

THERMAL DIFFUSIVITY MEASUREMENTS SOME SYNTHETIC SLAGS

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ABSTRACT

Thermal diffusivity measurements of synthetic slags containing SiO_2 , Al_2O_3 , CaO and MgO with additions of Na_2O were carried out using the three-layer laser flash method on a differential scheme in the temperature range 1625 to 1825 K. The aim of this study is to provide thermal diffusivity data needed both for subsequent modelling of the process of up-hill teeming and for an understanding of the thermal conductivities of silicate melts from a more general metallurgical viewpoint. Several compositions were selected in the low basicity region so that the samples are representative of the mould flux slags relevant to the process of up-hill ingot teeming of speciality steels. The results of the measurements indicate that the thermal diffusivity of the presently investigated slag compositions is dependent on the Na_2O concentration as well as the temperature. The observed trends are discussed and critically analysed.

I INTRODUCTION

The thermal diffusivity of liquid synthetic slags containing SiO_2 , Al_2O_3 , CaO and MgO with additions of Na_2O have been measured using a three-layered laser flash method on a differential scheme. The focus of this investigation is to increase the understanding of the heat transfer phenomena involving mould fluxes used in up-hill teeming of special steel. In up-hill teeming, the mould flux has several functions, the important among them being the protection of the steel meniscus against reoxidation from the atmosphere and the heat transfer control. The mould flux, originally in the form of a solid powder, transforms, upon heating, into different layers ranging from liquid slag to unreacted solid powder. This layer structure of the mould flux is schematically described in figure 1. The liquid slag layer prevents or minimises the reoxidation from the atmosphere of the steel meniscus but gives poor thermal insulation of the steel. The powdery layer on the other hand provides a good thermal insulation but has a low ability to exclude the atmosphere. One of the main operational parameters of the mould flux, is therefore the melting rate of the solid powder which is affected by the heat transfer through the liquid slag layer and in turn by the thermal diffusivity of the liquid slag layer.

The investigation of thermal property data of liquid silicate melts at high temperatures are still far from complete, as can be seen in the review on thermal conductivity and diffusivity data by Mills and Suza¹. The lack of such data makes a systematic discussion on the effects of temperature and structure of the melt on the thermal properties very difficult. The shortage of thermal property data for silicate melts also complicates accurate modelling and design of new and existing industrial processes and installations. Therefore a study like the present one finds its relevance and motivation in a variety of field such as pyrometallurgy, ceramic engineering, etc. Some of the earlier studies of the thermal diffusivity measurements that need be mentioned in this context are the measurements on continuous casting fluxes² and liquid calcium ferrite slags³ undertaken by Ohta et al. and on synthetic slags by Friedrichs et al⁴ al by the laser flash method together with thermal conductivity measurements on continuous casting fluxes by Goto et al.⁵, using the hot-wire method.

The thermal diffusivity measurements in this present study have been conducted using the laser flash method on cooling samples. The laser flash method has over the years been recognised as a versatile technique for thermal diffusivity measurements for a wide range of

materials, such as metals, plastics and slags in both solid and liquid state. A three-layered sample cell, consisting of the liquid slag sample sandwiched between an upper and a lower platinum crucible has been employed in this present study. Unlike thermal diffusivity measurements on solid samples, where the thickness can be accurately measured at room temperature and can easily be extrapolated to higher temperatures using the coefficient of linear expansion, measurements on liquid slags at high temperature always involve uncertainties in the estimation of the thickness of the liquid slag. Therefore, in the present work, a method, in which, two temperature response curves, originating from two separate laser pulses corresponding to two different sample thicknesses, with a known relative difference in thickness has been employed. The thermal diffusivity of the liquid sample can then be derived from these two temperature response curves without any knowledge of the absolute thickness of the liquid sample.

II. EXPERIMENTAL

A. Principle

The three layered cell arrangement used in this present investigation is schematically shown in figure 2. The three layers consist of the liquid slag specimen (layer 2), in the form of a thin film, sandwiched between two platinum containers (layer 1 and 3). The laser energy is absorbed by the top surface of the upper platinum container and travels through the sample to the lower platinum crucible. The temperature of the rear platinum surface was monitored through a gold-plated mirror, by collecting the radiation using a photovoltaic InSb infrared detector. The lower crucible containing the liquid slag sample was then lowered slightly and the measurement procedure was repeated to produce a second temperature response curve. A relative difference in the thickness of 0.2 mm of the slag layer between the first and the second measurement was obtained very accurately by the aid of a micrometer screw gauge.

From the temperature response curves at the initial time region, obtained from the two laser irradiations of the three-layered cell, the thermal diffusivity of the slag sample was evaluated with the a software based on differential three-layer analysis. For this, the procedure, based on the method developed by Ohta et al.⁶ was used. Their method is described below

$$\frac{\partial \ln(\theta \sqrt{t})}{\partial(1/t)} = \frac{(\eta_1 + \eta_2 + \eta_3)^2}{4} \quad (1)$$

where θ is the temperature response of the rear surface of the lower platinum crucible, t is the time, η_i is $l_i/\sqrt{\alpha_i}$, where l_i is the thickness and α_i the thermal diffusivity of the i -th layer respectively. A plot of $\ln(\theta \sqrt{t})$ against $1/t$ gives a straight line with the gradient $(\eta_1 + \eta_2 + \eta_3)^2/4$. From equation 1 the following two equations can be derived

$$\frac{l_2}{\sqrt{\alpha_2}} = -2\sqrt{\frac{\partial \ln(\theta_{(l_2)} \sqrt{t})}{\partial(1/t)}} - \eta_1 - \eta_3 \quad (2)$$

$$\frac{l_2 + \Delta}{\sqrt{\alpha_2}} = -2\sqrt{\frac{\partial \ln(\theta_{(l_2+\Delta)} \sqrt{t})}{\partial(1/t)}} - \eta_1 - \eta_3 \quad (3)$$

where $l_2 + \Delta$ and l_2 are the thickness of the liquid slag layer at the first and second laser radiation respectively, Δ is the relative difference in the thickness of the liquid slag layer obtained very accurately by rising the bottom crucible using the micrometer screw gauge. With knowledge of the thickness and thermal diffusivities of layer 1 and 3, the thickness and thermal diffusivity of the liquid slag sample can be determined. The relation between the thermal diffusivity measured at the first and second laser radiation and the corresponding sample thickness, with a given Δ can be described as the two lines in figure 3. The intersection between these two lines provides the thermal diffusivity α_2 and the thickness l_2 of the liquid slag sample.

B. Materials

Table 1 gives the supplier of the materials used together with their respective purities, as stated by the manufacturer. SiO_2 , Al_2O_3 , CaO , MgO was calcined at 1223 K in a muffle furnace to decompose any carbonate or hydroxide before use. The synthetic slag samples were prepared by mixing SiO_2 , Al_2O_3 , CaO , MgO and Na_2O in desired quantities in a ball mill, which was agitated for at least one hour.

C. Apparatus

A Sinku-Riko laser flash unit (model TC-7000H/MELT), with a maximum sample temperature limit of 1873 K was used for the present thermal diffusivity measurements. A schematic diagram of the same is presented in figure 4. The furnace heating elements, eight in number, are made of lanthan chromite. The sample was heated in argon atmosphere at the rate of $6 \text{ K} \cdot \text{min}^{-1}$. During the course of the experiments, the temperature of the liquid sample was measured with a Pt-13%Rh/Pt (R-type) thermocouple in an alumina tube placed in contact with the base of the sample container.

The platinum crucible containing the liquid slag sample has an inner diameter of 17 mm and a height of 11 mm. The upper platinum crucible has an outer diameter of 14 mm and a height of 20 mm. The thickness of the two platinum crucibles consisting of layers 1 and 3 is usually around 0.2-0.30 mm. Before the start of the thermal diffusivity measurements, the contact point between the upper and lower platinum crucibles was accurately determined, in order to obtain an equal sample thickness at all measurements. The cell arrangement was positioned in the even temperature zone of the furnace. After the attainment of the thermal equilibrium, the cell arrangement was exposed to the instantaneous laser energy pulse from a top-mounted Nd-glass laser (2.40 kV), in order to measure the thermal diffusivity of the liquid slag layer. The temperature distribution in the cell can be considered to be uniform prior to the instantaneous laser pulse.

D. Procedure

Before measuring the thermal diffusivities of liquid samples at high temperature, the alignment of the gold-coated mirror was verified by room temperature measurements of the thermal diffusivity of a solid stainless steel sample with a well-known thermal diffusivity value. Further, the operation of the three-layered laser flash method on the differential scheme, was also confirmed by measuring the thermal diffusivity of liquid LiNO_3 in the temperature range between 573 - 633 K.

The liquid slag samples were thermally equilibrated at each measurement temperature before the acquisition of at least 10 sets of temperature response curves. The thermal diffusivity of the samples was then calculated from these curves using the procedures described earlier. During the course of the experiments the upper and lower platinum crucibles were separated several times to avoid the presence of any gas bubble in the liquid slag sample.

III. RESULTS

Among the uncertainties arising from the experimental apparatus itself and the experimental method, the alignment of the gold-coated mirror and the presence of gas bubbles in the liquid slag sample should be mentioned. None of these can be completely excluded, especially at the high temperatures of the present experiments. Careful precaution have therefore been taken before and during every measurement to avoid and minimise the presence of gas bubbles in the liquid or any misalignment of the gold-coated mirror.

In the present investigation, five different synthetic slag compositions have been studied. The studied compositions can be divided into two groups, one consisting of three slag compositions where Na_2O was gradually added to a reference slag composition (A1) with a fixed weight ratio between SiO_2 , Al_2O_3 , MgO and CaO , which can be seen in table 2. The additions were made so that the content of Na_2O would represent 7.5 wt% and 15 wt% of the resulting slags A2 and A3 respectively. A second group also consisting of three different compositions, where the molar ratio between SiO_2 and Na_2O was altered while the molar ratio between Al_2O_3 , MgO and CaO was kept constant, as can be seen in table 3. An average thermal diffusivity value, calculated from at least 10 measurements at each temperature, for

those two sets of experiments as a function of temperature can be seen in figure 5 and 6 respectively

IV DISCUSSION

Figures 5 and 6 show that the thermal diffusivity of all the presently investigated slag compositions tend to increase as the temperature increases. It can also be seen from these two figures, that the slags with the lowest molar fraction of sodium oxide (A1 and B1) seem to have an exponential temperature coefficient, while the other slags, containing higher molar fractions of Na_2O , viz. A2 and A3 and B2 and B3 respectively, exhibit linear temperature dependencies.

The addition of cations to a silicate melt is expected to result in a gradual breakdown of the oxygen bonds within the silicate network, resulting in a gradually depolymerised melt. It has been proposed⁷ that the thermal resistance ($1/\lambda$) associated with the movement of phonons along the silicate chains or rings are relatively small compared to that associated with the movement of phonons from chain to chain. The thermal resistance ($1/\lambda$) would be expected to increase as the melt becomes progressively depolymerised. From the discussion above it can be interpreted that the thermal diffusivity should decrease as the silicate melt becomes more and more depolymerised. This behaviour could be seen if sample A1 and A2 in figure 5 and sample B1 and B2 in figure 6 are compared. However, a further increase of the sodium oxide content in the synthetic slags does not result in a further decrease of the measured thermal diffusivity. In this study, the two slag compositions with the highest Na_2O content, viz. A3 and B3 do not show the lowest thermal diffusivity, instead these two compositions shows roughly the same values as the two slag compositions containing no or very low concentrations of sodium oxide, A1 and B1 respectively. The apparent contradiction in the results shows clearly the important role played by the structure of the silicates in thermal conductivities of silicate melts. A deeper insight into the structural aspects of silicates and the effects of the different cations on the silicate chains and rings is necessary for a quantitative analysis of the present data. It would also be very interesting to compare the thermal diffusivities with other thermophysical properties of silicate melts like electrical conductivities and viscosities.

Figure 7 shows some typical result from a thermal diffusivity measurement of a liquid synthetic slag. Similar results were obtained for other sample although there are differences in detail. In this figure some scattering between individual measurements at the same temperature can be seen. The standard deviation of the measured values ranges from about $\pm 6\%$ at the lower measurement temperatures to about $\pm 15\%$ at the highest temperature. The slags containing the highest concentrations of Na_2O , A3 and B3 did show the largest scatter between individual measurements. The scattering in the experimental data are believed to be the result of uncertainties arising from the experimental apparatus and the experimental method, as for example the alignment of the gold-coated mirror and the presence of gas bubbles in the liquid slag sample. None of these sources of experimental uncertainties can be completely excluded, therefore careful precautions have therefore been taken before and during every measurement to avoid and minimise the presence of gas bubbles in the liquid or any misalignment of the gold-coated mirror.

Thermal energy can be transferred by conduction, convection and radiation or by a combination of these mechanisms. It is therefore necessary to separate the contributions from convection and radiation to the measured values of the effective thermal conductivity or diffusivity in order to give the true value of the thermal conductivity or diffusivity. The contribution from convection to the thermal conduction, arises from inhomogeneous sample temperature caused by the laser pulse. The effects of convection are very hard to estimate or calculate since the liquid slag sample is very thin, approximately 0.2-0.4 mm thick⁸. The convective part of the measured thermal diffusivity is believed to be kept at a minimum if a top mounted laser together with small sample dimensions and short measuring times are employed and can therefore be neglected⁹. The effects of the radiative heat transfer become more pronounced at high temperatures for semi-transparent mediums such as slags and glasses. A quantitative discussion of the radiative heat transfer in high temperature substances requires the optical properties such as the absorption coefficient of the sample in question¹⁰. Some previous studies contain attempts to separate the contribution from radiation and convection at high temperature from the measured thermal diffusivity values compensate for the effect of thermal radiation at high temperature^{10,11}. It is to be pointed out that in this present investigation this aspect has not been considered due to mutual contradictions in existing theories.

V SUMMARY

Thermal diffusivity measurements of liquid silicate slags on cooling samples have been conducted using the three-layered laser flash method on a differential scheme in the temperature interval between 1625 and 1825 K using the laser flash method. The synthetic slag compositions in the present investigation were selected so that the to some extent would correspond to the mould flux slag used in up-hill teeming of speciality steels. The result of these measurements shows that the thermal diffusivity of all the studied synthetic slag compositions increased with increasing temperature.

When SiO_2 was replaced with Na_2O a decrease in the thermal diffusivity was observed, up to a certain concentration of Na_2O . A further increase resulted in roughly the same thermal diffusivity values as for the slags with the lowest concentrations of Na_2O . This behaviour could to some extent be explained by considering the effect of such additions on the structure of the melt. In this study, no attempts to correct the measured thermal diffusivity values from the contribution due to thermal radiation at high temperature have been

VI ACKNOWLEDGMENT

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Table 1: Materials used in this present study.

Material	Purity	Supplier	Comment
Calcium Oxide, (CaO)	Anhydrous AR	Fisher Scientific, U.S.A.	Calcined at 1223 K For 24 hours
Silicon Oxide, (SiO ₂)	Pro Analysi	Merck, Germany	Calcined at 1223 K For 24 hours
Aluminium Oxide, (Al ₂ O ₃)	AnalaR	BDH, U.K.	Calcined at 1223 K for 24 hours
Magnesium Oxide, (MgO)	99.5%	Johnson Matthey, Germany	Calcined at 1223 K for 24 hours
Sodium Oxide, (Na ₂ O)		Merck, Germany	Kept in desicator at room temperature
Argon, (Ar)	Plus	Aga Gas, Sweden	

Table 2: Gradual addition of Na₂O to a reference slag composition

	X_{SiO_2}	$X_{Al_2O_3}$	X_{CaO}	X_{MgO}	X_{Na_2O}
A1	0.474	0.118	0.192	0.216	0
A2	0.440	0.109	0.178	0.200	0.073
A3	0.405	0.100	0.164	0.184	0.146

Table 3: Gradually replacing SiO₂ with Na₂O, while keeping molar ratio between CaO, Al₂O₃ and MgO was kept constant.

	X_{SiO_2}	$X_{Al_2O_3}$	X_{CaO}	X_{MgO}	X_{Na_2O}	X_{Na_2O} / X_{SiO_2}
B1	0.400	0.109	0.178	0.200	0.112	0.28
B2	0.440	0.109	0.178	0.200	0.073	0.17
B3	0.475	0.109	0.178	0.200	0.037	0.08

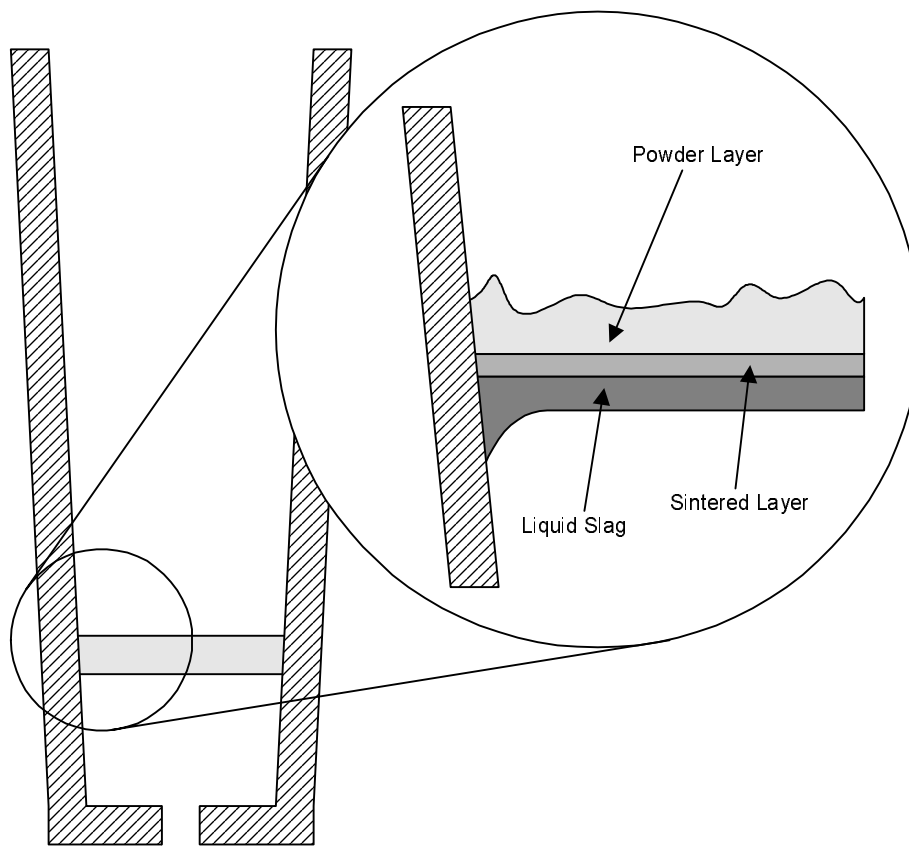


Figure 1: Schematic representation of the mould flux in the up-hill teeming mould

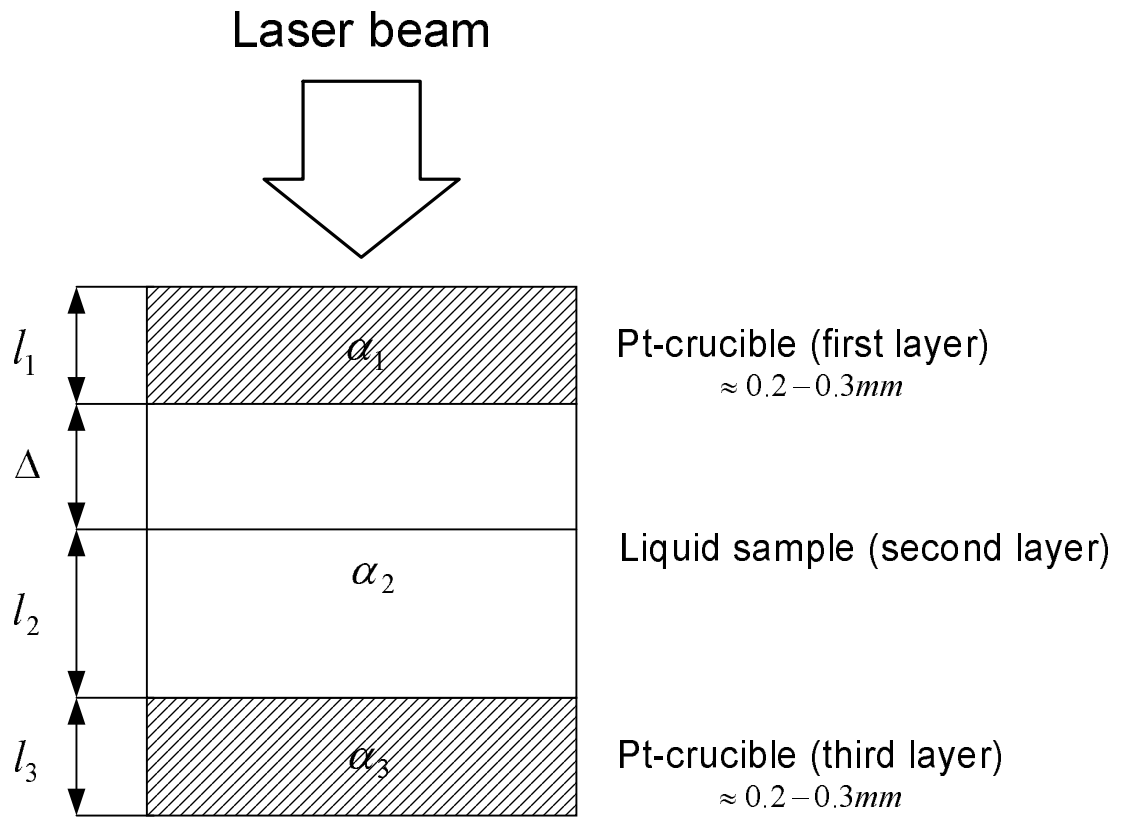


Figure 2: Schematic diagram showing the three-layered cell arrangement used in this present investigation.

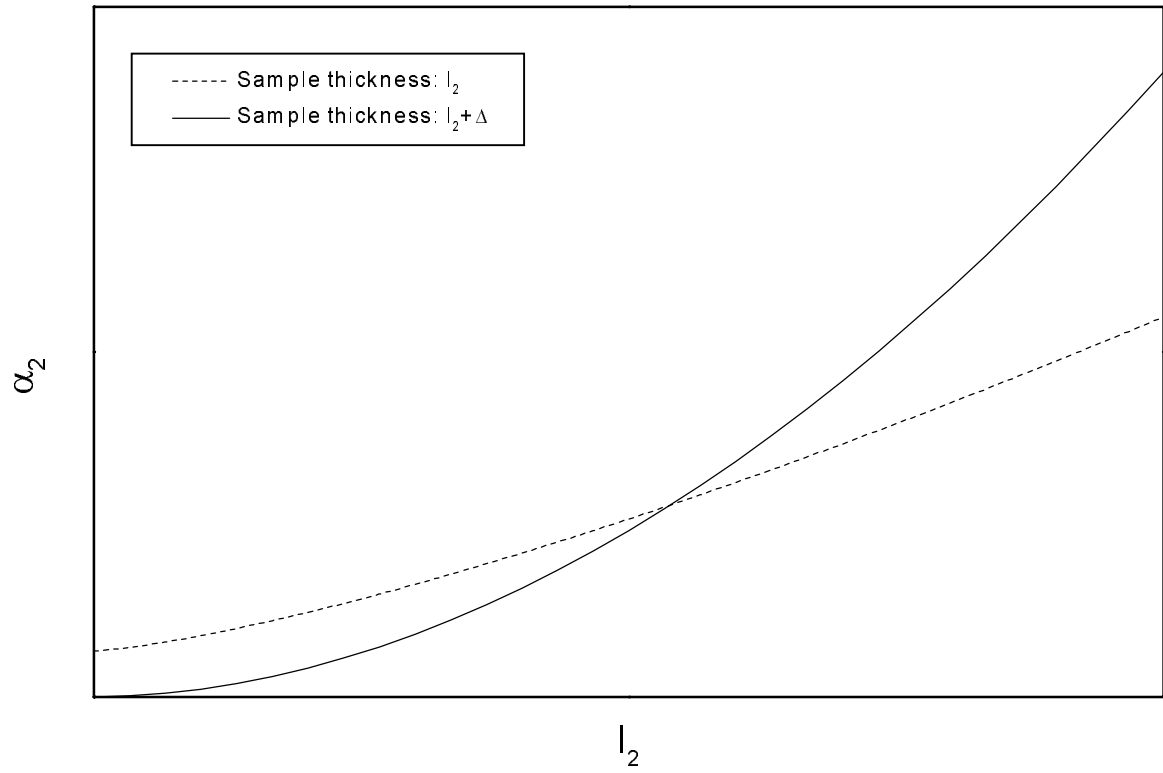


Figure 3: Principal description of the relation between the thermal diffusivity of the second layer and its thickness

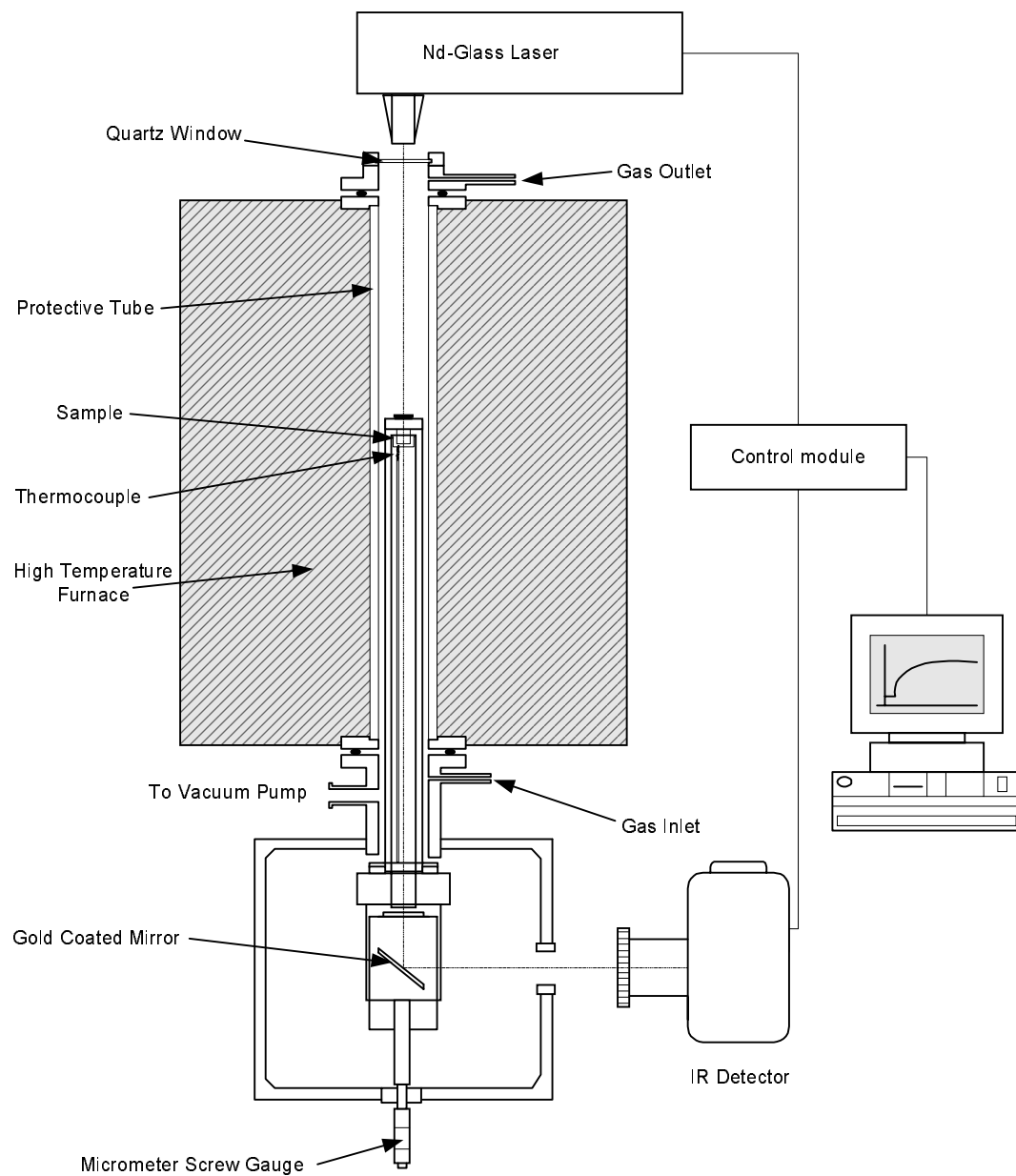


Figure 4: Schematic diagram showing the laser flash apparatus used in this present investigation.

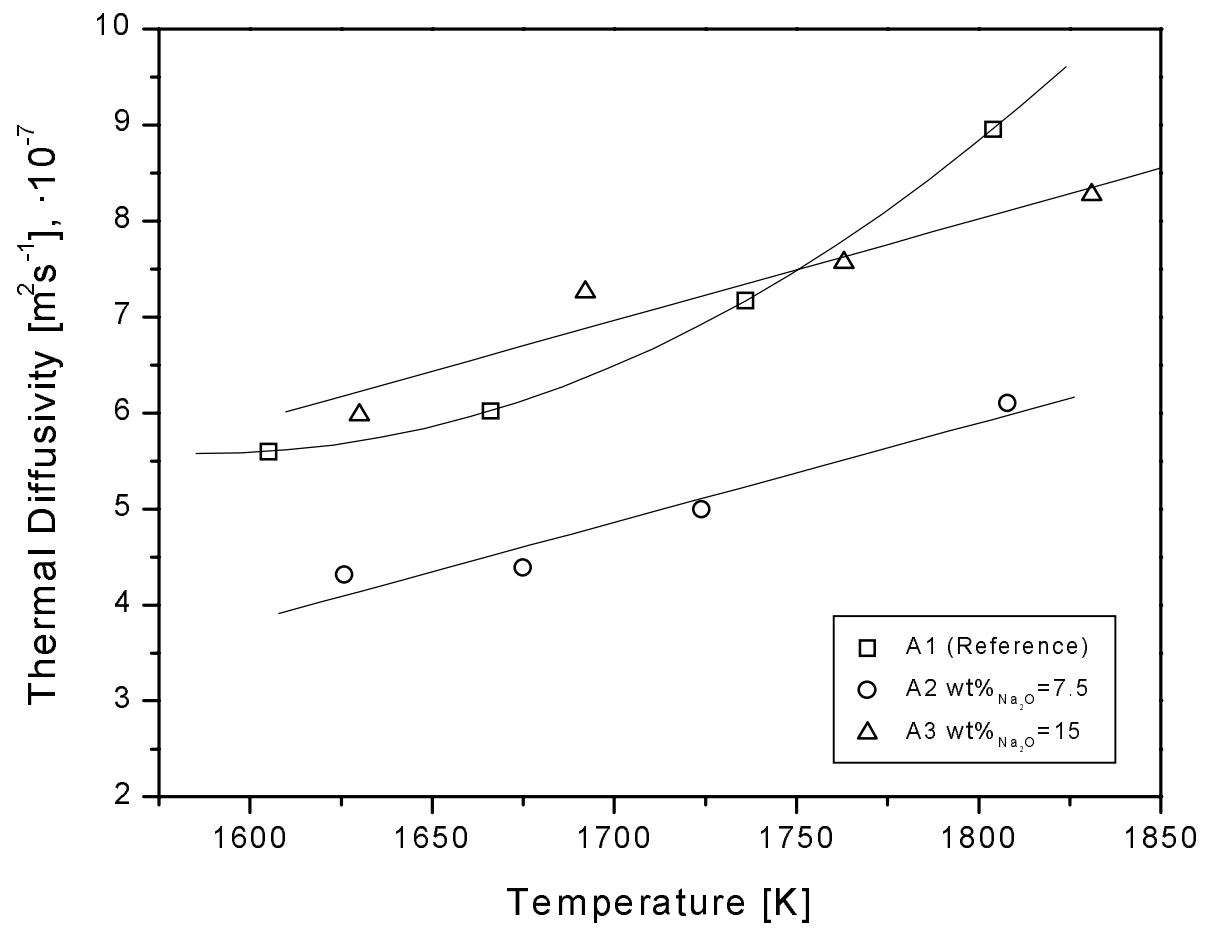


Figure 5: Average thermal diffusivity, calculated from at least 10 measurements at each temperature.

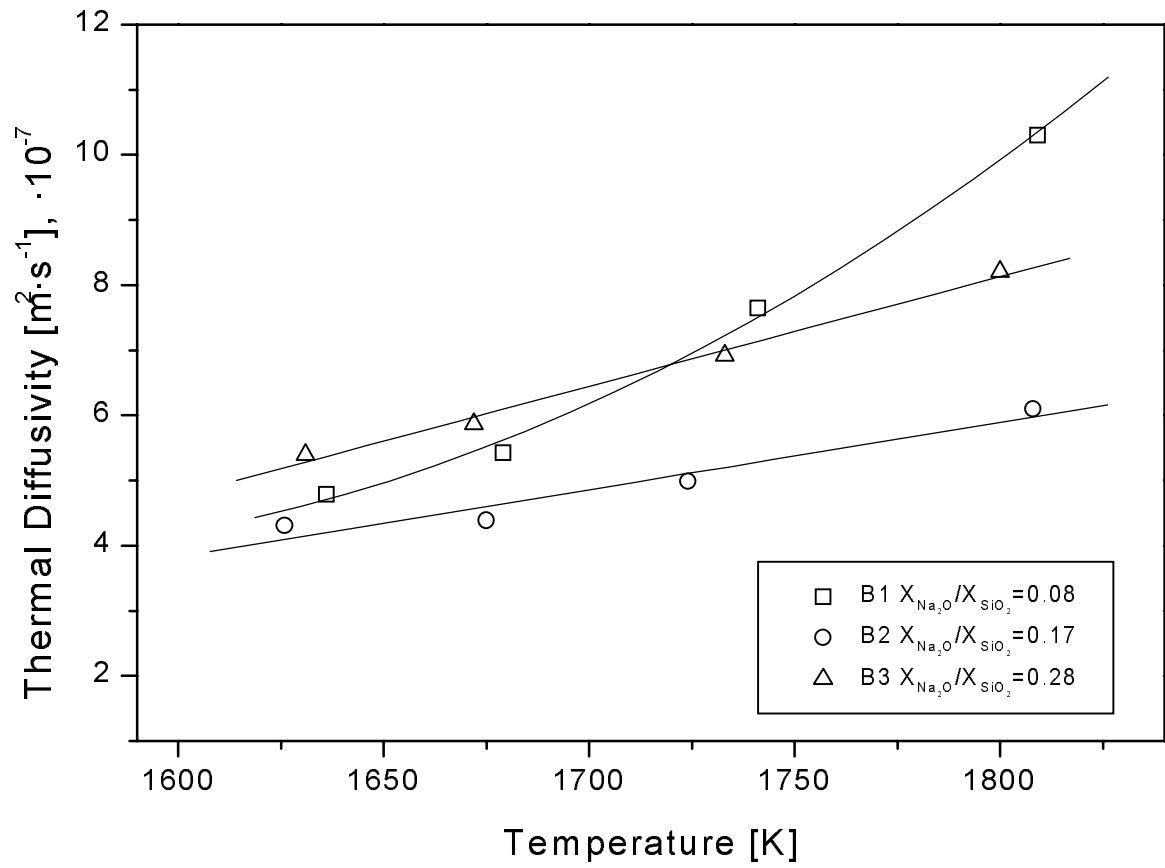


Figure 6: Average thermal diffusivity, calculated from at least 10 measurements at each temperature.

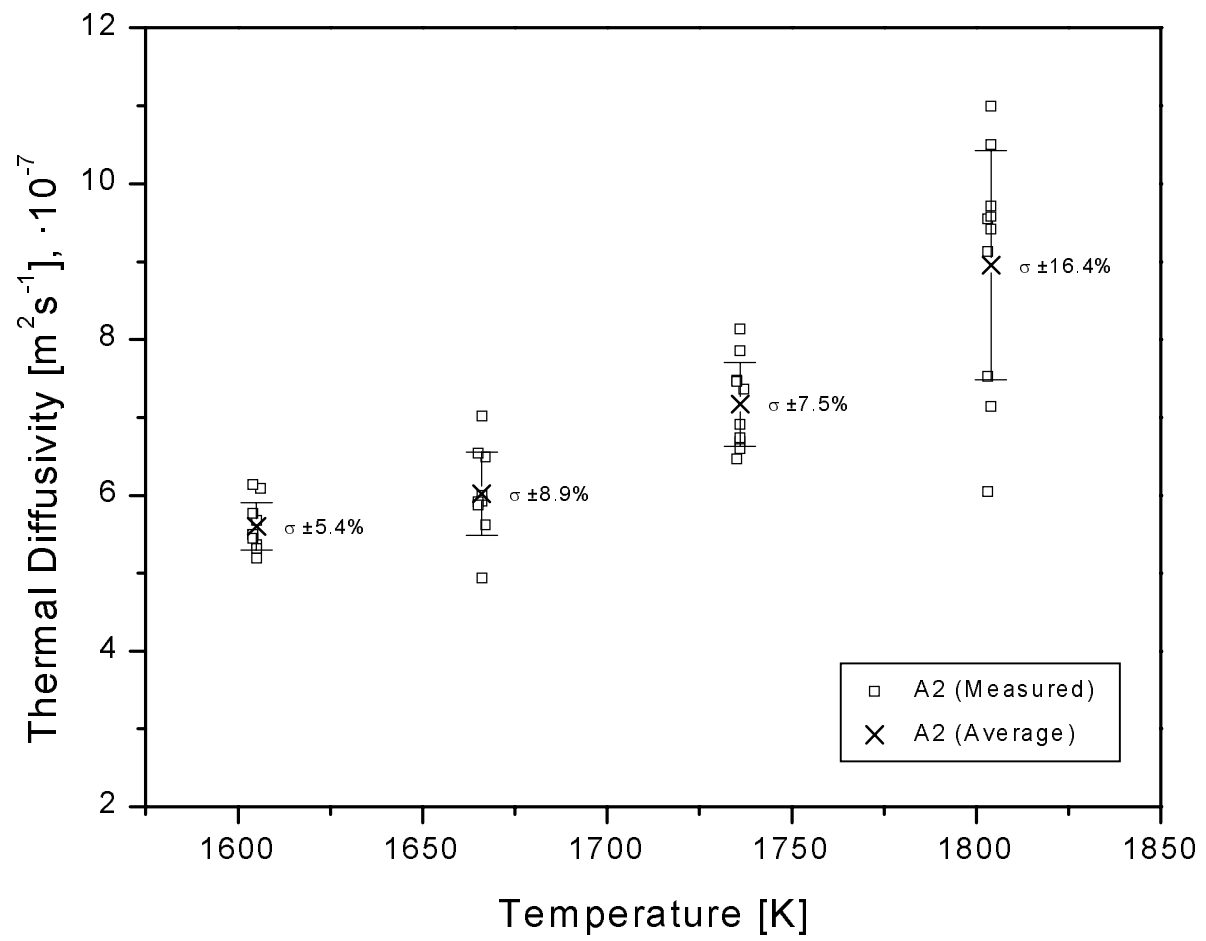


Figure 7: Measured thermal diffusivity values together with calculated average values.