AD-A191 755

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release; distribution is unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Naval Ocean Systems Center

6b. OFFICE SYMBOL *(if applicable)*
NOSC

7a. NAME OF MONITORING ORGANIZATION
Naval Ocean Systems Center

6c. ADDRESS *(City, State and ZIP Code)*
San Diego, CA 92152-5000

7b. ADDRESS *(City, State and ZIP Code)*
San Diego, CA 92152-5000

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
Director of Naval Laboratories

8b. OFFICE SYMBOL *(if applicable)*
DNL

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State and ZIP Code)*
Space & Naval Warfare Systems Command
Independent Research Programs (IR)
Washington, DC 20363-5100

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO.	TASK NO.	AGENCY ACCESSION NO.
61152N	ZT62	RR0000101	DN306 280

11. TITLE *(include Security Classification)*
Thermal Conductivity of Hard Anodized Coatings on Aluminum

12. PERSONAL AUTHOR(S)
T.R. Ogden

13a. TYPE OF REPORT
Professional Paper

13b. TIME COVERED
FROM June 1987 TO June 1987

14. DATE OF REPORT *(Year, Month, Day)*
November 1987

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
aluminum oxide, electrochemical method, thermal conductivity, anodization parameters

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

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(Keywords)

DTIC
ELECTE
MAR 2 1 1988
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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
T.R. Ogden

22b. TELEPHONE *(include Area Code)*
619-225-7479

22c. OFFICE SYMBOL
Code 633

DD FORM 1473, 84 JAN

83 APR EDITION MAY BE USED UNTIL EXHAUSTED
ALL OTHER EDITIONS ARE OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

88 3 16 065

AIAA'87

AIAA-87-2066

Thermal Conductivity of Hard Anodized Coatings on Aluminum

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AIAA/SAE/ASME/ASEE 23rd Joint Propulsion Conference

June 29-July 2, 1987/San Diego, California

THERMAL CONDUCTIVITY OF HARD ANODIZED COATINGS ON ALUMINUM

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ABSTRACT

Thermal conductivities of several commercial hard anodic coatings are measured using a transient heat-flow technique. These coatings were found to be effective heat insulators with thermal conductivities of the commercial coatings averaging 0.7 W/m/K. A laboratory anodization facility was assembled and the variation of thermal conductivity of the anodic coatings measured as a function of the anodization parameters. Preliminary results show that thermal conductivities as high as 1.3 W/m/K can be obtained in thick anodic coatings by optimizing the anodization parameters.

I. INTRODUCTION

The most effective method of protecting aluminum hardware against corrosion and abrasion is anodization, an electrochemical method of converting aluminum to aluminum oxide. Thick coatings of this type (15 or more micrometers in thickness) are known as "hard" anodize. In the marine environment these coatings are essential for corrosion and abrasion protection on high-efficiency, heat-transfer hardware used in propulsion systems.

Anodized coatings consist mainly of aluminum oxide, however, significant quantities of anion are present as well as water in the form of hydrated aluminum oxide. For example hard, anodic coatings formed in sulfuric acid contain about 15 percent sulfate anion and significant amounts of water, either free or bound in the form of mono- or trihydrates of aluminum oxide. If the coating is applied on an alloy of aluminum, then the impurities of that alloy are also incorporated into the film. Furthermore, these coatings are porous with a pore volume of about 5-20 percent. Figure 1 shows the idealized microscopic structure of an anodic oxide film on aluminum. There is an hexagonal structure with a pore at the center of each cell. Since the pore length is perpendicular to the plane of the film the porous nature of the coatings should be a relatively minor inhibiting factor in thermal conduction. Since the principal constituent of these coatings is aluminum oxide, it is commonly assumed that the thermal conductivity is somewhat less than that of aluminum oxide (about 30 W/m/K). This value of thermal conductivity is correct for polycrystalline aluminum oxide (corundum). The aluminum oxide contained in anodized coatings is, however, quasi-amorphous and, since the coatings also contain very large amounts of other compounds, it is not surprising that the thermal conductivity is very much lower than that of polycrystalline aluminum oxide. As a rule of thumb the thermal conductivity of an amorphous dielectric material, such as aluminum oxide, is usually about an order of magnitude lower than the thermal conductivity of the crystalline form of the same material.

Because anodized aluminum is produced in the form of relatively thin coatings and not in bulk, it is not easy to make an accurate, direct measurement of the thermal conductivity using conventional techniques. Definitive measurements of the thermal conductivity of hard anodized aluminum coatings cannot be found in the literature. Published values[1-5] cover a surprisingly wide range of almost two orders of magnitude, from 0.1 to 7 W/m/K, but some of these are the result of estimates based on indirect measurements. Apparently, the most reliable measurements are those of Shifrin[4] and Zil' berman[5]. Shifrin reported a thermal conductivity of 1.68 W/m/K. This measurement was made on a very thin, non-porous, barrier-type coating and in the plane of the film. Zil'berman et al. estimated the thermal conductivity of thicker, porous coatings formed in sulfuric acid to be 1.0 W/m/K. His estimate was based on the increase in temperature in samples of aluminum as they were being anodized, due to the electrical power dissipated in the film by the anodization process.

Thermal conductivities of thick, porous anodized aluminum coatings are reported for heat transfer normal to the plane of the coating. Several coatings were obtained from commercial vendors and are thought to be representative of the typical sulfuric acid-based anodic coatings on which the great majority of the commercial processes are based. The thermal conductivity of anodizations performed in the laboratory are also given and variations which can be obtained by modifying the anodization parameters.

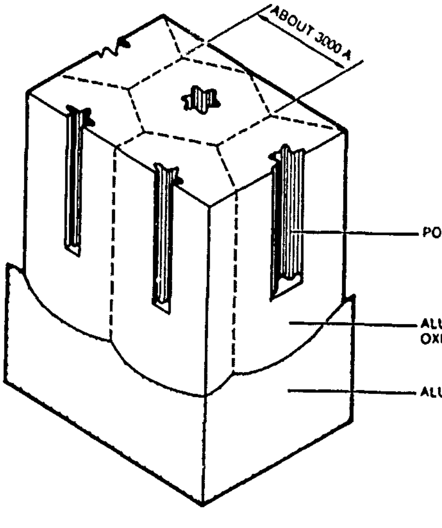

Fig. 1 Idealized structure of anodic oxide film.

II. THERMAL CONDUCTIVITY MEASUREMENTS

The transient heat-flow method used in this work to determine thermal conductivity was developed by Lee[6] to measure the thermal conductivities of polymer films. Advantages of the method compared to steady-state methods include: less instrumentation, quicker measurements, and lower sensitivity to heat losses.

Hardware and test procedures for the thermal conductivity measurements are fairly simple, are described thoroughly by Lee, and are discussed here only briefly. In any given test, hardware consists of a small aluminum block covered with an anodized coating of interest and a large copper block. Each block is a right circular cylinder with a small deep hole in the side where chromel-constantan thermocouples are soldered to monitor internal temperatures. The small block is made of 6061-T6 aluminum and has a height of 9.52 mm and a diameter of 12.7 mm. The large block is made of copper, and its dimensions are not critical except that its thermal mass should be much larger than that of the small aluminum test block. To prepare for a test, the large copper block is preheated to approximately 100 degrees C, while the small aluminum block is maintained at room temperature. At time zero, the two blocks are brought together, and contact is maintained uniformly by a pointed, spring-loaded plunger. A thin film of mineral oil is used between the blocks to improve heat transfer. (It will be seen later that the thermal resistance of this oil film does not affect the calculation of thermal conductivity.) As the blocks reach thermal equilibrium, their thermocouple voltages are digitized in a Data Translation Model 2805 data acquisition board and recorded in an IBM-PC compatible computer at a rate of approximately eight samples per second.

It is necessary in this transient heat-flow method to record temperature-history data for several small aluminum blocks having different thicknesses of a given anodized aluminum coating. The thickness of each coating is measured using an eddy current device, the accuracy of which was established by measuring coating thicknesses in microscopic sections of a number of blocks.

Based on the assumptions that: heat transfer across the anodized aluminum coating is governed by Fourier's first law of heat conduction; heat is transferred to the small aluminum block through the coating in a Newtonian heating process; and heat loss from the small aluminum block is negligible, Lee relates the temperature histories of the blocks to the thermal conductivity of the anodic coating in the equation

$$\frac{(T_1-T)}{(T_1-T_0)} = \exp\left\{\frac{-kAt}{CL}\right\}, \tag{1}$$

where T_1 is the initial temperature of the copper block; T_0 is the initial temperature of the aluminum block; T is the temperature of the aluminum block at any time, t; k is the thermal conductivity of the anodic coating; A is the contact area between the two blocks; C is the heat capacity of the aluminum block; and L is the thickness of the anodic coating.

If τ is defined as the time when

$$T_1-T = (T_1-T_0)/e\,, \tag{2}$$

then, from equation 1, the thermal conductivity of the coating is

$$k = \frac{CL}{A\tau}\,. \tag{3}$$

τ is determined from experimental data by first calculating the temperature difference between the aluminum and copper blocks as a function of time and then fitting an exponential function to this data using a least squares fit. Since the thermal resistance of the anodic coating, R, is defined as L/kA, it may also be written as

$$R = \frac{\tau}{C} = \frac{L}{kA} \tag{4}$$

using equation 3. If experimental values of R are plotted as a function of L, k may be found from the slope of the curve that fits the data. For a linear fit of the data,

$$k=1/mA\,, \tag{5}$$

where m is the slope of the line through the data. Note that this analysis is still valid when thermal resistances are present for an oil film, contact resistance, etc. as long as these resistances are constant for all of the aluminum blocks having different values of L. In other words, an additional constant (unknown) thermal resistance added to values of R will not change the slope of the plot of measured thermal resistance versus L.

Equation 4 is valid for Newtonian heating, that is when the Biot number, $Bi = R_{int}/R_{ext}$, defined along the heat transfer path between the two blocks, is small. R_{int} and R_{ext} are the internal and external thermal resistances of the small aluminum block. Bi numbers in this work were as high as 0.6. A correction factor was calculated and found to result in a correction smaller than the error in measurement (10-20 percent error for the measurements on anodic coatings.)

To check the accuracy of this method, thermal conductivities were determined for several polymers for which thermal conductivity data are available in the literature. A typical plot of external thermal resistance versus polymer thickness is shown in figure 2 for poly(vinylidene fluoride). The line in the plot is a least-squares fit of the four data points, and thermal conductivity is calculated from equation 5. Results for all the polymers considered are shown with accepted values for thermal conductivities[6,7,8] in table 1. Although the molecular weight and crystallinity of polymers tend to vary, and these factors affect thermal conductivity, the agreement in table 1 is good. The uncertainty in thermal conductivity indicated in table 1 is based on one standard deviation in the linear fit of thermal resistance versus thickness data as shown in figure 2.

The anodizations performed in the laboratory were carried out on aluminum coupons as described below. The coupons were anodized on both sides to thicknesses of 10-70 micrometers. The thermal resistance through the thickness of the coupons were measured as just described. Since the interior of the coupon was aluminum, there is some lateral thermal conduction in the coupon. A correction is necessary to calculate the thermal conductivity of the coating. This was done by measuring the thermal conductivity of a polymer sample in both configurations, as single sheets of different thicknesses as described above and double sheets sandwiching an aluminum coupon, then calculating an effective area for use in equation 5 when using the sandwich configuration. The effective area for the apparatus and coupon dimension described here is $A_{eff} = 1.54A$

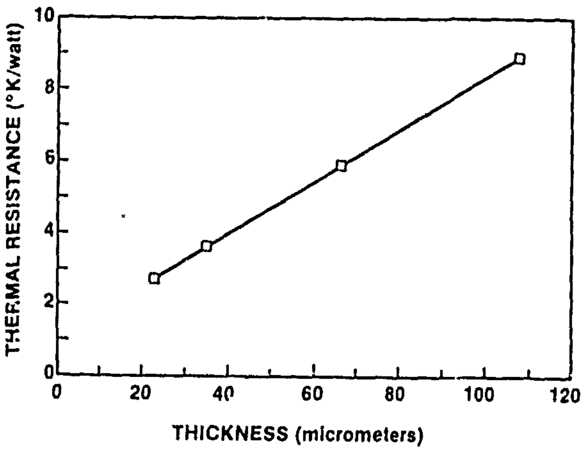

Fig. 2 Thermal resistance versus sample thickness for a typical polymer sample, poly(vinylidene fluoride).

Table 1
Thermal conductivities of selected polymers.

Polymer	Measured Value (W/m/K)	Accepted Value (W/m/K)
Poly(vinylidene fluoride)	0.126 ± 0.004	0.130
Cellulose Acetate	0.218 ± 0.01	0.203
Polyester	0.193 ± 0.01	0.218

III. ANODIC COATING PROCEDURE

The laboratory anodizations were carried out in a water jacketed beaker with a capacity of 2 liters. A refrigerated laboratory circulator was used to pump a cooled ethylene glycol solution through the outer jacketed area in order to maintain the anodization solution at a constant temperature. Anodizations were carried out at temperatures between 0 and 25 degrees with aqueous sulfuric acid and oxalic acid solutions, using triple deionized water. The aluminum samples were small coupons of 6061-T6 aluminum alloy of dimensions 2.54 cm x 2.54 cm x 25 micrometers. Before anodization, the coupons were degreased in acetone, etched for 3 minutes in an aqueous sodium hydroxide solution (50 gr/L), and desmutted in 300 ml/L nitric acid solution. Titanium leads (99.5% pure) were spot-welded to the aluminum coupons. A bar of lead was used as the cathode. The samples were rinsed for several minutes in deionized water after anodization. After the thermal conductivity measurement the anodized coatings were stripped from the aluminum base in an aqueous solution (100 mL/L sulfuric acid, 10 mL/L hydrofluoric acid) and the thickness of the coating was determined by measuring the thickness with a micrometer before and after stripping the coating and taking the difference.

IV. RESULTS AND DISCUSSION

Typical results from tests with thick anodized aluminum coatings are shown in figure 3, again, as external thermal resistance versus coating thickness. There is much more scatter in this data than there is in the polymer data. This is due to the fact that the polymer samples are flexible and give a much more consistent contact resistance for each sample. Different thicknesses of anodic coatings obtained commercially were applied on different aluminum blocks. Scatter in the anodic-coating data is caused by variations in thermal contact resistance due to small differences in flatness and surface roughness on the different aluminum blocks. The thickness of anodic coatings is very uniform, and their presence would not be expected to significantly change the machined flatness or surface roughness of the aluminum blocks.

Thermal conductivities determined in this work for anodic coatings from several industrial facilities are shown in table 2. All of the coatings are sealed with an aqueous sodium dichromate solution except sample 5. All of these samples were produced with sulfuric acid-based anodization processes. The concentrations of the aqueous electrolyte solutions were about 7-15 volume percent. Anodizations temperatures were about 0 degrees Celsius. The most important variable between the different commercial processes is the voltage and current waveforms used. This can significantly affect the properties of the coating and is frequently held proprietary by the vendor. Sulfuric acid-based anodizes are generally performed at 20-100 volts. The Sanford anodize, however, is based on a patented process which allows thick coatings to be applied at very low voltages (less than 20 volts.) Another variable among vendors and even between batches obtained from the same vendor is the condition of the anodization bath. The electrolyte is used for many anodizations and then is replaced after build up of dissolved aluminum and other impurities has become excessive. This as well as the initial water purity can be an important factor in the final condition of the coating. The thermal conductivities of the coatings measured ranged from about 0.5 to 1.0 W/m/K. The error in measurement was about 10 percent. Thus there is a fairly large variation in the thermal conductivities of the coatings even though they were produced with similar processes. It is impossible to determine the cause of the variations in thermal conductivities, however, because all the anodization parameters can not be obtained from the vendors, and because precise quality control is not a certainty.

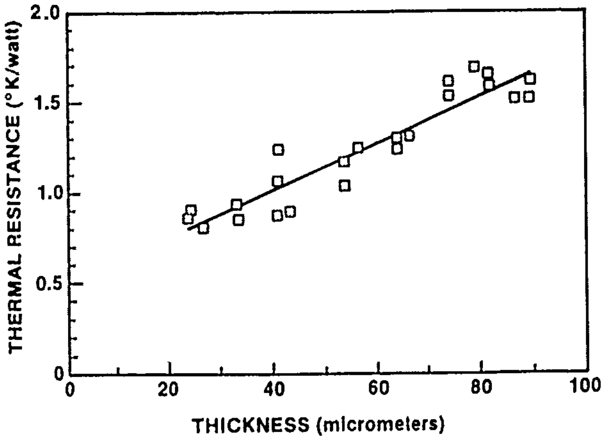

Fig. 3 Thermal resistance versus sample thickness for a typical thick anodic coating.

Table 2
Thermal Conductivities of several commercial anodic coatings.

Sample	Supplier	k (W/m/K)
1	Dyanco	0.61 ± 0.08
2	Dyanco	0.46 ± 0.07
3	Coast Plating	0.68 ± 0.10
4	Anadite	0.70 ± 0.08
5	Anadite (unsealed)	0.90 ± 0.09
6	Sanford	1.00 ± 0.12

In order to eliminate some of the uncertainties experienced with commercial vendors and to determine the factors which influence thermal conductivity of the coatings and the magnitude of the possible changes in thermal conductivity, in house anodizations were performed. Table III shows the results to date of thermal conductivity measurements made on samples produced in the laboratory in sulfuric acid. The average thermal conductivity of the sulfuric acid coatings is 0.77 W/m/K. This agrees well with the average of the thermal conductivities of the commercially produced coatings (0.73 W/m/K). The coatings produced in the laboratory were all unsealed, while all but one of the commercial coatings were sealed. The one measurement of sealed and unsealed coatings from the same commercial vendor suggests that sealing the coating reduces slightly the thermal conductivity of the coating, although more measurements are necessary in order to confirm this effect.

A large number of acids can be used to produce thick anodic coatings on aluminum. Sulfuric acid is almost exclusively used in the United States, because coatings produced with this acid have a number of desirable properties. Two of the most important reasons for the widespread acceptance of sulfuric acid in anodization electrolytes are; that it is economical to use because it produces coatings at relatively low voltages (low electrical power costs); and the porosity of the coatings produced in sulfuric acid is such that they readily absorb dye for decorative purposes. Neither of these factors are overriding concerns for coatings needed to protect expensive thermal propulsion systems.

Oxalic acid can be used in aqueous solution as an alternative to sulfuric acid to produce anodic coatings. Anodizations in this electrolyte are typically carried out at lower solution concentrations and at higher voltages than with sulfuric acid solutions. The anodic reaction starts above 100 volts at 0 C in a 1.0 weight percent solution. Coatings produced in this electrolyte contain lower percentages of anion impurities (about 3 percent oxalate) than sulfuric acid-based coatings and are thought to be at least as hard and abrasion resistant as those coatings produced in sulfuric acid. Anodic coatings produced in oxalic acid are known to be less porous than sulfuric- acid based coatings.

Table IV shows some measurements of thermal conductivities of coatings produced in oxalic acid and the corresponding anodization parameters. With the oxalic acid coatings there is a definite increase in thermal conductivity at lower concentrations. Figure 4 shows a plot of thermal conductivity versus concentration at temperatures from 0-5 K. It is impossible to vary one parameter and

Table 3
Thermal conductivities and anodization parameters of anodic coatings produced in the laboratory with sulfuric acid.

Temperature (C)	Concentration (Volume %)	Current Density (Amps/sq. dm)	Thermal Conductivity (W/m/k)
3	15	1.94	0.65
0	15	2.72	0.81
1	7	1.94	0.85

keep the others constant while anodizing. Lowering the concentration of the electrolyte tends to increase the anodization voltage when the current is held constant. More electrical power is dissipated in the anodic film at higher voltages and constant current, thus the temperature of the bath is increased. The temperature given is the maximum temperature reached by the bath during the anodization.

Table 4
Thermal conductivities and anodization parameters of anodic coatings produced in the laboratory with oxalic acid.

Temperature (C)	Concentration (Weight %)	Current Density (Amps/sq. dm)	Thermal Conductivity (W/m/K)
0.0	1.0	0.78	0.63
15	5.0	1.93	0.79
3	2.4	1.93	0.86
3	1.0	1.93	1.30
5	1.0	2.71	1.33

V. CONCLUSIONS

The thermal conductivity of typical commercial hard anodic coatings is about 0.7 W/m/K. The thermal conductivity of thick anodic coatings produced in an oxalic acid electrolyte is almost twice (1.3 W/m/K) that of sulfuric acid-based coatings. Other electrolytes or combinations of electrolytes can also be used to produce thick anodic coatings and the thermal conductivity of some of these will likely be greater than those systems measured to date. These measurements were performed on 6061-T6 aluminum alloy because it was desired to produce results with an alloy commonly used in structural applications. Once the compositional and morphological changes are identified which are responsible for the increased thermal conductivity and the anodization parameters are also identified which are responsible for these changes, then it should be possible to design an anodization process which produces coatings with significantly enhanced thermal conductivity.

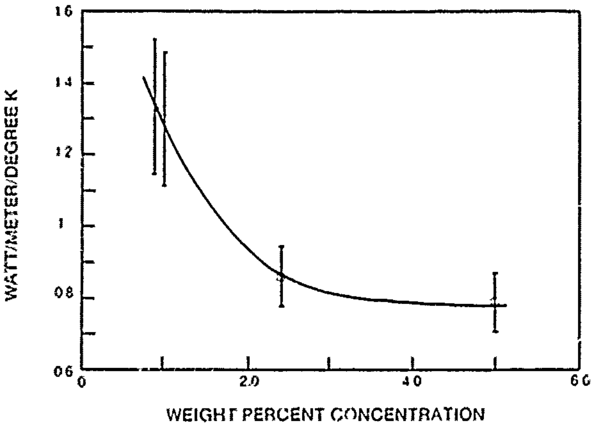

Fig. 4 Thermal conductivity of thick anodic coatings versus concentration of oxalic acid.

REFERENCES

1. N. Miura, Y. Fuura, and A. Kazami, J. Jap. Soc. Appl. Phy. Sup. 39 (1970) 211.

2. J.P. Gourber and C. Wyss, IEEE Trans. Mag-17 (1981) 1868.

3. W.E. Goldman, Electronic Products, (Oct. 1966) 7.

4. G.A. Shifrin and R.W. Gammon, NBS Special Publication No. 302, (1968) 405.

5. B.Ya. Zil'berman, N.P. Fedot'ev, and S. Ya. Grilikhes, Zh. Prikl. Khim. 36 (1963) 557-65.

6. H. Lee, Rev. Sci. Instrum. 53 (1982) 884.

7. Kynar Piezofilm data sheet, Pennwalt Corp., King of Prussia, PA, USA (1985).

8. D.R. Anderson and R.U. Acton, in: Thermal Properties, Encyclopedia of Polymer Science and Technology, ed. H.F. Mark, N.G. Gaylord, and N.M. Bikales (Interscience, New York, 1964)p.780.

ACKNOWLEDGMENTS

The author is grateful to J. T. Gilchrist for help in designing the thermal conductivity measurement apparatus. This work was supported by Independent Research and Independent Exploratory Development Funds of the Naval Ocean Systems Center.