PII: S0955-2219(97)00149-0

Effect of Addition of Niobium Oxide on the Thermal Conductivity of Alumina

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Abstract

Alumina is extensively used in the advanced ceramic industry, mainly for mechanical and electronic applications. However, the high melting point of Al_2O_3 necessitates a high sintering temperature of around 1923 K. In this work it was investigated the effect of niobium oxide additives on the thermal conductivity of alumina sintered at 1673 K, and at 1723 K. Niobia concentrations added ranged from 1 to 6% in weight. Thermal diffusivity was measured over the temperature range 373–1273 K using the laser flash method. The samples sintered at 1723 K containing ≥ 3% Nb_2O_5 show a continuous microstructure containing little porosity. Nb_2O_5 additions in the range 3–6% result in increases in thermal conductivity, the highest increase being noted for the 5 wt% addition. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Alumina is extensively used in the advanced ceramic industry, mainly for mechanical and electronic applications.[1] For such applications the electrical resistivity, loss factor, mechanical resistance and hardness are important properties. However, the high melting point of Al_2O_3 (2323 K) necessitates a high sintering temperature of around 1923 K. Various additives have been used to lower the sintering temperature, for the fabrication of electronic substrates, such as silica and eutectics of manganese and titanium oxides.[2] The reduction in the consolidation temperature is generally due to the formation of a glassy phase within the alumina.

Niobium oxide has also been used as a sintering additive, and preliminary results show that high densities and good mechanical strength can be obtained after sintering at temperatures as low as 1723 K.[3] The Nb_2O_5–Al_2O_3 equilibrium diagram (Fig. 1) shows a eutectic at 1698 K. Hence densi-fication can occur via the formation of a transient liquid phase.[4]

Although small amounts of niobium oxide (1–6% by weight) can improve the density and mechanical properties of Al_2O_3 sintered at temperatures as low as 1723 K,[3] the thermal properties may however be affected by the introduction of this additive.

The objective of this study is to investigate the effect of niobium oxide additives on the thermal conductivity of alumina sintered at 1673 where no liquid phase is expected, and at 1723 K where liquid phase sintering is anticipated. It is important that the niobia introduced as an additive should not produce a decrease in the thermal conductivity of the alumina if this material is to be used for electronic substrates. If a drastic decrease in the thermal conductivity occurs, the sintered material obtained, despite its higher density and improved mechanical properties will not be suitable for electronic applications. Niobia concentrations added ranged from 1 to 6% in weight. The experimental results were compared against results obtained for pure alumina.

Thermal diffusivity was measured over the temperature range 373–1273 K using the laser flash method.

2 Sample Preparation

Samples were prepared in the shape of discs, 10 mm diameter ×2 mm thickness. Alumina powder A-16 SG, (ALCOA), 99·79% purity, medium grain size < 0.5 μm, and niobium oxide powder 99·99% purity (Companhia Brasileira de Mineracao e Metalurgia, Brazil) were used as starting material. The two oxides were mixed in a vibratory mill and samples were prepared by a standard cold pressing process. Two batches of samples containing from 1 to 6% weight of niobia were prepared. The first series was sintered at 1673 K and the second series sintered at 1723 K. The samples were
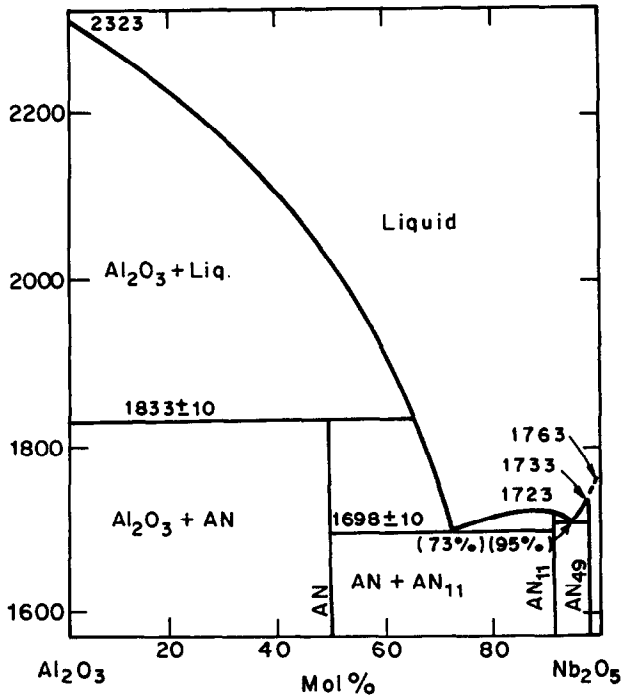
Fig. 1. The Al_2O_3–Nb_2O_5 equilibrium diagram.[4]

Table 1. Sample densities

		Percentage of Niobia						
Sintering temperature (K)	*Density (kg m^{-3})*	*0*	*1*	*2*	*3*	*4*	*5*	*6*
1673		3490	3540	3520	3600	3550	3510	3520
1723		3650	3590	3600	3710	3730	3720	3780

sintered for 2 h in air at the specified temperature. The sample densities obtained after sintering at these temperatures are shown in Table 1 as a function of the amount of niobium oxide added.

3 Experimental Technique

Thermal diffusivity measurements were carried out by using the heat pulse technique initially developed by Parker et al.[5] In this technique a uniform heat pulse of short duration compared with the transient time through the sample is incident on the front face of a disc specimen, and the temperature history on the rear face is recorded.

If no heat losses occur, the normalised temperature rise of the rear face is given by

$$V = 1 + 2\sum_{n+1}^{\infty}(-1)^n \exp(-n^2\omega^2) \qquad (1)$$

where:

$\omega = \pi^2\alpha t/L^2$

$V = \dfrac{T}{Tm} = $ dimensionless temperature rise of the rear face

$T = $ instantaneous temperature rise of the rear face of the specimen

$Tm = \dfrac{Q}{\rho CL} = $ maximum temperature rise of the rear face

$Q = $ input energy on the front face

$\rho = $ density

$C = $ specific heat/unit mass

$L = $ specimen length

Most users employ the half rise time $t_{1/2}$ for which ω is equal to 1·38, and hence the thermal diffusivity α is given by

$$\alpha = 1·38L^2/\pi^2 t_{1/2} \qquad (2)$$

Deviations for idealised behaviour that have been addressed in the scientific literature are finite pulse time effects[6–8] and heat losses.[9,10] The former may be avoided by selecting a suitable sample length but the latter are impossible to avoid at elevated temperatures. In the UMIST apparatus, the pulse profile has been determined and finite pulse time effects are corrected using the method of Taylor and Clark.[8]

$$\alpha = \dfrac{C_1 L^2}{C_2 t_{1/2} - \tau} \qquad (3)$$

where τ is the pulse dissipation time and C_1 and C_2 are constants whose values depend on the pulse shape. Heat losses are corrected using the method advocated by Cowan.[9] A schematic diagram of the UMIST apparatus[11] is shown in Fig. 2.

The pulse source is a solid state Nd glass laser ($\lambda = 1·067\,\mu m$) with a beam diameter of 16 mm. The energy output is in the range 5–95 J, and the pulse dissipation time is nominally 0·6 ms. The disc shaped sample coated with colloidal graphite to improve emissivity is mounted in a graphite holder which is sited inside a graphite susceptor. A lid, having a hole the same diameter as the sample, serves to cut off excess laser beam. The susceptor is located inside an induction coil located inside a vacuum chamber/pressure vessel which permits measurements over the temperature range 20–2750°C in either vacuum or an inert atmosphere such as argon, nitrogen or helium. The temperature of the sample is monitored either by a thermo-couple or an optical pyrometer.

Radiation from the rear face of the sample is collected via a lens and mirror system and transmitted to the detector assembly external to the vacuum chamber by an optical system. The radiation detector used is a InSb detector, sensitive to 5·5 μm and having a response time of 1·5 μs. The detector output signal is then amplified by using a commercially available amplifier. The
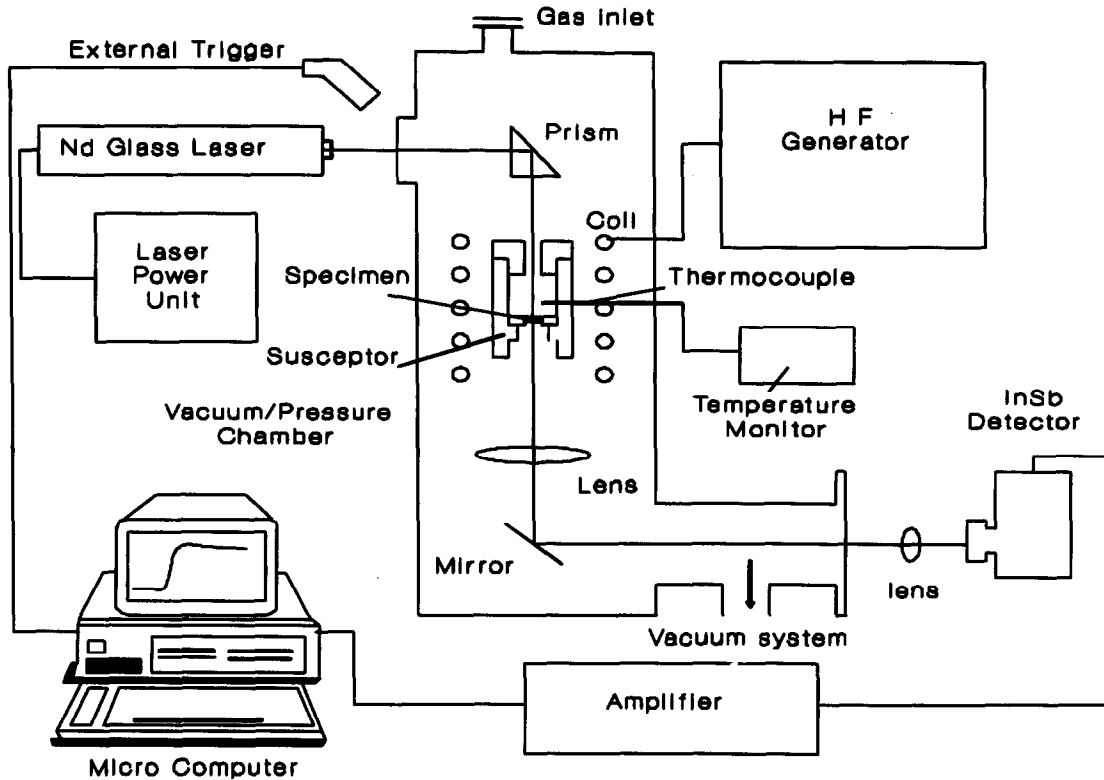
Fig. 2. Schematic of UMIST laser flash equipment.

amplified signal is then recorded and processed by a computer via an analog-to-digital convertor using software specially written for this purpose.

4 Results

Thermal diffusivities were measured from 373 to 1273 K. Figure 3 shows the experimental results obtained for the first series of samples sintered at 1673 K and Fig. 4 shows the results for the second series of samples sintered at 1773 K.
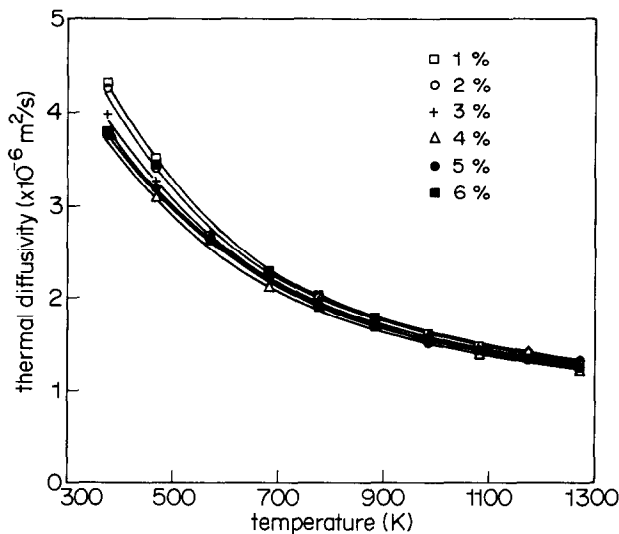
Thermal diffusivities were converted to thermal conductivities by multiplying by density and specific heat. The measured densities listed in Table 1 were used and the specific heats calculated for each composition using the Neumann–Kopp rule

$$C(T) = \sum_{n=1}^{n} F_i C_i(T) \qquad (4)$$

where F_i is the mass fraction of each phase and $C_i(T)$ the corresponding specific heat for the constituents Al_2O_3 and Nb_2O_5. Literature specific heat
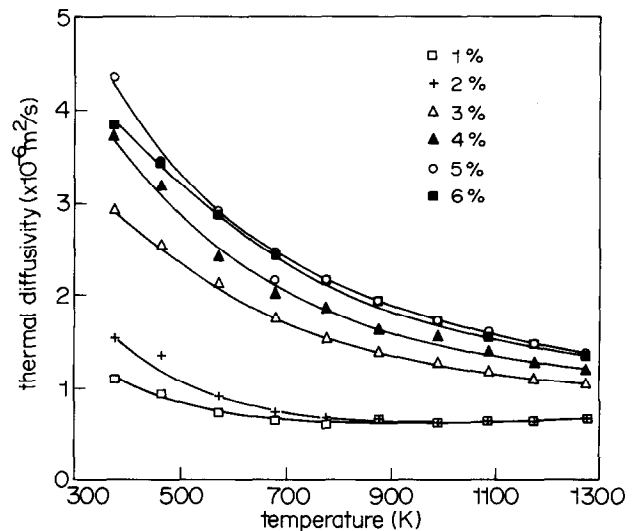

Fig. 3. Thermal diffusivity of samples sintered at 1673 K.

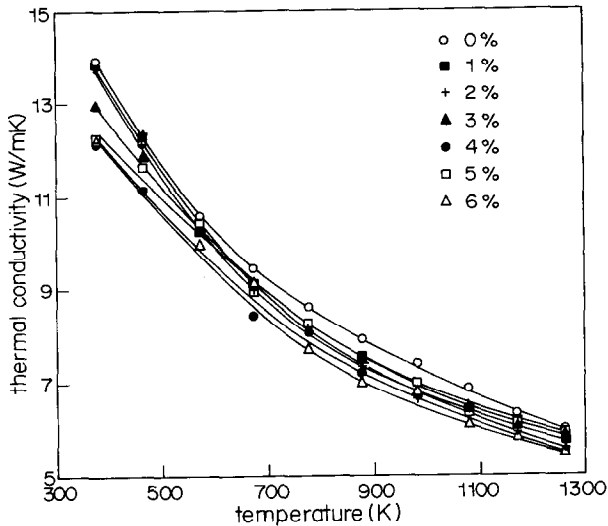**Fig. 4.** Thermal diffusivity of samples sintered at 1723 K.

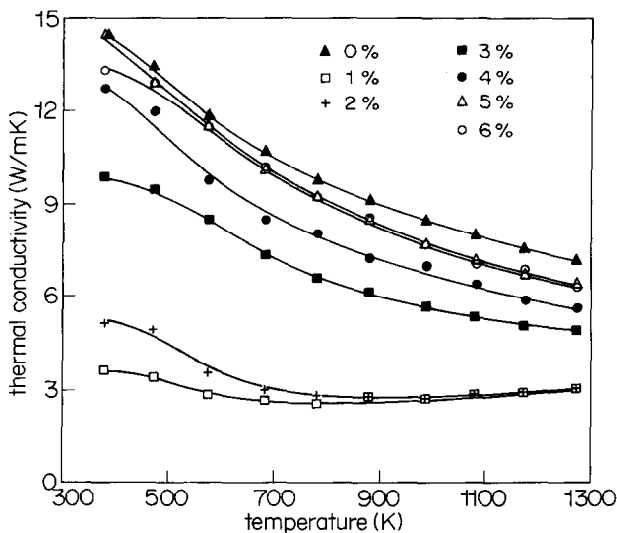**Fig. 5.** Thermal conductivity of samples sintered at 1673 K.

Fig. 6. Thermal conductivity of samples sintered at 1723 K.

data[12] were fitted by a least squares curve fitting method. For Al$_2$O$_3$ the specific heat is fitted by

$$C_p\left(\text{J kg}^{-1}\,\text{K}^{-1}\right) = 1\cdot076 \times 10^3 + 2\cdot249$$
$$\times 10^{-1}T - 4\cdot432 \times 10^{-5}T^2$$
$$- 3\cdot322 \times 10^7 T^{-2} \qquad (5)$$

and for Nb$_2$O$_5$ the specific heat is fitted by

$$C_p\left(\text{J kg}^{-1}\,\text{K}^{-1}\right) = 5\cdot847 \times 10^2 + 8\cdot175 \times 10^{-2}T$$
$$-4\cdot372 \times 10^{-6}T^2 - 9\cdot104 \times 10^6 T^{-2}$$
$$\qquad (6)$$

In Fig. 5 the derived thermal conductivities of the samples fired at 1673 K are plotted as a function of temperature and in Fig. 6 the thermal conductivities of the samples fired at 1723 K are

plotted. For comparison purposes, the thermal conductivities of samples of pure Al$_2$O$_3$ fired at the same sintering temperatures but without the use of sintering additives, are also included.

5 Discussion

The densities obtained for additions of 0 to 6% Nb$_2$O$_5$ listed in Table 1 show that for a sintering temperature of 1673 K the measured densities lie in the range 3490 kg m^{-3} to 3610 kg m^{-3}, i.e. 89·5 to 92·6% theoretical density. There is no systematic trend of density versus niobia content. At this temperature we would not expect any liquid phase to be formed to assist sintering and densification. Therefore, the effect of the Nb$_2$O$_5$ additions is to introduce Nb as an impurity on the alumina lattice which increases the phonon scattering. Hence, the net result is a small but detectable decrease in the thermal conductivity when compared to pure alumina as the amount of Nb$_2$O$_5$ increases.

(a)

(b)

Fig. 7. (a) Microstructure of sample containing 5% Nb$_2$O$_5$ sintered at 1673 K. (b) Microstructure of sample containing 5% Nb$_2$O$_5$ sintered at 1723 K.
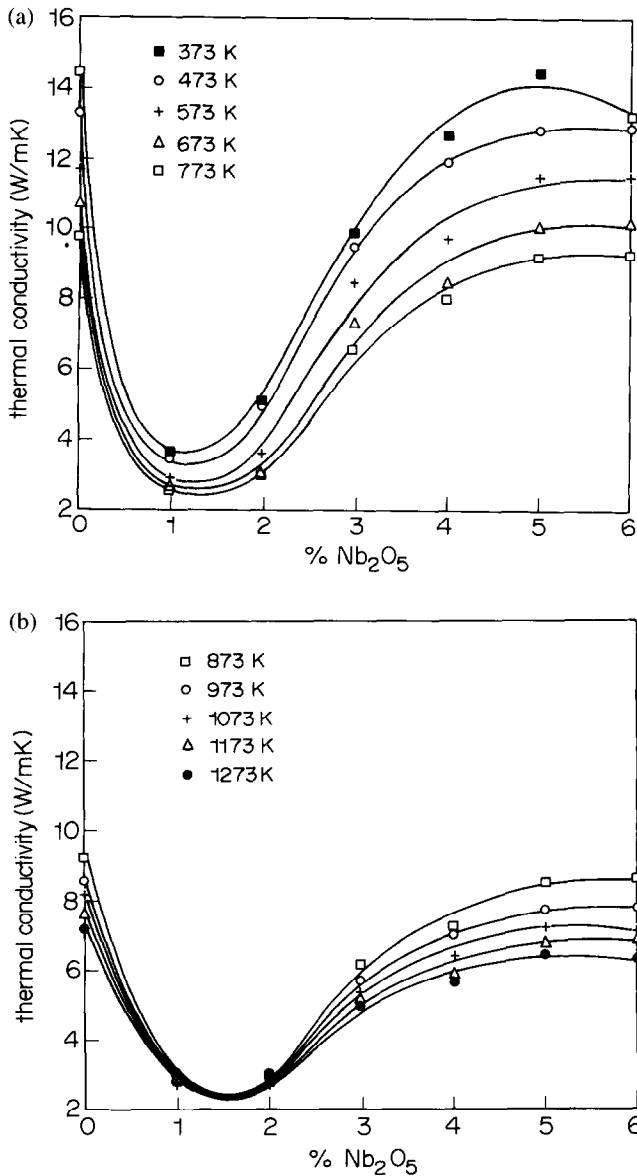
(a)

(b)

Fig. 8. Effect of Nb_2O_5 addition on thermal conductivity of samples sintered at 1723 K.

sharp fall in thermal conductivity compared with that of pure Al_2O_3 (Fig. 8) and this is accompanied by a relatively small decrease in density. However, Nb_2O_5 additions in the range 3–6% result in increases in thermal conductivity, the highest increase being noted for the 5 wt% addition. The difference in thermal conductivity between the samples sintered with 5 or 6 wt% Nb_2O_5, compared to that obtained with no sintering additive, is negligible. However, the densities obtained are significantly higher at 3720–3780 kg m^{-3}. These values of density are comparable with those obtained by sintering Al_2O_3 at 1873 K.[13] However, the thermal conductivity of the Al_2O_3/Nb_2O_5 samples is significantly lower than that of pure Al_2O_3 sintered at 1873 K (by some 25% at 373 K). This suggests that the benefit of higher density at a lower sintering temperature is, to a degree, offset by the fact that the phases present after solidification of the liquid phase appear to have a much lower thermal conductivity.

Acknowledgements

However, the densities of the samples sintered at 1723 K, where a liquid phase is expected to be formed during sintering, show initially a decrease in sintered density for Nb_2O_5 additions of 1 and 2% but a significant increase in sintered density when the Nb_2O_5 content exceeds 3%. Indeed, the porosity level is reduced to 3% when 6% Nb_2O_5 is added as a sintering additive.

The samples sintered at 1723 K containing $\geq$ 3% Nb_2O_5 show a continuous microstructure containing little porosity. In Fig. 7 the microstructure of a sample sintered with 5% Nb_2O_5 sintered at 1723 is compared with a specimen containing the same additive level but sintered at 1673. More porosity and the absence of a grain boundary phase are clearly present in the latter.

However, the effect of liquid phase sintering at 1723 K on the thermal properties is really quite dramatic. Additions of 1–2% Nb_2O_5 cause a very

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