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Thermophysical Properties of Fast Reactor Fuel

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Abstract

This paper identifies the fuel properties for which more data are needed for fast-reactor safety analysis. In addition, a brief review is given of current research on the vapor pressure over liquid UO_2 and $(\text{U,Pu})\text{O}_{2-x}$, the solid-solid phase transition in actinide oxides, and the thermal conductivity of molten uranium.

I. Property Needs

The most crucial thermophysical property needs for fast-reactor safety analyses have been identified in sensitivity studies on various safety codes. For fuel, these include: density of the liquid, heat capacity, electrical conductivity, vapor pressure, and thermal conductivity. Table 1 summarizes the current status of research on these five properties. A dash indicates that no experimental data are available.

Extensive measurements have been made on the thermodynamic properties of UO_2 but additional experiments are still needed for $(\text{U,Pu})\text{O}_{2-x}$. The most recent and precise measurements of the density of liquid UO_2 are the experiments by Drotning.¹ Heat capacity is obtained from enthalpy measurements. From analysis of the enthalpy data,² solid-solid phase transitions have been identified in both UO_2 and $(\text{U,Pu})\text{O}_{2-x}$. Because of limited data on the enthalpy of $(\text{U,Pu})\text{O}_{2-x}$ above 2600 K, the uncertainty in the temperature of the solid-solid phase transition is 50 K. Additional measurements of enthalpy at these high temperatures are needed to determine the phase-transition temperature more precisely. International agreement has been reached on an equation to represent the total pressure over UO_2 . Additional research is needed on the vapor pressure of $(\text{U,Pu})\text{O}_{2-x}$ before similar agreement may be attained.

The data on transport properties of fuels are not as complete as the data on thermodynamic properties. Additional data are needed for both electrical and thermal conductivity at high temperatures. Above 1400 K, the electrical conductivity data of Bates³ disagree with more recent

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measurements of Wright et al.⁴ and Alexis et al.^{5,6} by a factor of 3. Electrical conductivity experiments of $(U,Pu)O_{2-x}$ have been plagued by hysteresis problems, which result in different values for conductivity the heating and cooling cycles. Only the measurements from 600 to 1000 K by Schmitz and Couty⁷ are free of these problems. No measurements of electrical conductivity in the liquid state have been made for either fuel. Although many thermal conductivity and diffusivity measurements on solid actinide oxides have been made, additional measurements are needed above 2500 K for UO_2 and above 1800 K for $(U,Pu)O_{2-x}$. These high-temperature measurements are crucial in determining the significance of the solid-solid phase transition for thermal conductivity. The disagreement between the three experimental determinations of the thermal conductivity of liquid UO_2 at its melting point is discussed below.

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II. Current Research

The main areas of current research include the determination of vapor pressure over UO_2 and $(U,Pu)O_{2-x}$, the solid-solid phase transition in actinide oxides, and the thermal conductivity of molten urania.

(1.) Vapor Pressure

At a meeting of the International Working Group on Fast Reactors (IWGFR)⁸ in 1978, agreement was reached on an equation to represent the vapor pressure over liquid UO_2 . The error bars of this equation include most of the values of vapor pressure determined from calculations and experiments. However, at high-temperatures, some pressures determined from laser-pulse measurements⁹⁻¹⁰ are significantly higher than pressures calculated with this IWGFR equation.

Figure 1 compares the total pressure over $(U_{0.8}Pu_{0.2})O_{1.95}$ determined from calculations by Green, et al.¹¹ and by Bober et al.¹² with laser-pulse measurements by Ohse et al.¹³ The pressures obtained from the laser-pulse experiments are significantly higher than pressures calculated using thermodynamic methods. Both the calculations and the high-temperature experiments have several sources of uncertainty. Limitations of the calculations are as follows:

- (1) The lack of experimental oxygen potential data for the liquid means calculations in the liquid region are based on extrapolation methods.
- (2) Uncertainty in the critical point makes it difficult to incorporate critical behavior into the

calculations and to determine the temperature limitations of the calculations.

- (3) Values of the heat of vaporization determined from vapor pressure calculations of Green et al.¹¹ have an incorrect slope at high temperatures, which most likely arises because no critical behavior was included in their calculations.

Limitations of the laser-pulse experiments are as follows:

- (1) The laser-pulse experiments are extremely complicated, requiring much analysis and many corrections. In particular, it is difficult to be certain that all mass losses have been taken into account and all pertinent physical phenomena have been considered in the analysis.
- (2) For UO_2 , disagreement exists between the laser-pulse results of Ohse et al.⁹ and those of Tsai,¹⁴ with the values from thermodynamic calculations falling between the two experiments.
- (3) At high temperatures, pressures determined from laser-pulse measurements by Ohse et al. are significantly higher than values determined by other methods.

Both methods of determining the vapor pressure have limitations, however, comparing the two, elucidates the limitations of each and the areas where additional research is needed.

(2.) Solid-Solid Phase Transition in Actinide Oxides

A diffuse solid-solid transition has been observed in most fluorites and anti-fluorites. Its presence in uranium dioxide was first predicted by Bredig.¹⁵ In analysis of enthalpy data, Fink² identified a similar solid-solid phase transition in most reactor fuels. Table II gives the melting point, phase-transition temperature, and the ratio of these two temperatures for various actinide oxides. Note that this ratio is nearly constant. Lack of reliable enthalpy data for PuO_2 above 2000 K^{2,16} makes it impossible to determine the existence of a phase transition in this actinide oxide. Recently, this phase transition has been linked to fission gas release.¹⁷ The phase-transition temperature for $(\text{U,Pu})\text{O}_{2-x}$ as determined from enthalpy data² and creep data¹⁸ (2750 ± 50 K) is just below 2773 K, the temperature at which fuel swelling and fission gas release became pronounced in experiments by Randklev and Hinman¹⁸. Neutron scattering experiments are being performed at Harwell¹⁹ in an attempt to understand this transition in the actinide oxides. Further

research is needed to understand the following:

- (1) structure of the actinide oxides above the solid–solid phase transition,
- (2) link between the solid–solid phase transition and fission gas release so that a model can be formulated
- (3) impact of the phase transition on electrical conductivity, thermal conductivity, and thermal expansion.

(3.) Thermal Conductivity of Molten Urania

The thermal conductivities of molten UO_2 at its melting point as determined by three experiments disagree significantly. Kim et al.²¹ used a modulated electron beam to measure the thermal diffusivity of molten UO_2 clad in tungsten. Their recommended value for the thermal conductivity at the melting point is $11 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Otter and Damien²² measured the thermal diffusivity of molten UO_2 contained in tungsten using a laser-pulse technique. Their reported value for thermal conductivity is $8.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Tasman et al.²³ reported $2.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the thermal conductivity from determination of the depth of a molten layer of a UO_2 cylinder.

Each experiment has a number of possible sources of error. For example, the results reported by Kim et al.²¹ and Otter and Damien²² could differ from those reported by Tasman et al.²³ because of failure to appropriately account for conduction through the side walls of the tungsten container in the analyses or from the dissolution of tungsten in the molten UO_2 . In the experiment by Tasman et al.²³, questions have been raised concerning the validity of their steady-state assumption for an experiment of 5-s duration and the reliability of the determination of the melt depth via observation after solidification.^{17,24} Errors in the analytical models used in the analysis of each experiment are also possible.

Recently, Fink and Leibowitz²⁵ analyzed all three experiments using the transient heat transfer code THTB,²⁶ a three-dimensional finite difference program that is capable of handling conduction, convection, gray-body diffuse radiation, surface flux, internal heat generation, non-sink mass flow, and latent heat effects. Each experiment was modeled assuming values of thermal conductivity

from 2 to $10 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

The experiment by Kim et al.²¹ was modeled by two methods:(1) an ideal model assuming no side edge effects (corresponds to assuming an infinite diameter) and (2) a real model that takes into account heat transfer to the tungsten sides. The results of the THTB calculations for the ideal and real models differed significantly from the values calculated by Kim et al. A reanalysis of the analytic model of Kim et al. gave good agreement with the THTB analysis. From this reanalysis, Fink and Leibowitz concluded that errors were made in the original solution of the heat transfer equations by Kim et al.

Figure 2 compares the THTB transient (5 s) and steady-state (ss) analyses with the results reported by Tasman et al. The THTB analyses show that the sample had not reached steady state in the 5-s duration of the experiment. Thus, the low value reported by Tasman et al. is due, in part, to the application of a steady-state model. The difference between the steady-state value calculated by Tasman et al. and the value obtained from the THTB analysis is not understood at present.

Half times as a function of thermal conductivity determined using THTB to model the Otter and Damien experiment were compared with the half time for the mean thermal conductivity reported by Otter and Damien. This half time was determined from graphs given by Otter and Vandeveld²⁷ in their paper on the analysis of the French laser-pulse diffusivity experiments. For this half time, the THTB analysis gave a lower thermal conductivity than that reported by Otter and Damien. Insufficient data are available on this experiment to understand the source of the difference of the two analyses.

The results of these analyses using THTB and the results originally reported by the experimenters are summarized in Fig. 3. The differences in the values of thermal conductivity determined using the THTB analysis of each experiment are not nearly as great as those originally reported. The mean value of the THTB determined thermal conductivity values is $5.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

III. Conclusion

Table III shows the countries presently engaged in research. Despite the needs for additional experimental data, no measurements of enthalpy, heat capacity, density, or electrical conductivity

are being made. In the USA no experimental research on oxide fuel properties is being funded by the reactor safety program and only limited analytical work is being done. At Oak Ridge National Laboratory, Besmann²⁸ and Lindemer²⁹ are analyzing existing oxygen potential data. Tam et al.³⁰ at Argonne National Laboratory are studying the link between the phase transition and fission-gas release.

Oxygen potential models are being developed independently in the UK by Hyland³¹ and at Karlsruhe in the FRG. Experimental measurements of the vapor pressure over UO_2 by laser-pulse methods continue at Karlsruhe. Additional research on the thermal conductivity of molten UO_2 is being conducted both at Karlsruhe and the Commissariat a l'Energie Atomique in France. The solid-solid phase transition is being studied in the UK both by experiments at Harwell¹⁷ and by analytical investigations of the structure. In addition, the implications of this transition on heat capacity and thermal conductivity are being investigated.

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Table I. Status of Important Fuel Properties

Property	State	UO ₂	(U,Pu) _{2-z}
Density	Liquid	Data to 3250 K.	-
	Solid	Data to 3120 K.	Need data above 2600 K.
Heat Capacity		Phase transition 2670 K.	Phase transition 2750 K.
	Liquid	Data to 3531 K	-
Pressure		International agreement on IWGFR equation.	Disagreement high temp.
	Solid	Above 1400 K experiments disagree.	Data to 1100 K.
Electrical Conductivity	Liquid	-	-
	Solid	Need data above 2500 K.	Need data above 1800 K.
Thermal Conductivity	Liquid	Results of three experiments disagree.	-

Table II. Solid-Solid Phase Transition in Actinide Oxides

Material	Melting Point	Phase Transition	T_t/T_m
	T_m , K	T_t , K	
UO ₂	3120	2670	0.86
ThO ₂	3643	2950	0.81
PuO ₂	2701	-	-
(U,Pu)O ₂	3002	2750	0.92
(U _{0.08} Th _{0.92})O ₂	3609 ^a	2850	0.79
(U _{0.15} Th _{0.85})O ₂	3550 ^a	2950	0.83
(U _{0.30} Th _{0.70})O ₂	3460 ^a	2900	0.84

^a Calculated solidus based on ideal solution behavior

Table III. Countries Engaged in Fuel Properties Research

Need	Analytical	Experimental
Density	-	-
Heat Capacity	UK	-
Pressure	USA, UK	FRG
Thermal Conductivity	-	FRG, France
Electrical Conductivity	-	-
Phase Transition	USA UK	UK

Figure Captions

- (1) The total pressure over $(U_{0.8}Pu_{0.2})O_{1.95}$ determined from calculations by Green et al.¹¹ and by Bober et al.¹² compared with measurements by Ohse et al.¹³.
- (2) Calculated melt depth as a function of UO_2 thermal conductivity.
- (3) Comparison of the thermal conductivity of molten urania reported by the experimenters with that determined from analysis with the heat transfer code THTB.

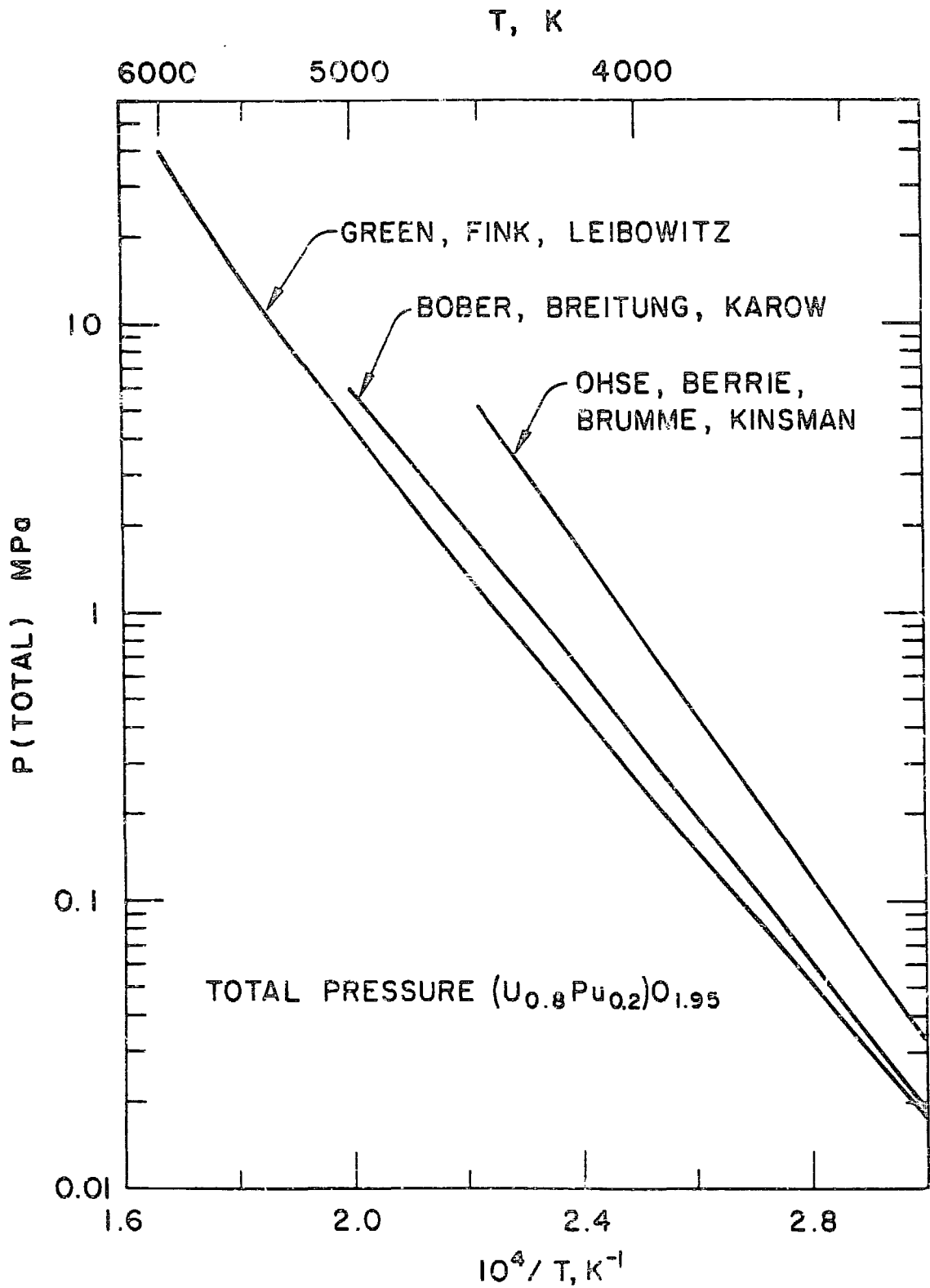


Fig 1

Calculated Melt Depth

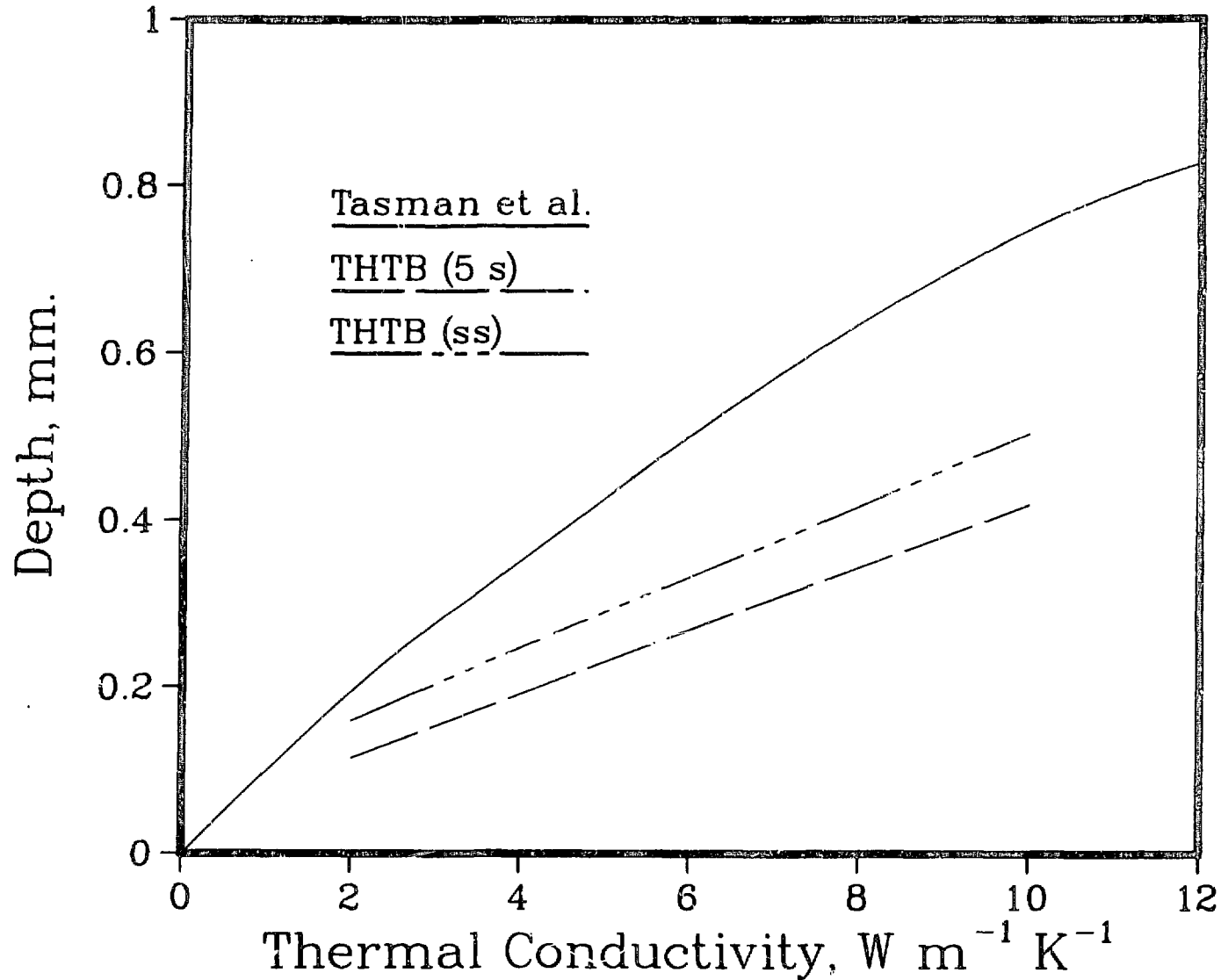


Fig. 2

Thermal Conductivity of Molten Urania

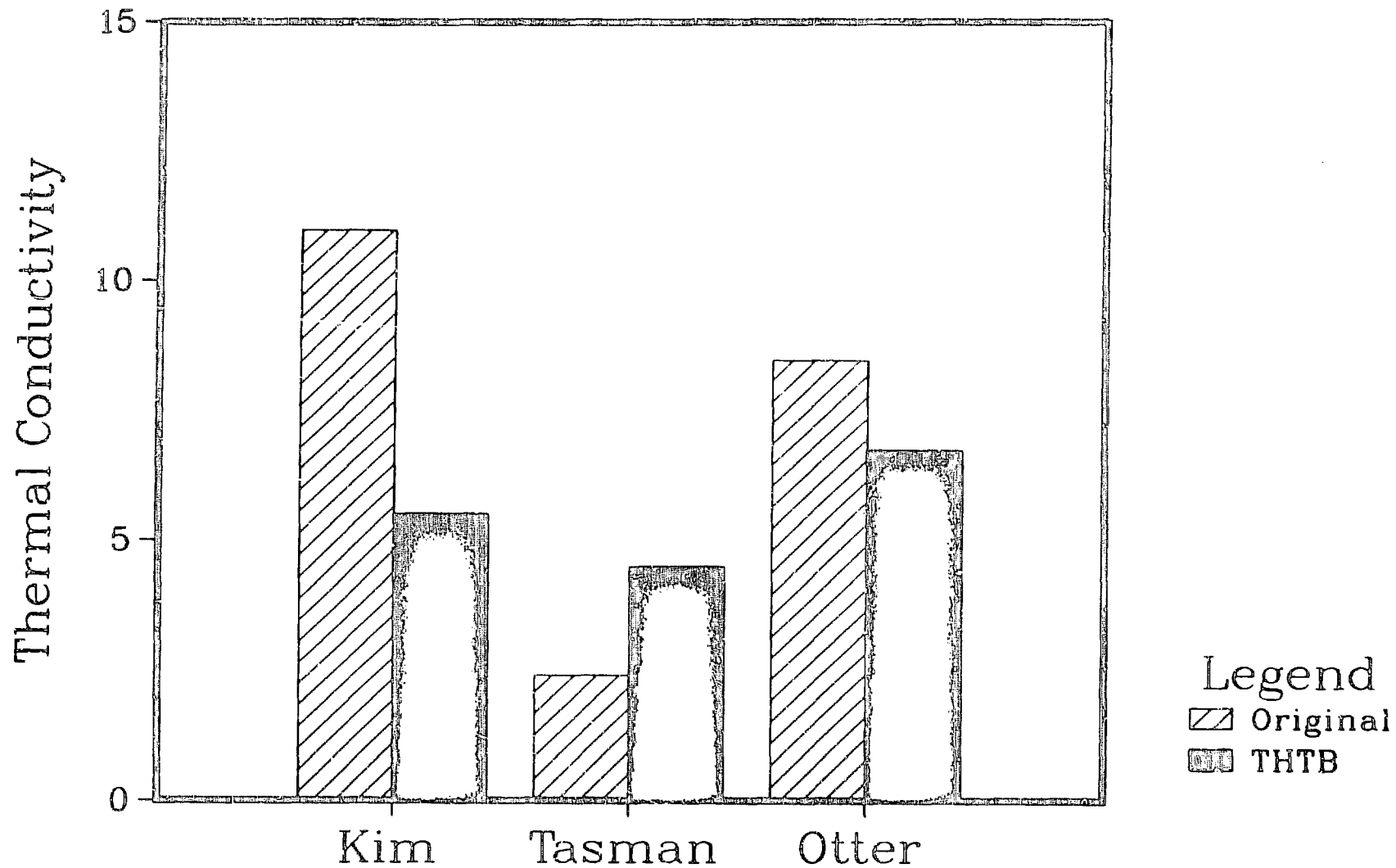


Fig. 3