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W. R. Even, N. J. Manesis, M. D. Skibo

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DIMENSIONAL INSTABILITIES IN Min-K 1400
ABOVE ITS EXPECTED SERVICE TEMPERATURE

W. R. Even
N. J. Manesis
Exploratory Chemistry - Division II

M. D. Skibo
Materials Development - Division I
Sandia National Laboratories, Livermore

ABSTRACT

The response of Min-K[®] 1400 to temperatures in excess of its recommended service limits has been investigated. Severe, irreversible shrinkage was observed at temperatures greater than 1000°C. The shrinkage was found to be anisotropic and related to the direction of fiber reinforcement. The extent and rate of shrinkage was quantified. There was no evidence of crystallization or new phase formation associated with the densification.

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INTRODUCTION

In the late 1960's the AEC, through the Albuquerque Operations Office, contracted with the Johns-Manville Corporation to study the development of a thermal insulation for use with radioisotopic thermal generators, RTG, under contract #AT(29-2)-2661⁽¹⁻³⁾. The work was based on modifications of an existing Johns-Manville product line called Min-k[®]. This product with its extremely low thermal conductivity, yet reasonable load-bearing properties, showed promise for RTG applications. The original material consisted of a low density silica particle/titanium dioxide opacifier matrix that was reinforced with asbestos fibers and consolidated with a binder. Due to possible RTG contamination problems, however, the asbestos and binder were removed from the formulation, and subsequent development of a system based on alternative high temperature fibers was pursued.

After extensive material evaluations, three compositions were chosen based on a $\text{SiO}_2/\text{TiO}_2$ matrix reinforced with quartz fibers having duplex diameters⁽¹⁾. These formulations resulted in low thermal conductivity, good structural integrity, and the low level of intrinsic contaminants necessary for RTG compatibility. Adsorbed water was a specific compatibility concern because polar solids having high surface areas are known to pose problems associated with water adsorption/desorption. Details concerning this issue can be found in a separate Sandia report⁽⁴⁾.

The properties of the commercially available Min-k[®] series are given in Table 1. In the specified service range, the insulation shows great structural stability. Shrinkage, a common problem with fiber/matrix composite insulation, is controlled to within a few percent. Although limited references to the material can be found in development quarterly reports⁽⁵⁻¹⁴⁾ and registered patents^(15,16), the manufacturer considers all information proprietary. Consequently, a literature search, including government reports and the open literature, turned up surprisingly little published information.

This work is undertaken to determine the response of Min-k[®] 1400 to temperatures above its maximum steady state service limit. The data are required to evaluate thermal effects on RTG part MC3500 in a fire scenario. In this high temperature environment, the behavior of materials associated with the RTG case and heat source cladding is affected by the insulating character of Min-k[®]. In a

fire, the insulation which normally maintains the temperature differential necessary for thermopile power production now isolates the radioisotope heat source from possible cooling paths. The temperatures generated internally may be in excess of the fire environment possibly leading to rupture of the heat source cladding. Thermodynamic modeling⁽¹⁷⁾ of such systems at high storage temperature indicates that this may be a possibility. Shrinkage or physical distortion of the insulation at these elevated temperatures could provide the radiative and convective pathways by which the RTG heat source could cool. In a Sandia study⁽¹⁸⁾, statistics were gathered concerning temperatures which exist during controlled jet fuel fires. It can be expected that 50% of aircraft fires will result in temperatures in excess of 1000°C, but a fire in the vicinity of 1000°C actually has the highest probability of occurring. Statistics also show that 90% of the fires will be less than one hour in duration.

While this research addresses a specific engineering response of Min-K[®] 1400, it also serves as a reference to existing literature concerning the material. The apparent onset of dimensional instability in Min-K[®] 1400 at temperatures in excess of 1000°C is examined, and the extent of shrinkage under these conditions is quantified.

EXPERIMENT

A representative 15 cm x 15 cm x 4 cm slab of Min-K[®] 1400 was acquired from Organization 2531. Test coupons were carefully cut from the center of the slab to avoid the possibility of introducing skin effects caused by manufacturing or contamination. The test specimens were 2.5 cm x 2.5 cm x 1.2 cm prisms having smooth, parallel faces to facilitate measurement. The orientation of each sample was fixed with respect to the quartz fiber mat which imparts an anisotropic reinforcement to the bulk as shown in Figure 1. The direction perpendicular to this mat exhibits the lowest thermal conductivity. There is a distinct tendency toward delamination of the insulation parallel to the reinforcing mat. The dimensions of all specimens were measured to within ± 0.1 mm parallel and normal to the mat.

A set of specimens was placed into the preheated furnace at each of six temperatures ranging from 1000⁰ - 1100⁰C in 20⁰ increments. All runs were made in air for times as long as 24 hours. The specimens were supported in a round-bottomed quartz "boat" to prevent contact contamination by the furnace. The temperature was controlled to within $\pm 30^{\circ}\text{C}$ of the desired temperature, and thermal equilibrium was established quickly compared to the sampling interval. After cooling, specimen dimensions were remeasured. Due to anisotropic shrinkage, slight physical distortion of the block surface produced an unavoidable error in the data.

SEM investigations were carried out on representative specimens fractured in bending. X-ray diffraction analysis was used to determine if new phase formation or crystallization had occurred during the thermal treatment. In an attempt to quantify any changes in mechanical properties after heating, hardness measurements were made of selected specimens.

RESULTS

As described by the material specifications in Table 1, the Min-K[®] 1400 is dimensionally stable within its service range (up to 750⁰C) and exhibits only marginal shrinkage at temperatures approaching 1000⁰C. Preliminary studies (see Figure 2) showed that the onset of shrinkage, and thus matrix densification, occurs in the exact temperature range suggested in the fire studies discussed above. The effects of time and temperature on the shrinkage of Min-K[®], both parallel and normal to the mat, are shown in Figures 3 and 4, respectively. Clearly, a major dimensional change occurs above 1000⁰C in this material. In general, the shrinkage observed normal to the mat direction can be as large as four times that within the mat direction. As expected, the rate and magnitude of shrinkage depends on the orientation of the fibrous mat. Apparently the quartz fibers minimize thermally induced contraction in the fiber direction, yet offer little resistance to transverse shrinkage. In Figure 3, shrinkage in the mat direction shows a monotonic increase in shrinkage rate at successively higher temperatures. The lines represent the least squares fit to the data; the slopes of which are given in Table 2. Within experimental error these lines may be considered to have a zero intercept. Normal to the mat direction (see Figure 4), the lines representing the steady state densification do not have zero intercepts. This initial offset is due to a rapid, physical collapse of the structure perpendicular to the mat direction. This direction is not

reinforced by the quartz fibers and has much less stability at these temperatures. It can be seen from the two highest temperature runs that these specimens more rapidly approach their equilibrium density and deviate from linearity after short time spans. Data associated with time spans less than one hour are presented in Figure 5. Again, the shrinkage behavior resembles that of longer exposures but with much larger slopes. Heating intervals less than 20 minutes were not attempted due to insufficient oven equilibration time. Errors associated with reproducibility and physical distortion can be estimated from Figure 6. Although the scatter is large, the mean values are well behaved.

A fire scenario does not represent a steady state process but rather a dynamic temperature environment. Because of this, the rate of change in shrinkage becomes important. Figures 7 and 8 show the rate of increase in shrinkage with temperature. These data are only representative of short time spans, as the change in rate must go to zero as the equilibrium density is approached. However, data displayed in these figures as well as that associated with the initial structure collapse would constitute the physical response of Min-K[®] 1400 in a fire situation. The time/temperature behavior within this specific range may, in fact, be shown to cross-correlate. The densification within the mat direction exhibits a 1.5 fold decrease in shrinkage time per 20°C of temperature rise. Thus, within the correlation errors, changes which take 10 hours to occur at 1000°C can be observed in approximately 4-1/2 hours at 1040°C. This time/temperature superposition is shown in Figure 9. The amount of equilibrium (24 hours) densification appears to be independent of orientation (see Figure 10). The shrinkage normal to the mat is seen to parallel the behavior within the mat direction but shifted by an amount related to the initial offset indicated in Figure 4. The manufacturer^(1, 19) attributes the densification to a sintering and a crystallization process. However, in these samples only crystallization associated with a thin surface layer and not with the bulk was detected. There are existing data⁽¹⁹⁾ which suggest a difference in shrinkage upon heating in air or vacuum. This is not surprising; an O₂ overpressure can affect vacancy concentrations in the SiO₂ surface. In this study, attempts were made to minimize specimen contamination, but it should be noted that contaminants in the actual RTG application could greatly affect the sintering or densification rate.

The SEM micrographs of fracture surfaces in Figures 11 and 12 confirm the particulate agglomeration during thermal exposure. It can be seen that there is little or no apparent bonding to the fibers. In the as-fabricated material and specimens experiencing either short times or low temperatures, the fracture surface shows evidence of fiber pull-out. As the shrinkage reaches equilibrium values, the failure mode changes to one in which fiber fracture is observed (see Figure 13). In an attempt to quantify the effect of densification on a mechanical property, hardness values of the insulation were measured. Although the hardness values shown in Figure 13 cannot be directly related to an engineering parameter, they parallel our observations of increased load-bearing capability. Qualitatively, the densified insulation still provides strong, rigid support.

SUMMARY

The Min-K[®] 1400 used in RTG part MC3500 undergoes severe, irreversible shrinkage at temperatures attainable in a jet fuel fire. This densification begins at 1000°C and increases rapidly with increasing temperature.

Sufficient data is available for computer modeling studies to address fire safety questions associated with Min-K[®] 1400 and the RTG.

REFERENCES

1. Collins, J. O., Jaunarajs, K. L., Reid, D. R., "Development of New 1400⁰-1800⁰ F Fibrous-Type Insulation for Radioisotope Power Systems," Albuquerque Operations Office, ALO-2661-12, 1967.
2. Collins, J. O., "Development of New 1400⁰-1800⁰ F Fibrous-Type Insulation for Radioisotope Power Systems," Vol. #1, Albuquerque Operations Office, ALO-3633-7, 1967.
3. Collins, J. O., "Development of New 1400⁰-1800⁰ F Fibrous-Type Insulation for Radioisotope Power Systems," Appendix A, Vol. #2, Albuquerque Operations Office, ALO-3633-7, 1967.
4. Nelson, G. C., Robertson, M. M., Meador, W., "Outgassing Studies of Formulation 2002 Min-K," SC-DR-710674, 1971.
5. RTG Project Quarterly Progress Report, 1 January - 31 March, Sandia National Laboratories, SLA 73-0533, 1973, p. 13, 27.
6. RTG Project Quarterly Progress Report, 1 September - 31 December, Sandia National Laboratories, SLA 73-0103, 1972, p. 39-
7. RTG Project Quarterly Progress Report, 1 July - 30 September, Sandia National Laboratories, SC-PR-720788, 1972, p. 32.
8. RTG Project Quarterly Progress Report, 1 April - 26 June, Sandia National Laboratories, SC-PR-720556, 1972, p. 11.
9. RTG Project Quarterly Progress Report, 1 January - 31 March, Sandia National Laboratories, SC-PR-720258, 1972, p. 50.
10. RTG Project Quarterly Progress Report, 31 December - 1 September, Sandia National Laboratories, SC-PR-720073, 1971, p. 35.
11. RTG Project Quarterly Progress Report, 1 July - 30 September, Sandia National Laboratories, SC-PR-710883, 1971, p. 42.
12. RTG Project Quarterly Progress Report, April - June, Sandia National Laboratories, SC-PR-710552, 1971, p. 9, 41, 46.
13. RTG Project Quarterly Progress Report, January - March, Sandia National Laboratories, 1971, p. 28.
14. Tye, R. P., "The Thermal Conductivity of Min-K TE-1400 in Different Environments, Test Report," Dynatech Corporation, 1973.
15. Patent No. 3634563.
16. Patent No. 2811457.
17. Hiller, C. C., (private communication, SAND Report to be published).

References - Cont.

18. Clarke, R. K., Foley, J. T., Hartman, W. F., Larson, D. W., "Severities of Transportation Accidents," Sandia National Laboratories, SLA-74-0001, 1976.
19. Collins, J. O., Intersociety Energy Conversion Engineering Conference, 1968 Record, 247 (1968).

TABLE I
PROPERTIES OF Min-K TE 1400*

<u>Thermophysical Properties</u>	
Maximum service temperature F. steady state*	1400
Nominal density, lbs/cu. ft.	20
Average transverse strength, psi (min) ASTM C-203	65
Compressive strength, psi 5% compression	75
8% compression ASTM	145
Linear shrinkage, %	1.0% after 2000 hrs. at 1400F
Thermal conductivity Btu in/sq ft Hr F	
600F	.21
800F	.23
1000F	.25
1200F	.27

*Data from product spec. sheet, Johns-Manville Corp., Denver, CO.

TABLE II
"LEAST SQUARES" EQUATIONS FOR MEAN SHRINKAGE *

Temperature (°C)	In Mat Direction		Normal to Mat Direction	
	Equation	Correlation Coeff.	Equation	Correlation Coeff.
1000	$Y = 0.17X + 0.24$	0.92	$Y = 0.95X + 1.03$	0.99
1020	$Y = 0.33X + 0.33$	0.95	$Y = 1.59X + 3.36$	0.95
1040	$Y = 0.90X - 0.19$	0.87	$Y = 2.64X + 5.16$	0.99
1060	$Y = 1.89X - 0.99$	0.95	$Y = 3.71X + 8.51$	0.99
1080	$Y = 2.09X + 0.24$	0.95	$Y = 3.11X + 14.7$	0.99
1100	$Y = 3.29X + 1.66$	0.98	$Y = 3.48X + 21.3$	0.97

0 - 1 Hr. Exposure:

1080	$Y = 6.60X - 1.10$	0.99	$Y = 12.0X + 9.10$	0.99
1100	$Y = 9.60X - 0.20$	0.99	$Y = 18.6X + 10.8$	0.99

*Note: This table reflects data shown in Figures 3 through 5 and is valid for only early times. Slope expressed in %/hr.
Y-intercept expressed in %.

FIGURE 1--Specimen geometry as cut from the test slab and indicating fiber mat orientation. The quartz fibers themselves are dispersed randomly within the plane of the mat.

FIGURE 2--Initial set of Min-K test specimens (a) as prepared, (b) after exposure to temperatures indicated for times less than 3 hours.

FIGURE 3--Shrinkage within the plane of the mat as a function of time and temperature. Lines are least squares fit.

FIGURE 4--Shrinkage normal to the plane of the mat as a function of time and temperature. Note non-zero intercepts.

FIGURE 5--Shrinkage of the test specimens reflecting the initial collapse of the structure.

FIGURE 6--Single Min-K shrinkage data set. Error represents sample-to sample variations, as well as physical distortion.

FIGURE 7--Rate of shrinkage in the plane of the mat as a function of temperature.

FIGURE 8--Rate of shrinkage normal to the plane of the mat as a function of temperature.

FIGURE 9--Master curve of time/temperature correlation, 1020°C chosen as reference.

FIGURE 10--Equilibrium shrinkage after 24 hours of exposure. Note offset associated with mat orientation.

(a)

(b)

(c)

FIGURE 11--SEM micrographs of Min-K fracture surfaces: (a) as received; (b) 4 hours at 1020°C; (c) 7 hours at 1020°C. Changes in surface morphology relate to matrix densification.

(a)

(b)

(c)

FIGURE 12--Evidence of fracture mode change from fiber pull out to fiber fracture. This change occurs only near equilibrium densification. Sample 24 hours at 1080°C.

FIGURE 13--Insulation hardness (Rockwell 15X) as a function of time. The increased matrix strength parallels insulation densification.

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