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ALO 3633-10
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DEVELOPMENT OF 400F-2200F FIBROUS-
TYPE INSULATIONS FOR RADIOISOTOPE
POWER SYSTEMS

Seventh Quarterly Progress Report
Report No. ALO 3633-10

October 1, 1968

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FEDERAL BUREAU OF INVESTIGATION
By *ALL*
10/31/1968

Report Period: July 1, 1968 to September 30, 1968

by
J. O. Collins
K. L. Jaunaraajs
D. R. Reid

JOHNS-MANVILLE RESEARCH & ENGINEERING CENTER
Manville, New Jersey

Prepared under
Contract AT(30-1)-3633

for the
Albuquerque Operations Office
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ABSTRACT

by

J. O. Collins

The study of the basic phenomenon of sintering, and particularly that of submicron silica and alumina particles was completed. Thermal stability, thermal conductivity, porosity, and electron microscope evaluations all point to a particle agglomeration at temperatures lower than expected for these oxides.

Materials studies were also completed for ALON-C, K_2CO_3 shrinkage inhibitor, and ZrO_2 opacifier combinations. In light of the agglomeration tendencies, the effect of the shrinkage inhibitor on the ALON-C must be studied over extended periods of life testing before the true product characteristics can be determined.

Comparison of opacified and unopacified Glasrock foam silica thermal conductivities at various densities showed the ineffectiveness of the opacifiers within the normal product density range.

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1. INTRODUCTION

This Seventh Quarterly Progress Report under Contract No. AT(30-1)-3633 covers the effort conducted during July, August, and September 1968.

The study of the basic phenomenon of sintering and the evaluation of ALON-C submicron alumina, and candidate shrinkage inhibitors were completed this quarter. The effect of K_2CO_3 shrinkage inhibitor on the agglomeration and conversion tendencies of ALON-C (from gamma to alpha) were investigated at 2200F in air and vacuum. ZrO_2 opacifier was also included as a variable in the various compositions studied. The use of porosimeter and electron microscope techniques, as well as thermal stability and thermal conductivity clearly described the effect of temperature and inhibitor on the response of the ALON-C particles to the test conditions.

The opacified Glasrock foam silica investigation continued with the evaluation of products containing 5 and 10 percent ZrO_2 , and 5 percent TiO_2 . Problems with the manufacture of the 10 percent TiO_2 product precluded its evaluation during this quarter. A parallel thermal conductivity evaluation of unopacified Glasrock foam silica at a range of densities was performed so that the effectiveness of the candidate opacifiers could be fully ascertained. All conductivity values were obtained on the Rapid Heat Meter apparatus.

II. PHASE I, TASK 5 - DETAILED EVALUATION

Thermal Conductivity Measurement Efforts. Since the inception of this contract, thermal conductivity determinations have consumed a major portion of the total effort, and constituted a primary evaluation tool in the development of the new insulation products. Much of this effort was conducted on a new Guarded Hot Plate unit capable of mean temperatures up to 2000F, and enclosed in a chamber permitting evaluation of the insulations in air, vacuum (10^{-5} mm Hg), or any gaseous media as desired. As with any new and highly sensitive piece of equipment, the initial period of operation was plagued with burned out heater elements, thermocouple failures, over-heating (due to accidental failure of the water cooling system), flooding of the test chamber (waterline split), etc. After each mishap, the equipment was restored to its original condition. In some cases, small additions were incorporated into the unit such as insulation between the test and guard sections of the heater plates to minimize lateral heat flow at the plates, installation of differential thermal couples between the test and guard sections to magnify any temperature differential between these points for greater adjustment accuracy, grounding of critical areas to prevent stray ac fields from affecting the readings, etc.

In general, however, there were two basic time intervals during which data were collected, these intervals being separated by a major rewinding of the heater plates. Prior to rewinding, the equipment appeared to be slightly unstable, particularly at the higher temperatures, as witnessed by a slight unsteadiness of the temperature and power readings. The equipment also appeared somewhat slow to respond to external adjustments of power. These conditions led to some speculation as to their effect upon the accuracy of the data. After rewinding however, both of these apparent problems disappeared, and it was believed that the equipment was producing reliable data. The specific reason for their disappearance could not be established.

During the "unsteady and slow" period of operation, the data obtained for the MIN-K materials in air corresponded very closely with those obtained in the ASTM C-177 Guarded Hot Plate Apparatus using the identical specimens. Similarly, the argon data appeared to be as expected, although no means of confirmation was available. The vacuum data, although "as expected" in the 500F mean temperature range, rose sharply with increasing temperature, thus making it appear that a small extrapolation of the data would have placed it above the air conductivity data.

Since the rewiring of the heater plates, all measurements taken in air and argon have been exceptionally low, and in some cases have shown little or no change with temperature. Conversely, the vacuum data was "as expected" at 500F, and continued to follow what one would describe as an orderly, progressive increase with temperature.

An analysis of the available data does permit one to arrive at the best and most logical thermal conductivity vs mean temperature relationship for MIN-K Formulation 1999, 2002, and 2020 in air and argon. (Both Formulation 1999 and 2002 have completed their retest following 2000 hrs exposure to elevated temperature. Formulation 2020 has just begun retest.) The scientific justification (aside from theoretical considerations) for choosing one set of vacuum data as being correct, and one set as incorrect however, is lacking at the present time.

Thermal Conductivity in Air. The case for the choice of conductivity values in air is probably the strongest. The various tests conducted in air, and the equipment used are outlined in Table 1. Those tests marked with an asterisk resulted in essentially the same conductivity vs mean temperature regression within 5 percent of the grand average of all 4 sets of data. These tests probably produced the correct data. This conclusion is strengthened by the confirmation provided by the ASTM C-177 Guarded Hot Plate tests. Of the tests conducted in air on the special atmosphere equipment following the rewinding, only one set of data (Formulation 2020) showed a progressive increase in conductivity with mean temperature. These data were too low to be accepted in light of the results on the same specimens tested in the ASTM C-177 equipment, however.

Thermal Conductivity in Argon. Prior to rewinding of the equipment, Formulations 1999 and 2002 were evaluated in argon. Their results were exceptionally close (a maximum spread of 0.004 Btu in/hr ft² °F), and in good relationship with the air values obtained within the same time period. If the thermal conductivity values in air which were confirmed by the ASTM C-177 test are accepted, then theoretical considerations dictate that the argon curve would be slightly lower and approximately parallel to the air curve. The full effect of the difference in conductivity between the two gases alone would not be realized in MIN-K, since the gaseous conduction portion of the total conduction of MIN-K is already less than that of the free gas.

The other data in argon (after rewinding) was 20 percent below the initial data at 500F mean temperature, increased gradually to 800F mean temperature, and subsequently appeared to level off between 800F and 1300F mean temperature. In light of this erratic behavior, these data were discarded, and the earlier data (before rewinding) were considered to carry greater validity. Table 2 summarizes the thermal conductivity tests conducted in argon.

Thermal Conductivity in Vacuum. Both Formulations 1999 and 2002, before extended thermal exposure, were evaluated in vacuum in the special atmosphere equipment prior to the major rewinding. Although these data were in excellent agreement, the extreme slope of the curves indicated that a crossing of the vacuum and air data might take place at 1400-1500F mean temperature. Subsequently, Formulation 2020, prior to extended exposure, was evaluated in vacuum following the rewinding of the heater plates, as were both Formulations 1999 and 2002, after extended exposure. All three materials followed what could be considered as the "proper" conductivity vs mean temperature relationship during the latter series of tests, with no indication of crossover with the air data. Table 3 summarizes the thermal conductivity tests conducted in vacuum.

TABLE I.
SUMMARY OF MIN-K THERMAL CONDUCTIVITY
EVALUATION IN AIR

<u>Formulation No.</u>	<u>Exposure Conditions Prior to Test</u>	<u>Test Equipment</u>	<u>Data Validity</u>
2002*	2000 hrs, 1200F 1 atm. argon	ASTM C-177 Guarded Hot Plate	Accepted
2020*	none	ASTM C-177 Guarded Hot Plate	Accepted
1999*	none	Special atmosphere equipment before rewinding	Accepted
2002*	none	Special atmosphere equipment before rewinding	Accepted
2020	none	Special atmosphere equipment after rewinding	Rejected
1999	2000 hrs, 1000F 1 atm. argon	Special atmosphere equipment after rewinding	Rejected
2002	2000 hrs, 1200F 1 atm. argon	Special atmosphere equipment after rewinding	Rejected

*All tests produced the same conductivity vs mean temperature regression within 5 percent of the grand average.

TABLE 2.
SUMMARY OF MIN-K THERMAL CONDUCTIVITY
EVALUATIONS IN ARGON

<u>Formulation No.</u>	<u>Exposure Conditions Prior To Test</u>	<u>Test Equipment</u>	<u>Data Validity</u>
1999	none	Special atmosphere equipment before rewinding	Accepted
2002	none	Special atmosphere equipment before rewinding	Accepted
1999	2000 hrs, 1000F, 1 atm. argon	Special atmosphere equipment after rewinding	Rejected
2002	2000 hrs, 1200F 1 atm. argon	Special atmosphere equipment after rewinding	Rejected
2020	none	Special atmosphere equipment after rewinding	Rejected

TABLE 3.
SUMMARY OF MIN-K THERMAL CONDUCTIVITY
EVALUATIONS IN VACUUM

<u>Formulation No.</u>	<u>Exposure Conditions Prior to Test</u>	<u>Test Equipment</u>
1999	none	Special atmosphere equipment before rewinding
2002	none	Special atmosphere equipment before rewinding
1999	2000 hrs, 1000F 1 atm. argon	Special atmosphere equipment after rewinding
2002	2000 hrs, 1200F 1 atm. argon	Special atmosphere equipment after rewinding
2020	none	Special atmosphere equipment after rewinding

Confirmation of either set of data at the Johns-Manville Research & Engineering Center is not possible, since only one special atmosphere conductivity apparatus is available for these elevated temperatures. Evaluations of MIN-K 2000 by Dynatech at the request of WANL in November 1967 resulted in a conductivity vs mean temperature relationship in vacuum ($2-4 \times 10^{-4}$ mmHg) slightly above that described by the original Johns-Manville data (before rewinding). Assuming that the increased opacification efficiency of the new formulations over MIN-K 2000 accounted for this difference, the Dynatech data and the initial Johns-Manville data appear to be in good agreement.

An examination of the Dynatech data in air and vacuum would also indicate a potential crossover. However, conversations with Dynatech personnel uncovered more recent tests on MIN-K 2000 at still higher mean temperatures. These data showed that the slope of the conductivity vs mean temperature curve in air increased sufficiently above 1200F to prevent the crossover of the vacuum curve. Thus, it would appear that the early (and higher) vacuum data are correct.

Summary of Thermal Conductivity Data. Figure 1 presents the composite of air and argon data considered to be the best obtained to date. Also shown are the two sets of vacuum data. A comparison of the conductivity values in Figure 1 at 1100F mean temperature with those predicted in the First Quarterly Progress Report (Report No. ALO-3633-1, Table 2) is given in Table 4. Good agreement between predicted and test values was obtained in air. The same might be said for the values in argon, although room for improvement of the predicted value does exist. If the recent vacuum data are accepted, the relationship between theory and test appears to be excellent. However, the first vacuum data, which generally substantiated the Dynatech data, was considerably higher than anticipated.

Since data confirmation by an independent source must be considered a strong case for validity, it would appear that the existing theory is in error. This is further accented by the trend of the magnitude of the error (-5.6%, -13.9%, and -33.6%) as the gaseous media is altered. However, before any additional theoretical analyses can be undertaken, further confirmation of the vacuum data must be obtained. To this end, the test equipment is being examined to determine the cause of the conflict in test values.

FIGURE 1.

BEST COMPOSITE OF THERMAL CONDUCTIVITY
DATA FOR FORMULATIONS 1999, 2002, and 2020

TABLE 4.

COMPARISON OF PREDICTED AND TEST THERMAL CONDUCTIVITY VALUES
FOR MIN-K AT 1100F MEAN TEMPERATURE

<u>Condition</u>	<u>Test Value</u> <u>Btu in/hr ft² °F</u>	<u>Predicted Value*</u> <u>Btu in/hr ft² °F</u>	<u>Deviation of Predicted</u> <u>From Test Value</u>
Air	0.267	0.252	-5.6%
Argon	0.244	0.210	-13.9%
Vacuum	0.144	0.138	-4.2%
Vacuum	0.208	0.138	-33.6%

*Table 2 of First Quarterly Progress Report, Report No. ALO 3633-1
assuming 2 micron opacifier size.

Conclusions Based Upon Tests to Date

Assuming that the above data analysis summarized in Figure 1 is reasonably accurate, several conclusions can be drawn regarding the thermal conductivity of Formulations 1999, 2002, and 2020:

1. The thermal conductivity of these three insulations in air prior to simulated service exposure is the same.
2. The thermal conductivity of Formulations 1999 and 2002 in argon prior to simulated service exposure is the same.
3. Prolonged exposure at elevated temperature in argon does not alter the thermal conductivity of Formulations 1999 and 2002 in air.

From these conclusions, it is reasonable to believe that:

1. The thermal conductivity in air, argon, or vacuum is not affected by the minor reinforcement media differences found in Formulations 1999, 2002, and 2020.
2. The thermal conductivity is not altered by prolonged service exposure within the limits of the conditions used under this evaluation.

These two beliefs have been considered valid since the inception of this effort, and data to date have not shown to the contrary.

III. PHASE II, TASK 2 - MATERIAL RESEARCH & DEVELOPMENT

Subtask 2.1 - Basic Studies

Effect of Opacifier Content. Previous evaluations of different opacifiers which were reported in the Fifth and Sixth Quarterly Progress Reports were carried out on an equal weight basis. That is, the experimental compositions contained 16 percent by weight of the opacifier, regardless of the molecular weight of the opacifier. During this quarter however, samples were prepared containing the different opacifiers on an equal mol basis. The amount of opacifier added was based on 16 percent by weight TiO_2 addition. ALON-C alpha was used exclusively for this series of specimens. Density and thermal conductivity (by the comparative method) measurements were taken after various heat treatments. These results are presented in Table 5. Included in Table 5 for direct comparison are the results presented in Table 6 of the Sixth Quarterly Progress Report where the opacifiers were added on an equal weight basis.

It can be seen from Table 5 that from a thermal conductivity standpoint, there was no significant overall advantage to adding the heavier opacifiers (Cr_2O_3 , ZrSiO_4 , ZrO_2) on an equal mol basis with TiO_2 . This would apply not only when comparing weight and mol additions of the same opacifier, but also when comparing TiO_2 and the other opacifiers on a mol basis. Only samples in the unfired condition, and samples heat treated at 2200F in air appeared to show an improvement when measured under vacuum conditions (comparing equal weight and equal mol additions for the same opacifier).

It can also be seen that there was a definite improvement in the thermal stability of the samples containing the heavier opacifiers added on an equal mol basis with the standard TiO_2 . This increased stability was probably the result of the additional amount of the more stable opacifier material in the sample composition. Because the thermal conductivity was not significantly affected, either beneficially or detrimentally, the addition of the opacifiers on a mol basis would probably be desirable from a thermal stability standpoint. This is particularly true of the ZrO_2 opacifier, since Cr_2O_3 and ZrSiO_4 are most likely ruled out because of volatility in vacuum (see Subtask 3.2 in the Sixth Quarterly Progress Report). It should be pointed out that the small negative changes in density resulted because of a slight increase in sample thickness after heat treatment.

Porosity. During the past quarter, porosity measurements were made on MIN-K type formulations containing ALON-C gamma and ALON-C alpha alumina. Measurements were made on samples which had been heat treated to 2000F or 2200F in either air or vacuum conditions. Both total porosity and pore size distribution values were obtained using an Amino-Winslow Porosimeter. This apparatus uses mercury penetration under pressure to determine pore sizes ranging from 0.035 to

TABLE 5.

THERMAL STABILITY AND THERMAL CONDUCTIVITY OF
ALON-C ALPHA SPECIMENS CONTAINING OPACIFIERS
ON AN EQUAL WEIGHT AND EQUAL MOL BASIS

Sample	Number	Basis of Opacifier Addition	5 hr Isothermal Heat Treatment	Density Before Heat Treatment pcf	Change in Density %	Thermal Conductivity @ 725F Mean Temp Btu in./hr ft ² of	
						Air	Vacuum
MIN-K/ALON-C alpha/TiO ₂	112-1	Weight	none	30.1	--	0.38	0.14
	BS-54	Weight	2000F, Air	32.1	1.2	0.38	0.14
	BS-53	Weight	2000F, Vac	29.9	2.3	0.42	0.14
	BS-64	Weight	2200F, Air	23.9	30.6	0.57	0.16
	BS-63	Weight	2200F, Vac	28.5	15.1	0.54	0.18
MIN-K/ALON-C alpha/Cr ₂ O ₃	112-2	Weight	none	30.5	--	0.35	0.15
	BS-56	Weight	2000F, Air	30.8	1.0	0.35	0.15
	BS-55	Weight	2000F, Vac	26.0	3.1	0.40	0.15
	BS-66	Weight	2200F, Air	29.7	25.3	0.51	0.17
	BS-65	Weight	2200F, Vac	24.1	6.6	0.53	0.20
MIN-K/ALON-C alpha/ZrSiO ₄	112-3	Weight	none	27.3	--	0.39	0.16
	BS-58	Weight	2000F, Air	29.8	2.3	0.40	0.16
	BS-57	Weight	2000F, Vac	31.9	3.1	0.39	0.15
	BS-68	Weight	2200F, Air	27.8	14.4	0.58	0.19
	BS-67	Weight	2200F, Vac	27.5	6.2	0.47	0.18
MIN-K/ALON-C alpha/ZrO ₂	112-4	Weight	none	28.9	--	0.36	0.15
	BS-60	Weight	2000F, Air	28.6	2.1	0.40	0.15
	BS-59	Weight	2000F, Vac	27.7	3.6	0.39	0.15
	BS-70	Weight	2200F, Air	27.0	16.3	0.56	0.18
	BS-69	Weight	2200F, Vac	27.6	14.5	0.50	0.17

(CONTINUED)

TABLE 5. (CONTINUED)

Sample	Number	Basis of Opacifier Addition	5 hr Isothermal Heat Treatment	Density Before Heat Treatment pcf	Change in Density %	Thermal Conductivity @ 725F Mean Temp Btu in./hr ft ² °F	
						Air	Vacuum
MIN-K/ALON-C alpha/TiO ₂	112-1	Mol	none	30.1	--	0.38	0.14
	BS-54	Mol	2000F, Air	32.1	1.2	0.38	0.14
	BS-53	Mol	2000F, Vac	29.9	2.3	0.42	0.14
	BS-64	Mol	2200F, Air	23.9	30.6	0.57	0.16
	BS-63	Mol	2200F, Vac	28.5	15.1	0.54	0.18
MIN-K/ALON-C alpha/Cr ₂ O ₃	115-1	Mol	none	36.4	--	0.36	0.12
	BS-82	Mol	2000F, Air	31.6	-2.8	0.41	0.15
	BS-81	Mol	2000F, Vac	32.5	-1.8	0.46	0.14
	BS-76	Mol	2200F, Air	33.2	13.0	0.44	0.13
	BS-75	Mol	2200F, Vac	33.8	9.2	0.47	0.14
MIN-K/ALON-C alpha/ZrSiO ₄	115-3	Mol	none	34.8	--	0.40	0.13
	BS-86	Mol	2000F, Air	27.4	-0.4	0.44	0.15
	BS-85	Mol	2000F, Vac	34.8	-0.3	0.48	0.15
	BS-80	Mol	2200F, Air	37.6	10.1	0.49	0.14
	BS-79	Mol	2200F, Vac	34.6	2.9	0.50	0.19
MIN-K/ALON-C alpha/ZrO ₂	115-2	Mol	none	31.6	--	0.36	0.12
	BS-84	Mol	2000F, Air	34.9	-0.3	0.45	0.14
	BS-83	Mol	2000F, Vac	36.2	0.8	0.45	0.14
	BS-78	Mol	2200F, Air	30.3	3.3	0.54	0.15
	BS-77	Mol	2200F, Vac	39.5	11.1	0.60	0.19

100 microns. Samples for porosity measurements were approximately 1/4 in. cubes cut from the interior of the experimental samples. Care was taken not to include the skin of any specimen. An average of three porosimeter tests was used to obtain the values reported for each sample. The results of these tests are shown in Figures 2 through 6.

Results showed that formulations containing gamma ALON-C had a greater number of fine pores needed for the MIN-K effect than formulations containing alpha ALON-C (compare Figures 2a and 2b with Figures 2c and 2d). Note that these fine pores still remained in samples heat treated in either air or vacuum up to 2000F (see Figures 3 and 4). This differed from the porosimeter results presented in the Fifth Quarterly Progress Report, April 1, 1968. However, in that report the samples also contained titania (TiO_2) which has been shown to exhibit a fluxing action at 2000F, particularly under vacuum conditions.

The loss of the MIN-K type pores after the 2200F heat treatment is quite obvious (see Figures 5 and 6). This occurred for both alpha ALON-C and gamma ALON-C compositions under both air and vacuum conditions.

It is of particular interest that the pore size tended to center around 0.1 to 0.5 microns regardless of the type of specimen or exposure condition. It has been suggested (by the paint industry) that submicron size particles of titania will agglomerate to a specific size at some temperature below the normal sintering temperature, and maintain this size until the normal sintering temperature is attained. This initial agglomeration of titania has been attributed to Vander Waal's forces. The current porosimeter data tended to support this hypothesis with respect to the ALON-C particles.

Electron micrographs of heat treated ALON-C also appeared to support this hypothesis. Figures 7 and 8 are "rubout" electron micrographs of ALON-C before and after heat treatment respectively. Before exposure to 2200F, the ALON-C was primarily gamma alumina with an average particle size of .03 microns. Note, however, that there were a number of considerably larger particles (Figure 7) which account for the wide distribution of pore sizes even in unfired ALON-C. After exposure to 2200F much of the ALON-C was converted to the alpha form. However, the alpha agglomerates or crystals did take on what appeared to be a certain limiting size as observed in Figure 8.

Only when the TiO_2 was present did the major pore size differ from 0.1 to 0.5 microns after heat treatment. This was because of the considerably larger alumina crystals which developed as a result of the fluxing action. Evidence of this may be seen in the porosity results (Figure 9) and the electron micrograph of MIN-K/ALON-C gamma/ TiO_2 (Figure 10) after exposure to 2000F in vacuum for 5 hours.

FIGURE 2.

PORE SIZE DISTRIBUTION AND TOTAL POROSITY OF UNFIRED ALON-C SPECIMENS

FIGURE 3.

PORE SIZE AND TOTAL POROSITY
OF MIN-K/ALON-C ALPHA SPECIMENS
EXPOSED TO 2000F FOR 5 HOURS

FIGURE 4

PORE SIZE AND TOTAL POROSITY
OF MIN-K/ALON-C GAMMA SPECIMENS
EXPOSED TO 2000F FOR 5 HOURS

FIGURE 5

PORE SIZE AND TOTAL POROSITY OF MIN-K/ALON-C ALPHA SPECIMENS
EXPOSED TO 2200F FOR 5 HOURS

FIGURE 6

PORE SIZE AND TOTAL POROSITY OF MIN-K/ALON-C GAMMA SPECIMENS
EXPOSED TO 2200F FOR 5 HOURS

Pore Size - Microns

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FIGURE 7.

ALON-C GAMMA
MAG: 27,500X

NEG 750-B

FIGURE 8.

ALON-C ALPHA
MAG: 27,500X

FIGURE 9.

TOTAL POROSITY AND PORE SIZE DISTRIBUTION
OF MIN-K/ALON-C/TiO₂ FORMULATION

FIGURE 10.

MIN-K/ALON-C GAMMA/TiO₂
2000F FOR 5 HR IN VACUUM
MAG: 27,500X

Scanning Electron Micrographs. Figures 11-14 are scanning electron micrographs of several MIN-K/ALON-C type bodies which were heat treated under both air and vacuum conditions. The scanning method permits direct observation of a freshly fractured surface, and results in a micrograph having a distinct three-dimensional appearance.

The electron micrographs which were taken this past quarter indicated that for MIN-K/ALON-C type bodies which have been heat treated up to 2200F under either air or vacuum conditions, there was no significant macro change other than an increase in density. This condition applied to both alpha ALON-C and gamma ALON-C formulations.

Figure 11 shows MIN-K/ALON-C gamma in the unfired state, while Figure 12 shows this body after a five hour exposure at 2200F in vacuum. Other than an increase in density, there was no major change noted. This same observation was made for the 2200F heat treatments in air as well as for heat treatments at 2000F in both air and vacuum. Figure 13 shows MIN-K/ALON-C alpha in the unfired state, while Figure 14 shows this body after a five hour exposure at 2200F in air. Again no major change was noted here or in the other heat treatments of this body.

The scanning electron micrographs of the Sixth Quarterly Progress Report showed that there was a significant change in the overall structure of MIN-K/ALON-C gamma/TiO₂ formulations with heat treatment particularly under vacuum conditions. (See Figure 15). These changes were due to the fluxing action of the TiO₂. Therefore, these electron micrographs indicate that if TiO₂ were not present, no significant macro changes in structure would take place with heat treatment regardless of the form of alumina (gamma or alpha) used.

Electron micrographs were also taken of MIN-K/ALON-C alpha/TiO₂ and MIN-K/ALON-C alpha/ZrO₂ samples. Several of these micrographs are presented in Figures 16-19. Again, with the exception of the density increase there was no major change in the overall structures after 2000F or 2200F heat treatments. In the presence of the more stable alpha ALON-C, TiO₂ did not exhibit the fluxing action which it did in the presence of ALON-C gamma.

In view of the evidence of the electron micrographs and the porosity data, it is concluded that if TiO₂ or similar flux were not present, all changes in MIN-K/ALON-C type formulations up to 2200F would be submicron in nature and would not involve sintering to form larger agglomerates.

FIGURE 11.

MIN-K/ALON-C GAMMA
UNFIRED CONTROL
MAG: 800X

FIGURE 12.

MIN-K/ALON-C GAMMA
2200F FOR 5 HR IN VACUUM
MAG: 800X

FIGURE 13.

MIN-K/ALON-C ALPHA
UNFIRED CONTROL
MAG: 800X

FIGURE 14.

MIN-K/ALON-C ALPHA
2200F FOR 5 HR IN AIR
MAG: 800X

FIGURE 15.

MIN-K/ALON-C GAMMA/TiO₂
2000F FOR 5 HR IN VACUUM
MAG: 800X

FIGURE 16.

MIN-K/ALON-C ALPHA/TiO₂
UNFIRED CONTROL
MAG: 800X

FIGURE 17.

MIN-K/ALON-C ALPHA/TiO₂
2200F FOR 5 HR IN VACUUM
MAG: 800X

FIGURE 18.

MIN-K/ALON-C ALPHA/ ZrO_2
2000F FOR 5 HR IN VACUUM
MAG: 800X

FIGURE 19.

MIN-K/ALON-C ALPHA/ ZrO_2
2200F FOR 5 HR IN VACUUM
MAG: 800X

Subtask 2.2 - Materials

Shrinkage Inhibitor Evaluation. It was concluded in the Sixth Quarterly Progress Report (Report No. ALO 3633-1, dated July 1, 1968, Tables 3 and 4) that 5 mol percent of K_2CO_3 was the optimum amount and type of shrinkage inhibitor for ALON-C gamma based on isothermal tests in air and vacuum at 2200F. This conclusion was based upon the evaluation of 20 pcf density 1-1/8 in. diameter x 1/2 in. thick discs made from ALON-C (gamma) submicron alumina, 5 weight percent ASTROQUARTZ 1/4 in. staple and 4 weight percent MICRO-QUARTZ fibers and 16 weight percent TiO_2 opacifier (where used). This test also confirmed previous data that TiO_2 acted as a flux for ALON-C and hence, should not be used as the opacifier at this temperature.

Subsequent effort during the most recent quarter investigated the effect of ZrO_2 opacifier and K_2CO_3 inhibitor on the shrinkage of similar sized discs made with both gamma and alpha ALON-C, and pressed to 30 pcf density. This increase in density was considered desirable from a handling standpoint in the case of the gamma ALON-C specimens, and a necessity in the case of the specimens made from the more dense alpha ALON-C. ASTROQUARTZ and MICRO-QUARTZ fibers were also incorporated into the specimens at the same weight percent amounts indicated for the earlier experiments. The test time at 2200F was extended to include a 24-hr exposure as well as a 2-hr exposure. Table 6 presents the average linear shrinkage (diameter only) of these specimens.

From this evaluation series, it appeared that the inhibitor was more effective than the opacifier in preventing shrinkage as expected, although previous work indicated that 16 weight percent of zirconia in combination with MIN-K/ALON-C gamma also provided a slight inhibiting action (Fifth Quarterly Progress Report, Report No. ALO-3633-8, Table 8, and Table 5 of this report). Similarly, the effect of both the inhibitor and zirconia opacifier together was not noticeably different from that of the inhibitor alone. This is significant in that it showed that the combination of all of these materials did not result in a catastrophic shrinkage.

Table 6 also points out, as expected, that the ALON-C alpha specimens were more stable than the ALON-C gamma specimens. It has been shown previously, however (Sixth Quarterly Progress Report, Report No. ALO-3633-9, Table 6), that ALON-C alpha no longer has the desirable pore size distribution to yield the low thermal conductivity values in a gaseous media characteristic of MIN-K. This is also shown from the porosity data presented under Subtask 2.1 above.

Finally, initial evaluations of ALON-C gamma in combination with titania opacifier (Fifth Quarterly Progress Report, Report No. ALO-3633-8, Table 8) showed the shrinkage of the specimen to be considerably greater in vacuum than in air. This characteristic was found, in subsequent evaluations, to be peculiar

TABLE 6.

LINEAR SHRINKAGE OF MIN-K/ALON-C
CONTAINING INHIBITOR AND OPACIFIER
AFTER EXPOSURE TO 2200F (ISOTHERMAL)

Type of ALON-C	16 Wt % Opacifier	Inhibitor	Percent Linear Shrinkage*			
			in air		in vacuum	
			2 hr	24 hr	2 hr	24 hr
gamma	ZrO ₂	--	15.8	15.4	18.4	19.3
gamma	--	K ₂ CO ₃	4.6	11.0	7.9	14.4
gamma	ZrO ₂	K ₂ CO ₃	4.4	11.0	8.8	13.2
alpha	ZrO ₂	--	4.9	11.7	8.8	10.5
alpha	--	K ₂ CO ₃	2.1	6.5	5.3	7.4
alpha	ZrO ₂	K ₂ CO ₃	4.4	9.6	6.5	8.5

*Average of two specimens

to this combination of materials. Thus, although most of the shrinkage values shown in Table 6 are slightly higher following the vacuum exposure than following the air exposure, minimal significance should be attributed to this difference at this time.

The effect of ZrO_2 opacifier content on the thermal stability of MIN-K/ALON-C gamma discs after 2 hr at 2200F in air and vacuum was then determined. The opacifier content ranged from 16 weight percent to 28.3 weight percent, the latter content representing the mol percent equivalent to 16 weight percent of TiO_2 used in the lower temperature MIN-K formulations. No shrinkage inhibitor was used to mask the effect of the zirconia. All specimens were 30 pcf nominal density. Table 7 summarizes these results.

It would appear that greater amounts of zirconia helped to stabilize the composition in air, but was slightly detrimental to the stability in vacuum. Comparison of the shrinkage values for the 16 weight percent specimens tested in air as shown in Tables 7 and 6 (15.7 vs 15.8 percent) indicates excellent agreement, and hence, the trend in air may be real. A similar comparison of the shrinkage values of the same specimens tested in vacuum (17.5 percent vs 18.4 percent), although still considered in good agreement, tends to negate what might appear at first glance to be a trend.

All work on the thermal stability of the ALON-C - fiber - opacifier - inhibitor combinations had been conducted on small (1-1/8 in. diameter x 3/8 to 1/2 in. thick) specimens. Although gross effects due to composition changes could be established, minor effects - differences of several percent - could not be considered significant due to the potential error involved in measuring these small samples. Consequently, a test series was conducted with larger specimens molded from a formulation which was processed in the same manner (batching and Henschel mixing) as that used for the other pilot plant formulations studied under both phases of this contract.

Formulation 2041, shown in Table 8 was chosen as the optimum combination of ingredients for this larger scale thermal stability evaluation. The most obvious difference between this formulation and previous formulations (not only those devised for the small scale materials evaluation discs, but also the lower temperature "standard" formulations such as 1999, 2002, and 2020), was the elimination of the MICRO-QUARTZ fiber. MICRO-QUARTZ was shown to have an adverse effect on the thermal stability of Formulation 2020 unless it was prefired prior to batching (Phase 1 Final Report, Report No. ALO 3633-7, dated October 2, 1967). At 2200F, this effect would probably have been magnified still further. Since some fiber was required to impart handleability to the molded product, ASTROQUARTZ, a more temperature stable fiber, was retained in the formulation.

TABLE 7.
EFFECT OF ZIRCONIA CONTENT ON LINEAR SHRINKAGE
OF MIN-K/ALON-C GAMMA
(2200F isothermal, 2 hr)

<u>Weight % ZrO₂</u>	<u>Average Linear Shrinkage*</u>	
	<u>in air</u>	<u>in vacuum</u>
16.0	15.7	17.5
20.0	15.6	17.3
21.2	14.2	18.0
24.2	13.2	18.6
25.6	12.3	18.0
28.3	12.3	19.0

*Average of two specimens

TABLE 8.
MIN-K FORMULATION 2041

<u>Constituent</u>	<u>Weight Percent</u>
ALON-C gamma	74
ASTROQUARTZ 1/4 in. staple	5
ZrO ₂	16
K ₂ CO ₃	5*

*Represents 5 mol percent based upon ALON-C gamma content

Blocks 9 x 9 x 1 in. were pressed from the pilot plant mix to 20 and 30 pcf nominal densities. They were then cut to 3 x 2 x 1 in. specimens and measured to the nearest 0.001 in. Unlike the small disc specimens, they were not stored in dessicators until tested, but remained at the 72F, 40%RH room condition. These specimens were subjected to 2, 24, and 168 (1 wk) hr exposures to 2200F (isothermal) in air and vacuum. Tables 9 and 10 summarize the shrinkage results.

The first observation from both tables of data was that the 30 pcf density specimens were more stable than the 20 pcf density specimens. A second, and probably more important observation was that the shrinkage rate appeared to lessen considerably (on the average) in air after 24 hr, whereas it showed more indication of continuing beyond 168 hr in vacuum. Thus, the original hypothesis that submicron alumina particles shrink more in vacuum than in air (although subsequently tied to the TiO_2 opacifier as the prime cause for this phenomenon), may in fact hold true, given sufficient time at temperature.

During the tests in air, a considerable amount of moisture was noted within the furnace system (see Sixth Quarterly Progress Report, Report No. ALO 3633-9 for a full description of the equipment). As previously noted, these specimens were not stored in a dessicator prior to test, and hence, absorbed considerable quantities of moisture due to the hygroscopic nature of the K_2CO_3 inhibitor. Four specimens of Formulation 2041 at 20 pcf density and four specimens at 30 pcf density were dried at 400C (752F) in air for 18 hr, and subsequently retested for shrinkage at 2200F for 24 hr in air. Weight loss as a result of drying was 7 percent, and an additional 3 percent (both based upon the undried weight) was driven off as a result of the 2200F firing. The results of this shrinkage test are given in Table 11.

On the average, the shrinkage in air after drying was about 75 to 78 percent of that shown in Table 9, although the effect was more pronounced on the thickness shrinkage than the length and width shrinkage. This would indicate that the moisture either contributed directly to the shrinkage, or prevented the K_2CO_3 from inhibiting the agglomeration of the ALON-C particles. It would not be unreasonable to assume also that had the specimens been completely dry prior to test, an additional improvement in thermal stability may have been realized.

Based upon the known effect of drying upon the shrinkage after 24 hrs at 2200F, Table 12 was prepared. All numbers in italics represent estimates based on the 24-hr exposure data (Table 11). This "adjustment", shown in Table 12, does not alter the basic conclusion that, over prolonged exposure, Formulation 2041 probably would shrink more in vacuum than in air. It becomes doubtful that the shrinkage data in vacuum would be altered by pre-drying the specimens when one considers the heating cycle employed for all tests. The specimens were placed in the furnace, heated to 1000F, and held at this temperature overnight (approximately 18 hr) under active vacuum. Heatup to 2200F was then

TABLE 9.

LINEAR SHRINKAGE OF FORMULATION 2041 IN AIR
AT 2200F ISOTHERMAL

Nominal Density pcf	Firing Time hr	Average Shrinkage, % *		
		Length	Width	Thickness
20	2	6.5	6.6	7.6
20	24	12.1	12.3	15.8
20	168	12.8	13.4	28.4
30	2	5.3	5.3	4.8
30	24	10.2	9.7	12.3
30	168	10.2	10.7	17.6

*Average of four specimens

TABLE 10.

LINEAR SHRINKAGE OF FORMULATION 2041 IN VACUUM
AT 2200F ISOTHERMAL

Nominal Density pcf	Firing Time hr	Average Shrinkage, % *		
		Length	Width	Thickness
20	2	3.8	4.0	3.8
20	24	7.1	7.3	7.8
20	168	15.1	15.2	18.5
30	2	3.2	3.4	3.4
30	24	6.7	7.0	6.5
30	168	13.2	13.3	15.5

*Average of four specimens

TABLE II.

LINEAR SHRINKAGE OF FORMULATION 2041 IN AIR
AT 2200F FOLLOWING 400C DRYING

Nominal Density pcf	Firing Time hr	Average Shrinkage, % *		
		Length	Width	Thickness
20	24	9.5	10.3	11.2
30	24	7.6	8.2	8.0

*Average of four specimens

TABLE 12.

ESTIMATED LINEAR SHRINKAGE OF FORMULATION 2041 IN AIR
AT 2200F ISOTHERMAL

Nominal Density pcf	Firing Time hr	Average Shrinkage, % *		
		Length	Width	Thickness
20	2	5.1	5.5	5.4
20	24	9.5	10.3	11.2
20	168	10.0	11.3	20.2
30	2	4.0	4.5	3.1
30	24	7.6	8.2	8.0
30	168	7.7	9.1	11.4

*Average of four specimens

accomplished the following day in about 3 hr, also under active vacuum. Consequently, it is believed that essentially all of the moisture was removed from the system before the temperature reached a critical point, thus eliminating any adverse effect on the specimens.

X-ray diffraction data were obtained for typical specimens subjected to the 2200F exposure. These tests were qualitative in nature, but did provide an order-of-magnitude estimate of the extent of conversion from the gamma alumina form of ALON-C. Table 13 summarizes these results. It is apparent that the inhibitor suppressed the formation of alpha alumina, enhanced the formation of amorphous alumina (balance in each case assumed to be amorphous since no significant quantities of any other crystalline forms were detected), and minimized, or at least retarded the agglomeration of the submicron particles as indicated by the shrinkage data.

TABLE 13.

QUALITATIVE X-RAY DIFFRACTION ANALYSIS
OF FORMULATION 2041 FOLLOWING 2200F EXPOSURE

<u>Firing Time</u> <u>hrs</u>	<u>Form and Amount of Alumina</u>	
	<u>Air</u>	<u>Vacuum</u>
2	Trace of alpha, balance amorphous	Trace of alpha, balance amorphous
24	Moderate alpha (40 - 60%), balance amorphous	Trace of alpha, balance amorphous
168	Moderate alpha (40 - 60%), balance amorphous	Moderate alpha (40 - 60%), balance amorphous

IV. TASK 3 - LOAD BEARING INSULATION FOR 400-1800F SERVICE

Subtask 3.1 - Load-Bearing Insulation to 1400F

No further work was done on this subtask during this quarter. Formulation 2002 at 35 pcf density is currently awaiting its turn in the special atmosphere thermal conductivity apparatus for evaluation in argon.

Subtask 3.2 - Load Bearing Insulation for 1800F Service

The Sixth Quarterly Progress Report described the manufacture and evaluation of Glasrock foam silica containing 15 percent by weight of TiO_2 , ZrO_2 , ZrSiO_4 , and CrO_3 for purposes of opacification. Based upon the evaluation tests, ZrSiO_4 and Cr_2O_3 were eliminated from further consideration because of their excessive outgassing tendencies, particularly at 1800F under active evacuation conditions. Part 2 of the Program Plan was then initiated during this quarter to evaluate the remaining two candidates at the 5 and 10 percent levels of addition.

Manufacture. The manufacture of Glasrock silica foam containing 5 and 10 percent (nominal) ZrO_2 was conducted in the same manner as the previous product containing 15 percent ZrO_2 . No basic difficulties were encountered. It is estimated that the pore size was slightly smaller and more uniform as a result of the lower opacifier content. Comments by the manufacturer indicated that the lower additive content appeared to have less effect upon the unfired characteristics of the foamed slab (internal sag, drying cracks, etc.) than the original 15 percent level. Consequently, less control over slurry properties such as percent solids and pH would be required under production conditions.

Similar success was not achieved with the 5 and 10 percent TiO_2 products. Although the 15 percent TiO_2 product was successfully manufactured and evaluated, the first run of the 10 percent TiO_2 product resulted in a complete loss of all usable material due to excessive cracking and crazing of the product. The 5 percent TiO_2 specimens also cracked and crazed, but a judicious choice of test samples permitted the product evaluation to be conducted.

Subsequent trials of the 10 percent TiO_2 product finally resulted in a satisfactory product. This was attributed to more intimate mixing of the TiO_2 with the silica slip prior to casting. Samples of this product were received at the end of this quarter. Based upon the evaluation of the 5 percent TiO_2 , 5 and 10 percent ZrO_2 , and the unopacified products (see subsequent discussions), the initial evaluation will be limited to thermal conductivity at 800F mean temperature.

Density. The density of the 5 percent TiO_2 , and the 5 and 10 percent ZrO_2 opacified products is summarized in Table 14. In general, the product density was considered satisfactory. Maximum uniformity was obtained with the 5 percent TiO_2 product, while the major variation in the ZrO_2 products occurred in the thermal stability specimens, which also were the smallest of the test specimens.

Strength. The effect of 5 and 10 percent ZrO_2 and 5 percent TiO_2 on the cold crushing strength of the product is summarized in Table 15. A comparison with previous tests on the 15 percent opacified products (Sixth Quarterly Progress Report, Report No. ALO 3633-9, Table 10) showed that the reduction in ZrO_2 content had little effect (695 psi vs 730 psi) on the average crushing strength at room temperature. This should be anticipated since the strength was already in the 500-750 psi range of the standard unopacified product. The reduction in TiO_2 content from 15 percent to 5 percent however, resulted in a significant increase in strength (355 psi to 600 psi). Thus, it would appear that the TiO_2 at the 15 percent level did have a physical or chemical effect upon the silica structure, even though none was visible. It will be noticed that the average silica density of these three products, the factor which probably controls the strength of the product, was between 25 and 30 pcf (normal for the unopacified product).

Chemical Analysis. The chemical analysis of three experimental products is given in Table 16. Four specimens were analyzed from various parts of a slab. The results indicated good uniformity, and, with the possible exception of the 10 percent ZrO_2 product, that the target opacifier contents were achieved with reasonable success. References to "silica density" either above, or in subsequent sections utilized the data of Table 16 to calculate the density of the silica contained within the product.

The analysis of these specimens was conducted by X-ray emission spectrography utilizing a lithium tetraborate fusion technique. Two grams (2.0000g) of -100 mesh sample were fused with 10.0000g $\text{Li}_2\text{B}_4\text{O}_7$ in a platinum crucible. The homogeneous melt was cast on a hot aluminum plate and allowed to solidify in the form of a glass button. The bottom surface of the button was wet ground and polished on a metallographic wheel fitted with a No. 320 grit paper. The X-ray intensities of zirconium (ZrK alpha) and of titanium (TiK alpha) were measured according to appropriate X-ray spectrographic techniques, and compared with the respective intensities of standard buttons of known composition prepared from spectrographically pure oxides in exactly the same manner. The accuracy of this technique had been established at ± 0.1 percent (i.e. 8.8 ± 0.1 percent).

TABLE 14.
PRODUCT DENSITY OF
OPACIFIED GLASROCK SPECIMENS

	Average Density, pcf		
	<u>5% ZrO₂</u>	<u>10% ZrO₂</u>	<u>5% TiO₂</u>
Slabs before cutting*	28.1	29.4	29.3
Conductivity samples (2) (12 x 12 x 1 in.)	28.1	29.7	29.2
Permanent Set (4) (4 x 4 x 1 in.)	28.0	29.1	29.2
Thermal Stability (4) (3 x 2 x 1 in.)	29.2	27.6	29.3
Probable Average**	28.2	29.3	29.3

*Number and size varied depending upon degree of breakage during shipment.
**Added weight given to the larger samples.

TABLE 15.
COLD CRUSHING STRENGTH
OF OPACIFIED GLASROCK

<u>Opacifier</u>	<u>Average Cold Crushing Strength, psi</u> <u>(4 tests)</u>
5% ZrO ₂	736
10% ZrO ₂	726
5% TiO ₂	600

TABLE 16.
OPACIFIER CONTENT OF
GLASROCK SPECIMENS

<u>Opacifier</u>	<u>Opacifier Content, %</u>			<u>Avg</u>
	<u>Top</u>	<u>Middle</u>	<u>Bottom</u>	
ZrO ₂	4.4	4.6	4.6	4.6
	4.6			
ZrO ₂	8.8	8.8	8.8	8.8
			8.8	
TiO ₂	5.1	5.1	5.1	5.1
	5.1			

Thermal Stability. The thermal stability of the opacified Glasrock specimens (3 x 2 x 1" in size) is given in Table 17. Each value represents an average of the length, width, and thickness of three specimens subjected to 1800F for 168 hours. No significant difference in shrinkage was found either between specimens, or between measurement direction of a particular specimen. Thermal stability of all specimens was considered satisfactory.

Permanent Set. Four 4 x 4 x 1" specimens of each Glasrock composition were subjected to 1800F hot face and a constant load of 200 psi for 168 hours. Table 18 shows the permanent set of each specimen (thickness direction) in terms of inches resulting from the load. A comparison of these data with those presented for the 15 percent opacified products (Sixth Quarterly Progress Report, Report No. ALO-3633-9, Table 15), shows that the TiO_2 content had little or no effect upon the load carrying capability of the product. Conversely, the average permanent set of the ZrO_2 products was definitely related to the ZrO_2 content (0.005", 0.008", and 0.010" for the 5, 10 and 15 percent products respectively). This was somewhat unfortunate in light of the manufacturing problems connected with the TiO_2 products. At this point, ZrO_2 was the prime opacification candidate, but its presence in the silica matrix appeared to affect the long term load carrying capability.

Thermal Conductivity. The thermal conductivity of all opacified Glasrock specimens is presented in Table 19. Also shown is the total product density and the silica density (based upon the average chemical analyses). To complete the conductivity analysis of Glasrock, a series of tests was conducted on varying densities of the unopacified product. These results are also shown in Table 19. All tests were conducted on the Rapid Heat Meter apparatus which has been proven to be an excellent technique for obtaining comparative data (within ± 2 percent reproducibility), although dependent upon calibration with the Guarded Hot Plate apparatus for its ± 5 percent accuracy. All tests were conducted at a nominal 800F mean temperature with a total temperature drop of approximately 450F across the specimen. Actual mean temperatures ranged from 770F to 805F, but for practical comparison purposes, they shall be considered equal for all tests.

Figure 20 is a comparison of all of the data in Table 19 on a thermal conductivity vs product density basis. It is apparent that the data fall into two distinct groups: opacified, and unopacified specimens. Additionally, there appears to be a difference in slope of the two regressions. On this basis, one must conclude that the opacified products are more efficient than the unopacified products (at least within the normal product density range of 25-30 pcf.).

However, since it is reasonable to assume that the load-bearing characteristics are a function of the silica density (barring chemical reaction with the silica to the detriment of the product), the comparison was also made on a thermal conductivity vs silica density basis. Figure 21 shows this comparison. Although it is considerably more subtle, the opacified and unopacified products appeared again to follow two different average regressions.

TABLE 17.
THERMAL STABILITY OF OPACIFIED
GLASROCK SPECIMENS

<u>Opacifier</u>	<u>Average **Linear Shrinkage, %</u>	
	<u>Air</u>	<u>Vacuum</u>
5% ZrO ₂	0.23	0.09
10% ZrO ₂	0.44	0.08
5% TiO ₂	0.26	0.20

*168 hr at 1800F isothermal

**Average of 3 specimens each measured for length, width and thickness shrinkage.

TABLE 18.
PERMANENT SET OF OPACIFIED
GLASROCK SPECIMENS*

<u>Sample</u>	<u>Permanent Set (Thickness Direction)</u> <u>inches</u>
5% ZrO ₂ - 1	0.005
- 2	0.005
- 3	0.007
- 4	0.003
- Average	0.005
10% ZrO ₂ - 1	0.006
- 2	0.009
- 3	0.004
- 4	0.011
- Average	0.008
5% TiO ₂ - 1	0.000
- 2	0.005
- 3	0.004
- 4	0.002
- Average	0.003

*1800F hot face, 200 psi, 168 hr

TABLE 19.

THERMAL CONDUCTIVITY AND DENSITY OF
ALL OPACIFIED AND UNOPACIFIED GLASROCK SPECIMENS

Sample No.	Opacifier Amt and Type	Density, pcf			Conductivity @ 800F Btu in./hr ft ² °F
		Product	Opacifier*	Silica**	
1	5% ZrO ₂	28.0	1.3	26.7	1.24
2	5% ZrO ₂	27.8	1.3	26.5	1.24
3	10% ZrO ₂	30.2	2.6	27.6	1.34
4	10% ZrO ₂	29.4	2.6	26.8	1.29
5	15% ZrO ₂	28.0	4.0	24.0	1.28
6	15% ZrO ₂	28.0	4.0	24.0	1.26
7	5% TiO ₂	29.2	1.5	27.7	1.38
8	5% TiO ₂	29.0	1.5	27.5	1.36
9	15% TiO ₂	29.6	4.2	25.4	1.28
10	15% TiO ₂	29.4	4.2	25.2	1.26
11	15% ZrSiO ₄	27.2	3.9	23.3	1.15
12	15% ZrSiO ₄	27.1	3.9	23.2	1.14
13	15% Cr ₂ O ₃	25.0	4.0	21.0	1.01
14	15% Cr ₂ O ₃	24.6	3.9	20.7	0.99
15	none	30.4	---	30.4	1.40
16	none	29.3	---	29.3	1.33
17	none	28.4	---	28.4	1.35
18	none	28.6	---	28.6	1.40
19	none	27.3	---	27.3	1.31
20	none	27.3	---	27.3	1.32
21	none	25.4	---	25.4	1.25
22	none	25.2	---	25.2	1.24

*Based on analysis

**By difference

FIGURE 20.

THERMAL CONDUCTIVITY - PRODUCT DENSITY
RELATIONSHIP FOR OPACIFIED AND
UNOPACIFIED GLASROCK

(770F - 800F MEAN TEMPERATURE)

FIGURE 21.

THERMAL CONDUCTIVITY - SILICA DENSITY
RELATIONSHIPS FOR OPACIFIED AND
UNOPACIFIED GLASROCK
(770F - 800F MEAN TEMPERATURE)

Disregarding however the possibility of the existence of two regressions, it must be concluded from the existing data that the thermal conductivity was a function primarily of the silica density, that opacification did not improve the thermal conductivity of products of equal silica density, and that equal strengths and insulation efficiencies could be achieved either with or without opacification.

It is not intended to analyze theoretically the data obtained to date. However, to complete the experimental effort, the 10 percent TiO_2 product, and a specially made low density unopacified product will be tested for thermal conductivity at 800F mean temperature.

V. CONCLUSIONS

A. Phase I, Task 5 - Detailed Evaluation

1. The thermal conductivity data prior to the latest rewinding of the special equipment appear valid for Formulations 1999 and 2002 in air. These values were confirmed by Guarded Hot Plate ASTM C-177 tests which also included Formulation 2020.
2. Data obtained at the same time in an argon atmosphere must also be accepted as valid based on known and theoretical effects of the change in gas within the insulation.
3. Vacuum data were also widely divergent (before and after rewinding), and further investigation of the equipment operation are necessary for clarification as to which set of data is correct. Theoretical considerations would accept the more recent and lower data, although tests by an independent laboratory on similar materials confirm the earlier and higher data.

B. Phase II, Task 2 - Material Research & Development

1. Porosimeter data on ALON-C formulations indicated that the pore size, and hence the particle size tended towards some limiting size when subjected to 2200F in air or vacuum. Rub-out electron micrographs of the particles appeared to confirm this phenomenon.
2. Scanning electron micrographs, which show the three dimensional structure of the specimen, indicated no significant change in the structure as a result of the heat treatments. It would appear therefore that the changes are micro rather than macro in nature.
3. Zirconium dioxide was considered to be the best substitute for TiO_2 as opacifier in combination with ALON-C, and was found not to affect adversely the thermal stability of composition containing ALON-C.
4. Formulation 2041 containing ALON-C gamma, K_2CO_3 inhibitor, ZrO_2 opacifier and ASTROQUARTZ fiber showed slightly greater shrinkage in vacuum than in air after 168 hrs exposure to 2200F (isothermal). Twenty pound density specimens tended to shrink slightly more than 30 pound density specimens.

5. The thermal stability in air at 2200F was adversely affected by the presence of 10 percent moisture absorbed by the K_2CO_3 inhibitor as a result of exposure to room conditions prior to test.
6. Since previous testing indicated K_2SO_4 to be almost equivalent to K_2CO_3 as a shrinkage inhibitor, further consideration of K_2SO_4 might be warranted under a product development phase to reduce the moisture pickup of the product.
7. The use of ASTROQUARTZ silica fiber may have contributed less to the thermal stability of Formulation 2041 than a more exotic fiber having higher temperature capability. An investigation into more suitable fibrous reinforcements would be necessary if a product development and evaluation program were initiated.
8. Crystallization, particle size, and thermal stability changes, all of which are interrelated, appear to take place over a prolonged period of time. Thus, the suitability of any proposed product could be established only after long-term testing at the anticipated service conditions with respect to both temperature and atmosphere.

C. Task 3 - Load-Bearing Insulation for 400-1800F Service

1. The manufacture of Glasrock silica foam opacified with ZrO_2 appeared successful, whereas that for the TiO_2 product encountered considerable difficulty.
2. A comparison of thermal conductivity data for opacified and unopacified Glasrock foam silica indicated that, on an equal silica density basis, opacification was not reducing the thermal conductivity of the product.

VI. EIGHTH QUARTER EFFORT

1. Study further the thermal conductivity data obtained on the special equipment since rewinding to determine the cause of the data variations.
2. Evaluate the successfully made 10 percent TiO_2 Glasrock product to determine if additional evaluation (load-bearing in particular) is warranted.