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KINETICS OF REFRACTORY FIBER GLASS DEVITRIFICATION

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ABSTRACT

The kinetic model of Johnson-Mehl-Avrami was successfully applied to the devitrification of two alumina-silica based refractory glass fibers during the period of single phase crystallization. The volume fraction crystallized was found as a function of time and temperature. Linear shrinkage in a fiber was calculated as a function of volume fraction crystallized. This allows the practical prediction of performance of a fiber based on linear shrinkage at the actual use temperature.

INTRODUCTION TO KINETICS OF DEVITRIFICATION.

The generally accepted equation for the kinetics of glass crystallization is the Johnson-Mehl-Avrami (JMA) equation (1):

$$f_c = 1 - e^{-kt^n} \tag{1}$$

where f_c = volume fraction crystallized,
k = rate constant
t = time
n = Avrami coefficient.

Rearranging this equation gives (2),

$$\ln(-\ln(1-f_c)) = n\ln(k) + n\ln(t) \tag{2}$$

So, a plot of $\ln(-\ln(1-f_c))$ versus $\ln(t)$ gives a slope of n and an intercept of $(n \ln(k))$.

If an Arrhenius temperature dependence is assumed for the rate constant, the following equations apply:

$$\textit{Arrhenius equation:} \quad k = \nu e^{(-E/RT)} \tag{3}$$

Rearrangement of the Arrhenius equation gives:

$$\ln(k) = \ln(\nu) - \left(\frac{E}{R}\frac{1}{T}\right) \tag{4}$$

So, a plot of $\ln(k)$ versus $1/T$ gives a slope of $-(E/R)$ and an intercept of $\ln(\nu)$.

Devitrification data [Lo 1991] was available in the form of weight percent residual glass, %G, and the composition of the glass as wt% oxide for three commercial glass fibers heated at listed temperatures and times. From this information, the volume fraction crystallized may be calculated as in equation (5):

$$f_c = \frac{1}{1 + \frac{w_g}{\rho_g w_c \Sigma \frac{w_i}{\rho_i}}} \tag{5}$$

w_g = wt fraction glass = %G/100
w_c = wt fraction crystal = $1-w_g$
ρ_c = density of the crystal = $1/\Sigma(w_i/p_i)$
where w_i = wt fraction of each crystal phase
and ρ_i = density of each crystal phase present.
$\rho_{t,T}$ = density at time (t) and temperature (T) = $[w_g/\rho_g + (w_c)\Sigma(w_i/\rho_i)]^{-1}$
and f_c = volume fraction crystallized = $w_c(\rho_i/\rho_c)$

Using equation (5), and the devitrification data for the three commercial refractory fibers [Lo 1991], the volume fraction crystallized, f_c, at a given time (15 - 1800 s) and temperature (1366 K to 1700 K)* was calculated (see Table 1). The volume fraction crystallized at each time was plotted in the form of equation (2) and n and k were calculated from the slope and intercept for each temperature. The rate constant and temperature data was plotted in the form of equation (4), and the activation energy and frequency factor were calculated from the slope and intercept. Figure 1 and Figure 2 illustrate this for the ACS fiber. This procedure is the same as that outlined by Speyer [1994. p.66].

These equations are also applied to non-isothermal analyses such as differential thermal analysis (DTA). In a DTA study, the temperature may be increased at a constant rate and the temperature of the sample, relative to a reference, is measured. Crystallization is observed as an exothermic peak. Some assumptions are necessary for this application to be valid. The major assumption is that nucleation is completed at some lower temperature than that at which crystal growth occurs. Bansal et al. [1983] derive the following equation (equation (6)) for the analysis of this data:

$$\ln(T_p^{2/a}) - \ln(E/R) - \ln(\nu) + (E/R)T_p \tag{6}$$

where Tp = crystallization temperature (exothermic peak),
a = crystallization rate,
R = ideal gas constant,
E = activation energy, and
ν = kinetic frequency factor.

Thus, a plot of $\ln(T^{2/a})$ vs. 1/T should give a line with a slope of (E/R) and an intercept of $\ln(E/R)-\ln(\nu)$.

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* 1700 K = 1427°C = 2600°F
1589 K = 1316°C = 2400°F
1477 K = 1204°C = 2200°F
1366 K = 1093°C = 2000°F.

KINETIC CALCULATIONS AND RESULTING PARAMETERS

Isothermal analysis:

The devitrification data [Lo 1991] for the three commercially available refractory glass fibers was plotted as described in the above procedure. The reaction rate constant, k, and the Avrami coefficient, n, (related to the mechanism of crystallization) are found from the first plot using equation (2). The resulting kinetic parameters (n and k) may be found in Table 2.

The activation energy for crystallization, E, and the pre-exponential in the Arrhenius equation (the frequency factor), ν, are found from the slope and intercept of the second plot (Figure 2) as in equation (4). The resulting kinetic parameters (E and ν) may be found in Table 3.

Non-isothermal analysis:

DTA runs were completed for the AS fiber at four different heating rates. Information relating to the exothermic peaks observed is listed in Table 4. Since there is some scatter in the data, it would have been useful to have obtained more data, but time constraints prevented this. One of the concerns with this analysis is in the differences in the peak shapes observed. The peak shape may indicate that different mechanisms are active and dominating for the same fiber on different runs, possibly due to inhomogeneities in the glass or contamination of the fiber surface with dust or oil from handling prior to placement in the sample crucible. One interpretation of peak shape is that sharp peaks indicate bulk crystallization and broad peaks indicate surface crystallization. [Ray & Day, 1990 p.440]

The data given in Table 4 for the non-isothermal kinetic study of these fibers using the DTA was plotted using the form of equation (6) for the three choices of crystallization temperature. The resulting kinetic parameters (E and ν) may be found in Table 5.

DISCUSSION OF KINETIC PARAMETERS

Isothermal analysis:

If the devitrification process follows the model described here (JMA and Arrhenius equations), this analysis should give valuable information about the mechanism of crystallization (time dependence of nucleation and growth) and the temperature dependence of the rate of crystallization.

The mechanism of crystallization can be determined from the value of the Avrami coefficient [Speyer 1994 p.67, Bansal et al. 1983, Henderson 1979, Rogers 1970]. In the literature, n is usually taken to be between one and four, with one representing surface nucleation and four representing homogeneous nucleation with spherical growth [Speyer 1994]. A complete description of the theory of the interpretation of the Avrami coefficient as it applies to devitrification was not found in the literature, and it is difficult to say what a value of approximately 0.2 (as was seen in this analysis in Table 2) would mean. The smallest coefficient given in the literature is 0.5 for instantaneous nucleation with diffusion controlled growth in one dimension [Rogers 1970]. However, Sestak [1971] derives an equation with several mechanism coefficients to describe a process. It may be that some of the assumptions (such as complete nucleation prior to crystal growth which is assumed for the non-isothermal analyses) do not apply to devitrification in these fibers and a more complex equation is needed.

The above analysis appears to indicate that the activation energy (Table 3) for crystallization is least for the ASZ fiber and greatest for the ACS fiber. However, this does not agree with the experimentally observed behavior as evidenced by the data given as wt% crystallized as a function of time being least for the ASZ fiber. There are multiple factors in this. One difference is that the wt% crystallized was defined differently for the ASZ fiber since more than one phase is crystallizing simultaneously. Additionally, the crystallization of the ASZ fiber does not proceed directly to the equilibrium phases, so although the long term crystallization of tetragonal zirconia can be calculated, this has no actual validity since the tetragonal zirconia will be transformed to monoclinic zirconia and then zircon during the course of devitrification of the ASZ fiber. The theory cannot take into account the subsequent nucleation and growth of these multiple and competing phases. Therefore, only the kinetic parameters calculated for the AS and ACS fibers should be used for comparison.

An initial error analysis based on the equations reveals that there is only a small uncertainty in the value of the activation energy (about 5%), while the value of the frequency factor is far less certain (on the order of 100% uncertainty). It should be noted that this error analysis did not take into account any uncertainty in n and also that the uncertainties of E and ν were calculated independent of each other.

Non-isothermal analysis:

The non-isothermal analysis was intended to give an independent source for the above kinetic information for comparison. Unfortunately, there was a great deal of scatter in the limited data obtained. The scatter could be due to inherent inhomogeneities in the fibers affecting the nucleation process. Also, it is uncertain whether the mechanism involved in the fiber crystallization was controlled (constrained to one mechanism) during the tests. Contamination of the fibers could have resulted in a dominance of surface nucleation over bulk nucleation on some occasions. This may have produced unnecessary scatter in the data.

Perhaps more importantly, the uncertainty regarding the nucleation process may invalidate the application of this technique. Since the application of the JMA equation to the non-isothermal analysis involves some rather restrictive conditions for the nucleation process, this analysis is less useful than the isothermal analysis.

CALCULATION OF VOLUME FRACTION CRYSTALLIZED AS A FUNCTION OF TIME AND TEMPERATURE USING MODELED KINETIC PARAMETERS

The kinetic parameters (E, ν, and average n) calculated from the isothermal data using the JMA and Arrhenius equations for the AS and ACS fibers were used to create 3-d surface plots of fraction crystallized as a function of time and temperature using the equation

$$f_c = 1 - \exp\left(-\left(t\nu\exp\left(-\frac{E}{RT}\right)\right)^n\right) \tag{7}$$

These plots are Figure 3 and Figure 4. The contour plots accompanying the 3-d surface plots show volume fraction crystallized for varying temperature and time. These contour plots are very useful since they allow a user to easily determine a practical use temperature for each fiber. For example, if the user wanted to keep the volume fraction crystallized below 0.6, the ACS fiber could be used at temperatures less than 1350 K; however, the AS fiber could only be used at temperatures less than 1300 K. Unfortunately, it can also be seen from these plots that it is impossible to completely prevent devitrification in these fibers at the temperatures of interest.

The volume fraction crystallized at 1700K was calculated using the isothermally derived kinetic parameters for the AS and AS fibers using equation (7) and a series of temperatures ranging from 1800 sec (for experimental comparison) to 2 years (a reasonable use period). The same equation was rearranged to calculate the activation energy that would be needed to prevent the majority of crystallization (vol.fr.<0.1) at the same temperature and times. For the AS fiber the activation energy, E, must be greater than 830 kJ/mol, and for the ACS fiber it must be greater than 970 kJ/mol to keep the volume crystallized less than 10%. These are very large activation energies since activation energies for devitrification of conventional network forming glasses are reported to be between 100 and 300 kJ/mol [Negran and Glass 1979].

The same equation was also rearranged to calculate the temperature below which crystallization would be less than 10%. For the AS fiber, this is 1130°C, and for the ACS fiber it is 1140°C.

CALCULATION OF LINEAR SHRINKAGE AS A FUNCTION OF VOLUME FRACTION CRYSTALLIZED

While the volume fraction crystallized does provide a useful measure of fiber performance, another measure that is more accepted in industry is based on the percent shrinkage in a fiber mat. It has been shown elsewhere [Curtis 1993] that the length or width shrinkage in a typical fiber mat is derived from the linear shrinkage in the length of a fiber. Furthermore, this linear shrinkage is caused by the change in material density upon devitrification as given by the following equation:

$$\mathit{Linear\,Shrinkage} = 1 - \frac{\rho_g}{\rho_{t,T}} \tag{8}$$

where ρ_g = initial density (density of the glassy fiber),
$\rho_{t,T}$ = density after heating at time, t, and temperature, T.

The maximum linear shrinkage possible due to devitrification can be found when $\rho_{t,T}$ equals the final or equilibrium crystal density, ρ_c. The crystalline density can be found by knowing the final distribution of crystalline phases and the density of each phase by the rule of mixtures for densities (the additive rule for specific volume):

$$\frac{1}{\rho_c} = \sum\left(\frac{w_i}{\rho_i}\right) \qquad (9)$$

where w_i = weight fraction of crystalline phase in the material
and ρ_i = the density of each crystalline phase (from literature).

The final distribution of crystalline phases in the material may be found from the appropriate phase diagram. Therefore, to predict the shrinkage due to devitrification for a new fiber composition, only the composition and the glass density need to be known. The density of the glass can be measured using the pycnometer method [Reed 1988 p.106, Andrews 1928 p.33-36], but if the fiber has not been manufactured yet, it is necessary to be able to predict the density of the melt-spun glass.

The most frequently used method of predicting glass density from the composition was developed by Huggins and Sun. [1943, Morey 1954 p.224] They tabulate sets of specific volume factors for many oxides over different composition ranges relative to Si content. Unfortunately, when these specific volume factors were used to calculate the densities of the commercial AS, ASZ and ACS fibers, the calculated density was consistently lower than the measured (pycnometer) density. This may indicate some difference in the glass structure of the melt spun glass or a difference in the composition range studied. Therefore, specific volume factors were derived for the melt-spun glass fibers using the measured densities as follows: [Scholes 1975 p.385]

Derivation of specific volume factors for glass density in melt spun fibers.

The following equation applies for the density of glass (ρ_g) based on composition. (This is the additive rule for specific volume.)

$$\frac{1}{\rho_g} = \mathbf{A}w_A + \mathbf{S}w_S + \mathbf{C}w_C + \mathbf{Z}w_Z \qquad (10)$$

where w = weight fraction of oxide component in the glass phase where S=SiO_2, A=Al_2O_3, Z=ZrO_2, and C=Cr_2O_3, and **S**, **A**, **Z** and **C** are empirical constants (specific volume factors) for each of the components in the glass.

Density was measured for the three commercially available fibers using a pycnometer, and the density of vitreous silica is commonly available in the literature. This data is presented in Table 6.

Substituting the data from Table 6 into (10) and solving for the variables, empirical specific volume factors can be derived for these glass fibers. The empirical specific volume factors for SiO_2, Al_2O_3, ZrO_2 and Cr_2O_3 (**S**, **A**, **Z**, and **C** respectively) can be found in Table 7. These empirical specific volume factors can be used to calculate density of the glass in a melt spun fiber over a wide range of compositions. Of course use of these factors will result in densities which are most accurate for compositions near to those of the measured fibers.

Aside: As a measure of the power of the various oxides to increase the density of vitreous silica, the hypothetical oxide glass density was calculated. The hypothetical glass density is simply the inverse of the empirical specific volume factor. The higher the hypothetical glass density, the more power the oxide has to increase the glass density of the mixture. The hypothetical oxide glass densities are as follows: ρ-Al_2O_3 = 3.05, ρ-ZrO_2 = 10.67, and ρ-Cr_2O_3 6.31 Mg/m^3. This shows that the addition of alumina does not greatly increase the glass density, while the addition of zirconia or chromic oxide does greatly increase the glass density relative to vitreous silica.

The ability to predict the maximum amount of linear shrinkage in a fiber (composed of any combination of silica with alumina, zirconia and/or chromic oxide) due to devitrification based solely upon the composition of the fiber, as described above, is very important since it provides for the design of a fiber with minimum shrinkage within the compositional constraints of manufacture. However, it does not say anything about the use temperature of the fiber if devitrification is not allowable. For that, the kinetic theory must be applied.

At some time and temperature at which devitrification in a fiber is only partially complete, the following equations apply. For a fiber containing only alumina and silica,

$$\frac{1}{\rho_g} = Sw_{Sg} + Aw_{Ag} \tag{11}$$

where S = 0.455 and A = 0.328.

$$\begin{gathered} w_{Sg}w_g + w_{Sc}w_c = w_S \\ w_{Ag}w_g + w_{Ac}w_c = w_A \\ \textit{and } w_S + w_A = 1 \end{gathered} \tag{12}$$

where w_{Sg} = weight fraction of silica in the glass phase
w_{Ag} = weight fraction of alumina in the glass phase
w_{Sc} = weight fraction of silica in the crystal phase
w_{Ac} = weight fraction of alumina in the crystal phase
w_g = weight fraction of glass phase in the fiber
w_c = weight fraction of crystalline phase in the fiber
w_S = weight fraction of silica in the fiber
w_A = weight fraction of alumina in the fiber

Rearrangement of equation (12) gives

$$w_{Sg} = \frac{w_S - w_{Sc}w_c}{w_g} \quad \textit{and} \quad w_{Ag} = \frac{w_A - w_{Ac}w_c}{w_g} \tag{13}$$

So, the density of the glass can be found by substituting the equations for weight fraction of each component in the glass (equation (12) into equation (10)). This is simply a convenient re-statement of equation (10) using quantities that may more easily be known. The density of a glass containing components other than alumina and silica can be calculated by including the specific volume factors of the additional components into the equations. Specific volume factors for Cr_2O_3 and ZrO_2 in melt-spun glass fibers have been described above.

For any glass fiber that is partially devitrified,

$$w_g + w_c = 1 \tag{14}$$

Calculation of intermediate density as a function of volume fraction crystallized

To find linear shrinkage in a fiber as a function of time and temperature, it is necessary to find $\rho_{t,T}$. The volume fraction crystallized, f_c, is known as a function of time and temperature, so if $\rho_{t,T}$ can be found as a function of f_c, the result will be a model for linear shrinkage as a function of time and temperature.

$$\frac{1}{\rho_{t,T}} = \frac{w_c}{\rho_c} + \frac{w_g}{\rho_g} \tag{15}$$

$$\frac{w_g}{\rho_g} = \frac{1-(1-w_g)}{\rho_g} = \frac{1}{\rho_g} - \frac{w_c}{\rho_g} \tag{16}$$

The basic definition of volume fraction crystallized, f_c , is

$$f_c = \frac{V_c}{V_{total}}$$

$$so,\ f_c = \frac{V_c}{V_{total}} = \frac{\frac{m_c}{\rho_c}}{\frac{m_{total}}{\rho_{total}}} = \left(\frac{m_c}{m_{total}}\right)\left(\frac{\rho_{total}}{\rho_c}\right) = w_c\frac{\rho_{t,T}}{\rho_c} \tag{18}$$

$$and\ \frac{w_c}{\rho_c} = \frac{f_c}{\rho_{t,T}}\ \ or\ \ w_c = \frac{f_c\,\rho_c}{\rho_{t,T}}$$

So, substituting these relationships for f_c into equation (8), the following equation (equation (19)) is obtained

$$\frac{1}{\rho_{t,T}} = \frac{f_c}{\rho_{T,t}} + \frac{1}{\rho_g} - \frac{\rho_c f_c}{\rho_g \rho_{t,T}} \tag{19}$$

Factoring ($\rho_g\ \rho_{t,T}$) out in the denominator gives equation (20):

$$\rho_g = f_c \rho_g + \rho_{t,T} - f_c \rho_c \tag{20}$$

Rearrangement of this gives equation (21), $\rho_{t,T}$ as a function of f_c:

$$\rho_{t,T} = \rho_g + f_c(\rho_c - \rho_g) \tag{21}$$

Substituting this into the equation for linear shrinkage gives equation (22), linear shrinkage as a function of volume fraction crystallized, fc. Volume fraction crystallized has been modeled as a function of time and temperature.

$$LinearShrinkage = 1 - \frac{\rho_g}{\rho_g + f_c(\rho_c - \rho_g)} \tag{22}$$

Calculation of linear shrinkage as a function of time and temperature

Using the above relationships for linear shrinkage as a function of density, density as a function of volume fraction crystallized, and volume fraction crystallized modeled as a function of time and temperature using the JMA and Arrhenius kinetic theory, linear shrinkage in a fiber can be found as a function of time and temperature. Equation (22) was used to calculate this relationship. The major difficulty that exists in this calculation is the treatment of the crystal phase(s). The kinetic model is good only for a single phase crystallizing. The kinetic model has been sucessfully used to describe the crystallization of the AS and ACS fibers when only one phase (mullite) is crystallizing. However, at longer times, a second phase crystallizes in the AS and ACS fibers. This lowers the final crystal density because the initial crystalline phase, mullite, has a density of 3.23 Mg/m^3 while the second crystalline phase, cristobalite, has a density of 2.3 Mg/m^3. Therefore, several plots are presented here for each fiber. The first set of plots, Figure 5 and Figure 8 are of linear shrinkage as a function of time and temperature over the time and temperature range of the kinetic model. The second set of plots, Figure 6 and Figure 9, are the same function over a longer time span. This shows what the shrinkage would be at long times if mullite were the only phase crystallizing. The third set of plots, Figure 7 and Figure 10, show the long term shrinkage more accurately because the density of the crystal phase is taken to be the density of the final equilibrium crystalline composition. However, the third set of plots are not as accurate for the short times. To get a completely accurate plot over the entire time span of interest, the crystal and glass compositions in these fibers would need to be modeled in the time and temperature range of interest. This would most likely require an experimental basis. The parameters used in the calculation of these plots are presented in Table 8.

CONCLUSION.

The devitrification kinetics of alumina-silica based refractory insulating fibers can be modeled using the JMA theory and practical information regarding potential use conditions can be extracted. Linear shrinkage or volume fraction crystallized can be determined at any time and temperature and as a result, a practical maximum use temperature can be predicted. However, the model is only good during the period of single phase crystallization which occurs at short times. Therefore, some adjustments have been made to the linear shrinkage model to account for the densities of the actual phases crystallizing.

NOMENCLATURE.

A	empirical specific volume factor for Al_2O_3 in glass
a	crystallization rate,
ACS	alumina - chromic oxide - silica
AS	alumina - silica
ASZ	alumina - silica - zirconia
C	empirical specific volume factor for Cr_2O_3 in glass
E	activation energy
f_c	volume fraction crystallized
k	rate constant
n	Avrami coefficient
S	empirical specific volume factor for SiO_2 in glass
t	time
t-ZrO_2	tetragonal zirconia
T	absolute temperature, K, (unless specified as °C)
Tp	crystallization temperature (exothermic peak)
R	ideal gas constant
V	volume
w	weight fraction
w_c	weight fraction crystal
w_g	weight fraction glass
w_i	weight fraction of each crystal phase in total crystal material
Z	empirical specific volume factor for ZrO_2 in glass
ρ	density
ρ_c	density of the total crystalline material
$\rho_{t,T}$	intermediate density
ρ_i	density of each crystal phase present
ν	kinetic frequency factor

Subscripts:

S	silica, SiO_2
A	alumina, Al_2O_3
g	glass
c	crystal
t	time
T	temperature

for example,

$\rho_{t,T}$	density after heating at time, t, and temperature, T
w_{S_g}	weight fraction of silica in the glass phase
w_g	weight fraction of glass phase in the fiber

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Table 1. Volume fraction, fc, crystallized as determined from x-ray data. (Derived from Lo, 1991.)

	time,t	volume fraction crystallized, fc, at Temp, T (K)			
Fiber	(s)	1700	1589	1477	1366
AS	15	0.187		0.139	
	30	0.249		0.157	0.032
	45	0.212		0.210	0.054
	60	0.326		0.278	0.082
	600	0.592	0.373	0.306	0.243
	1200	0.655	0.443	0.313	0.243
	1800	0.662	0.450	0.294	0.243
ACS	15	0.324	0.279	0.148	0.063
	30	0.324	0.263	0.186	0.100
	45	0.318	0.279	0.194	0.136
	60	0.341	0.279	0.224	0.138
	600	0.531	0.409	0.290	0.159
	1200	0.632	0.461	0.263	0.164
	1800	0.751	0.466	0.302	0.159
ASZ	15	0.314	0.273	0.061	
	30	0.297	0.335	0.123	
	45	0.341	0.315	0.230	
	60	0.349	0.341	0.208	
	600			0.308	0.091
	1200			0.271	0.132
	1800			0.328	0.094
ASZ(t-ZrO2)	15	0.14596	0.12696	0.01389	
	30	0.18404	0.16441	0.03533	
	45	0.22247	0.16468	0.10841	
	60	0.30217	0.22247	0.09445	
	600			0.30204	0.10836
	1200			0.32257	0.12697
	1800			0.30206	0.14557
ASZ(mullite)	15	0.63753	0.55989	0.13785	
	30	0.59742	0.6733	0.26958	
	45	0.67379	0.63502	0.47779	
	60	0.67495	0.67379	0.43644	
	600			0.59612	0.18310
	1200			0.51878	0.26882
	1800			0.63455	0.18090

Note: for the ASZ fiber, fc(n)=mass n cryst./max. mass n possible

fc(tZ) = vol. fr. of $tZrO_2$ crystallized/max $tZrO_2$ possible (19 wt%)

fc(M) = vol. fr. of mullite crystallized/max mullite possible (44.57 wt%)

Note: for the ASZ fiber, the equil. cryst. phases are zircon, mullite and SiO_2.

Table 2. Kinetic parameters, n and k, from first plot of a series of isothermal data for three commercial refractory fibers.

Fiber	Temp.(K)	n	k
AS	1700	0.369	9.2x10^{-4}
	1589	0.235	7.0X10^{-5}
	1477	0.168	2.6X10^{-6}
	average:	0.257	
ASZ(t-ZrO$_2$)	1700	0.557	2.2x10^{-3}
	1589	0.390	3.8x10^{-4}
	1477	0.611	2.0x10^{-4}
ASZ(mullite)	1700	0.093	4.5x10^{-2}
	1589	0.198	3.2x10^{-2}
	1477	0.286	7.3x10^{-4}
ACS	1700	0.266	9.5x10^{-4}
	1589	0.165	3.3x10^{-5}
	1477	0.144	4.9x10^{-7}
	1366	0.153	1.4x10^{-8}
	average:	0.192	

Table 3. Kinetic parameters, E and ν, from the second plot of a series of isothermal data for three commercial fibers.

Fiber	E (kJ/mol)	E(kcal/mol)	ν (1/s)
AS	550	131	7.7x10^{13}
ASZ(t-ZrO$_2$)	221	53	1.1x10^{4}
ASZ(mullite)	393	94	9.6x10^{10}
ACS	651	155	7.9x10^{16}

Table 4. DTA of the AS fiber.

Rate (°C/min)	Height (μV)	FWHM (°C)	start (°C)	cryst.pt. (°C)	max.pt (°C)	Run/date
30	23.44	4.31	989	1004	1012	k2 6/16
30	24.56	6.46	991	1002	1011	k30-2 6/22
50	33.95	6.03	1003	1011	1022	k50 6/16
50	12.19	11.25	992	1008	1018	k50-2 6/22
70	28.35	9.48	1004	1015	1026	k70-2 6/22
70	19.85	9	1005	1015	1024	k70 6/16
90	25.49	13.15	1008	1016	1029	k90 6/22

FWHM = full width at half max.
start = temperature at first deviation from baseline
cryst.pt. = temp. at intersection of extrapolation of baseline and linear portion of peak rise
max.pt. = temp. at max. of exothermic crystallization peak.

Table 5. Kinetic parameters, E and ν, from non-isothermal analysis for AS fiber.

Temp.	E (kJ/mol)	E(kcal/mol)	ν (1/s)
start	197	47	6.2
cryst.	305	73	14.8
max.	254	61	9.6

Table 6. Composition and density of commercial melt-spun fibers and vitreous silica (literature).

Fiber	Composition (wt%) Al_2O_3	SiO_2	ZrO_2	Cr_2O_3	Density (Mg/m^3)
vit.SiO_2	0	1	0	0	2.20
AS	0.48	0.52	0	0	2.546
ASZ	0.32	0.49	0.19	0	2.895
ACS	0.40	0.53	0	0.07	2.614

Table 7. Empirical specific volume factors for calculating the density of melt-spun fibers from the composition in weight percent.

Component	Factor	
SiO_2	S	0.4545
Al_2O_3	A	0.3278
ZrO_2	Z	0.0937
Cr_2O_3	C	0.1585

Table 8. Parameters used in the calculation of linear shrinkage as a function of time and temperature.

Fiber	ν (s^{-1})	ν (day^{-1})	E (kJ/mol)	E/R (K)	n	ρ_g (Mg/m^3)	initial ρ_c (Mg/m^3)	final ρ_c^* (Mg/m^3)
AS	$7.7x10^{13}$	$6.65x10^{18}$	550	$6.6x10^4$	0.2574	2.54	3.23	2.79
ACS	$7.9x10^{16}$	$6.8x10^{21}$	651	$7.83x10^4$	0.1916	2.61	3.35	2.87

* initial crystalline phase is mullite or mullite s.s.

* final $1/\rho_c$ is based on the equilibrium crystal composition:

final $1/\rho_c = .397/2.32 + .603/3.23$ for the AS fiber, and

final $1/\rho_c = .372/2.32 + .628/3.35$ for the ACS fiber.

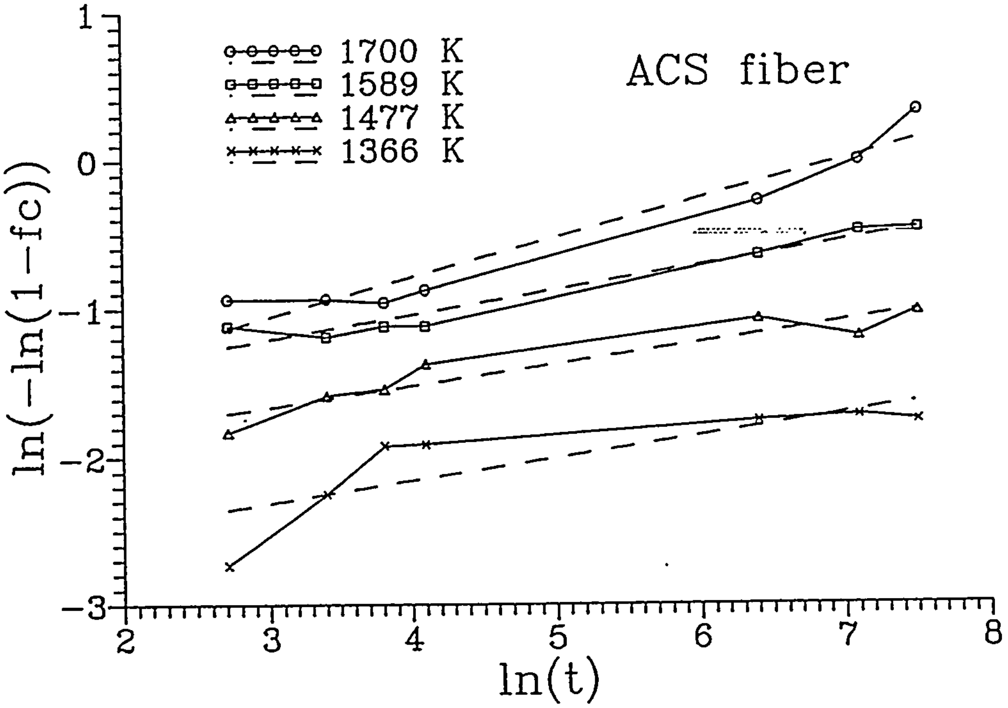


Figure 1. Plot for finding kinetic parameters n and k from a series of isothermal heat treatments for the ACS fiber.

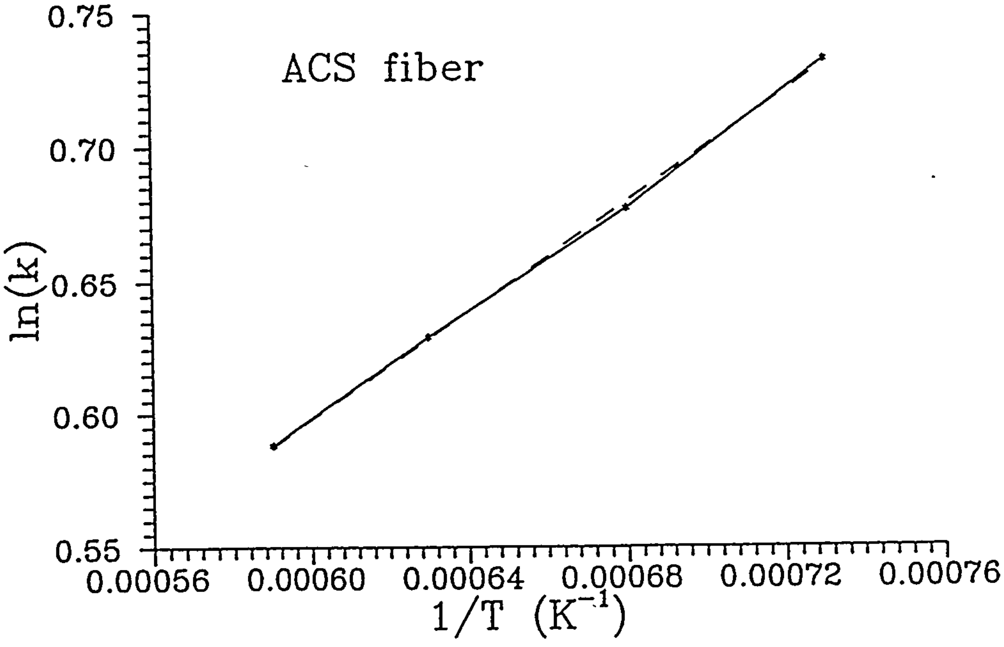
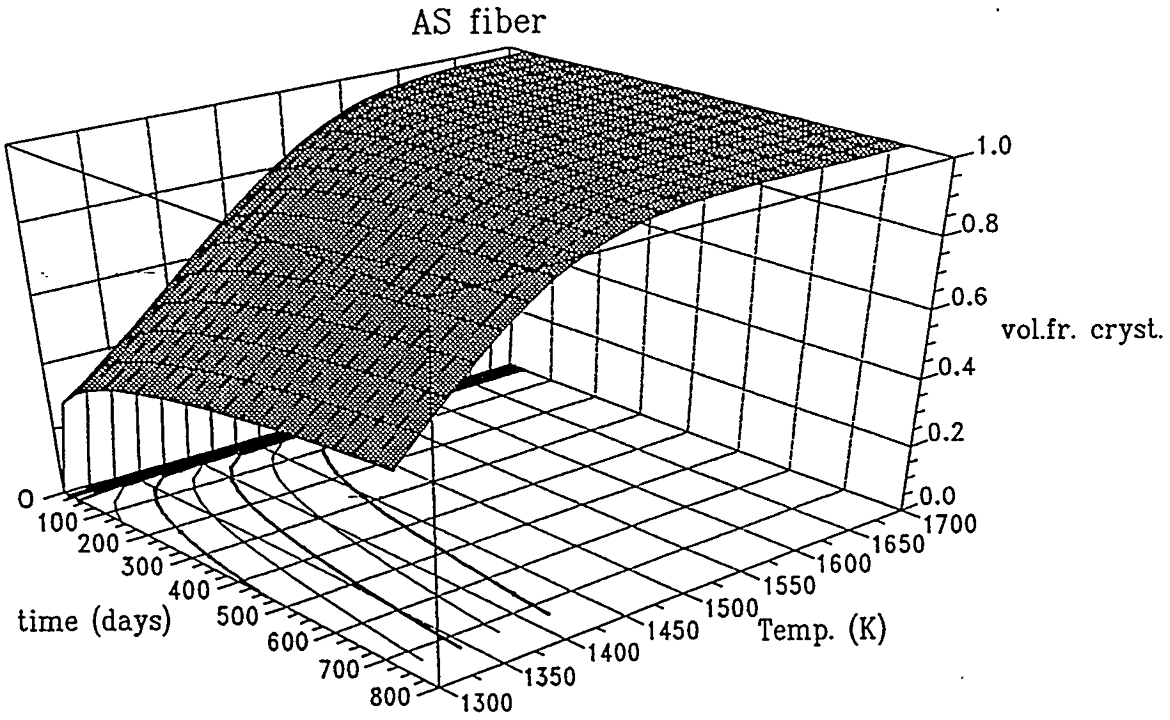


Figure 2. Plot for finding kinetic parameters E and ν from a series of isothermal heat treatments for the ACS fiber.



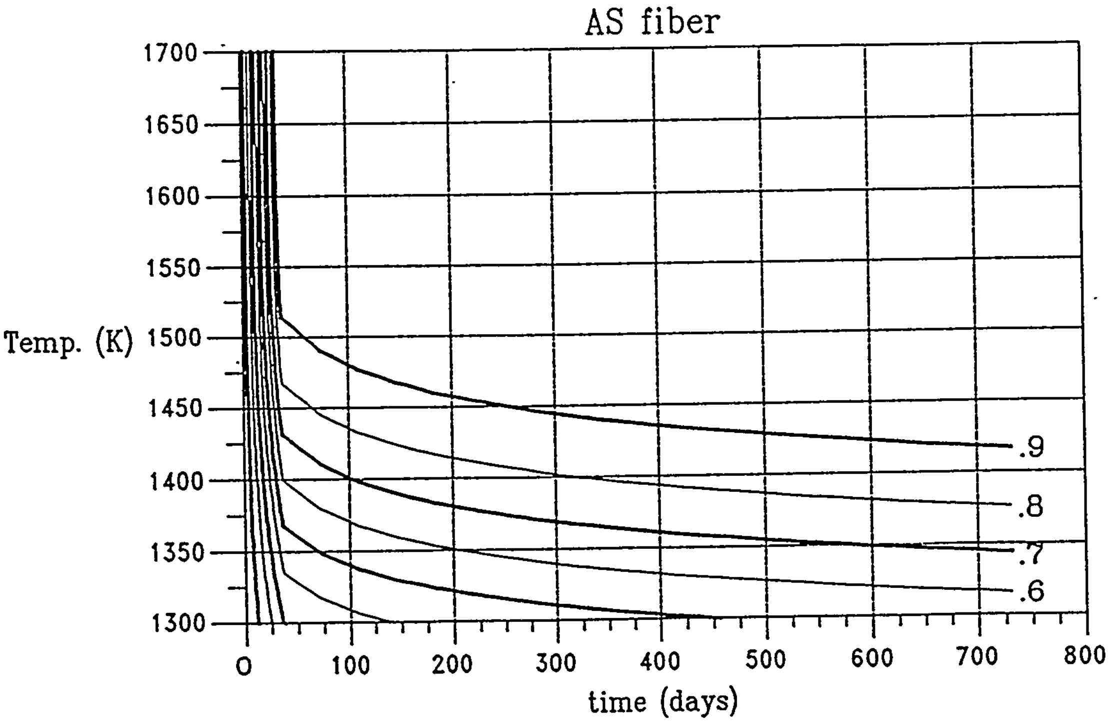


Figure 3. Volume fraction crystallized calculated from kinetic parameters derived from isothermal data for the AS fiber.

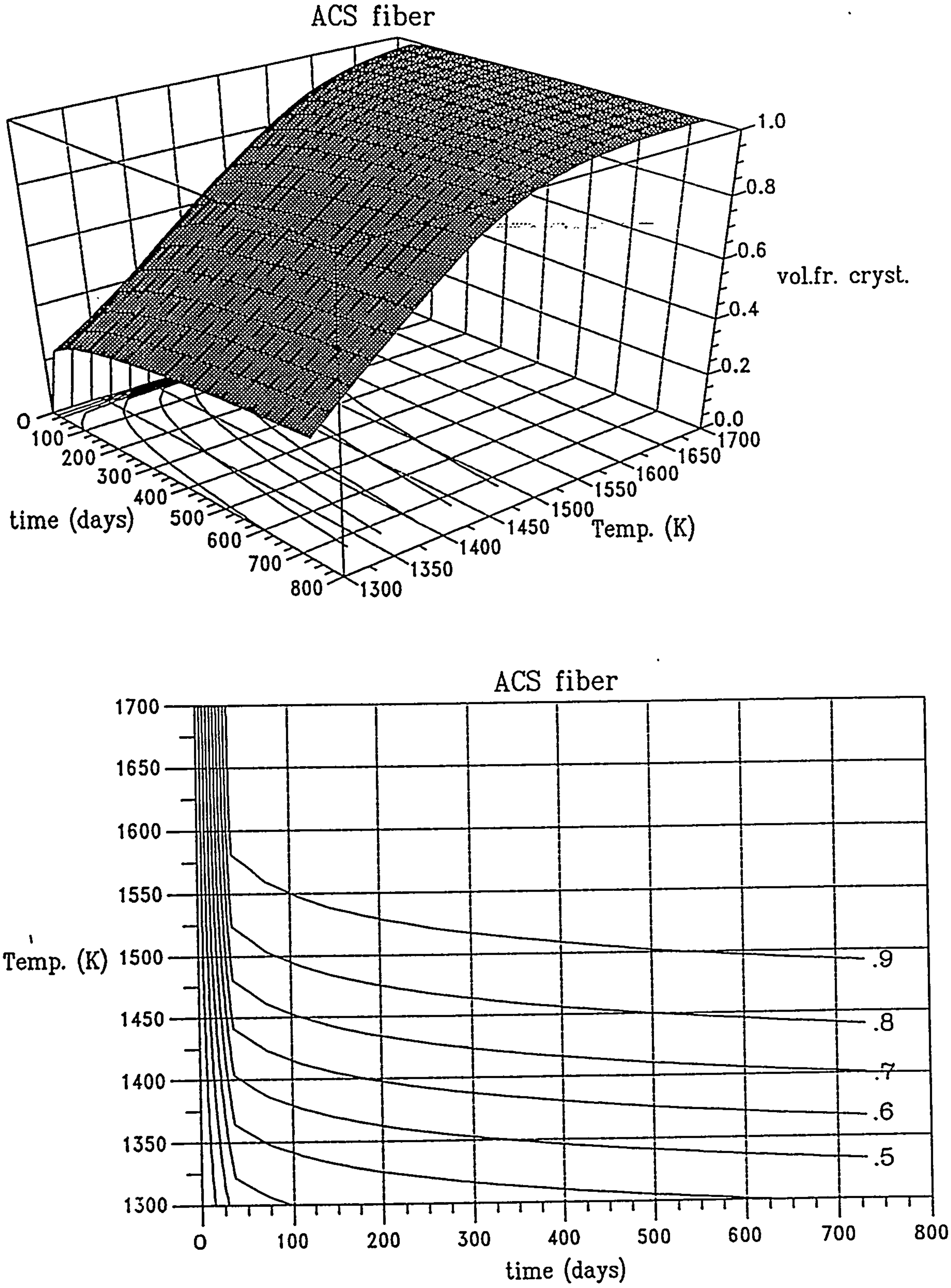


Figure 4. Volume fraction crystallized calculated from kinetic parameters derived from isothermal data for the ACS fiber.

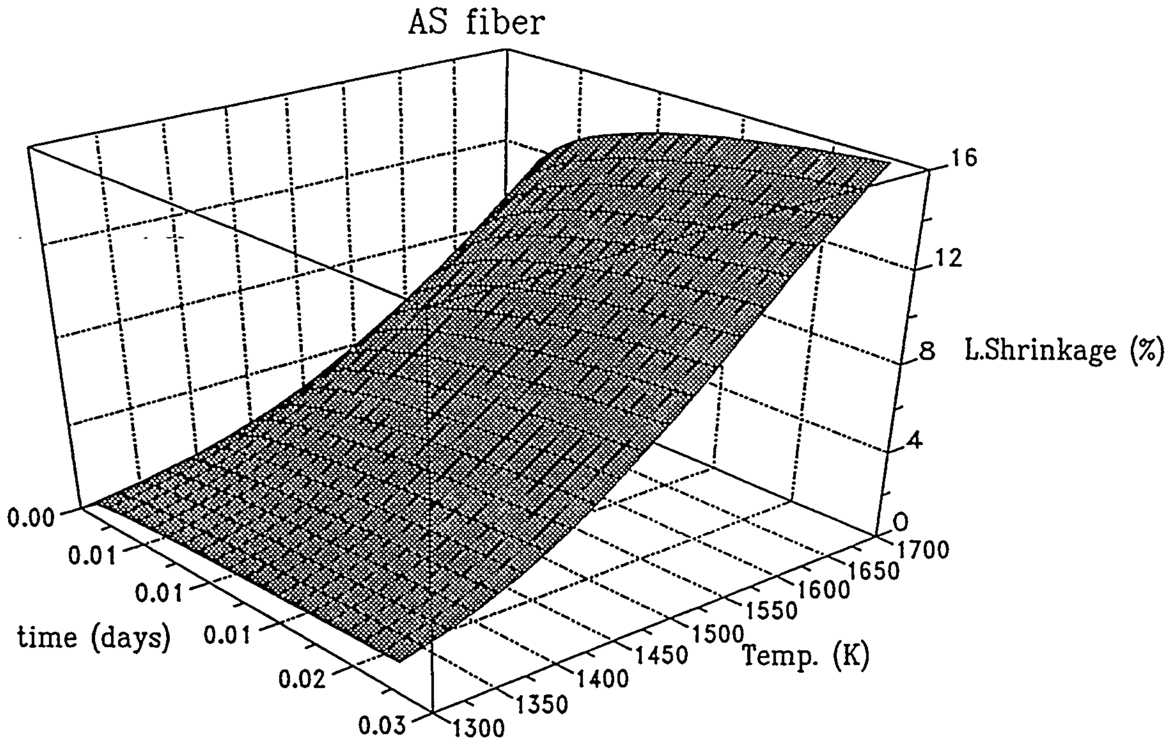
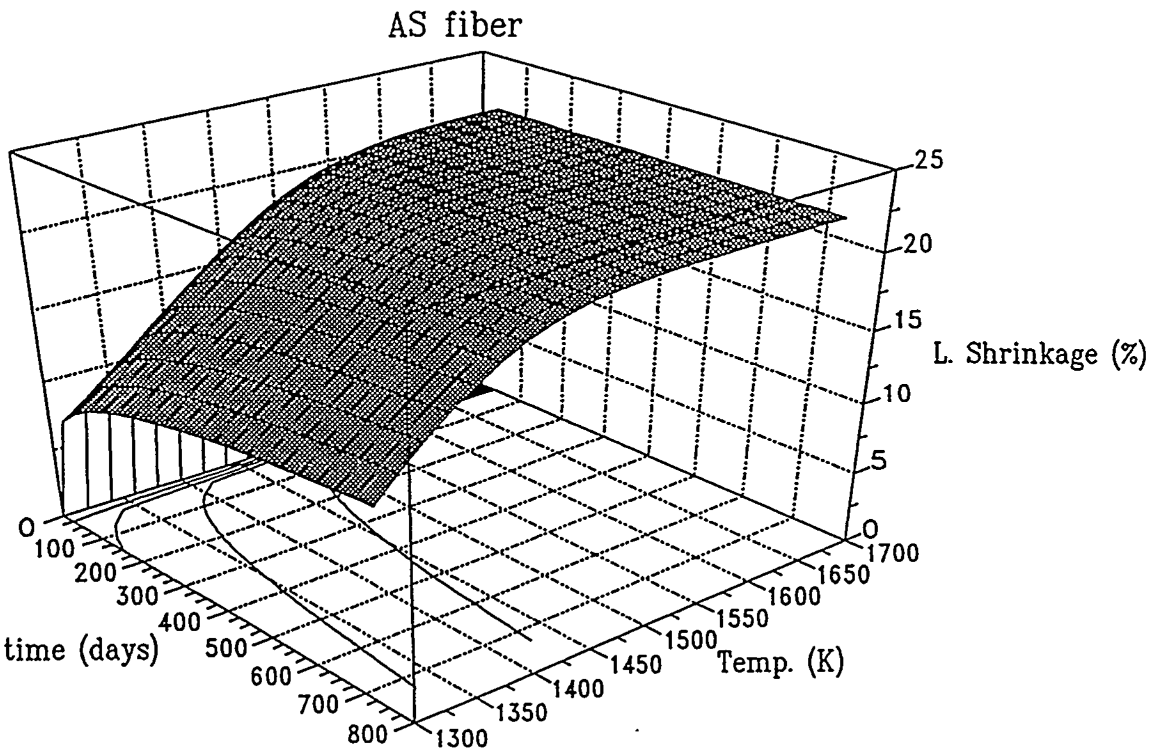


Figure 5. AS fiber at t = 0-1800 sec, T= 1093°C to 1427°C (2000°F to 2600°F). Glass density = 2.54 Mg/m^3 and crystal density= 3.23 Mg/m^3 (mullite).



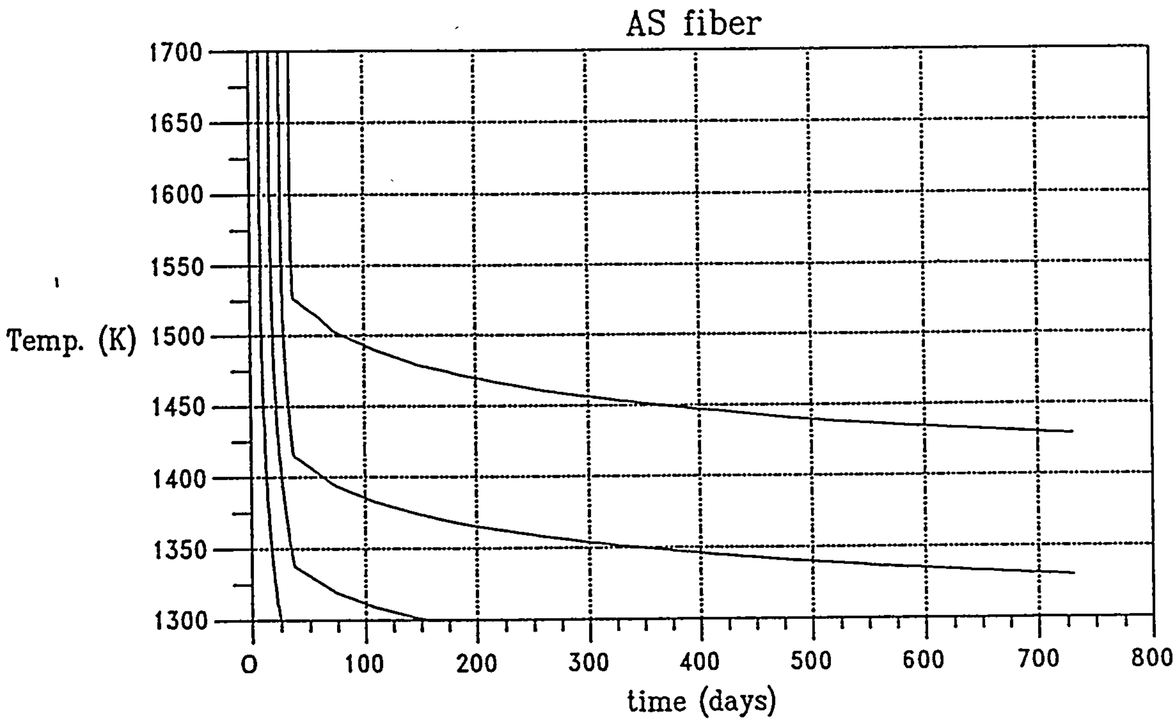
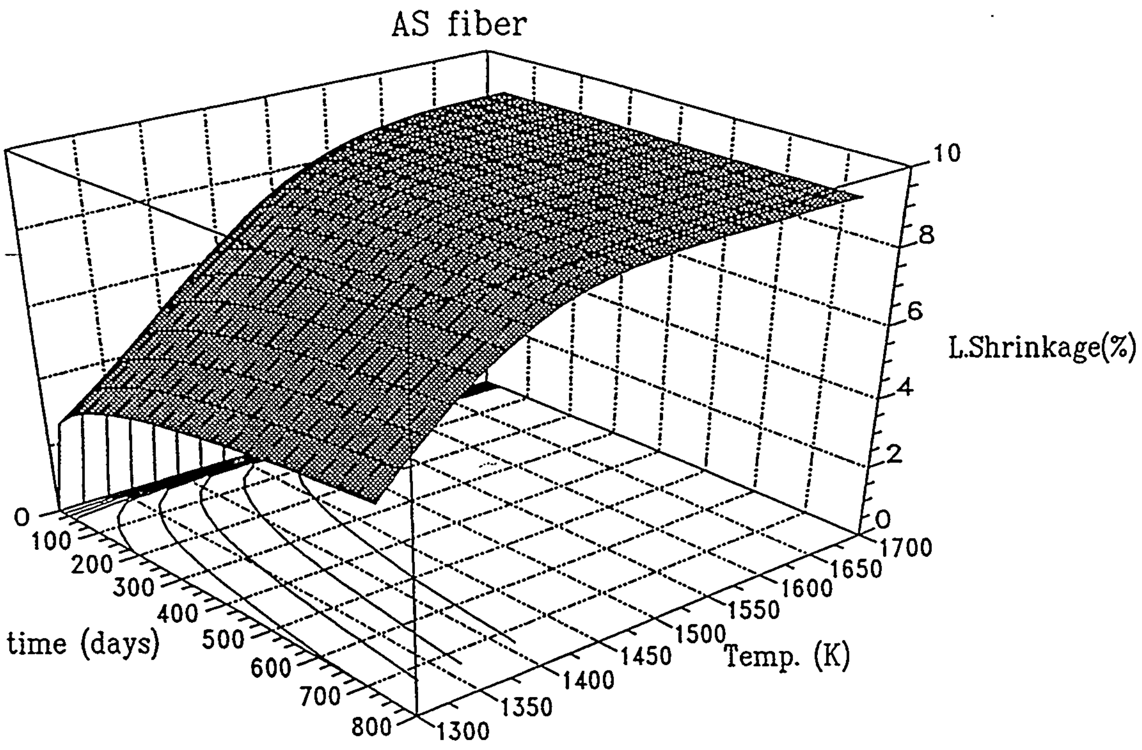


Figure 6. AS fiber at t = 0-730 days, T= 1093°C to 1427°C (2000°F to 2600°F). Glass density = 2.54 Mg/m^3 and crystal density= 3.23 Mg/m^3 (mullite).



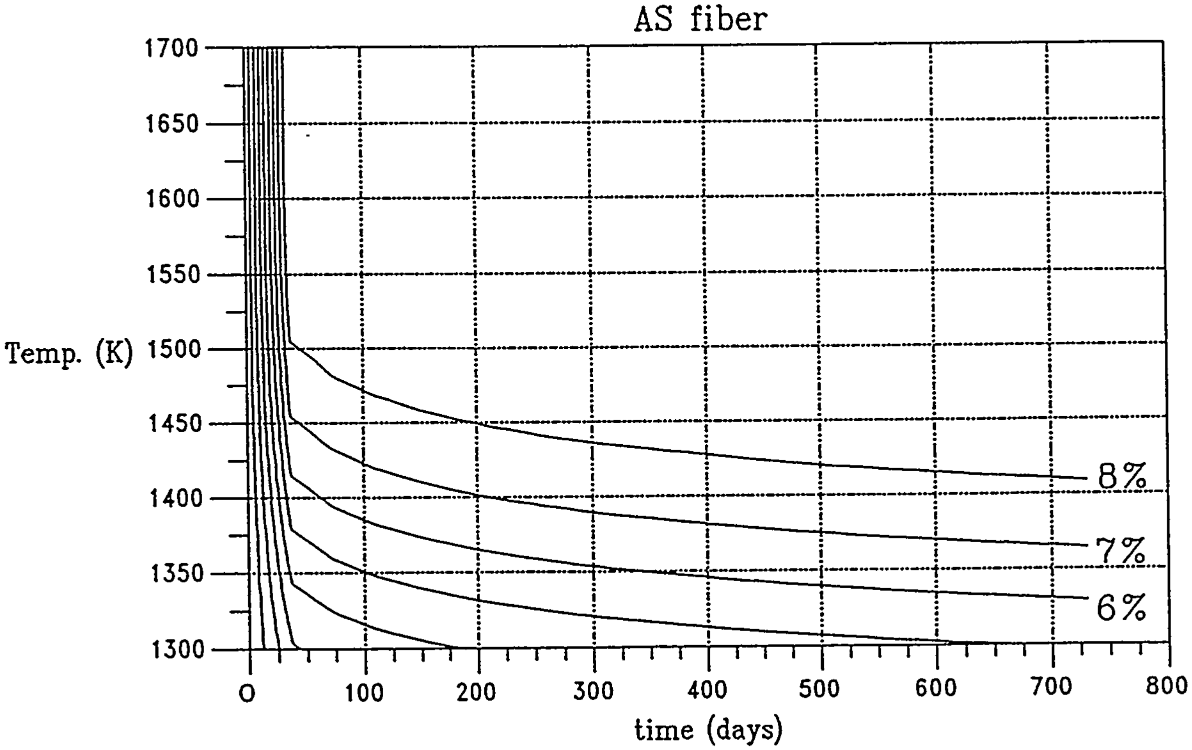


Figure 7. AS fiber at t = 0-730 days, T= 1093°C to 1427°C (2000°F to 2600°F). Glass density = 2.54 Mg/m^3 and crystal density= 2.79 Mg/m^3 (equilibrium crystal composition).

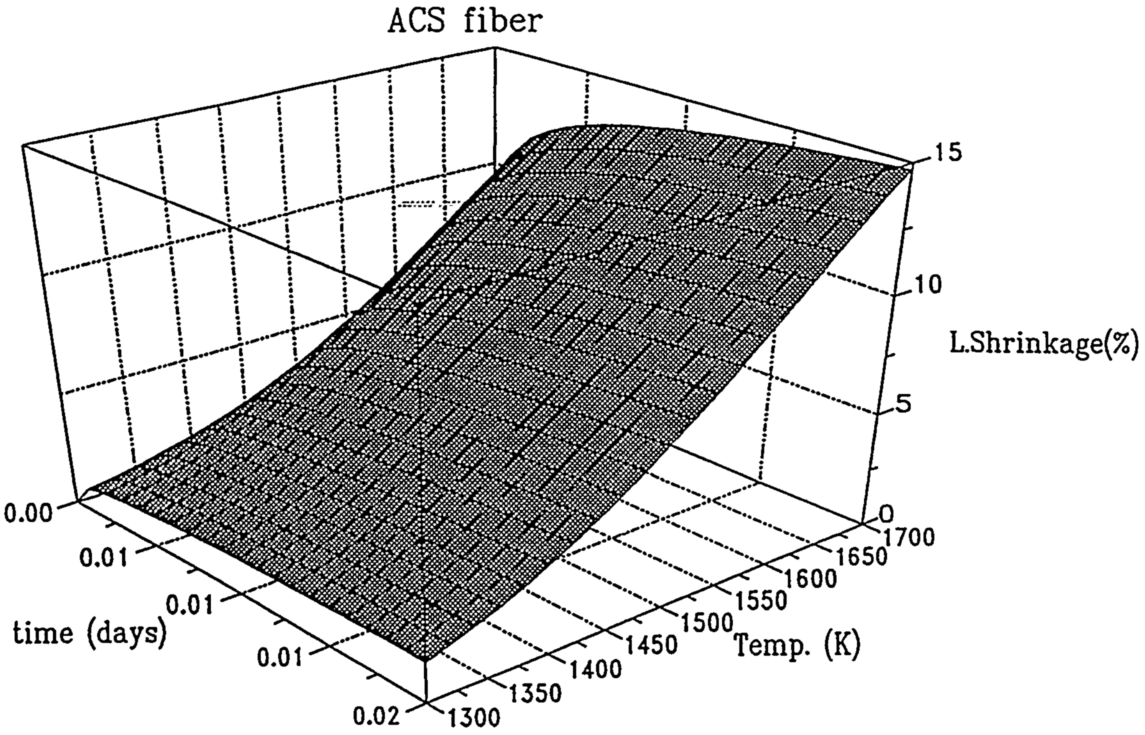


Figure 8. ACS fiber at t = 0-1800 sec, T= 1093°C to 1427°C (2000°F to 2600°F). Glass density = 2.61 Mg/m^3 and crystal density= 3.3 Mg/m^3 (mullite ss).

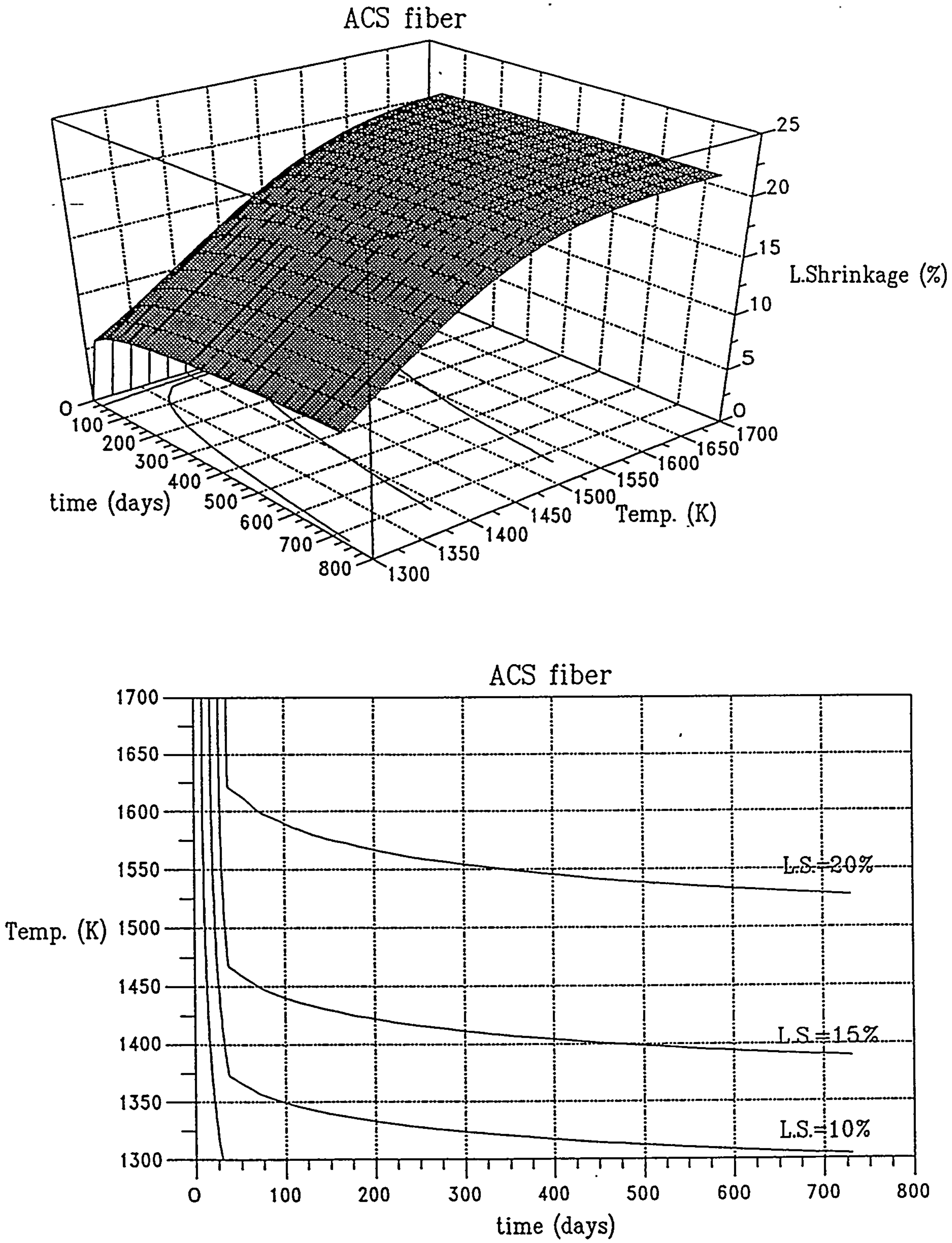


Figure 9. ACS fiber at t = 0-730 days, T= 1093°C to 1427°C (2000°F to 2600°F). Glass density = 2.61 Mg/m^3 and crystal density= 3.3 Mg/m^3 (mullite ss).

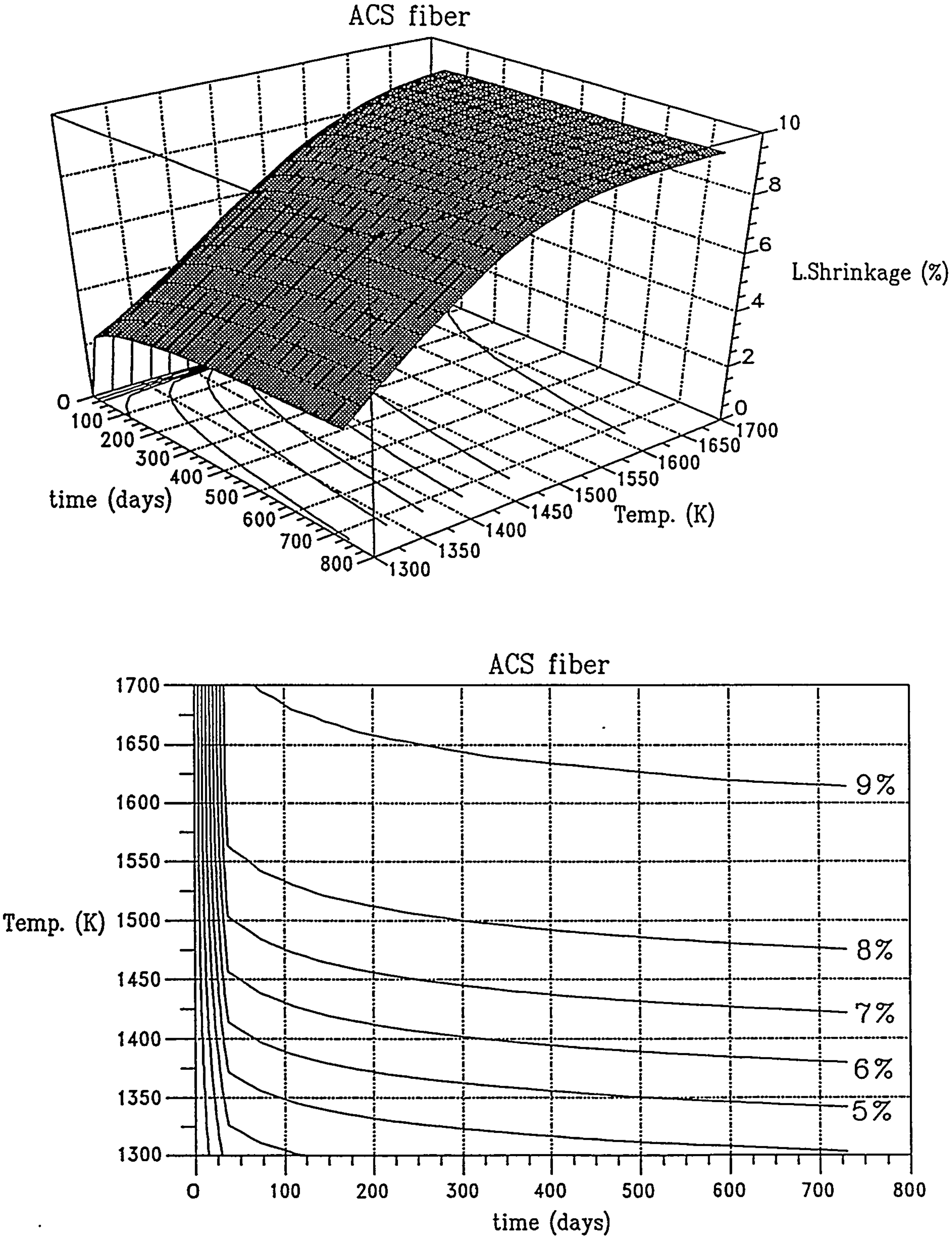


Figure 10. ACS fiber at t = 0-730 days, T= 1093°C to 1427°C (2000°F to 2600°F). Glass density = 2.61 Mg/m^3 and crystal density = 2.87 Mg/m^3 (equilibrium crystal composition).