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Studies on a probable correlation between thermal conductivity, kinetics of devitrification and changes in fiber radius of an aluminosilicate ceramic vitreous fiber on heat treatment

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Abstract

Degradation in heat insulation properties of vitrified ceramic fiber blankets has commonly been observed during prolonged use in heat treatment furnaces The associated physico-chemical property changes during such a heat treatment process has been studied under laboratory conditions with systematic time–temperature variations. Alumino-silicate ceramic fiber blanket .samples were subjected to temperature variations from 1100 to 1350 °C and soaking time variations from 1 to 4 h. Additionally, scanning electron microscopic studies of the fibers were undertaken to study progressive shrinkage of the fibers with rise in time and temperature. Quantitative estimation of mullite formation from devitrified fiber was made through an X-ray diffraction (XRD) study. Association of these two concurrent phenomenon made kinetics of devitrification process study difficult and established mathematical kinetics relationship valid for cylindrical (fiber) samples namely $(1-\alpha)^{0.5}=(1-kt/r)$ [H.S. Roy, J. Thermal Analysis 36 (1990) 743–764] (where, α, fraction reacted in time t, r, fiber radius and k, reaction rate constant, yielded wide variation in k values. A modification in fiber radius was thus made taking its n th relationship (where n is an empirical constant), such that the factor n took care of the concurrent phenomenon of mullitization associated shrinkage behavior. Plots were made between ln $(1-(1-\alpha)^{0.5})$ vs. ln kt. The slope gave the value of n ln r. A value of $n=1.7$–1.8 was consistent for all the data points with fiber diameter varying between 1.0 and 3.5 μ. The modified equation for this type of reaction can thus be established as $(1-(1-kt/r^{1.7-1.8})$. The radiant energy heat transfer at higher temperature which characterizes different varieties of ceramic blankets is disclosed in a relationship $k_T=a\ T^b$ (where k = thermal conductivity, T = temperature and a, b are constants). Log–log plot of k_T vs. T yields values of $b=1.3$–1.5 and the equation connecting quantity of heat transfer, Q, temperature, T, and fiber blanket thickness Z, can be correlated as $Q \propto (a(T1^b-T2^b)/Z^b$. This indicates that the use of a common temperature $(T1+T\ 2)/2$ and an average k at that temperature leads to misleading results unless a correction in Z as Z^b is brought into the equation. The value of Z modified as Z^b finds favor on our observation of $b=1.3$–$1.5 \approx n=1.3$–1.5 as mentioned earlier and appears to have given rise to a correlation between thermal conductivity and kinetic parameters involving kinetics of mullitization reaction, reaction rate constant and shrinkage in fiber radius with heat treatment.

Keywords: C. Thermal conductivity; Correlation; Kinetics; Devitrification; Ceramic fiber

1. Introduction

Adoption of production of a wide variety of steel products in the continuous casting–rolling process with rapid changes and alteration in furnace temperature as required in metallurgical treatment has necessitated furnace lining with ceramic fiber insulation as this reduces heat content of the lining significantly as compared with refractory/monolithic lining.

These fibers are either vitreous or crystalline in nature having alumina content 32–50% and belong to aluminosilicate/alumina–silica–zirconia variety. Crystalline variety shrinks less than the glassy variety and the shrinkage in transverse direction is more than that along longitudinal direction. In general it is observed that the glassy variety transforms into crystalline variety slightly below 1100 °C, and formation of mullite and cristoballite follows with progressive temperature rise which results in depletion of alumina in the matrix (Fig. 1).

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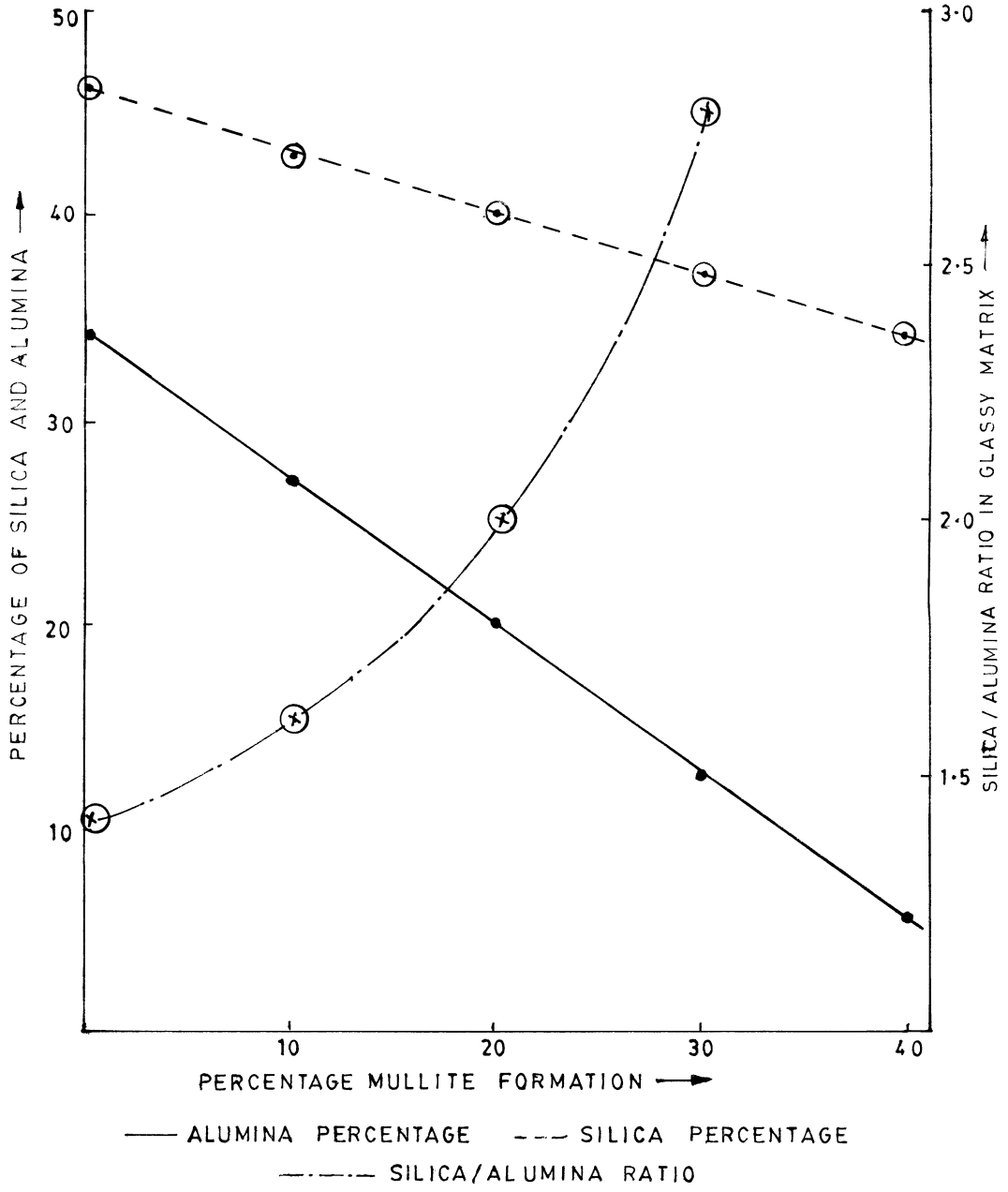

Fig. 1. Relationship between percentage mullite formation, silica/alumina ratio and percentage of silica and alumina in ceramic fiber.

The formation of crystalline phases with higher density as compared with the vitrified mass results in progressive shrinkage of the fibers with temperature, associated with micro-pore reduction formed during fabrication. Reaction kinetics study as a result is complex in nature and in this article an attempt has been made to correlate them which has resulted in modification of the established mathematical relationship [1,2] of rate kinetics equation incorporating the reaction product (α), kinetic constant (k), time (t) and fiber radius (r) valid for cylindrical samples.

2. Theory

The relationship connecting all these earlier mentioned parameters is of the following type

$$(1-\alpha)^{0.5} = 1-kt/r \tag{1}$$

If it is presumed that the radius has nth relationship due to reasonings mentioned as earlier, then (1) modifies into

$$(1-\alpha)^{0.5} = 1 - kt/r^n \quad (2)$$

or,

$$\ln(kt) - n \ln(r) = \ln(1-(1-(1-\alpha))^{0.5}) \quad (3)$$

A plot of $\ln(1-(1-\alpha)^{0.5}$ vs. $\ln(kt)$ will thus yield a straight line and the intercept on the y-axis will give the value of $n \ln r$ from which n can be found out.

2.1. Determination of k—reaction rate constant

Determination of reaction rate constant, k, can be carried out following the standard relationship

$$K \propto 1/t \propto e^{-Q/RT} \quad (4)$$

where k, reaction rate constant; t, time; T, temperature; Q, activation energy; and R, gas constant.

Or,

$$\ln(1/t) = \ln A - Q/RT \quad (5)$$

where ln A = proportionality constant. A plot of ln $(1/t)$ vs. $(1/T)$ will give Q/R from which Q can be found out.

The value of K can be found out from the relationship $K \propto e^{-Q/RT}$ for various temperatures.

2.2. Determination of $\propto$

For determination of $\propto$ (the relative amount of mullite formed) standard equation correlating mass absorption coefficients of mullite, glass and cristoballite and observed peak area under mullite peak at $2\theta = 31^\circ$ (Cu-$K\alpha$ radiation) was taken into calculation through the following standard relationship as suggested by Klugh and Alexander [3]

$$I_A/I_0 = X_A \ \mu_A/X_A \ (\mu_A - \mu_B) + \mu_B \quad (6)$$

where I_A, intensity of interference due to component A; I_0, intensity of interference due pure component; X_A, amount of A in mixture; and μ_A, μ_B = mass absorption coefficients of A and B, respectively.

The values of mass absorption coefficients of mullite and the probable phases are given in Table 1. From the table it will be observed that $(\mu_A - \mu_B)$ is negligible [4] and Eq. (6) transforms into $I_A/I_0 = K X_A$ and the peak heights/peak areas give the amount of mullite formed directly.

2.3. Determination of fiber radius

A small portion of the raw and heat-treated fibers were suspended in acetone and kept under ultrasonic vibration from which a drop was placed on milimeter sized copper wire gauge which served as sample holder. Diameter of the micron sized samples were automatically found out from a computer programmed scanner fitted with the SEM.

Table 1
Values of mass absorbtion coefficients

Substance	Value (μ)
Mullite (3:2)	32.57
(2:1)	31.86
Alumina	31.78
Silica	34.59
Non-crystalline matrix	
0.9 SiO_2 0.1 Al_2O_3	34.31
0.8 SiO_2 0.2 Al_2O_3	34.03
0.7 SiO_2 0.3 Al_2O_3	33.74
0.6 SiO_2 0.4 Al_2O_3	33.46

3. Experimental

The fiber used in this study had the following composition.

Alumina = 40–45%
Silica = 50–55%
Iron oxide, Titania, Magnesia. Calcia and alkalies = $<1.0\%$

The physical parameters of the fiber is disclosed in the following properties: Bulk density, kg/m ^{3} = 128, Fiber diameter, micron (most occurring range)—2.3–2.5 shot content,% max.—15, tensile strength, kg/cm^2—5.5–10.5.

Small sized fiber blocks (2×2 cm) cut out from the ceramic fiber role were heat treated in a SiC furnace at temperatures 1100–1350 °C with various soaking periods ranging between 1 and 4 h. X-ray diffraction studies were carried out on the samples to find out the amount of mullite formed. Siemens make powder diffractometer (type D-500) fitted with Siemens X-ray generator (40 Kv, 40 mA) was run with 1° divergent slit, chart speed 0.5 cm/min, goniometer speed 0.5°/min and 4 s time constant. The powder was compacted in a cellophane holder secured with cellophane window. Traces were obtained for $2\theta = 20$–40° (dA° = 4.44 A°–2.25 A°) and identification of peaks confirmed mullite formation. The inter planer spacing (dA° = 2.524 A°) and its corresponding peak area (I_A) (Fig. 2) were measured for all the heat-treated samples. SEM study indicate the original diameter (Fig. 3) and shrinkage of the fibers after heat treatment were measured for each individual samples through SEM studies as previously stated. The significant observation is progressive reduction of fiber diameter with rise in time and temperature with maxima

and minima as 3.5 μ and 1.0 μ The most occurring range was also automatically computed. Following the relationship as mentioned in Eq. (5) plots were made between $1/t$ vs. $1/T$ (Fig. 4) and the activation energy and subsequently reaction rate constant, K, was found out at each temperature.

The amount of mullite formed was calculated using Eq. (6). Plot of ln Kt vs. ln $(I-(1-\alpha)^{0.5})$ was made as shown in Fig. 5. The correlation coefficient of the data points were better than 94%. Values of n were calculated from different variations in diameter as 1–3.5 μ and were observed to lie between 1.7 and 1.8.

Thermal conductivity measurement of the fiber samples were carried out through the standard procedure, ASTM C 892–78. This is a standard specification for thermal conductivity measurement at high temperature and gives either ASTM 201–68 or ASTM C 177–78 as alternate acceptable test method and specifies maximum allowable apparent thermal conductivity blankets having densities between 96 and 128 kg/m ^{3} over a temperature range between 0 and 1400 °C [5,6].

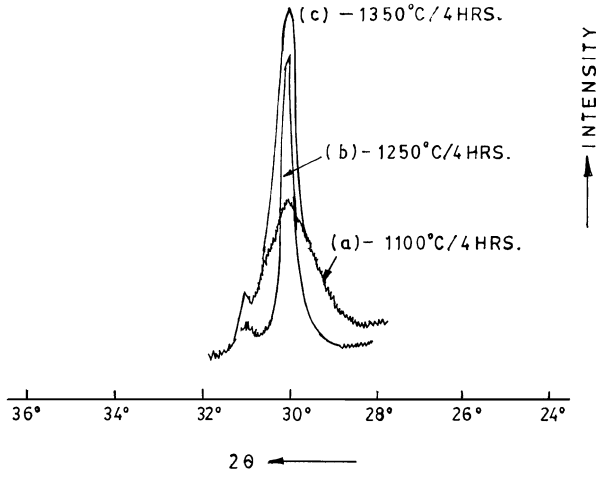

Fig. 2. Peak intensity comparison of mullite under $d^{\circ} = 2.524$ A°.

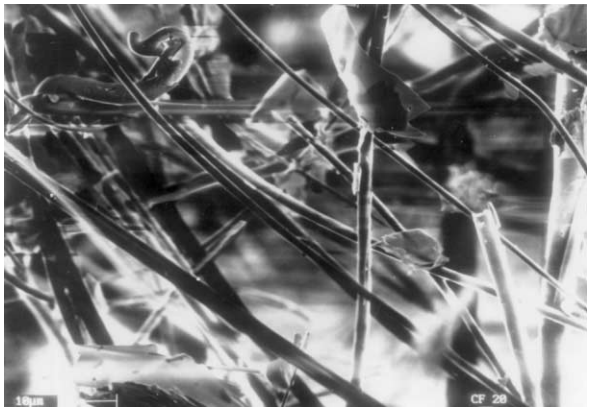

Fig. 3. SEM photograph of fiber.

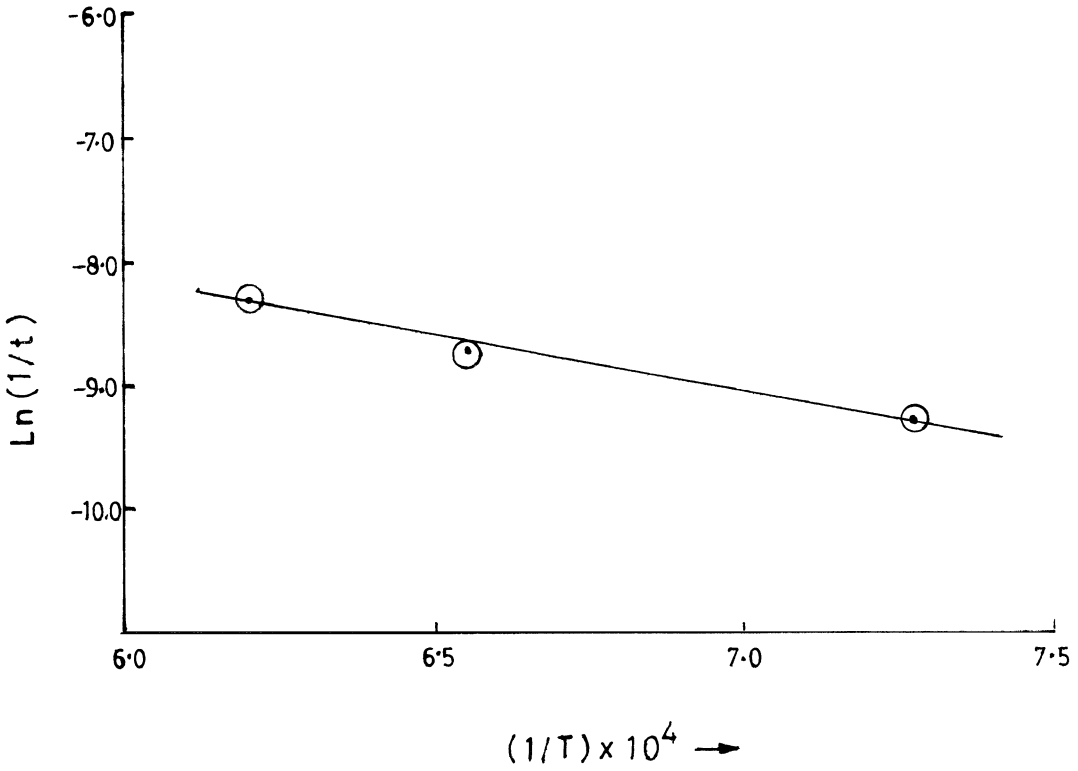

Fig. 4. Plot of ln $(1/t)$ vs. $(1/T)$ for determination of activation energy value.

This investigation was conducted to relate the apparent thermal conductivity of fiber blankets to temperature and mean fiber diameter through ASTM C 201–68 test procedure. Ceramic fiber blankets included major Indian manufacturer (in collaboration with M/S Morgan Thermal Ceramics Ltd, UK) and a sufficient number of 0.4×0.3 M samples were cut from blanket rolls (roll dimension 7.3×0.61 M, thickness 13–50 mm). Figs. 6 and 7 represents thermal conductivity relationship with temperature of a few specific samples with alumina and silica variations as mentioned earlier.

4. Results and discussion

Characterization of ceramic fibers is disclosed in thermal conductivity vs. temperature relationship (Fig. 6) and in ln (thermal conductivity) vs. ln (temperature) relationship (Fig. 7). While in Fig. 6 the relationship is observed non-linear, in Fig. 7, a linear relationship is observed in all the different samples studied. The values of slope appears in the range between 1.3 and 1.5. The common use of an average temperature and an average, k, will lead to misleading results. The above equation

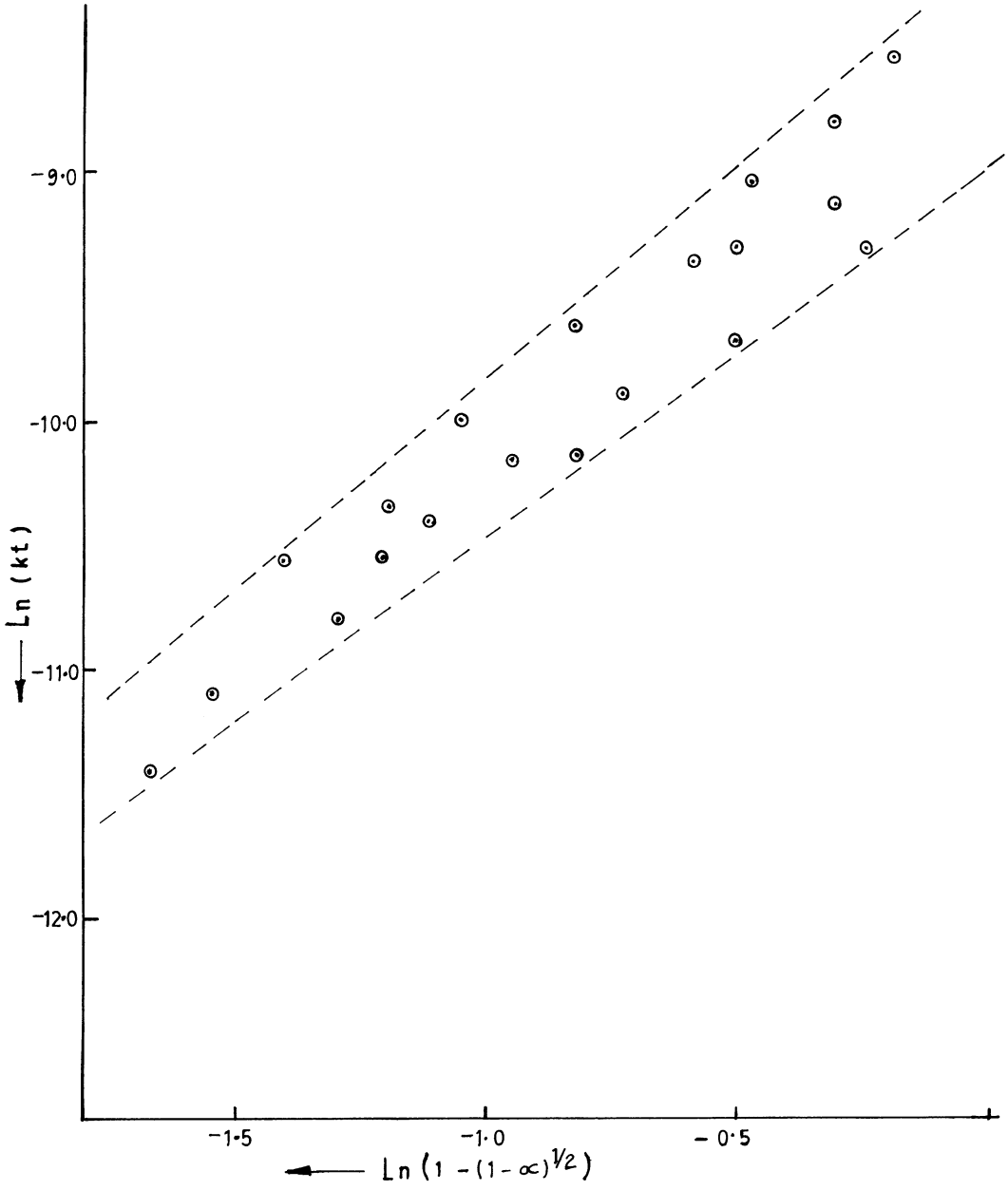

Fig. 5. Plot of ln (kt) vs. ln $(1-(1-\alpha)^{0.5})$ for determination of exponent n.

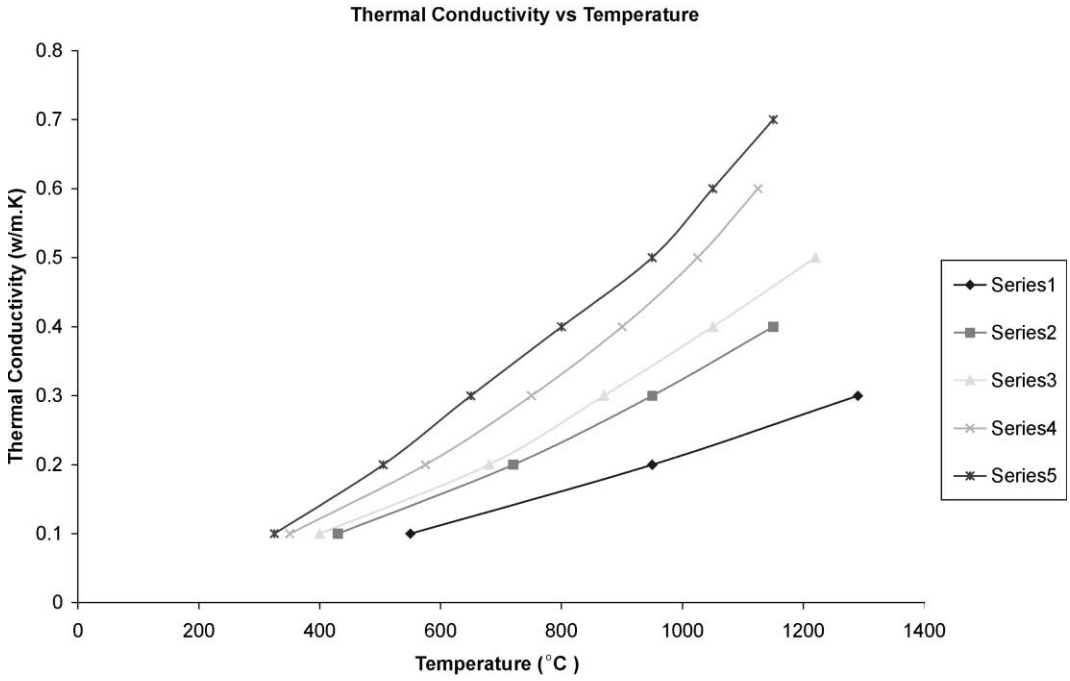

Fig. 6. Thermal conductivities of fiber refractories vs. temperature.

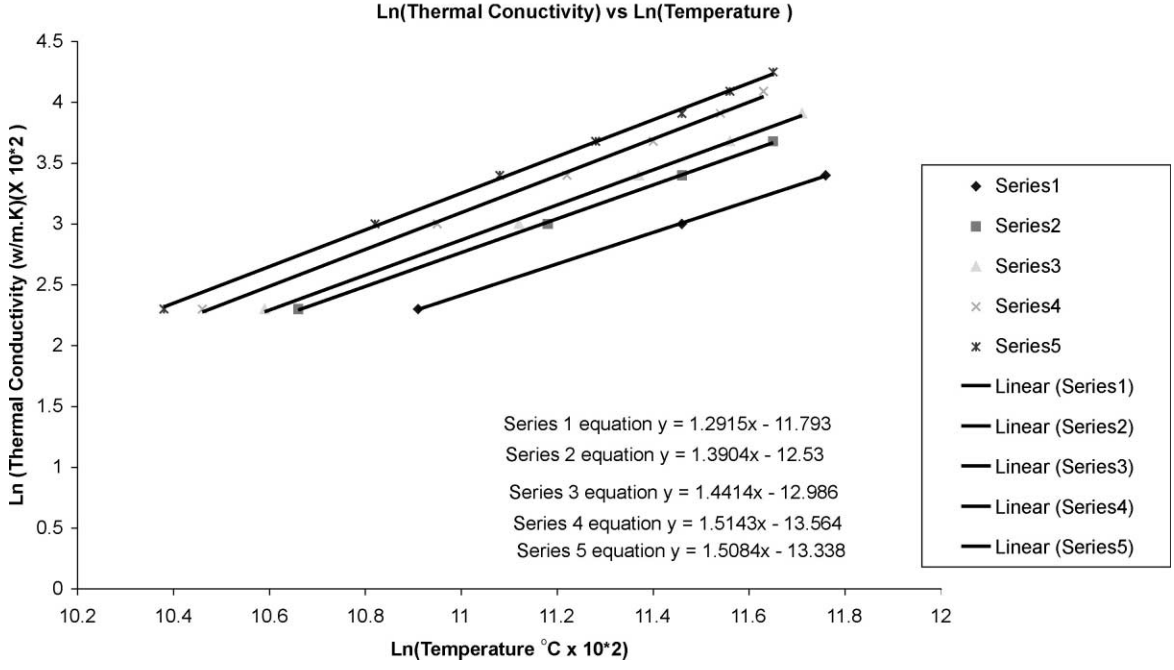

Fig. 7. ln (Thermal conductivity) vs. ln (temperature) of fiber refractories.

lends support from dimensional analysis also, as shown below.

$$K = \mathrm{a}\ T^n$$

$$Q \propto\ (\mathrm{a}\ (T1^n - T2^n)/Z^n$$

Presence of shots in the fiber, variable void volume fraction (dependent on the ratio of bulk density to theoretical density) affect the thermal conductivity values significantly. However, a straight forward relationship connecting mullitisation, fiber radius change and thermal conductivity appears interesting observation in this

case. As regards practical application, selection of fiber composition and correct fiber specification for prolonging the furnace lining life from the present observed correlation may give useful guidelines both to the manufacturers and the users, in future.

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