and obtain reliable conductivity data to 4500°F.

A variety of means for improving strength were investigated. Reinforcement with zirconia fibers provided a slight strength increase, but not sufficient; zirconium metal additions did not increase strength and are expensive; modifications to the particle size distribution also proved to be ineffective. Although variations in the organic binder system were found to alter the drying characteristics and the green strength of the foams, they contributed no permanent strengthening after firing. Zirconium diboride additions oxidized rapidly and weakened the foam structure. Coatings of metallic Mo did not improve strength, although they may have reduced thermal conductivity to a slight degree. Colloidal silica-base bonds were investigated briefly, but their foaming properties were poor and their silica content renders them unattractive.

Major improvement in the high-temperature strength of zirconia foams was successfully achieved by the development of magnesium oxychloride and oxysulfate bonds, which provide a slower hardening action allowing full foaming action and also stabilize the zirconia on firing. Modulus of rupture values, although dependent on foam density, were significantly higher than with calcia-stabilized foams. An average strength of 349 PSI was obtained from ten samples with densities in the range 0.90 to 1.09 g/cc, by firing to only 1550°C. Two foams had strengths over 700 PSI.

Shapes the size of a brick can be prepared easily. All parameters for making such foams to specified densities in a reproducible manner have not been entirely resolved, although the effects of changing the percentage of water and foaming agent are established. Rapid oven drying definitely reduces both strength and density. With 2 to 4% equivalent MgO content, the zirconia is still largely unstabilized.

The second objective, obtaining reliable heat transfer measurements to 4500°F, was greatly aided by the successful improvements in strength. For the first time, using MgO-stabilized foams, heater temperature could be measured at 2500°C (4532°F) without deformation or fracture of the specimen and thermal conductivity data obtained.

All thermal conductivities measured in this contract were recalculated to obtain coefficients for mean temperatures over four different thermal gradients. Using a wider gradient reduced the scatter and permitted smooth curves to be constructed. Discarding those readings in which the heater temperature was used as one reference temperature eliminated errors which had caused an anomalously low conductivity curve, although these errors apparently approach zero at 4000°F and above.

Although variations in density of the foam probably contribute to differences in conductivity values, it was noted that the major cause of variation was associated with difference in composition. The data were grouped on this basis and averaged at 500°F intervals, allowing "average" thermal conductivity curves to be drawn for both calcia-stabilized and magnesia-stabilized zirconia foams. The latter have conductivity values which are half again as high as the former. This degree of difference may be due to the nature of the additive, the amount, its effect on structure or a combination of these factors.

Using the mean temperature for each gradient reading did not permit conductivity to be determined directly to temperatures higher than about 3700°F. However, by extrapolation and from the convergent curves obtained from several gradients above 4000°F, it is believed that a thermal conductivity of about 25-30 BTU/ft^2/hr/in/°F is a reasonable value for a typical magnesia-stabilized zirconia foam at 4500°F. Variations in density and other characteristics may change the coefficient by a factor of two, especially at intermediate temperatures.

Comparison with thermal conductivity data on dense refractory oxide ceramics shows that these zirconia foams are superior as thermal insulators up to 3500°F over all dense oxides except possibly ceria. The high porosity causes increases in radiative heat transfer approaching the theoretical rate; however, this rate of increase is apparently attenuated by grain boundary scattering by the particles and also by reflection from the pore walls. At 4500°F, zirconia foam has a heat transfer coefficient no more than double that of dense zirconia, but its low density makes it attractive for many applications.

5. RECOMMENDATIONS

5.1 Zirconia foams should be stabilized with about 3% equivalent MgO, added as an oxychloride or oxysulfate cement; these can be fired at more economical temperatures to yield a fine pore structure, porosities in the range 80-85%, and high bond strength permitting use at hot face temperatures of 4500°F.

5.2 Parameters for the reproducible production of such foams should be established.

5.3 Thermal conductivity measurements should be made on an apparatus modified to provide a small temperature difference over a long dimension, with the object of measuring conductivity directly at mean temperatures approaching 4500°F.

5.4 Other means of producing foam structures by high-temperature bubble formation should be investigated; such foams would presumably be even stronger.

5.5 The thermal cycling ability of these foams should be investigated, and correlated with the degree of stabilization.

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