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Thermal Conductivity of Consolidated Al/Cu_2O Thermites

Gary D. Miller and Lowell D. Haws

June 17, 1980

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Contents

Abstract

Knowledge of the thermal conductivity, λ, of Al/Cu_2O consolidated thermites is required in order to model the reaction and, in turn, understand and predict thermite burn rates, ignition temperatures, and sensitivities. Two methods, laser-flash and comparative, were evaluated. The comparative method was found to be the method of choice. Results of the λ measurements are reported as functions of temperature, part density, and aluminum particle shape.

Introduction

Thermitic reactions have been used for a long time as chemical heat sources for applications ranging from welding train rails to disablement of enemy tanks and personnel carriers [1]. These reactions are characterized by rapid heat production but minimal gas evolution. The generalized expression for a thermitic reaction is:

$$aM + bM'_x O_y = M_a O_{by} + bxM' \qquad (1)$$

where M is a reactive metal; M' is a relatively stable metal; and a,b,x, and y are small integers indicative of the reaction stoichiometry. The thermitic reaction of interest in this study is:

$$2\ Al + 3\ Cu_2O \longrightarrow 6\ Cu + Al_2O_3 + 580\ cal \cdot g^{-1} \qquad (2)$$

High density composites of a stoichiometric mixture of finely divided aluminum and Cu_2O powders were developed jointly by Haws and co-workers at Monsanto Research Corporation and Latkin at Lawrence Livermore Laboratory for use as heat sources [2]. The hot pressing process for fabrication of these composite parts has been described elsewhere [2]. The principal advantages of the consolidated thermite heat sources over loose powders are safer handling, easier ignition, machinability, and minimization of gas evolution from expansion of interstitial air in the mix.

In order to model the reaction of consolidated thermites and hence gain an understanding of how combustion in them is initiated and propogated, several chemical and physical properties must be measured. Techniques and results of measurement of one of the most important of these, the thermal conductivity, λ, is the topic of this report.

Measurement techniques

Both the comparative method and the laser-flash method were used for the thermal conductivity measurements. The two methods yielded slightly different conductivities for samples of identical composition and density. As will be explained below, these differences may be attributed to differences in the sample size requirements of the two methods because different sample sizes require different processing conditions in order to achieve the same sample density.

Comparative method

Comparative method conductivity measurements were made using the Dynatech Corporation model TCFCM-N20 thermal conductivity instrument. The method is described in detail elsewhere [3]. Briefly, a consolidated thermite disc 1.75 in. in diameter by 0.625 in. thick is placed in a stack between two Inconel 702 reference standard discs having dimensions similar to the sample as shown in Figure 1. The stack of sample and reference discs is then placed between a set of identical stainless steel upper and lower heating blocks fitted with resistance wire heaters. Chromel-Alumel thermocouples are inserted into predrilled holes in the sample and reference standards at the points shown in Figure 1. The thermocouples are threaded through 0.064 in. diameter, double-bore ceramic insulator rods which make snug fits in the thermocouple holes in the sample and reference to ensure good thermal contact. A temperature gradient is applied through the stack by setting the upper heater at a temperature higher than that of the lower heater.

Equating the heat flow through the reference discs to that through the sample leads to the relation:

$$\lambda_s = \frac{1}{2}\left(\frac{\Delta X}{\Delta T}\right)_s \left[\left(\lambda\frac{\Delta T}{\Delta X}\right)_{tr} + \left(\lambda\frac{\Delta T}{\Delta X}\right)_{br}\right] \qquad (3)$$

where s = sample

tr = top reference

br = bottom reference

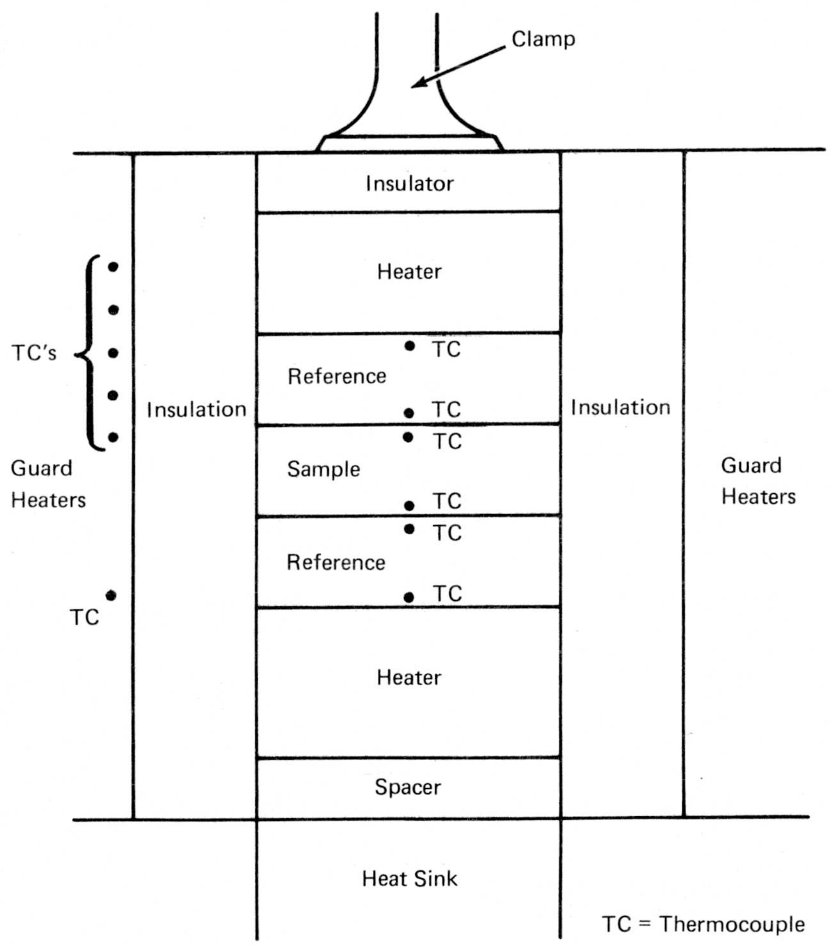

FIGURE 1 - Cross sectional veiw of sample-reference stack used in comparative method.

ΔT = the temperature difference across the sample or reference disc

and ΔX = the distance betwen the two thermocouples in the sample or reference disc.

The average temperature of the sample, T_{avg}, is given by:

$$T_{avg} = T_4 + \Delta T_{sample}/2 \qquad (4)$$

where T_4 is the temperature at the lower sample thermocouple. The validity of Eq. (2) is ensured by minimizing radial heat flow, which is accomplished in two ways. First, the sample reference stack is surrounded by a set of cylindrical guard heaters (see Figure 1) which are controlled to keep the temperature of the guard equal to the temperature at an adjacent height in the stack. Second, the space between the stack and the guard heaters is filled with ceramic insulating powder. When an experiment is run, temperatures in the guard area are noted. If the guard temperature is not within 0.1C° of that at the adjacent height in the stack, the system is allowed to equilibrate until this requirement is met.

Laser-flash method

The flash method was developed approximately 30 yr ago, before the development of laser technology. In the early applications, a xenon flash lamp was used as the light source. A complete description of the theoretical framework for the flash method and the early experimental instrumentation is given by Parker et al. [4]. A description of an updated instrument using a laser light source has been described by Etter et al. [5]. Briefly, an infrared laser pulse is incident on the front of a sample disc of 0.25 in. diameter and about 0.040 in. thick. Temperature as a function of time is followed at a thermocouple on the back surface of the sample disc. The thermal diffusivity, α, is determined from the equation:

$$\alpha = 1.38\, L^2/\pi^2 t_{\frac{1}{2}} \qquad (5)$$

where L is the sample thickness and $t_{1/2}$ is the time required for the back surface of the sample to reach one half of its final temperature rise. From the diffusivity the thermal conductivity was calculated according to

$$\lambda = \rho c\, \alpha \qquad (6)$$

where ρ is the density and c is the specific heat of the sample. The uncertainty in α was estimated to be less than 1%. The densities required for the calculation were determined simply from the mass and dimensions of the samples. Uncertainties in the densities are therefore negligible. The specific heats of the samples of thermite were determined by differential scanning calorimetry (DSC). The experimental uncertainty was taken to be equal to the reproducibility which was only ± 10%. The average value of the specific heat found for a stoichiometric mixture of Al/Cu_2O powders was 0.122 $cal \cdot g^{-1} \cdot K^{-1}$ [6]. A properly weighted average of the published specific heats of Al and Cu_2O also gives the results, c = 0.122 $cal \cdot g^{-1} \cdot K^{-1}$ [7]. In view of the large uncertainty in the experimental result, the good agreement may be fortuitous. In any case, essentially all the uncertainty in λ is a result of the uncertainty in c, which is propogated according to the equation:

$$\frac{\delta\lambda}{\lambda} = \frac{\delta\rho}{\rho} + \frac{\delta c}{c} + \frac{\delta\alpha}{\alpha} \qquad (7)$$

where δ denotes the uncertainty in the quantity it precedes.

Evaluation of the two methods

The advantages of each method are summarized in Table 1. It is clear from the table that the only disadvantage in the comparative method is its slowness (about one hour per determination versus only a few minutes for the laser-flash method). It has the advantage of being more precise and of requiring no additional measurements. The larger sample size required by the comparative method appears to be a disadvantage but is actually an advantage for this application. The consolidation conditions (temperature-time) required to achieve a desired part density are different for different size parts. Therefore, to make a sample having the same density and temperature history as a real thermite part the sample and part must be roughly the same size. The sample diameter in the comparative method matches prototype part dimensions closely enough to allow the sample and the prototype to both have the same density and temperature history. This reason alone is justification enough for choosing the comparative method over the laser-flash method. In addition, when its higher precision and the fact that no additional measurements are required are taken into consideration, it must be concluded that the comparative method is the method of choice for thermal conductivity determinations on consolidated thermites.

Because of the problem discussed above of different sample sizes requiring different consolidation conditions to achieve the same density, there are no directly comparable results between the two methods. Data were obtained using both methods on samples having roughly the same density. Figure 2 shows the comparison of the conductivities obtained using the two methods over the temperature range 0-400°C. Table 2 summarizes the differences in the processing conditions for the samples of Figure 2. Other important physical data on the samples are also included in Table 2. It is easily seen that for the flaked aluminum samples the flash method gives lower values of λ than the comparative method does. Part of this difference is the result of the density difference, 85.6 (flash) versus 89.6% of the theoretical maximum (comparative), between the two samples. The remainder of the difference is the result of either consolidation condition differences or systematic error

Table 1 - COMPARISON OF COMPARATIVE AND LASER-FLASH METHODS FOR THERMAL CONDUCTIVITY DETERMINATIONS

	Comparative	Laser Flash
Uncertainty	±7%	±10%
Speed	slow	fast
Data Processing	moderate amount	moderate amount
Sample Size	1-3/4 in. diameter disc	1/4 in. diameter disc
Additional measurements required	none	specific heat

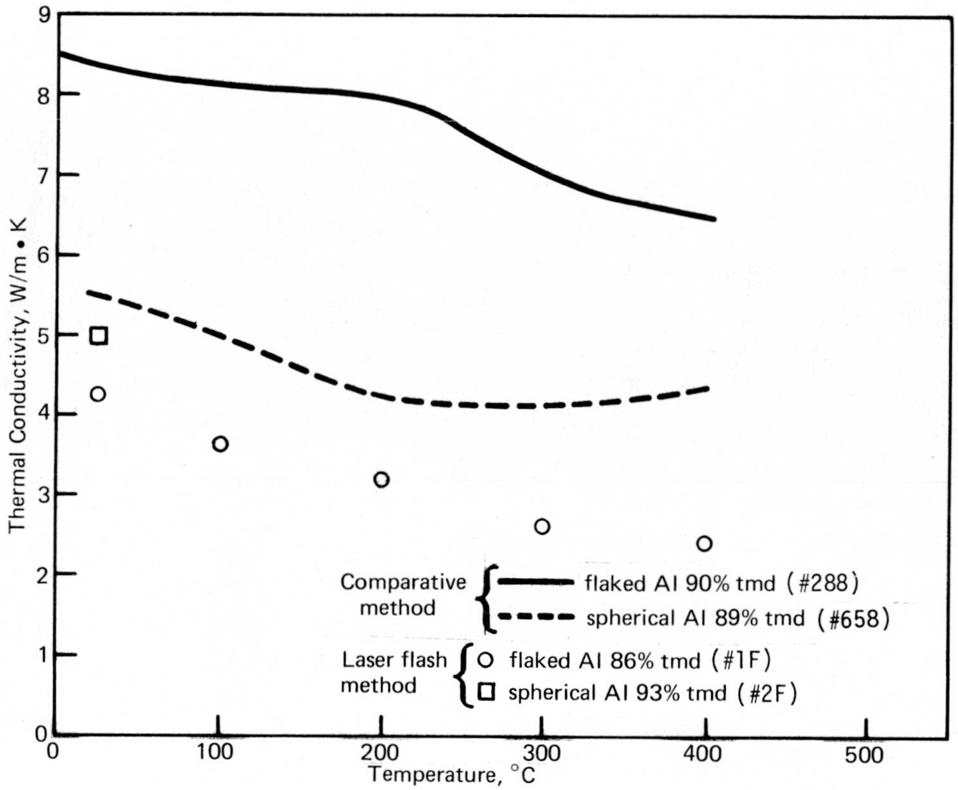

FIGURE 2 - Comparison of laser-flash and comparative method thermal conductivities.

Table 2 - COMPARISON OF FLASH AND COMPARATIVE THERMAL CONDUCTIVITIES AT 25°C

Sample No.	1F	2F	288	658
Type Al	Flaked	Spherical	Flaked	Spherical
Shape	disc	disc	disc	disc
Height (cm)[a]	0.107	0.119	1.588	1.600
Diameter (cm)[a]	0.635	0.635	4.445	4.445
Mass (g)[a]	0.1531	0.1855	115.	116.
ρ (g/cm^3)[a]	4.53	4.91	4.74	4.69
% theoretical max. p	85.6	92.8	89.6	88.7
c (cal/g-K)[b]	0.122	0.122	0.122	0.122
α (cm^2/s)[c]	0.0186	0.0198	---	---
λ (W/m-K)[d] flash	4.3	5.0	---	---
comp.	---	---	8.3	5.4
Processing conditions				
Temperature (°C)	425	425	480	480
Time (min)	15	15	60	60
Pressure (psi)	10,000	10,000	10,000	10,000

[a]Uncertainties considered negligible compared to others in calculation.

[b]Relative uncertainty = ±10%.

[c]Relative uncertainty taken to be equal to reproducibility of ±2%.

[d]Relative uncertainties are ±12% for flash method, ±7% for comparative method.

in one or both of the methods. For the spherical aluminum samples, the conductivities as determined by the two methods are nearly equal. Correction for the difference in densities (the effect of density on λ is discussed in a later section) would cause the flash method again to yield lower values than the comparative method.

Results

The thermal conductivity of consolidated thermites was studied as a function of three parameters, temperature, density, and aluminum particle shape (flaked or spherical). The results (all of which were determined by the comparative method) of the temperature and density studies are shown in Figure 3. The composition of the samples represented in Figure 3 is 11 wt % flaked Al/89 wt % Cu_2O (the stoichiometric composition). Inspection reveals that the thermal conductivity decreases slightly with increasing temperature for all densities ranging from 63 to 90% of theoretical maximum density (tmd). As expected, at constant temperature the thermal conductivity increases with increasing density. No attempt was made to fit the curves of Figure 3 to analytical forms, although this would present no problem if there were a need to do so.

The data of Figure 3 were inverted to show the density dependence of the thermal conductivity at selected temperatures (100,200,300 and 400°C). By reading conductivities and densities from Figure 3 at each selected temperature, $\lambda(\rho)_T$'s were found by fitting the data to the quadratic form:

$$\lambda(\rho)_T = a + b\rho + c\rho^2 \qquad (8)$$

Table 3 shows the best fit values determined by a quadratic least squares program for a, b, and c. From Eq. (8) and Table 3 the conductivity of Al/Cu_2O thermite of any density can be accurately predicted at or near any of the selected temperatures.

As was alluded to previously, two types of aluminum were used in the thermites of this study. One type is flaked aluminum on which the studies described above were performed. The second type is spherical aluminum. Previous studies had shown that the spherical aluminum formulation was less electrically conductive than the flaked aluminum thermite composite. This result was explicable from photomicrographs that showed that the latter type of thermite was traversed in all directions by continuous paths of aluminum, whereas the former was characterized by isolated spheres of aluminum in a continuum of Cu_2O. The present studies are consistent with the electrical conductivities and photomicrographs, as the thermal conductivity shown in Figure 4 of flaked aluminum thermite is significantly higher than that for the spherical aluminum thermite. This study was done only for thermites of density ρ = 89% tmd, but the qualitative effect is expected to be the same at all practical densities.

Another type of thermite composite that was studied is one in which sperical particles of the eutectic Al-Si composition replace the aluminum flakes or spheres in normal thermite. The Al-Si/Cu_2O composite is used as an igniter material for the normal thermite composites. It is believed that the easier ignition characterisitcs of the Al-Si/Cu_2O thermite are the results of its lower electrical and thermal conductivity. Figure 5 shows the results of

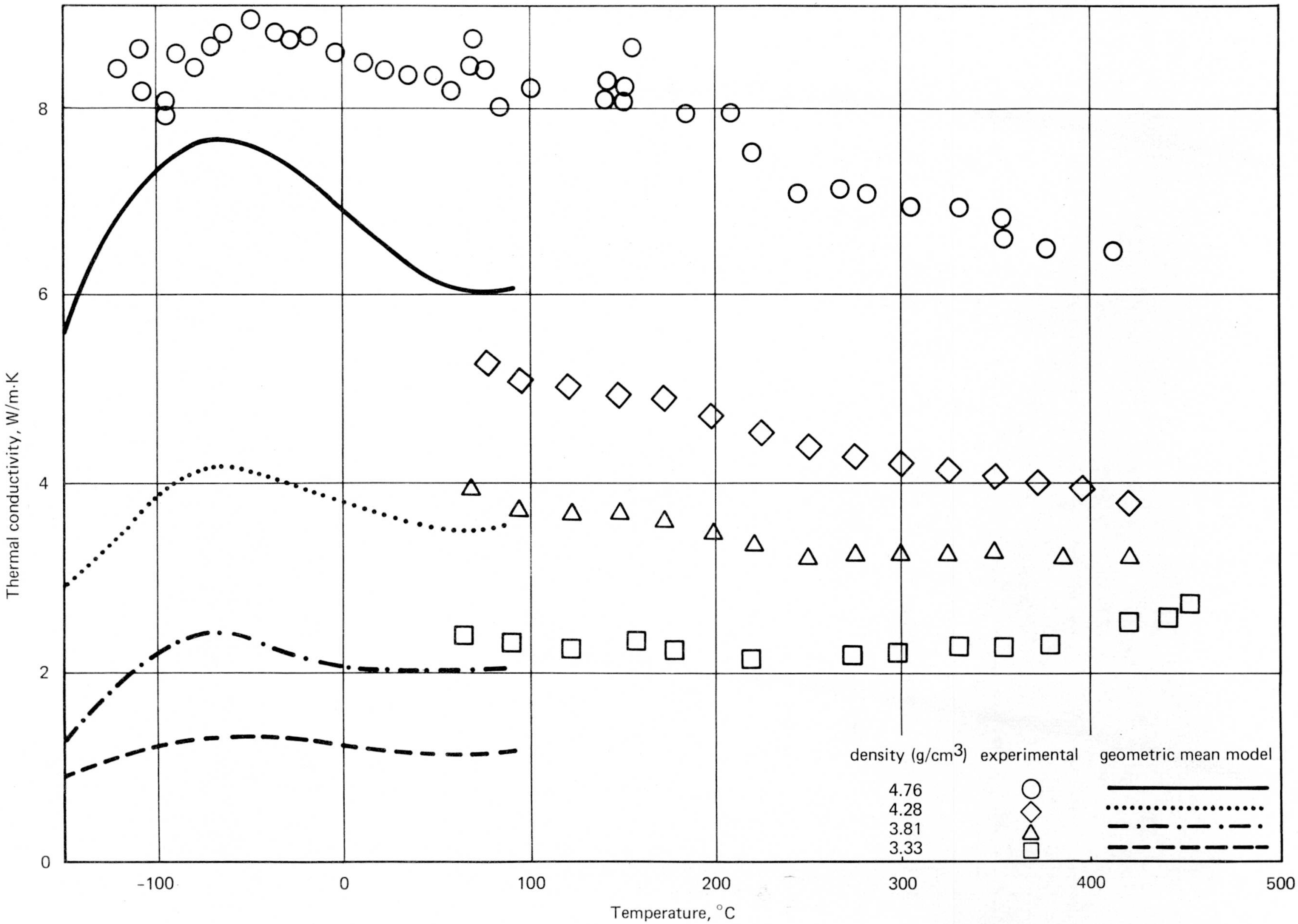

FIGURE 3 - Thermal conductivities of flaked Al/Cu_2O thermite composites are plotted as functions of temperature at four densities. The lines plotted for comparison with the points were obtained by taking the geometric mean of the component (including air) thermal conductivities

Table 3 - BEST FIT COEFFICIENTS FOR THE DENSITY DEPENDENCE OF THE THERMAL CONDUCTIVITY

$\lambda(\rho) = a + b\rho + c\rho^2$ [a]

Temperature (°C)	a	b	c	r^z
100	19.68	-61.47	54.01	0.9910
200	20.75	-64.14	55.25	0.9893
300	23.09	-68.00	55.56	0.9827
400	23.37	-66.62	53.09	0.9815

[a] λ in W/m-K and ρ in %tmdx10^{-2}.

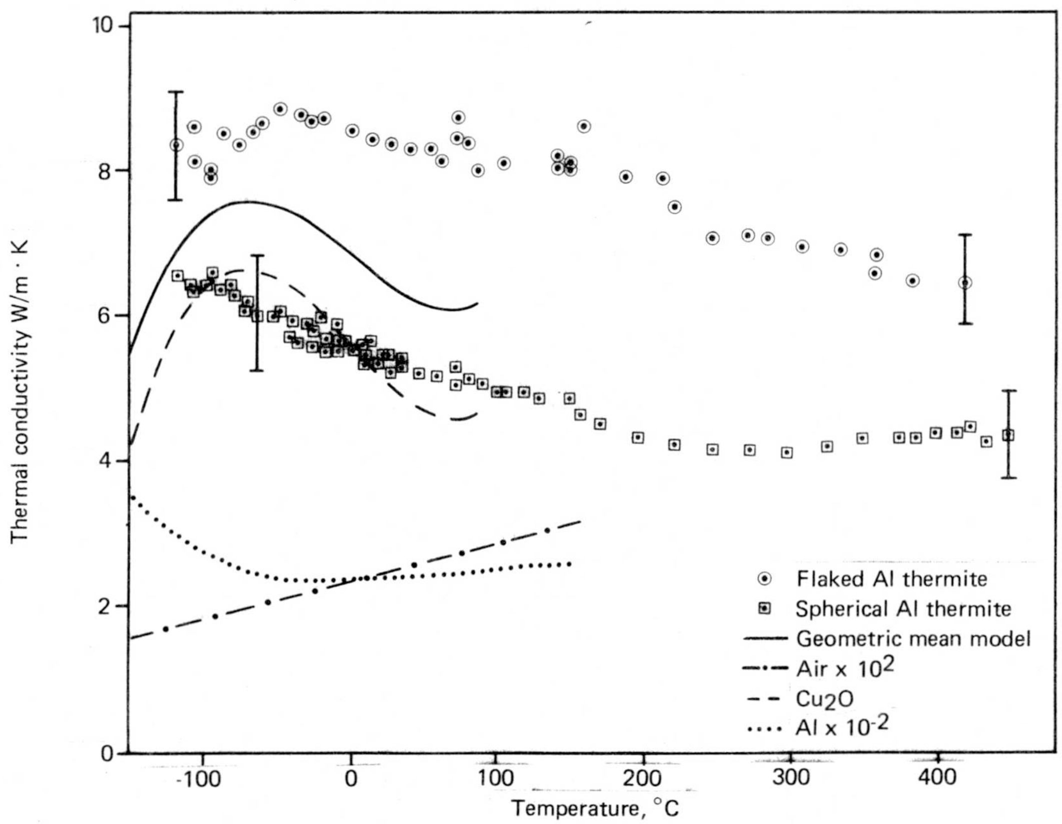

FIGURE 4 - Thermal conductivity of flaked and spherical Al thermites at 90% tmd.

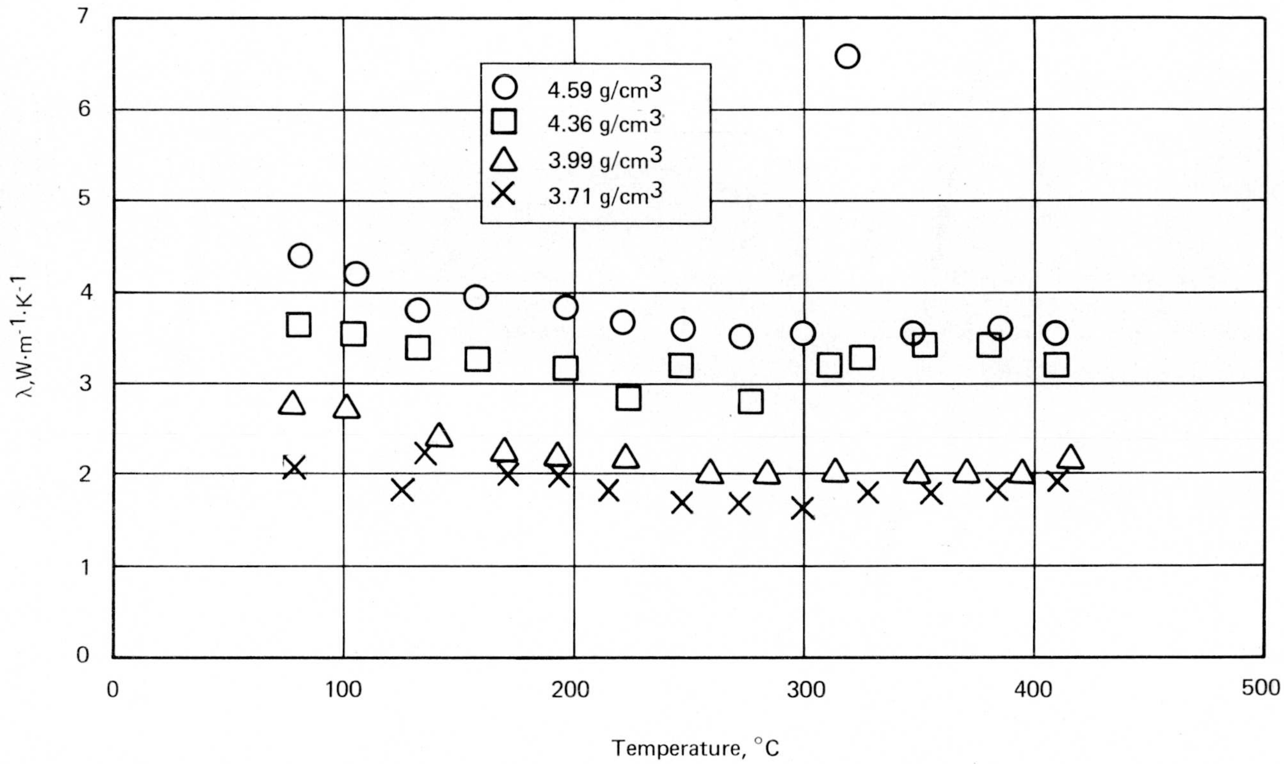

FIGURE 5 - Thermal conductivities of Al-Si/Cu_2O thermite composites are plotted as functions of temperature at four densities.

determinations of λ as a function of T for four densities ranging from 3.71 to 4.59 $g \cdot cm^{-3}$. The temperature dependence shows the same slight decreasing trend found with the Al/Cu_2O composites. As expected, the thermal conductivity increases with increasing thermite density. Comparison of Figure 5 with Figure 3 indicates that for a comparable density the thermal conductivity of the Al-Si/Cu_2O composites is about half that of flaked Al/Cu_2O composites. No fits of either the temperature or density dependence to analytical expressions have been attempted. There would be no problem in doing this, however, if the need existed.

One final type of thermite studied was a 50-50 (by weight) Al-Mg/Cu_2O blend. The thermal conductivity for this blend compacted to 4.45 $g \cdot cm^{-3}$ is shown in Figure 6. The temperature dependence is essentially the same as that for pure aluminum and Al-Si thermites. Notice that if one compares similar density compacts (see Figures 3 and 5) at any given temperature the order of thermal conductivities is Al-Mg>Al>Al-Si. Thus, it is evident that the conductivity of the blend can be altered by changing the material with which the aluminum is alloyed.

Models for thermal conductivities of composites

Several theoretical models have been proposed to describe the conductivity of composite materials. They are the series, parallel, and geometric mean models. The expressions relating the composite to the component phase thermal conductivities are,

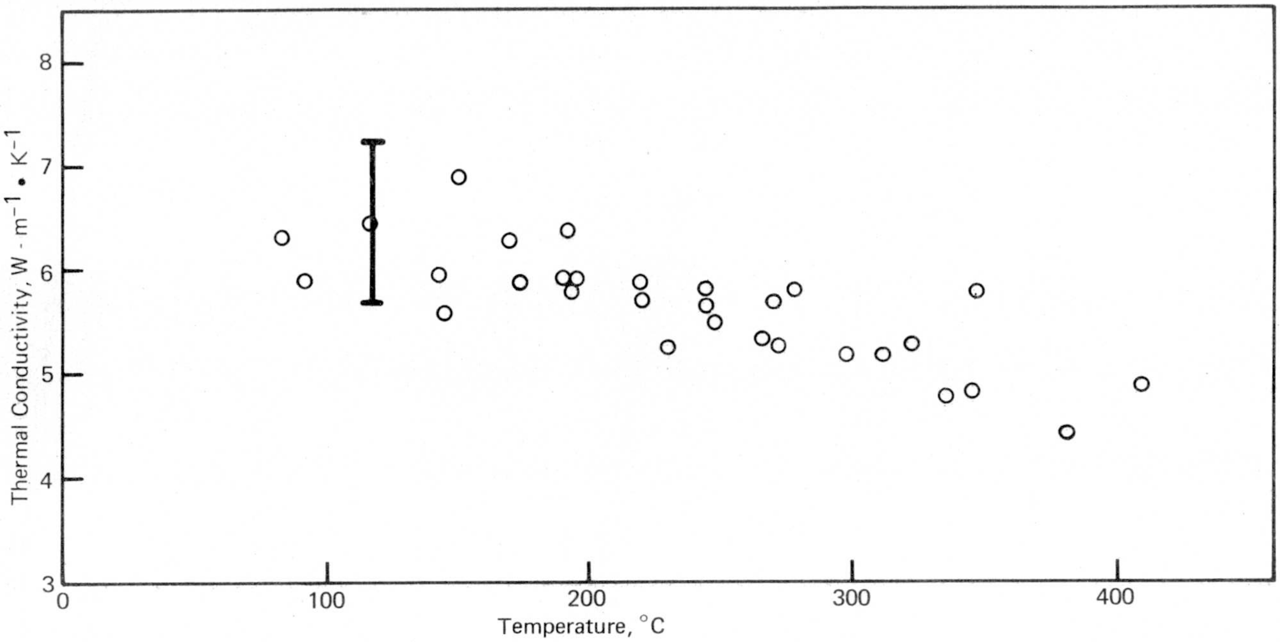

FIGURE 6 - Thermal conductivity of Al-Mg/Cu_2O at density = 4.45g/cm^3.

respectively:

$$\frac{1}{\lambda_s} = \sum_i \frac{F_i}{i} \tag{9}$$

$$\lambda\rho = \sum_i F_i \lambda_i \tag{10}$$

$$\lambda_{GM} = \prod_i \lambda_i^{F_i} \tag{11}$$

where λ_i is the conductivity of the ith component phase, and F_i is its volume fraction in the composite. The series and parallel models have been found to be very poor predictors of the thermal conductivities of consolidated Al/Cu_2O thermites. For example, the series model yields a value of $\lambda_s = 0.31\ W{\cdot}m^{-1}{\cdot}K^{-1}$, and the parallel model yields a value of $\lambda\rho = 50.83\ W{\cdot}m^{-1}{\cdot}K^{-1}$, for stoichiometric Al/$Cu_2O$ thermite at temperature, T = 370K and density, ρ=90% tmd. The experimental value for flaked and spherical aluminum formulations are, respectively, 8.2 and 5.0 $W{\cdot}m^{-1}{\cdot}K^{-1}$. The geometric mean model, which corresponds physically to a completely random distribution of phases, gives a value in fairly good agreement with experiment of $\lambda_{GM} = 5.65\ W{\cdot}m^{-1}{\cdot}K^{-1}$. Figure 3 shows the calculated geometric mean conductivities for each density at which measurements were made. The calculations were made for temperatures below 90°C only, because the thermal conductivity of Cu_2O is not available above this temperature. The agreement between experiment and the model is within 10 to 25% for 90% tmd flaked Al/Cu_2O thermite. The agreement becomes worse as the density is decreased.

Temperature history and thermal conductivity

The question arises as to whether the process of heating the thermite sample to the desired test temperature has in itself any effect on λ, resulting from physical changes or perhaps some small amount of reaction progress. To check this, a sample of 89.6% tmd 11 wt % flaked Al/89 wt % Cu_2O consolidated thermite was allowed to age in the TCFCM-N20 thermal conductivity instrument at 377.9°C for 1000 hr. The conductivity was determined at roughly 24-hr intervals by applying a small temperature gradient across the sample. Figure 7 is a plot of the resulting conductivity as a function of time data. The conductivity at first drops, then rises slowly back to approximately its initial value. It was noticed that the aged thermite was harder to cut with a hacksaw than unaged thermite was. The reason for this behavior cannot be explained at this time. It can, however, be concluded that the thermal conductivity of 90% tmd thermite is essentially not affected by its temperature history below 380°C.

The situation is quite different for low density thermites. A slight increase in conductivity with temperature was noted for the low density samples at temperatures above 350°C (see Figure 3). In order to check whether this was a real effect or one induced by the heating process itself, conductivity determinations were repeated for 63% tmd thermite after short aging periods (4-10 hr) at moderate temperatures (300-500°C). The results of this experiment are shown in Figure 8. The conductivities after approximately 4, 8, and 10 hr are successively higher than the data from the initial set of measurements. This experiment makes two points clear. First, the slight increase at the high temperature end of the 63% tmd conductivity curve (Figure 3) is caused by some physical or chemical change induced by the heating

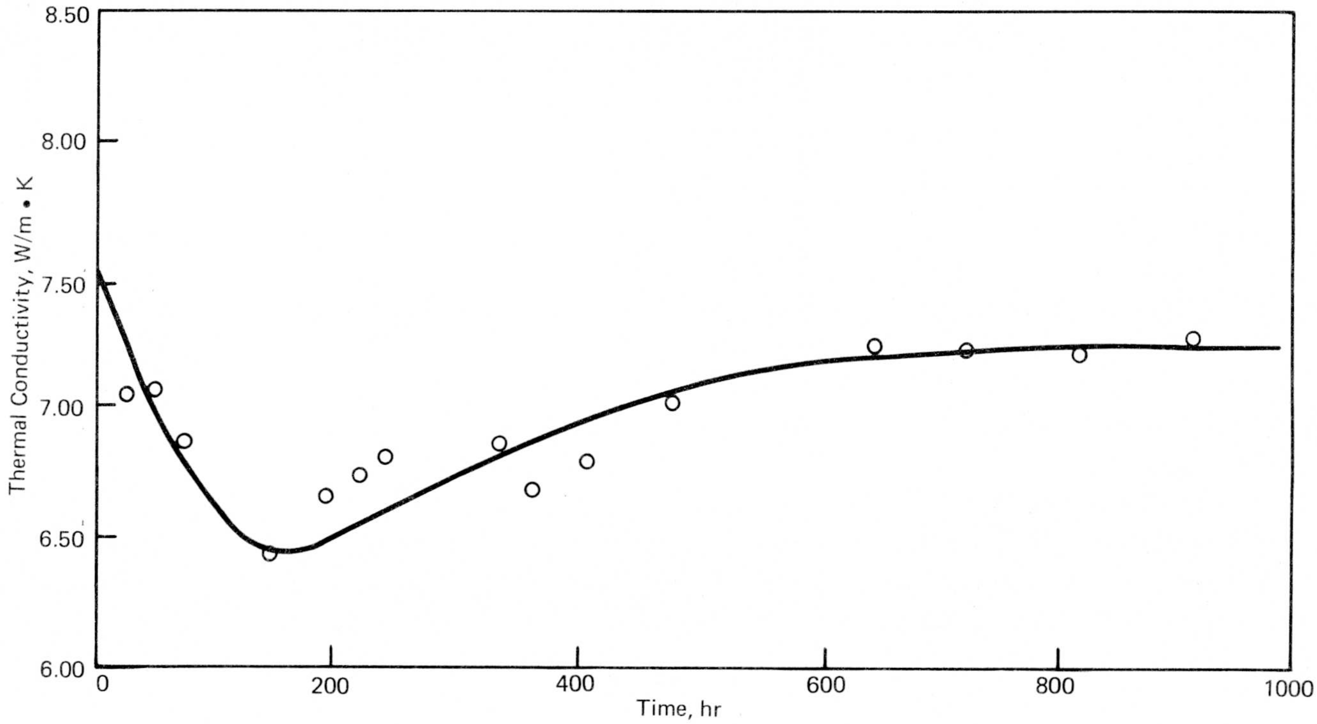

FIGURE 7 - Thermal conductivity as a function of time for thermite part 288 at 377.9°C.

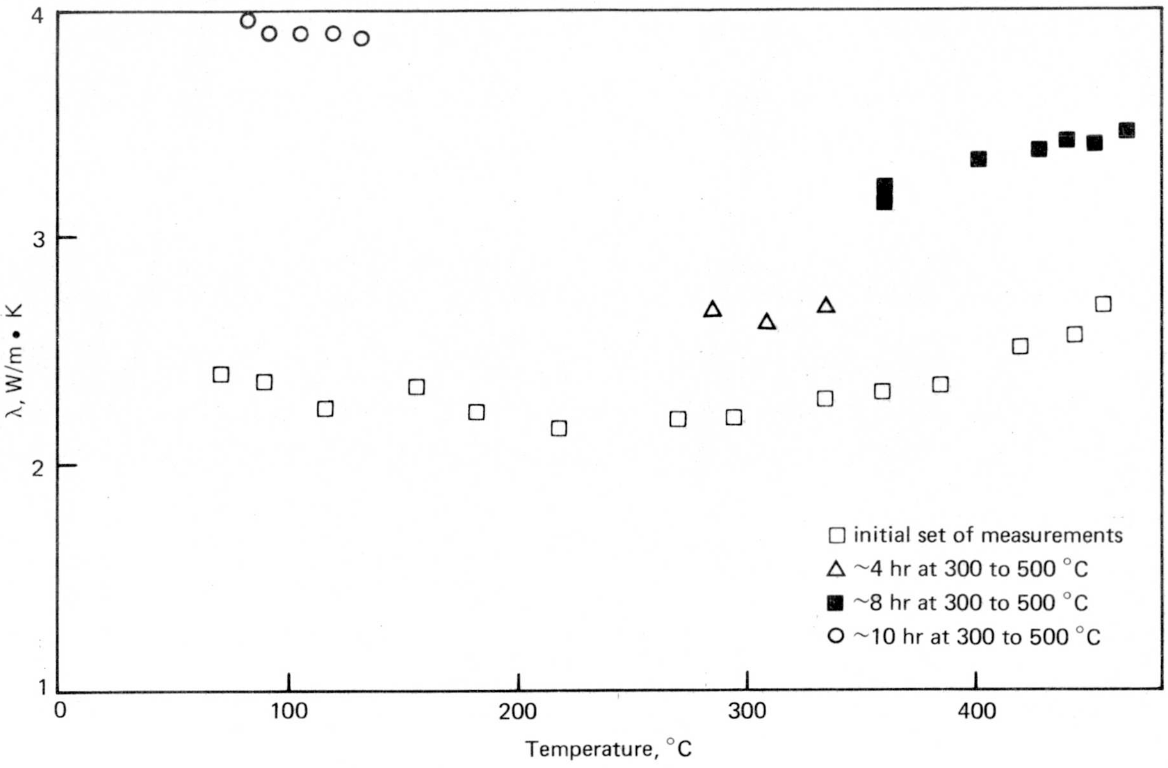

FIGURE 8 - Effect of temperature history on 63% tmd thermite.

process itself. This experimental artifact is unavoidable, but can be minimized by heating quickly and making measurements as soon as the desired temperature is reached. Second, when data are acquired for conductivity-temperature curves, the low temperature data should be acquired first to avoid perturbing these measurements by whatever changes occur during the heating process. Finally, it should be noted that the deleterious effects of sample heating have been noticed with low density thermites only. There seems to be no problem with high density thermite composites ($\rho > 80\%$tmd). The reason for this density dependence is unknown at this time. A clue is given, however, by the observation that the density of the 63%tmd thermite sample had increased to 66%tmd after the completion of the aging experiment described above. Evidently, low density thermite tends to shrink when heated even in the absence of significant external pressure.

Conclusions

1. Thermal conductivity decreases with increasing temperature for all Al/Cu_2O thermite formulations studied.
2. Thermal conductivity increases with part density for parts fabricated with flaked aluminum.
3. Parts fabricated from flaked aluminum have a higher thermal conductivity than parts fabricated from spherical aluminum.
4. The conductivity of flaked and spherical aluminum thermite parts are not all that different, however, and the geometric mean model agrees

closely with the measured conductivities of both types of thermite.

5. For similar part density, Al-Si/Cu_2O thermite has a lower thermal contivity than either flaked or spherical Al/Cu_2O thermite.

6. The comparative method is the method of choice for determining the thermal conductivity of Al/Cu_2O consolidated thermites.

7. Long term aging (1000 hr at roughly 380°C) has no substantial effect on the thermal conductivity of 90% tmd flaked Al/Cu_2O consoliated thermite.

8. Even relatively short term aging (1 to 5 hr at 300-400°C) has a substantial effect on the thermal conductivity of Al/Cu_2O thermite having a density of less than 80% tmd.

9. It is good practice, when determining conductivity-temperature data, to obtain the lowest temperature data first in order to minimize effects of sample heating.

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