

# High Conductivity, Low Cost Aluminum Composite for Thermal Management

April 28, 1997

## Sponsored by

Defense Advanced Research Projects Agency (DOD)  
(controlling DARPA Office)

ARPA Order No. 611, Amdt. 05

Issued by U.S. Army Missile Command Under

**Contract # DAAH01-96-C-R231**

**Contractor:** Technical Research Associates, Inc.  
2257 South 1100 East  
Salt Lake City, UT 85106

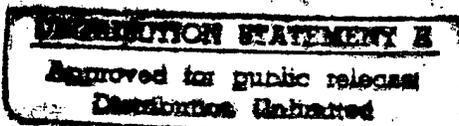
**Effective Date of Contract:** September 30, 1996  
**Contract Expiration Date:** March 30, 1997

**Principle Investigator:** Jared L. Sommer, Ph.D.

**Telephone Number:** (801)-485-4994

**Short Title of Work:** Aluminum/Graphite Composites

19970506 054



DTIC QUALITY INSPECTED 3

# DISCLAIMER NOTICE



**THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.**

# DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF COLOR PAGES WHICH DO NOT REPRODUCE LEGIBLY ON BLACK AND WHITE MICROFICHE.

## Technical Abstract

In order to produce an inexpensive packaging material that exhibits high thermal conductivity and low CTE, Technical Research Associates, Inc. (TRA) has shown in Phase I the feasibility of incorporating natural flake graphite in an aluminum matrix. TRA has developed a proprietary coating technique where graphite flakes have been coated with a thin layer of molybdenum/molybdenum carbide (approximately 0.2 microns). This barrier coating can protect the graphite flake from chemical reaction and high temperature degradation in molten aluminum-silicon alloys. Methods to successfully vacuum infiltrate coated flake with molten aluminum alloys were developed.

The resulted metal matrix composites exhibited lower CTE than aluminum metal. The CTE of the composites were significantly lower than aluminum and its alloys. The CTE can potentially be tailored for specific applications. The in-plane thermal conductivity was higher than the aluminum matrix alloy. The thermal conductivity and CTE of the composite may be significantly improved by improving the bond-strength of the molybdenum-coating on the graphite flake. The flake can potentially be incorporated in the molten aluminum and pressure die-cast to align the flakes within the aluminum matrix. By preferentially aligning high conductivity graphite flakes within a plane or direction, the thermal conductivity of the resulting composite will be above pure aluminum in the alignment direction.

## Acknowledgements

This research has been sponsored by the Defense Advanced Research Projects Agency of the Department of Defense, under the Small Business Innovative Research Program, Contract # DAAH01-96-C-R231. TRA appreciates the help and support of DOD.

DTIC QUALITY INSPECTED 3

# Table of Contents

I. Introduction .....	6
II. Background .....	6
III. Technical Approach .....	8
IV. Phase I Technical Objectives .....	10
V. Phase I Work Plan .....	10
VI. Experimental Approach and Results .....	11
A. Materials .....	11
B. Coating Graphite Flake with Molybdenum Carbide .....	13
1. Flake Coating Process .....	13
2. Flake Characterization .....	14
C. Aluminum Infiltration of Graphite Flake .....	15
1. Vacuum Sealing of Flake in Aluminum Foil Bag .....	16
2. Design of Graphite Mold for Vacuum Infiltration .....	17
3. Aluminum Infiltration of Fiber Cloth .....	18
4. Infiltration of Graphite Flake .....	19
5. Influence of Aluminum Oxide Skin Layer on Infiltration .....	22
D. Alignment Techniques .....	24
1. Flake Alignment .....	24
2. Binders .....	26
E. Characterization of the Composite Material .....	26
1. Volume Fraction and Density Measurements .....	26
2. Measurement of Thermal Expansion Coefficient .....	27
3. Measurement of Thermal Conductivity .....	28
F. Raw Materials Cost Analysis .....	30
G. Thermal Model of Composite System .....	31
VII. Future Work .....	34
VIII. Conclusions .....	35
IX. Tables .....	36
X. Figures .....	38

## List of Figures

<b>Figure 1-</b> SEM Micrograph of 3061 Graphite Flake. . . . .	39
<b>Figure 2-</b> Molybdenum-Coated 3061 Graphite Flake Infiltrated with Copper . . . . .	40
<b>Figure 3-</b> SEM Photograph of Molybdenum-Coated Graphite Flake . . . . .	41
<b>Figure 4-</b> Close-up of Molybdenum-Coated Graphite Flake . . . . .	42
<b>Figure 5-</b> Aluminum Foil Vacuum Bag Ultrasonically Welded on Three Sides. . . . .	43
<b>Figure 6-</b> Process used to Vacuum Infiltrate Coated Flakes with Molten Aluminum Alloy. . . . .	43
<b>Figure 7-</b> Configuration Used to Make Long CTE Specimens . . . . .	44
<b>Figure 8-</b> Al/Gr Composite (2.0" long) with Tapered Graphite Die. . . . .	44
<b>Figure 9-</b> Uncoated EWC-600 Graphite Cloth Infiltrated with 443 Aluminum-Silicon Alloy and Held for 20 Minutes at Temperature. Uncoated Graphite Cloth Severely Reacted with Aluminum Matrix. (Scale: 1 cm = 20 $\mu$ m). . . . .	45
<b>Figure 10-</b> Molybdenum-Coated Graphite Fiber Cloth Infiltrated with 443 Al-Si Alloy at 1000°C and Held for 20 Minutes. Graphite Fibers Remain Virtually Unreacted. (Scale: 1 cm = 20 $\mu$ m). . . . .	46
<b>Figure 11-</b> Mo-Al-C Ternary Phase Diagram at 1000°C . . . . .	47
<b>Figure 12-</b> Composite Containing Molybdenum-Coated Graphite Flake in 443 Alloy Matrix. Protective Molybdenum-Coating Prevented Graphite Flake Reaction with Matrix. (Scale: 1 cm = 40 $\mu$ m). . . . .	48
<b>Figure 13-</b> Micrograph of Al/Gr Composite (Sample B). Significant Flake Reaction Occurred Because of Defective Molybdenum Coating. (Scale: 1cm = 40 $\mu$ m) . . . . .	49
<b>Figure 14-</b> Microstructure of Al/Gr Composite (Sample D). Less Reaction with Flake Resulted in Higher Thermal Conductivity and Lower CTE. (Scale: 1cm = 80 $\mu$ m). . . . .	50
<b>Figure 15-</b> Extrusion Device Used to Align Graphite Fibers. . . . .	51
<b>Figure 16-</b> Alignment of Graphite Flakes By Extrusion Process . . . . .	51
<b>Figure 17-</b> Experimental Thermal Expansion Coefficient of Al/Gr Composites Compared to Alloy 443 and Pure Al as a Function of Time. . . . .	52
<b>Figure 18-</b> Dimensions of "Penny-Shaped" Inclusion used in Modeling Composite Randomly-Oriented Graphite Flake. . . . .	53
<b>Figure 19-</b> Calculated Thermal Conductivity of Al/Gr Composites for Randomly Packed and Aligned Flakes as a Function of Flake Volume Fraction and Thermal Conductivity. . . . .	54
<b>Figure 20-</b> Steady-State Temperature Distribution for Aluminum Plate with 20 W/cm <sup>2</sup> Heat Source on Surface and Bottom Edge Maintained at 20°C. ( $K_x = 180$ W/mK). . . . .	55
<b>Figure 21-</b> Steady-state Temperature Distribution of Al/Gr Composite Plate with 20 W/cm <sup>2</sup> Heat Source and Bottom Edge Maintained at 20°C . ( $V_f = 0.5$ , $K_{flake} = 250$ W/mK, and $K_{comp} = 215$ W/mK). . . . .	56
<b>Figure 22-</b> Steady-state Temperature Profile of Al/Gr Composite with 20 W/cm <sup>2</sup> Heat Source on Surface and Bottom Edge Maintained at 20°C. ( $K_{flake} = 350$ W/mK, $K_{comp} = 265$ W/mK). . . . .	57

## List of Tables

<b>Table 1-</b> Weight Percent of Impurities in #1 Flake and 3061 Graphite Flake from Asbury Graphite. ....	36
<b>Table 2-</b> Measured CTE on Composite Samples .....	36
<b>Table 3-</b> Flash Thermal Diffusivity Results for Al/Gr Composites. Sample D (30% Graphite) was tested at TPRL. Sample B (25% Graphite) was tested at ORNL. ....	37
<b>Table 4-</b> Calculated Composite Thermal Conductivity as Function of Flake Thermal Conductivities and Flake Volume Fraction. ....	37

## I. Introduction

Electronic components continue to increase in complexity and functionality while decreasing in size. Each generation of microprocessor has needed to dissipate progressively more thermal energy, despite efforts to reduce operating voltages and implement advanced power management. For example, the Intel Pentium™ microprocessor (200 MHz) typically dissipates between 15-17 watts of thermal energy, while the Pentium Pro™ processor (200MHz) dissipates approximately 37 watts of power<sup>1</sup>.

Thermal energy is dissipated through a combination of heat sinks, fans, recirculating fluids, and heat pipes. Aluminum heat sinks are an indispensable part of thermal management techniques. Aluminum offers high thermal conductivity (180 W/ mK), low density (2.7 g/cc), and low cost. On a specific conductivity basis (conductivity divided by density) it is about six times as thermally efficient as copper, and slightly more efficient than magnesium.

The long-term objective of this effort is to develop a heat transfer material that has greater thermal conductivity, lower density, lower CTE, and cost than aluminum heat sinks. The objective of this Phase I is to develop heat sink material which would exhibit thermal and physical properties attractive to electronic applications and that would be cost competitive with aluminum heat sinks using low cost raw materials and potential for low cost production.

## II. Background

Among composite materials, aluminum/graphite and copper/graphite composites are leading materials for use in high-performance electronic systems. The use of aluminum matrix (Al/Gr) composites for packaging material have been severely limited because of the cost of graphite fibers and problems with corrosion. The high cost of the composite material is a direct result of the following factors:<sup>2</sup>

---

<sup>1</sup> Data from Intel Technical Support and Intel Product Data sheets, available through Intel's web site, [www.intel.com](http://www.intel.com). (1997).

<sup>2</sup> Schmidt, K.A., and C. Zweben, "Application of Composites in Packages", Electronic Materials Handbook ASM International, Vol.1 (1989), pp.1126-1128.

- **High Material Costs-** Typically, high thermal conductivity graphite fiber costs approximately \$ 100 per pound for every 100 W/mK. For example, the cost of graphite fibers exhibiting thermal conductivities of 400 W/mK is approximately \$400/lb.
- **High Fabrication Costs-** Carbon is not spontaneously wet by molten aluminum. To incorporate the carbon into the aluminum matrix, molten aluminum must be forced in between the fiber interstices by high pressure (>1000 psi). Other techniques that have been used are foil lay-up with subsequent hot-pressing, plasma spraying, and sputtering processes. These are all expensive fabrication techniques.

Therefore, the cost of producing the metal matrix composite material incorporating graphite fibers have been prohibitively expensive in applying the technology to high-volume commercial electronics.

Molten aluminum eventually wets carbon at high temperatures, high pressures, or long reaction times. The "wetting" is primarily a result of a  $Al_4C_3$  reaction product that forms at the aluminum/carbon interface. Unfortunately, aluminum carbide easily hydrolyzes under moist conditions to form aluminum hydroxide.

An ideal electronic packaging material would be fabricated from materials that exhibit high thermal conductivity and low density. The thermal expansion coefficient of the packaging material should be tailorable to the electronic components to maintain reliability of the electronics during use by reducing residual stress caused by thermal mismatch. The fabrication costs preferentially must be low enough to compete with monolithic aluminum packaging materials. The packaging materials should also exhibit good corrosion resistance.

Unfortunately, the elements on the periodic table are somewhat limited in economically providing thermal and physical properties superior to aluminum. Although beryllium is more thermally conductive and less dense, the metal is more expensive than aluminum and the oxide is toxic. Only carbon can meet these stringent requirements. However, processing the carbon to a usable packaging material can be expensive. To achieve sufficiently high thermal conductivity, the graphitic basal planes must preferentially aligned in one plane or the carbon must be deposited as a diamond-like film. Both processes require high capital equipment costs, long processing times, and

often high cost precursor materials. Natural crystalline graphite is inexpensive. However, it is difficult to achieve good thermal contact between grains in order to achieve high continuous thermal conductivity throughout the material.

The thermal conductivity of natural graphite parallel to the basal plane (approximately 350 W/mK) is high in comparison to aluminum (180 W/mK).<sup>3</sup> Natural flake graphite is also relatively inexpensive. Typically, 50 mesh flake graphite (93% pure) costs from 50 to 60 cents per pound. The smaller mesh size graphite flake (<200 mesh) costs approximately 40 cents/lb. The natural flake graphite is used extensively in plastics and rubbers to increase the thermal conductivity.

### III. Technical Approach

In order to produce an inexpensive packaging material that exhibits high thermal conductivity and low density, Technical Research Associates, Inc. (TRA) has shown in Phase I the feasibility of incorporating natural flake graphite in an aluminum matrix. For the past five years, TRA has been developing copper/graphite fiber metal matrix composites for use as heat sink and packaging materials. TRA has developed a proprietary coating technique where graphite fibers have been coated with a thin layer of molybdenum/molybdenum carbide (approximately 0.2 microns) using solution chemistry. TRA demonstrates in Phase I that this barrier coating can protect the graphite flake from chemical reaction and high temperature degradation in molten aluminum-silicon alloys. Methods to successfully vacuum infiltrate coated flake with molten aluminum alloys were developed.

The fabricated metal matrix composites exhibited lower density than aluminum metal. The CTE of the composites were significantly lower than aluminum and its alloys. The in-plane thermal conductivity of the composite was higher than the aluminum matrix alloy. The thermal conductivity and CTE can be significantly improved by improving the bond-strength of the molybdenum-coating on the graphite flake. Tests also show that the flake can potentially be incorporated in the molten aluminum and pressure die-cast to align the flakes within the aluminum matrix.

---

<sup>3</sup> Neubert, T.J., J. Royal, A.R. Van Dyken, "The Structure and Properties of Artificial and Natural Graphite," Argonne National Laboratory, Report ANL5524, February 1956, p. 28.

By improving the composite and fabrication processes, the resulting composite may have specific advantages over conventional aluminum/graphite composite materials:

- **Potentially High Thermal Conductivity and Tailorable Thermal Expansion Coefficient.** By preferentially aligning high conductivity graphite flakes within a plane or direction, the thermal conductivity ( $K$ , of the resulting composite will be above pure aluminum ( $K = 180$  W/mK).
- **Corrosion Resistant-** Corrosion resistant Al/Gr composites have been recently produced by Wendt et al.<sup>4</sup> by alloying the aluminum matrix with up to 26 at.% (55 wt%) molybdenum by a sputtering process. The composites were electrochemically tested and found to be three orders of magnitude more corrosion resistant than conventional Al/Gr composites. The corrosion rate of the metal matrix composites was anodically controlled; i.e., the rate did not depend on the fiber/matrix area ratio. The steady-state galvanic current densities were very low in comparison to the pure aluminum as a result of the molybdenum addition. The molybdenum addition may shift the corrosion potential of the aluminum without influencing the morphology of the protective aluminum oxide skin layer. By surrounding each individual graphite particle with a thin layer of molybdenum/molybdenum carbide, the composite may exhibit excellent corrosion resistance. By initially coating the individual fibers with the molybdenum coating, the formation of the aluminum carbide may also be prevented.

---

<sup>4</sup> Wendt, R.G., W.C. Moshier, B. Shaw, P. Miller, and D.L. Olson, "Corrosion - Resistant Aluminum Matrix for Graphite-Aluminum Composites," Corr. Sci., vol. 50, 11, (1994), pp. 819-826.

## **IV. Phase I Technical Objectives**

The objectives of this Phase I feasibility demonstration were the following:

1. Model a composite heat sink material consisting of an aluminum matrix with high conductivity flake graphite dispersed within it.
2. Demonstrate that the flake graphite can be uniformly coated with a layer to promote wetting.
3. Develop simple, low cost methods to incorporate the flake graphite into the aluminum matrix.
4. Evaluate the thermal properties of the aluminum/flake graphite composite.
5. Develop a simple cost model to evaluate major costs and areas for improvements.

## **V. Phase I Work Plan**

The Phase I Work Plan will consist of the following Tasks:

- |         |   |
|---------|---|
| Task 1. | Acquire Suitable High Conductivity, Low Cost Graphite Flake               |
| Task 2. | Develop a Thermal Model for the Composite System                          |
| Task 3. | Coat the Graphite Flake with Molybdenum Carbide                           |
| Task 4. | Develop Methods of Incorporating the Flake into Molten Aluminum           |
| Task 5. | Characterize the Aluminum/Graphite Flake Composite                        |
| Task 6. | Develop Cost Model; Compare Projected Properties with Measured Properties |
| Task 7. | Final Report and Sample Preparation                                       |

## VI. Experimental Approach and Results

### A. Materials

Various types of graphite flake that exhibited potentially high thermal conductivity and low cost were acquired from commercial suppliers. Typically, natural graphite flake containing high levels of carbon (99% C) is more expensive than the lower grades of graphite flake (50 cents/lb) but should exhibit higher thermal conductivity.

Two graphite flake grades, #1 Flake and 3061, from Asbury Graphite Mills, Inc. (Asbury, NJ) were investigated. Other graphite flakes were obtained from other vendors but not tested because ash analysis was not available. The #1 Flake is approximately 93% carbon and contains graphite flakes larger than +50 mesh ( $>300\mu\text{m}$ ). The flake cost is approximately \$1/lb. The size of the 3061 graphite flake ranges between -20 and +50 mesh (300 to  $850\mu\text{m}$ ). The graphite flake is approximately 99% carbon and costs \$3/lb. Other potential materials for further research include Grade 599 natural graphite flake which is also available from Asbury Graphite. This grade is approximately 99.6% carbon and costs \$0.99/lb. This grade of flake contains approximately 20% fines smaller than  $250\mu\text{m}$ .

Asbury's #1 and 3061 flake are relatively large in diameter. Large graphite flakes have the advantage that they are easily aligned during casting or post-processing (i.e. extrusion, etc.). The large graphite flakes also exhibit lower surface area and require less coating per pound than the smaller graphite flakes. However, the large flake tends to have a higher impurity level in comparison to smaller flake, and as a result, may exhibit lower thermal conductivities than smaller flake sizes. Medium-sized graphite flakes with high carbon content are used in resins to increase the polymeric resin thermal conductivity. Producing heat sink material with graphite flake will be a compromise between larger particles (which require less coating per pound and is easier align) and smaller size flake (which is less expensive, exhibits higher thermal conductivity, and may be easier to cast).

The chemical analysis of the 3061 and #1 flake type is shown in Table 1. When the natural

graphite flake is pyrolyzed in air to measure ash content, the residual ash remains in the same form and shape as the original graphite flake, suggesting that the oxides are dispersed evenly and interconnected within the graphite matrix. The degree of oxide dispersion and its effect on the thermal conductivity of the graphite flake is unknown.

An SEM micrograph of the 3061 flake is shown in Figure 1. The face of each flake is quite smooth but jagged on the edges. The graphite flakes consist of layered carbon basal planes held together by weak van der Waal forces. The carbon atoms are held together within each plane by strong directional covalent bonds. These strong covalent bonds are primarily responsible for the high in-plane thermal conductivity. Because of the strong covalent carbon bonds, the surface of the flake is relatively inert and difficult to coat.

Aluminum (99%) and aluminum alloy 443 were investigated in Phase I. Alloy 443 is a casting alloy that exhibits excellent castability. This is a result of lower liquid metal viscosity with increased silicon content. The alloy also exhibits low shrinkage porosity and a narrow freezing range.<sup>5</sup> It is used in permanent and sand-casting for producing pipe and marine fittings and shows generally good corrosion resistance. The thermal conductivity of the alloy is approximately 145 W/mK- or about 65% that of pure aluminum.<sup>6</sup> The alloy composition was analyzed by Met-Chem Testing Laboratories (Salt Lake City, UT). It contained approximately 6.43% Si, 0.002% Cu, and other minor constituents. The alloy is specified to have a Mg of 0.05%. This alloy was investigated because it consists primarily of silicon as its only alloying agent.

Alloy 537, an aluminum-magnesium alloy containing approximately 7% Mg and other minor elements, was also briefly investigated.

---

<sup>5</sup> Wang, L., M. Makhlouf, and D. Apelian, "Aluminium Die Casting Alloys: Alloy Composition, Microstructure, and Properties- Performance Relationships," Int. Mat. Rev., **40**, (6), 1995, pp. 221-238.

<sup>6</sup> Metals Handbook, Desk Edition, H.E. Boyer and T.L. Gall, eds., ASM International, Metals Park, OH, 1985, p. 6.55.

## **B. Coating Graphite Flake with Molybdenum Carbide**

### **1. Flake Coating Process**

Over the past 10 years, Technical Research Associates have developed several methods of coating graphite fibers and surfaces with a thin uniform layer of a molybdenum/molybdenum carbide compound. (The molybdenum/molybdenum carbide coating will be referred to as the "molybdenum coating" in this report.) The technology to coat graphite fibers with an adherent molybdenum coating is highly developed. Technical Research routinely coats continuous, woven, or discontinuous fiber with coatings that are 0.1-0.2 $\mu$ m thick and are wettable by molten copper. Since copper does not form a stable surface oxide layer to inhibit wetting, molten copper was used as a "screening" metal in Phase I to determine if the molybdenum-based coating on the natural graphite flake was both adherent to the flake surface and wettable.

One of the principle objectives in Phase I was to find a process to successfully coat graphite flake with a molybdenum coating that would wet molten copper. The surface chemistry of the graphite flake is quite different from graphite fibers. Most of the edges of the graphitic basal planes within pitch-based graphite fibers radiate outward, perpendicular to the fiber surface (like spokes on a bicycle). The edges of the planes are more reactive than the face of the planes. Since the natural graphite flakes consist of the carbon basal planes stacked parallel within the plane of the flake, the graphite flake is somewhat less reactive than graphite fibers.

Various coating techniques were investigated to produce a wettable coating on the flake surface. The natural graphite flakes were initially coated with a molybdenum precursor solution using similar coating procedures used to coat pitch-based graphite fibers. The solution was applied to the flakes and dried to evaporate the solvent. The flakes were then thermally treated at 1100°C in an inert atmosphere to convert the coating to a combination of molybdenum carbide and molybdenum metal.

The coating procedure used to coat graphite fibers had to be modified to coat the natural flake. Problems included the coating spalling off the surface of the flake during drying and heat-treatment and residual coating-byproducts bridging between the individual flakes, causing the coated flake to clump together after processing. The clumps were difficult to break apart. After varying the

coating procedure through several iterations, we found that the flake could be effectively coated with molybdenum by drying the saturated graphite flake with high air flow (>90 ft/sec at 100°C), heat-treating the dried flake in air to 700°C, and then further heat-treating the flake briefly in an inert atmosphere at 1100°C. Flakes with a good molybdenum coating adhered to each other but were easily separated with a spatula. Virtually no bridging of the coating occurred between the flakes. Some residual by-product still remains on the flake. Further research will refine the reproducibility of the coating process.

To test wettability of the coated flake, approximately 0.5 grams of coated graphite flake was wrapped in copper foil and heated above 1150°C. If the coating was good, the coated flakes floated to the surface of the molten copper but remained wet by liquid metal. However, flakes with a defective coating floated to the surface of the molten copper (unwet by copper) and were easily brushed off the surface of the copper after solidification. Figure 2 shows a sample of flake with a good molybdenum coating infiltrated with molten copper. The flake is completely wet by the molten copper.

Reproducing the molybdenum coating on flake surfaces has been influenced both by the variability of the graphite flake and the coating conditions. Some coatings adhered well to the surface of the graphite during infiltration. Many times, however, the applied molybdenum coating spalled off and did not protect the graphite surface. The good and defective coatings looked similar under the optical microscope. Many variables influence the adherence of the molybdenum coating, such as reaction time and temperature, humidity, solution age, coating thickness, gas flow, and solution concentration. With further development, we believe a reliable coating process for flake graphite can be developed. Both 3061 Flake and #1 flake was successfully coated with the molybdenum coating.

## **2. Flake Characterization**

An SEM micrograph of the molybdenum-coated 3061 flake is shown in Figure 3. Residual molybdenum coating by-products dust the surface of the flakes. Underneath this by-product, a thin submicron coating of molybdenum and molybdenum carbide coats the entire surface of the graphite flake. A close-up of the coated graphite flake surface is shown in Figure 4. As a result of the thinness of the coating, the as-received flake and coated flake appear very much alike under the

optical and scanning microscope. However, the coated flake is silver-colored and wettable by molten copper.

The density of the coated flake was measured at TerraTek (Salt Lake City, UT) using a helium pycnometer. The density of the flakes were measured using different cell sizes and pressures. The density of the uncoated and molybdenum-coated 3061 flake was measured to be 2.260 and 2.630 g/cm<sup>3</sup>, respectively, with an error of  $\pm 0.005$  g/cm<sup>3</sup>. These densities can be compared to pure aluminum and Alloy 443, which have densities of 2.7 and 2.68 g/cm<sup>3</sup>, respectively.

The increase in flake density is approximately 16.4% higher than the as-received graphite flake. With further development, we believe it is reasonable to fabricate coated flake with a density of approximately 2.5 g/cm<sup>3</sup>. Coated flakes that exhibit densities similar to aluminum may be desirable in order to insure that the graphite flake disperses well, without segregating or floating within the aluminum matrix, during casting.

Previous research at TRA has shown using x-ray diffraction Auger spectroscopy that the molybdenum-coating on fiber materials is a mixture of molybdenum and molybdenum carbide. Assuming that the coating primarily exists on the flat surfaces of the graphite flake and exhibits a density of 9.5 g/cm<sup>3</sup> (average of Mo and Mo<sub>2</sub>C densities), the coating thickness calculates to approximately 0.2 $\mu$ m. Previous TEM micrographs of molybdenum-coated graphite fiber revealed that the coating thickness lies between 0.1- 0.2 $\mu$ m.

### **C. Aluminum Infiltration of Graphite Flake**

The principle problem associated with incorporating graphite flake in aluminum is overcoming the resistance of the aluminum oxide layer. Two methods were investigated to infiltrate the molybdenum-coated graphite flake with molten aluminum, 1) vacuum sealing the coated flake in an aluminum bag, and 2) vacuum infiltrating the flake within a graphite mold. Experimental details and results of each method is described below:

## 1. Vacuum Sealing of Flake in Aluminum Foil Bag

The objective of this task was to vacuum bag the coated graphite flake within an aluminum foil bag. The sealed bag would then be submerged in molten aluminum, melting the foil bag, thus allowing the liquid aluminum to penetrate the flake material.

In Phase I, Technical Research worked with Stapla to ultrasonically join aluminum foil together to form sealed aluminum bags. Two types of aluminum foil were investigated, textured and plain. Textured aluminum foil was investigated because Stapla has extensive experience in welding the textured foil for producing sealed aluminum foil oven bags. Both foils were approximately 0.0015" (40 $\mu$ m) thick and described commercially as "extra heavy duty." These foils have a higher resistance to tearing during the welding process. A sample of a 3"x 4" welded aluminum bag is shown in Figure 5. The bag seams are ultrasonically welded on three sides using 3kW of power at a frequency of 20kHz.

Our approach was to vacuum seal the edge of the aluminum bag with a sealing compound and then to permanently weld the aluminum bag parallel with the sealed edge. After welding, the glued edge would then be cut off, producing a vacuum-sealed aluminum bag containing molybdenum-coated graphite flake. In order to vacuum seal the graphite flake within the bag, a vacuum autoclave was used. The autoclave was designed for vacuum sealing electronic components within epoxies or silicon molding compounds. The unsealed edge of the aluminum bag was clamped between two 0.5" Teflon rods and suspended vertically within the autoclave with the unsealed edge pointing upwards. The autoclave was then closed, evacuated, and refilled with helium gas. The chamber was then re-evacuated. Two-part RTV silicon rubber (GE Silicone RTV11) or 20 minute epoxy (Duro brand) was poured on the unsealed edge of the aluminum foil bag. After curing, the sample was withdrawn from the autoclave.

The performance of this vacuum sealing technique was evaluated by sealing a cubic inch of polyurethane sponge within an aluminum bag. The edges of the bag were pre-sealed on three edges using silicone rubber adhesive. When the evacuated bag was exposed to atmospheric pressure and withdrawn from the autoclave, the enclosed sponge was completely squashed and remained so for four weeks.

Home Mojal at Stapla Ultrasonics investigated two types of ultrasonic welding heads under

various pressures, vibrational frequencies, and power levels to hermetically seal the aluminum foil. A standard rough-finish head and a cross-hatched serrated head were investigated. The serrated head was designed to be more aggressive, focusing more vibratory energy into the seam. Unfortunately, Stapla had difficulties in producing hermetically sealed edges using ultrasonic welding. Welded aluminum foil seams could be made "water-tight" but not "vacuum-tight". Welding conditions were not found to prevent gas from leaking through small fissures within the welded seam in Phase I. Therefore, we concentrated on an alternative vacuum infiltration technique.

## 2. Design of Graphite Mold for Vacuum Infiltration

As an alternative to vacuum-sealing the flake material in aluminum bags, an alternative method was investigated to infiltrate the flakes with aluminum.

In order for the aluminum to wet ceramic or metallic surfaces, the tenacious aluminum oxide skin on the molten aluminum must be overcome to allow intimate contact between the molten aluminum and substrate surface. Many studies have shown that the aluminum oxide skin acts as a barrier and impedes substrate wetting.<sup>7,8</sup> A partial pressure as low as  $10^{-36}$  atmospheres of oxygen at  $1000^{\circ}\text{C}$  is required thermodynamically to disassociate the aluminum oxide skin.<sup>9</sup> The aluminum oxide skin can also be disrupted by flowing the liquid aluminum (to continually replenish the surface) or by mechanically breaking the outer skin layer.<sup>10</sup>

Various mold designs were also investigated to vacuum infiltrate coated flake and cloth while simultaneously breaking up the aluminum oxide skin layer. The most successful mold design and

---

<sup>7</sup> Laurent, V., D. Chatain, and N. Eustathopoulos, "Wetting of SiC by Aluminum and Al-Si Alloys", *J. Mater. Sci.*, **22**, (1987), p. 244.

<sup>8</sup> Brennan, J.J., and J.A. Pask, "Effect of Nature of Surface on Wetting of Sapphire by Liquid Aluminum," *J. Amer. Ceram. Soc.*, **51**, (1968), p. 569.

<sup>9</sup> Gaskell, D. R., *Introduction to Metallurgical Thermodynamics*, 2<sup>nd</sup> Ed., McGraw-Hill, New York, (1981).

<sup>10</sup> Jung, W., H. Song, S-W Park, and D-Y. Kim, "Variation of Contact Angles with Temperatures and Time in the Al-Al<sub>2</sub>O<sub>3</sub> System," *Met. Mat. Trans B*, **27B**, 2, (1996), pp. 51-55.

infiltration process is shown graphically in Figure 6.

The flake was placed in the bottom of a tapered graphite crucible. A tapered plug with a machined hollow cone in the center was then firmly inserted to seal the plug against the walls of the crucible. The aluminum or aluminum alloy was then placed on top of the plug, as shown in Step 1. The graphite flake was infiltrated by evacuating the chamber, melting the aluminum within the crucible (Step 2), and then refilling the chamber with nitrogen to force the molten aluminum in the evacuated flake (Step 3). The expanding nozzle entrance was designed to continually break up the aluminum oxide skin as the molten aluminum flowed into the lower chamber containing the coated flakes. The flakes were infiltrated with atmospheric pressure, with no external pressure required.

The mold configuration was modified to make longer flat specimens suitable for CTE and thermal conductivity testing. A 0.5" wide by 2.0" long channel was machined in the graphite plug section, as shown in Figure 7. Specimens 1.0" long were also fabricated. The molybdenum-coated flake was 'dry-packed' or dampened with methanol and packed into the machined channel in the graphite mold. Using the same infiltration principle as described above, the flake was infiltrated with the molten aluminum. A fabricated 2.0" long Al/Gr composite sample and the tapered dies are shown in Figure 8.

### **3. Aluminum Infiltration of Fiber Cloth**

Initially, uncoated and molybdenum-coated graphite fiber cloth (EWC-600 Fiber Cloth produced by Amoco Performance Company, Alpharetta, GA) since the fiber coating process is quite reliable. The fiber cloth was vacuum infiltrated at 1000°C with the 443 aluminum alloy and held for 20 minutes at that temperature. These graphite fibers are originally 10 $\mu$ m in diameter and are either circular in cross-section or "pac-man" shaped.

#### **a. Uncoated Graphite Fibers**

The microstructure of the infiltrated composite containing uncoated graphite fibers is shown in Figure 9. Because of the high temperature, the molten aluminum reacted with the surface of the unprotected graphite fiber forming aluminum carbide, according to the following chemical equation:



The fibers are no longer cylindrical but appear to be severely degraded and almost consumed by the chemical reaction. The sharp angular precipitates projecting out of the fiber surface is characteristic of aluminum carbide. This was confirmed by microprobe analysis.

#### **b. Molybdenum-Coated Graphite Fibers**

The graphite fibers were coated with a 0.2  $\mu\text{m}$  thick molybdenum coating and infiltrated with the same aluminum alloy under the same infiltration conditions. A micrograph of the resulting composite structure is shown in Figure 10. The cross-section of the graphite fibers are still circular (or "pac-man" shaped). Only a very small amount of reaction product exists at the interface because of the excellent protection afforded them by the molybdenum coating.

The x-ray diffraction scan of the composite cross-section shows that the detectable level of molybdenum in the sample was so small that its signal may have been lost in the background noise. Only aluminum, silicon, and carbon were readily detectable. Although the molybdenum coating is thin (approximately 0.2 $\mu\text{m}$  thickness), the graphite fibers were protected by the molten aluminum alloy at high temperatures during infiltration. This experiment simply illustrates that the molybdenum coating, if correctly applied to the surface of the graphite, can protect the graphite flake and its thermal properties from degradation.

### **4. Infiltration of Graphite Flake**

#### **a. Pure Aluminum Infiltration**

Infiltration of the graphite flake with pure aluminum was very difficult. No composite samples were made or tested with a pure aluminum matrix because of incomplete infiltration. Vacuum infiltration required that a good gas seal existed at the molten aluminum/graphite crucible interface within the riser section. Often, the aluminum would melt but not seal against the crucible walls because of the tenacious oxide skin layer on the outside of the aluminum. As a result, the nitrogen gas would leak around the molten aluminum and fill the mold before infiltration was possible.

In order to break the oxide skin layer, a small graphite plunger was placed on the surface of the aluminum. When the aluminum melted, the weight of the plunger would break the oxide surface of the molten aluminum. Some packed flake was partially infiltrated with the aluminum by evacuating and back-filling the flake-filled mold with nitrogen numerous times to break up the oxide skin layer on the molten aluminum. However, the pure aluminum quickly oxidized and would not seal against the graphite mold.

The liquid aluminum that did infiltrate a small part of the flake appeared to react with the graphite surface. This may have been due to the high temperatures, long liquid metal exposure period, or degradation of the molybdenum barrier coating. According to the Mo-Al-C ternary diagram<sup>11</sup> at 1000°C, many possible phases may exist at the flake/aluminum interface, as shown in Figure 11. At 1000°C, the solubility of molybdenum in molten aluminum is approximately 2.3 atomic percent- or about 7.5 weight percent. The molten aluminum reacts with molybdenum metal to form molybdenum aluminides, such as  $\text{MoAl}_4$ ,  $\text{Mo}_3\text{Al}$ , and  $\text{MoAl}$ . Carbon is poorly soluble in these molybdenum aluminides. Some protection may be afforded the graphite flake at low temperatures by these aluminides forming. Packing the molybdenum-coated flake at high volume fraction may decrease dissolution due to the higher localized dissolved molybdenum concentration within the packed flake bed.

The 'molybdenum coating' also contains molybdenum carbide ( $\text{MoC}$  or  $\text{Mo}_2\text{C}$ ). This may also protect the flake. Aluminum carbide ( $\text{Al}_4\text{C}_3$ ) or  $\text{Mo}_3\text{Al}_2\text{C}$  (m.p. 1700°C) may form at the interface. However, the chemical reaction or dissolution rates are unknown.

#### **b. Infiltration with Aluminum-Silicon Alloys**

Graphite flake infiltration with Alloy 443 was successful, depending on the adherence of the molybdenum coating on the graphite flake surface. The silicon addition increased the fluidity, decreased the surface tension, and appears to lower the transition temperature where the aluminum oxide skin would not interfere with wetting. Figure 12 shows the microstructure of the coated graphite flake within the 443 alloy matrix. The flakes are well dispersed with the 443 alloy matrix.

---

<sup>11</sup> Ternary Alloys, G. Petzow and G. Effenberg, eds., ASM Inter., vol. 3, (1990), p. 507.

The flake was vacuum infiltrated at 1000°C and held for approximately 4 minutes at temperature. The molybdenum coating was well bonded to the surface of the graphite flake in this sample. Aluminum carbide does not appear to be present at the matrix/flake interface. The composite microstructure shows the characteristic interdendritic silicon phase within the Al-Si matrix.

Atomic microprobe was used to determine the composition of the matrix near the vicinity of the incorporated flake. The analysis showed that a small amount of molybdenum was present near the flake material. The molybdenum coating appeared to prevent the aluminum alloy from chemically reacting with the graphite flake. Some silicon segregated at the aluminum/flake interface, most likely forming a thin layer of molybdenum disilicide. This reaction layer may have prevented the graphite flake from reacting with the aluminum alloy, even for long periods of time in the molten state. As noted previously, molybdenum-coated graphite fiber could be held at 1000°C for 20 minutes in the 443 alloy without chemical degradation. On the other hand, uncoated graphite fiber infiltrated with the same aluminum alloy and experimental conditions were severely degraded. The Mo-Si-Al ternary diagram was not found for 1000°C.

In order to show the effectiveness of the molybdenum-disilicide coating, a molten 537 alloy (Al-7Mg) was vacuum-infiltrated into molybdenum-coated graphite fiber at 1000°C. Microscopic examination revealed that the aluminum-magnesium alloy reacted with and degraded the coated graphite fibers after holding the fibers in the molten liquid for only 5 minutes. This suggests that the molybdenum-coating may require some silicon in the matrix to protect the fiber surface by forming a thin MoSi<sub>2</sub> layer.

A few small crystalline precipitates were found scattered within the aluminum matrix. Microprobe analysis shows these precipitates are made of molybdenum and silicon, possibly molybdenum disilicide. The coating may have contained excess molybdenum which dissolved in the aluminum matrix and reprecipitated within the matrix. In Phase I, we have only demonstrated the feasibility of coating the graphite flake with molybdenum; therefore, the coating properties have not been optimized.

The microstructures of two composite samples (Samples B and D) that were tested for CTE and thermal conductivity are shown in Figures 13 and 14. The original graphite flake volume fractions of Samples B and D were approximately 25 and 30%, respectively. The molybdenum-

coated graphite flake has reacted quite heavily in both samples, particularly in Sample B. These samples were vacuum infiltrated at approximately 1000°C for approximately 20 minutes to insure complete infiltration. Unfortunately, the molybdenum coatings were not sufficiently adherent to the graphite flake in these samples. The microstructure reveals that the silicon in the aluminum alloy has reacted with the graphite flake to form a thick SiC reaction layer, displacing the graphite flake. Residual graphite flake "slivers" remain within a thick grey reaction layer. The Al-Si matrix appears depleted of interdendritic silicon precipitates. A substantial amount of angular molybdenum disilicide precipitates is within the aluminum matrix, suggesting that molybdenum-coating did not adhere to the surface of graphite flake. The flake was, therefore, unprotected and was almost consumed by the molten aluminum alloy. The graphite flake in sample B appears to be approximately 80% reacted with the aluminum alloy. Very little porosity was found in the Sample B.

Approximately 40-50% of the graphite flake in sample D (Figure 14) remains in the matrix. The remaining graphite substantially influenced the thermal properties of the composite material. These two composite samples will be discussed further in the Characterization of the Composite Materials Section (E).

### **5. Influence of Aluminum Oxide Skin Layer on Infiltration**

The aluminum-silicon alloy infiltrated relatively easy in the molybdenum-coated flake in comparison to the pure aluminum alloy. The aluminum-silicon alloys exhibit excellent fluidity characteristics. The surface tension of liquid aluminum lowers only slightly with the addition of silicon, but then remains almost constant at higher silicon percentages up to 12%.<sup>12</sup>

The wetting transition temperature experimentally appeared to be much lower than pure aluminum. We found the molybdenum-coated graphite fiber to be partially wet by the aluminum alloy as low as 925°C. There is evidence of this mentioned also in the open literature. Laurent et al. found that the wetting transition temperature is moderately decreased by alloying the aluminum with silicon

---

<sup>12</sup> Aluminum: Properties and Physical Metallurgy, J.E. Hatch, ed., ASM Intl, Metals Park, OH, 1984.

on SiC substrates.<sup>13</sup>

As discussed by Olson et al., silicon in molten aluminum modifies the point defect chemistry of the aluminum oxide skin layer, enhancing the aluminum vacancy concentration, thereby increasing the aluminum diffusion rate through the oxide skin layer to the substrate material.<sup>14</sup> Kaptay suggests that molten aluminum will wet all ceramic surfaces if the oxide skin layer could be overcome. The silicon may modify the aluminum oxide skin sufficiently to promote wettability at lower temperature and, at the same time, react with the molybdenum coating to produce a thin barrier coating.

We found experimentally that partial infiltration with the pure aluminum only occurred above 1100°C. The adherent aluminum oxide skin layer acts as a barrier to prevent wetting of the coated-graphite surface. The aluminum oxide forms a network on the surface of the molten metal which can hold the liquid together in the original shape of the solid aluminum. Many researchers have shown that surface properties (surface tension, reactivity, etc.) of molten aluminum are more characteristic of super-cooled liquid Al<sub>2</sub>O<sub>3</sub> than molten aluminum, particularly as the partial pressure of oxygen within the system is increased.<sup>15,16</sup>

As suggest by Kaptay, the contact angle of molten aluminum on a wide range of ceramic substrates will fall below 90° above approximately 950°C in low vacuum environments.<sup>17</sup> This “transition temperature” is most likely due to the Al<sub>2</sub>O<sub>3</sub> reacting with the liquid aluminum forming gaseous Al<sub>2</sub>O, according to the following chemical reaction:

---

<sup>13</sup> See Laurent, et al., (1987).

<sup>14</sup> Chidambaram, P.R., G.R. Edwards, and D.L. Olson, “Wetting of Ceramic by Molten Metals: Rate Controlling Phenomena,” Proceedings of AIME-TMS, October 20-24, 1991, Metal Science of Joining, Held in Cincinnati, OH., (1992), Warrendale, PA, pp. 67-71.

<sup>15</sup> Kaptay, G., “On Surface Properties of Molten Aluminum Alloys of Oxidized Surface,” Mat. Sci. Forum, 77, (1991), pp. 315-330.

<sup>16</sup> Naidich, J.V., “The Wettability of Solids by Liquid Metals,” Prog. Sur. Mem. Sci., v. 14, D.A. Cadenhead and J.F. Danielli, eds., Academic Press, N.Y., (1981), pp. 353-484.

<sup>17</sup> See Kaptay, G., (1991).



The formation of this mono-oxide breaks up the aluminum oxide skin layer, allowing the liquid aluminum to wet the underlying substrate. Since the vapor pressure of  $\text{Al}_2\text{O}$  decreases at lower temperature, the transition temperature should decrease as the pressure of the system is lowered. The transition temperature of aluminum on molybdenum substrates is also reported to be above  $900^\circ\text{C}$ , most likely due to the aluminum oxide skin layer.<sup>18</sup>

## D. Alignment Techniques

### 1. Flake Alignment

Flake alignment in the composite is important for many reasons. These include: 1) more CTE control, 2) higher in-plane thermal conductivity, and 3) high flake volume fraction within composite matrix. Packing methods included direct manual dry- and wet-packing, vibration, and extrusion. Various binders were also investigated. Details of the methods follow:

#### a. Direct Manual Packing

Various methods were investigated to pack and align the graphite flake material to various packing densities. The packing technique used most often was to dry pack the flakes into the mold. Pressure applied to the surface of the flake tended to align the flakes somewhat to face perpendicular to the direction of the applied pressure. Typically, this method produced composites containing approximately 25-30% volume fraction of flake graphite.

#### b. Vibration

In order to achieve higher packing densities, the molds containing the flake were vibrated to align the graphite flake within the graphite molds. The final packing density is dependent upon the

---

<sup>18</sup> Shebo, P., P. Gutka, A. Govalda, I. Ivan, and L. Taborski, Kavale. Mater., **13**, no. 5 (1975), pp. 654.

vibrational frequency and amplitude, time, flake size and aspect ratio, and mold size. The flakes were vibrated in a dry condition. Methanol was also added in some experiments to the graphite flake to increase the volume fraction by decreasing interparticle friction between the individual flakes.

The vibrational techniques were unsatisfactory. The dry flakes were difficult to manage because of their low density. Ubiquitous static charges caused the graphite flakes to cling to the mold walls. When the methanol-based slurry was tested, the flakes easily suspended in the methanol. Vibrational waves within the liquid caused the flakes to distribute unevenly. Therefore, alternative techniques were investigated.

### **c. Extrusion**

Molybdenum-coated graphite flake was mixed in a solvent to a thick paste and extruded through a convergent nozzle in order to pack and align the graphite flake at high volume fractions. The extrusion die was fabricated by heating four layers of heat-shrink tube around an aluminum mold and the cut-off end of a 10 cc syringe, as shown in Figure 15. The aluminum mold was removed after the tube conformed around the mold. The sides of the heat-shrink were cut in order to facilitate removal of the flake after extrusion. A Teflon-coated screen was taped at the end of the extruder to allow excessive solvent to exit during the extrusion process.

As the plunger was pushed in, the flakes aligned by the convergent laminar flow of the solvent, as shown in Figure 16. The slurry needed to be extruded at fairly high velocities (over 5 cc/sec) in order to keep the flakes suspended within the lubricating solvent. At low flow rates, the individual flakes would contact each other. The high contact friction would cause the flakes to seize before the flakes could be fully extruded. The extrusion process produced aligned graphite flake preforms with volume fractions as high as 45 percent. The initial slurries before extrusion contained between 20 and 30 volume percent graphite flake. The solvent was removed by evaporating at 100°C.

Water was used as a solvent, although isopropanol, methanol, or other organic liquids could be used. Since liquid aluminum at 700°C has the same viscosity as water at room temperature, these extrusion experiments demonstrate that graphite flakes within a liquid medium can be aligned at high volume fractions. By incorporating the graphite flake into molten aluminum or an aluminum alloy,

the composite slurry may be die-cast or pressure die-cast, producing aluminum heat-sink materials with aligned graphite flakes.

## **2. Binders**

Binders were investigated as a method of holding the coated graphite flake together as the aligned flake preform was transferred into the graphite mold for aluminum infiltration. The binder must be soluble in the solvent used to align the flake, hold the flake together after solvent removal, and be burn off without leaving a significant amount of impurities that may contaminate the wettability of the flake or the thermal properties of the aluminum matrix.

The most effective binder found was Good-Rite K-702 Polyacrylate Binder, produced by BF Goodrich. This binder is a monomer acrylic acid and has a molecular weight of approximately 250,000 g/mole. Methanol solutions containing approximately 2% binder held the flakes after the methanol was removed. After heating the flakes above 300°C in air to burn off the binder, the flakes could be infiltrated with copper, demonstrating that wettability of the molybdenum-coated graphite flakes were not significantly affected by the binder. The polyacrylate binder is stabilized with a small amount of NaOH. However, the sodium did not interfere with wettability. The monomer could theoretically be stabilized with  $\text{NH}_4\text{OH}$  and leave no residual impurities after heat-treatment.

Water was used also as a binder. After extruding the flake material in water, the preform was frozen with liquid nitrogen. The preform could then be removed and transferred, after which the water was removed by evaporation. The water tended to damage the molybdenum coating, however, rendering the flake unwettable by copper or aluminum.

One sample with aligned graphite flake held together with a binder at lower volume fraction (approximately 20 volume percent) was successfully infiltrated with aluminum.

## **E. Characterization of the Composite Material**

### **1. Volume Fraction and Density Measurements**

Water displacement techniques were investigated to calculate the volume fraction of flake within the composite from calculated densities. However, the densities of the 443 aluminum alloy

and the molybdenum-coated flake were very similar, therefore, the margin of error was quite high. Chemical dissolution of the composite matrix was the best approach to determine volume fraction. The matrix of one composite containing "dry-packed" flake was dissolved. The results showed that the dry-packed composites contained approximately 25 volume percent graphite flake. The "wet-packed" sample was calculated to contain approximately 30% graphite flake.

In Phase I, the flakes were manually packed into the graphite dies before infiltrating with aluminum. The flake orientation and volume fraction, therefore, varied somewhat throughout the composite structure. However, no macrochanneling occurred in the flake during aluminum infiltration.

## 2. Measurement of Thermal Expansion Coefficient

The coefficients of thermal expansion (CTE's) of various samples were measured using a Theta Industries dilatometer between room temperature and 100°C. All composite samples tested were fabricated with the 443 aluminum alloy. This alloy exhibits a CTE of approximately 22.1 ppm/°C.<sup>19</sup>

Results of four samples that were tested for average CTE are shown in Table 2. Plots of CTE versus temperature for the four composite samples are combined in Figure 17. These CTE's are compared to pure aluminum and 443 Alloy. Both manually dry-packed composites exhibited CTE's in the range of 14-14.5 ppm/°C, suggesting that the volume fractions and flake orientations within the composites may have been very similar. All samples show a significant drop in CTE in comparison to the aluminum alloys. The wet-packed sample exhibited a CTE ranging from approximately 11-12 ppm/°C- or about half the CTE of the monolithic alloy.

The microstructures of samples B and D were shown previously in Figures 13 and 14. Since the molybdenum coatings were not sufficiently adherent to the graphite flake in these samples, the aluminum matrix reacted with the graphite flake. Only small amount of residual graphite flake remains within the reaction layer as a result of a weakly bonded molybdenum coating. As a result, the thermal expansion coefficient is approximately 14-15 ppm/°C.

---

<sup>19</sup> See Metals Handbook, (1985).

The graphite flake in sample D (Figure 14) was only partially reacted. As a result, the composite exhibited a lower CTE due to the low CTE of the graphite flake. The CTE is almost half of the 443 base alloy. The thermal expansion coefficient within the plane of the flake should be negative or approximately 0 ppm/°C. Even though the flake reacted with the matrix alloy, the remaining graphite was sufficient to significantly lower the CTE of the composite.

Coating graphite flake with a thin adherent molybdenum coating is very possible, as shown previously in Figure 12. However, as mentioned previously, reliable molybdenum coating conditions for graphite flake have not yet been established. By improving the reliability of the molybdenum coating, aluminum/graphite flake composites will exhibit CTE's as low as 4-6 ppm/°C. This may allow the composite material to be directly bonded to silicon electronic components and improve heat transfer.

### **3. Measurement of Thermal Conductivity**

The CTE's of Samples B and D were measured at Thermal Properties Research Laboratory (TPRL-- Purdue University) and Oak Ridge National Laboratory (CIMTECH), respectively, using laser flash diffusivity. TPRL measured thermal conductivity through the thickness and along the axis of the sample. The specific heat of each sample tested TPRL was measured. The specific heat of the sample tested by ORNL was estimated by rule-of-mixtures. The densities of Samples B and D were measured to be 2.57 and 2.66 g/cm<sup>3</sup>, respectively.

In order to measure thermal conductivity down the length of the sample, the composite material was sectioned, super-glued, and stacked together and both sides of the material were machined parallel to each other and then turned to a 0.5" diameter cylinder. The laser was then focused on the flat end face. Heat conducted parallel to the glued joints. The results from these tests are shown in Table 4. Sample B showed a thermal conductivity of approximately 88 W/mK. The published thermal conductivity value for Alloy 443 is 145 W/mK. However, only a small amount of residual graphite flake remained in the composite matrix as a result poor adhesion of the molybdenum coating on the graphite flake surface.

The thermal conductivity of Sample D from TPRL along the length of the sample is approximately 153 W/mK at room temperature, which is higher than the 443 alloy matrix. Although

the graphite is approximately 50% reacted with the aluminum and contains approximately 10% porosity, the thermal conductivity is quite high. Substantially higher thermal conductivities will be possible when the molybdenum coating layer on the graphite flake is improved. The through-thickness thermal conductivity is lower because of the anisotropic nature of the graphite flake material. By aligning well-coated graphite flake within an aluminum matrix, we expect to achieve thermal conductivities as high as 300 W/mK with CTE's as low as 4 ppm/°C.

In addition to improving the adherence of the molybdenum coating, there may be several ways to improve the conductivity in the composite:

- 1) **Other types of natural graphite may exhibit higher thermal conductivity** than was tested in Phase I. Only one flake was investigated in Phase I (Flake 3061 from Asbury Graphite). This flake has silica and other impurities dispersed throughout the graphite matrix. Other flakes exist that have different graphitic structures and that originate from other parts of the world. In Phase II, we will investigate other types of flakes from various manufacturers and methods to align the flake within the composite material.

Natural graphite flake has been added to polymeric resins by researcher at Advanced Ceramics to produce composites that exhibit in-plane thermal conductivities as high as 82 W/mK. The resin itself exhibits a thermal conductivity less than 1 W/mK. In addition, the composite samples contained 25% porosity and many impurities. This suggests that the flake used exhibited very high thermal conductivity.

- 2) **Graphite flake with a smaller mesh-size is available.** These flakes exhibit lower impurity levels at a less cost. Large graphite flake was used in Phase I to investigate methods to produce good flake alignment.
- 3) **Flake Orientation.** High thermal conductivity exists within the plane of the graphite flake. However, thermal conductivity perpendicular to the flake is very low, as can

be seen in the thru-thickness conductivity measurement. The more aligned the flake is in the composite, the higher resulting thermal conductivity. Flake alignment will be further investigated in Phase II.

## **F. Raw Materials Cost Analysis**

Typical extruded aluminum alloy heat sink material is made from 6063 alloy. The alloy contains 0.2-0.6% Si, 0.35% Fe, 0.4-0.9% Mg, and other minor elements. The alloy costs approximately \$0.90/lb before extrusion and exhibits a thermal conductivity of approximately 217 W/mK.

The cost of graphite flake begins at \$0.40/lb for smaller flake and increases upwards, depending upon flake size, purity, range of mesh-size, and source. We will assume that we will use small diameter graphite flake that exhibits high thermal conductivity and costs approximately \$0.70/lb (\$1.54/kg). Using a kilogram of graphite flake as a basis, the main cost of the proprietary coating solution is the molybdenum compound used in the precursor solution. TRA has purchased the molybdenum compound from vendors for approximately \$65/kg. The price drops substantially as the quantity purchased increases.

As a basis, we will assume one pound of composite material at 40% volume fraction graphite flake. Using the unoptimized Phase I coating procedure to coat the graphite flake, the raw material cost for the molybdenum compound is approximately \$0.053 per gram of graphite flake. Therefore, the total composite material cost is approximately \$4.23/lb of Al/Gr composite material. However, the current coating procedure produces excess molybdenum by-products. If the coating procedure could be optimized to produce a molybdenum coating with a 12% weight gain over the plain flake with little or no excess molybdenum by-products, the price would reduce to \$2.03/lb composite for raw materials.

The composite material requires a substantial amount of processing in comparison to the extruded aluminum alloys. The flakes will be coated with the molybdenum precursor and heat-treated to produce the molybdenum/molybdenum carbide coating. Inexpensive methods to infiltrate the coated flake with molten aluminum alloys will be further investigated to lower these processing costs.

Although this is still substantially more than monolithic alloys, the composite material will potentially exhibit substantially higher thermal conductivity than monolithic alloys currently in use. The thermal expansion coefficient of current aluminum heat sink material is approximately 23.4 ppm/°C and exhibits a density of 2.7 g/cm<sup>3</sup>. The CTE of the composite heat sink material may be reduced to 4-5 ppm/°C with densities around 2.65 g/cm<sup>3</sup>. The aluminum composite may be used as an electronic packaging substrate. The CTE will be tailorable to meet specific electronic needs and applications, thereby justifying the cost of the composite material.

### G. Thermal Model of Composite System

A modeling study was performed using Finite Element Analysis (FEA). The program used, "Visual Stardyne," is made by Research Engineers, Inc. (Yorba Linda, CA). The objective of these modeling experiments was to determine the sensitivity of an aluminum/graphite flake composite to different thermal conductivities of the graphite flake. Aligned and randomly oriented flake is considered in the model, with graphite volume fractions between 30 and 50 volume percent. Flake thermal conductivities ranging from 250 to 350 W/mK were considered.

For the aligned flake case, the thermal conductivity, specific heat, and density of the composite material was calculated using rule-or-mixtures, i.e.:

$$X_f V_f + X_m (1 - V_f) = X_c \quad (3)$$

where  $X_f$ ,  $X_m$ , and  $X_c$  represents the particular thermal property of the fiber, matrix, and composite material.  $V_f$  is the volume fraction of aligned graphite flake within the matrix.

For the case of randomly oriented graphite flake, the theoretical study of Hatta and Taya<sup>20</sup> was used to calculate the average thermal conductivity of the composite. The graphite flakes were modeled as "penny-shaped" inclusions within the aluminum matrix, as shown in Figure 18. The half-

---

<sup>20</sup> Hatta, H. and M. Taya, "Effective Thermal Conductivity of a Misoriented Short Fiber Composite," *J. Appl. Phys.*, **58**, (7), 1985, pp. 2478-86.

thickness of the graphite flake,  $a_3$ , is assumed to be much less than the flake radius  $a_1$ . Hatta's model is analogous to Eshelby's equivalent inclusion method for elasticity.<sup>21</sup> The composite thermal conductivity for a composite containing randomly oriented inclusions is given by the following equation:

$$\frac{K_c}{K_m} = 1 - \frac{V_f(K_m - K_f)[(K_f - K_m)(2S_{33} - S_{11}) + 3K_m]}{3(K_f - K_m)^2 (1 - V_f) S_{11} S_{33} + K_m(K_f - K_m)R + 3K_m^2} \quad (4)$$

where  $S_{ij}$  are second-order tensors and are functions of the graphite flake dimensions. The equations defining these tensors and the value of  $R$  for a "penny-shaped" inclusion are as follows:<sup>22</sup>

$$S_{11} = \frac{\pi a_3}{4a_1}, \quad S_{33} = 1 - \frac{\pi a_3}{2a_1} \quad (5)$$

$$R = 3(S_{11} + S_{33}) - V_f (2S_{11} + S_{33}) \quad (6)$$

The thermal conductivity of the aluminum was assumed to be 180 W/mK with a specific heat of 0.21 cal/gK. This is a typical value for aluminum metal. The specific heat of the graphite flake was assumed to be 0.18 cal/g K. The flake half-thickness,  $a_1$ , and the flake radius,  $a_3$ , was 10 $\mu$ m and 1mm, respectively. The thermal conductivity of the flake was also assumed to be isotropic for the randomly oriented model, since Hatta-Taya model only contained solutions for isotropic penny-shaped inclusion properties. The anisotropic solution has not been published.

---

<sup>21</sup> Eshelby, J.D., Proc. Roy. Soc., **A241**, (1957), p. 376.

<sup>22</sup> Taya, M. and R. J. Arsenault, Metal Matrix Composites: Thermomechanical Behavior, Pergamon Press, Elmsford, N.Y., (1989), p. 255.

A summary of the calculated composite thermal conductivities for various flake volume fractions is shown in Table 4. The table contains calculated data for both pure aluminum, randomly-packed, and aligned flake composites. The data is also presented in graphic form in Figure 19. The thermal conductivities of the composite materials steadily increases with increasing flake thermal conductivity and volume fraction. Thermal conductivities for the randomly-packed and aligned flake composites are very similar for a given volume fraction, mainly because isotropic flake properties were used in the model. The thermal conductivity of the random model would be lower if anisotropic values for the flake were used. The thru-thickness thermal conductivity of flake is approximately 25-50 W/mK.

The effectiveness of the composites that exhibit higher thermal conductivity can be illustrated by finite element analysis. In the model, we assume that a 2" x 2" x 0.060" aluminum plate exhibits a thermal conductivity of 180 W/mK. One edge of the plate is maintained at 67°F (20°C). A heat source of 20 W/cm<sup>2</sup> is placed on the surface of the plate opposite to the cooled edge. The steady-state heat distribution for aluminum is shown in Figure 20. This can be compared with Figures 21 and 22 which show the steady-state temperature distribution of composite plates containing 50 volume percent aligned graphite flakes with thermal conductivities of 250 and 350 W/mK, respectively (Cases D and E in Table 4). The temperatures are much lower as would be expected for the composites with higher thermal conductivities. The maximum temperature of the aluminum case is approximately 84°C, while those of the aligned composites for cases D and E are approximately 81 and 78°C, respectively.

## VII. Future Work

- 1) Higher conductivity aluminum alloys will be investigated.
- 2) Coating techniques will be investigated to improve the chemical bonding of the molybdenum coating on the surface of the graphite flake.
- 3) Techniques will be investigated to further improve the alignment of the graphite flakes within the composite matrix.
- 4) Techniques to lower the wetting transition temperature of aluminum and aluminum alloys will be investigated.
- 5) Methods will be investigated to economically produce molten aluminum/graphite slurries.
- 6) Techniques to completely surround the composite with aluminum during cast will be investigated to improve the corrosion resistance of the composite material.

## VIII. Conclusions

The Phase I work and successes can be summarized as follows:

- 1) Natural graphite flake was successfully coated with a submicron layer of molybdenum/molybdenum carbide.
- 2) Methods were developed to successfully vacuum infiltrate the molybdenum-coated flake with molten aluminum alloys.
- 3) The molybdenum coating protected graphitic surfaces from significant chemical reaction with liquid aluminum-silicon alloys at 1000°C for periods longer than 20 minutes. Uncoated graphite reacted to form  $Al_4C_3$  and severely degraded when infiltrated under the same conditions. The protection may be a result of a thin layer of molybdenum disilicide forming on the graphite surface. This protection should improve the resistance to Al/Gr composite exfoliation in marine environments, typically caused by chemical reaction with the aluminum carbide with water to form voluminous aluminum hydroxide by-products.
- 4) The composites were shown to exhibit densities approximately the same as aluminum.
- 5) The thermal expansion coefficients of the Al/Gr composites were significantly lower than the base aluminum-silicon alloy. The CTE of the composite may be tailored to specific applications by adjusting flake volume fraction and orientation.
- 6) The in-plane thermal conductivities of the composite material were found to be higher than the base aluminum-silicon alloy. Higher conductivity alloys should produce further improvements.
- 7) Extrusion techniques were investigated to align graphite flake to a preform with almost 50 volume percent flake. These alignment processes suggest that a molten aluminum composite slurry may be pressure cast into dies to align the graphite flakes within the composite matrix.

## IX. Tables

**Table 1- Weight Percent of Impurities in #1 Flake and 3061 Graphite Flake from Asbury Graphite.**

Oxide	Weight Percent in Flake	
	#1 Flake	3061
Silicon Dioxide	2.40	0.14
Aluminum Oxide	0.47	0.11
Iron Oxide	0.80	0.09
Calcium Oxide	1.62	0.20
Magnesium Oxide	0.86	0.07
Sulfur Trioxide	0.77	0.36
Other	0.13	0.03

**Table 2- Measured CTE on Composite Samples**

Sample	Packing Method	Approx. Vol. %	CTE Range (ppm/C)
443	Alloy	N/A	22.1
A	Dry-packed	25%	14.0-14.8
B	Dry-packed	25%	14.1-14.5
C	Binder	20%	16.0-16.7
D	Wet-packed	30%	11.5-12.0

**Table 3-** Flash Thermal Diffusivity Results for Al/Gr Composites. Sample D (30% Graphite) was tested at TPRL. Sample B (25% Graphite) was tested at ORNL.

Sample	Orientation	Temp (°C)	$C_p$ (W sec/gm/K)	Diffusivity (cm <sup>2</sup> / sec)	K (W/mK)
B	In-plane	25	0.781 (est.)	0.439	88
D	Thru-thickness	23	N/A	N/A	51
	In-plane	23	0.832	0.689	153
	“ ”	50	0.875	0.655	153
	“ ”	75	0.905	0.623	150
	“ ”	100	0.931	0.591	147

**Table 4-** Calculated Composite Thermal Conductivity as Function of Flake Thermal Conductivities and Flake Volume Fraction.

Case	Flake Properties		Thermal Conductivity (W/mK)	
	$V_f$	$K_f$ (W/mK)	Random	Aligned
Aluminum	--	---	---	(180)
A	0.3	250	200	201
B	0.3	350	225	231
C	0.3	450	248	261
D	0.5	250	213	215
E	0.5	350	257	265
F	0.5	450	299	315

## **X. Figures**

(Beginning next page)

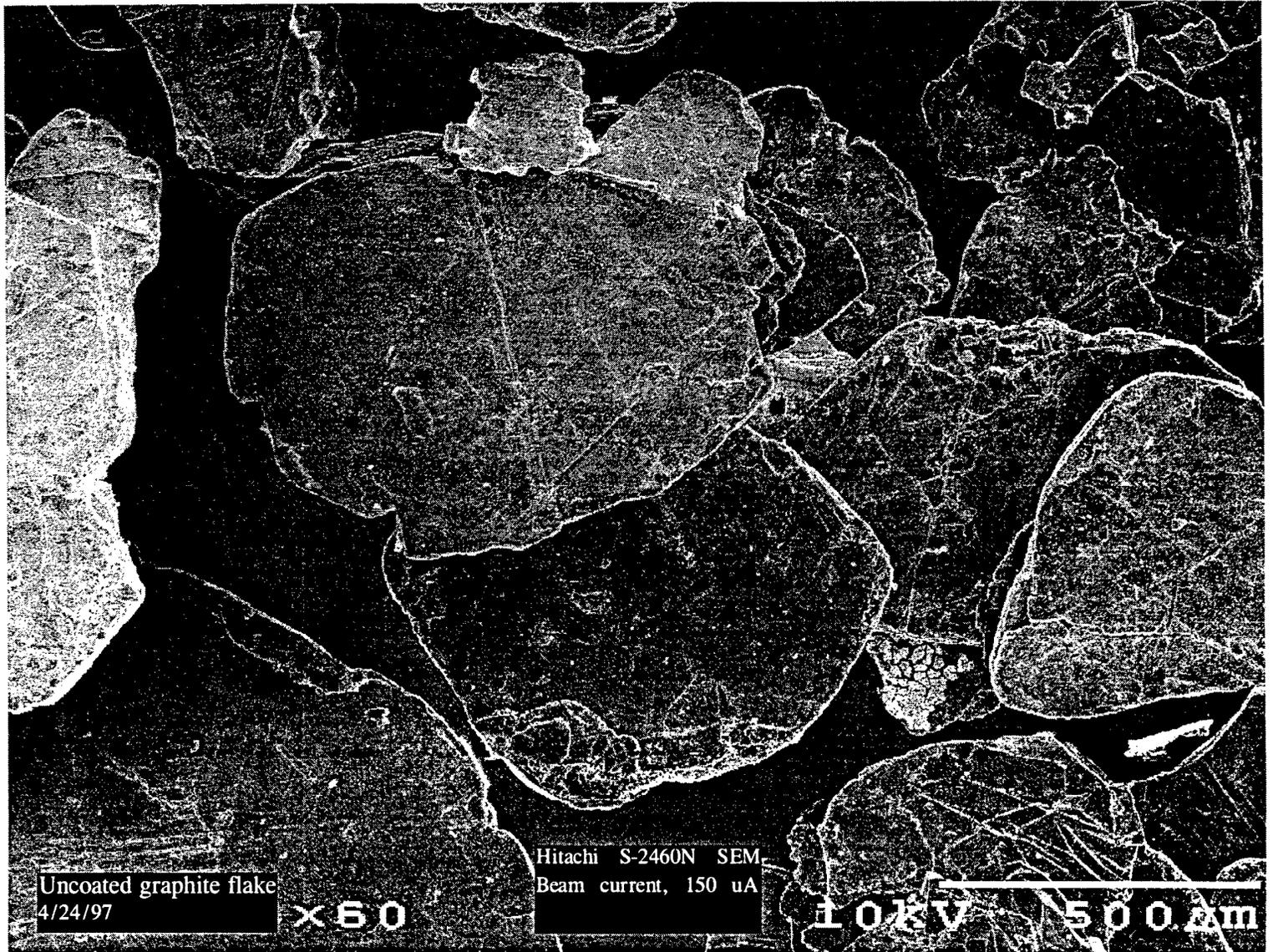
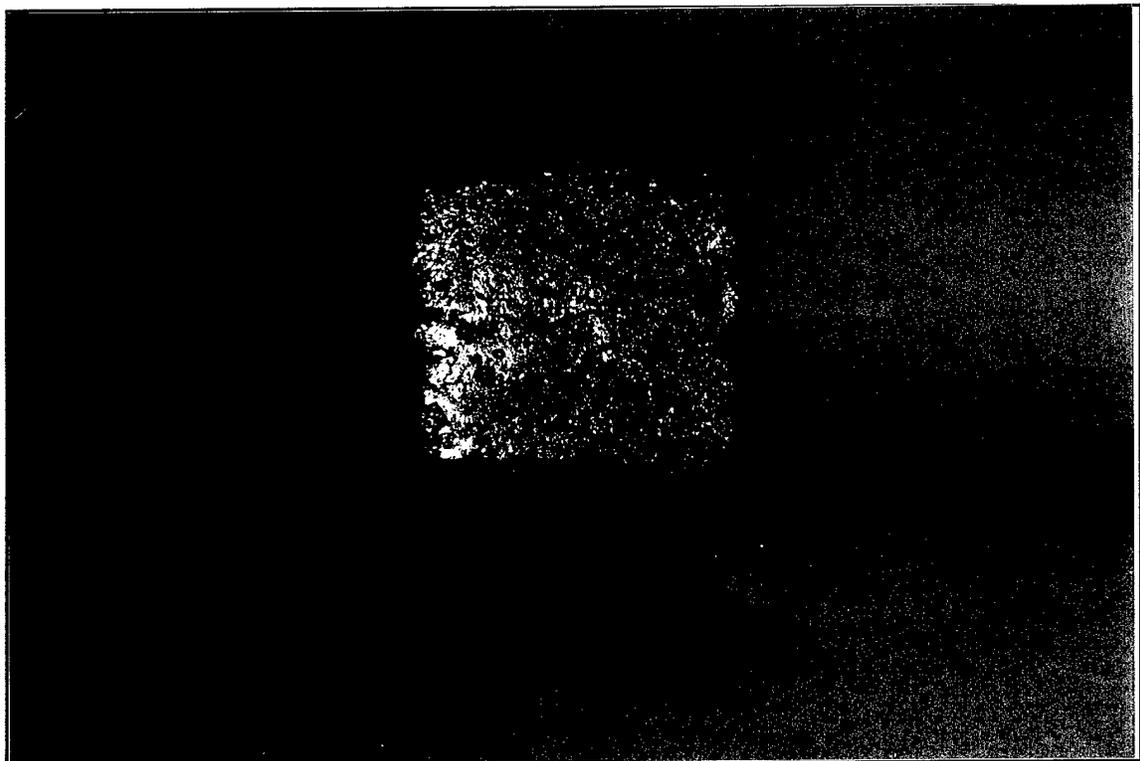


Figure 1- SEM Micrograph of 3061 Graphite Flake.



**Figure 2-** Molybdenum-Coated 3061 Graphite Flake Infiltrated with Copper

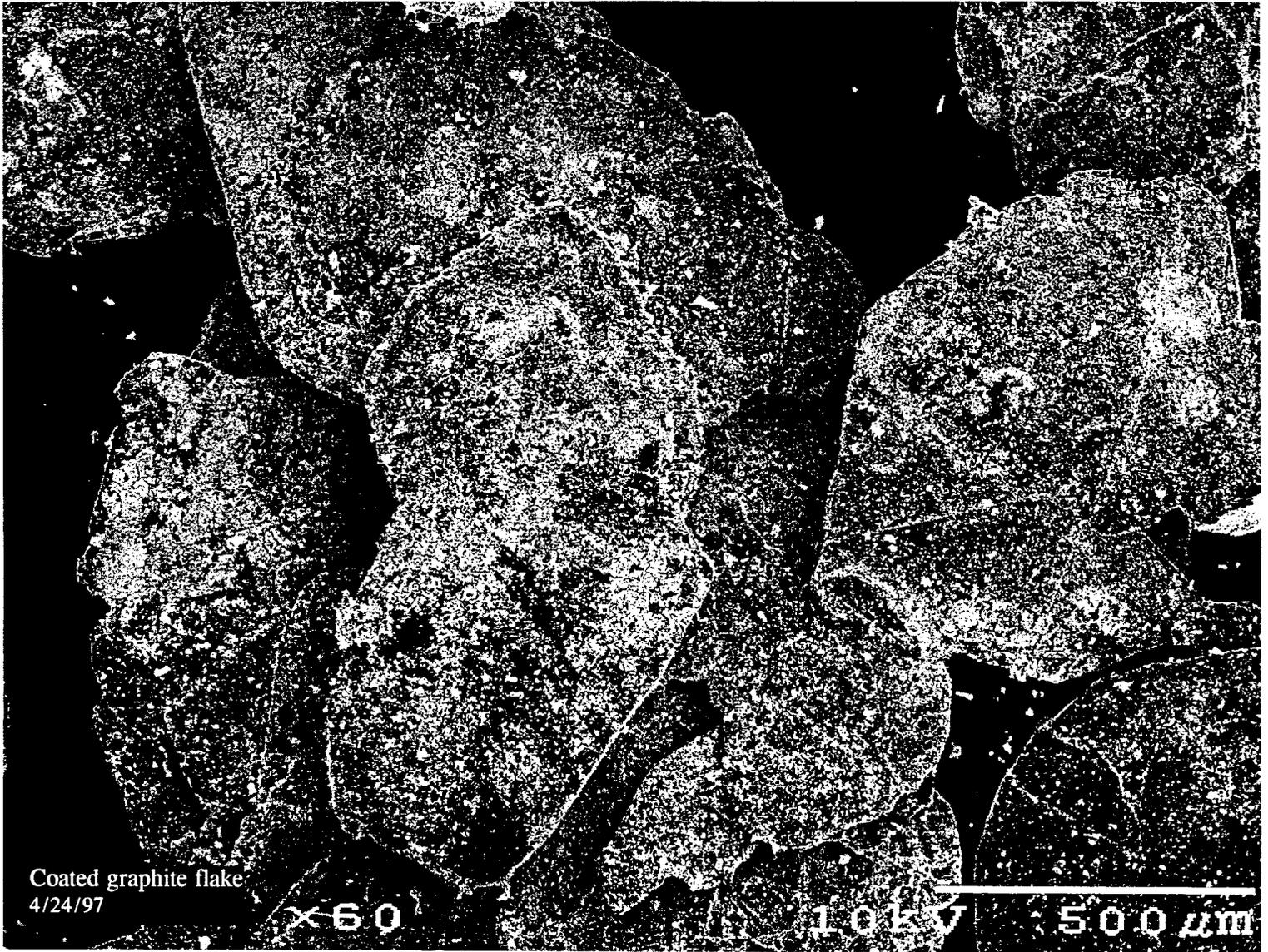


Figure 3- SEM Photograph of Molybdenum-Coated Graphite Flake

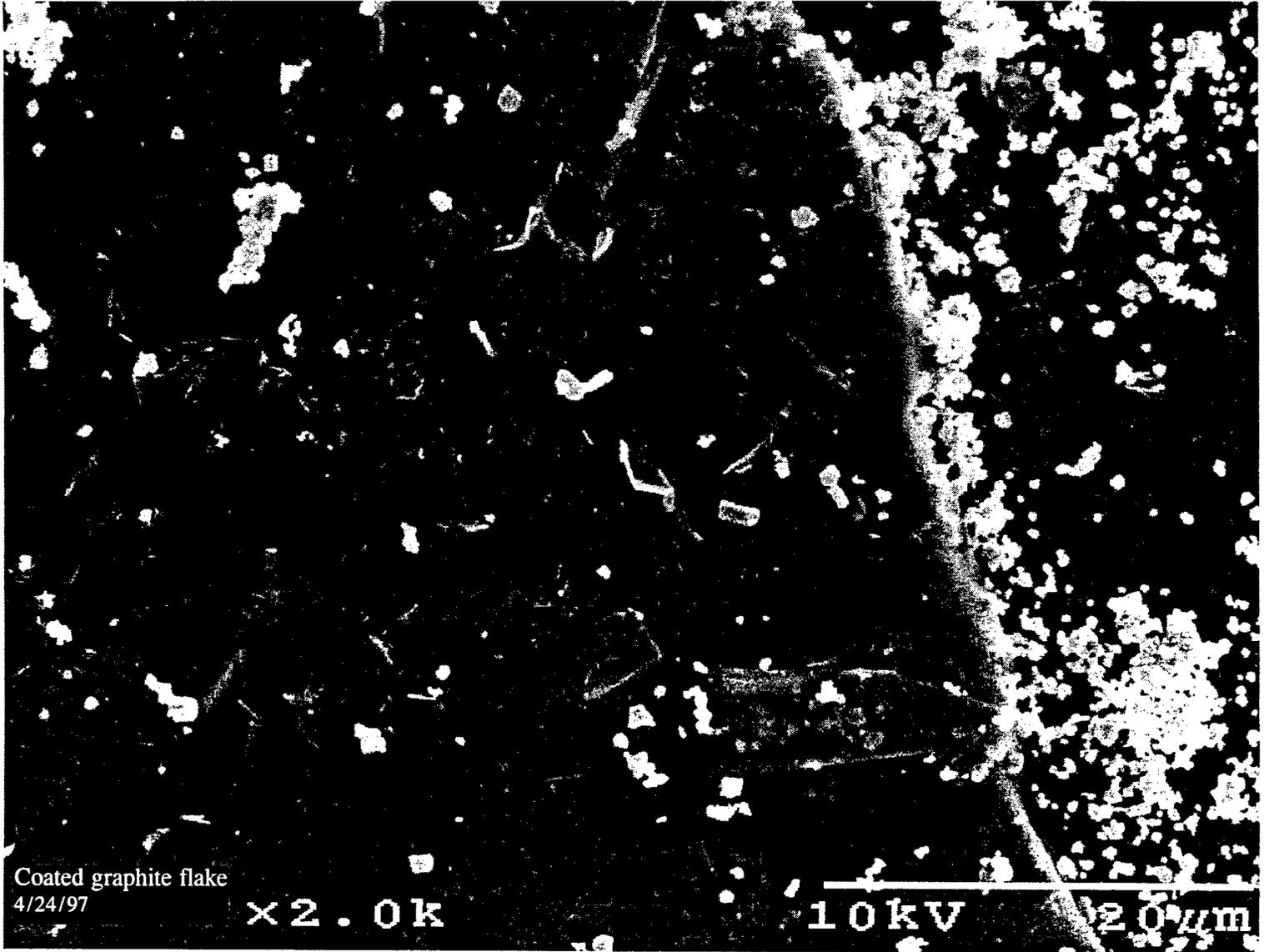
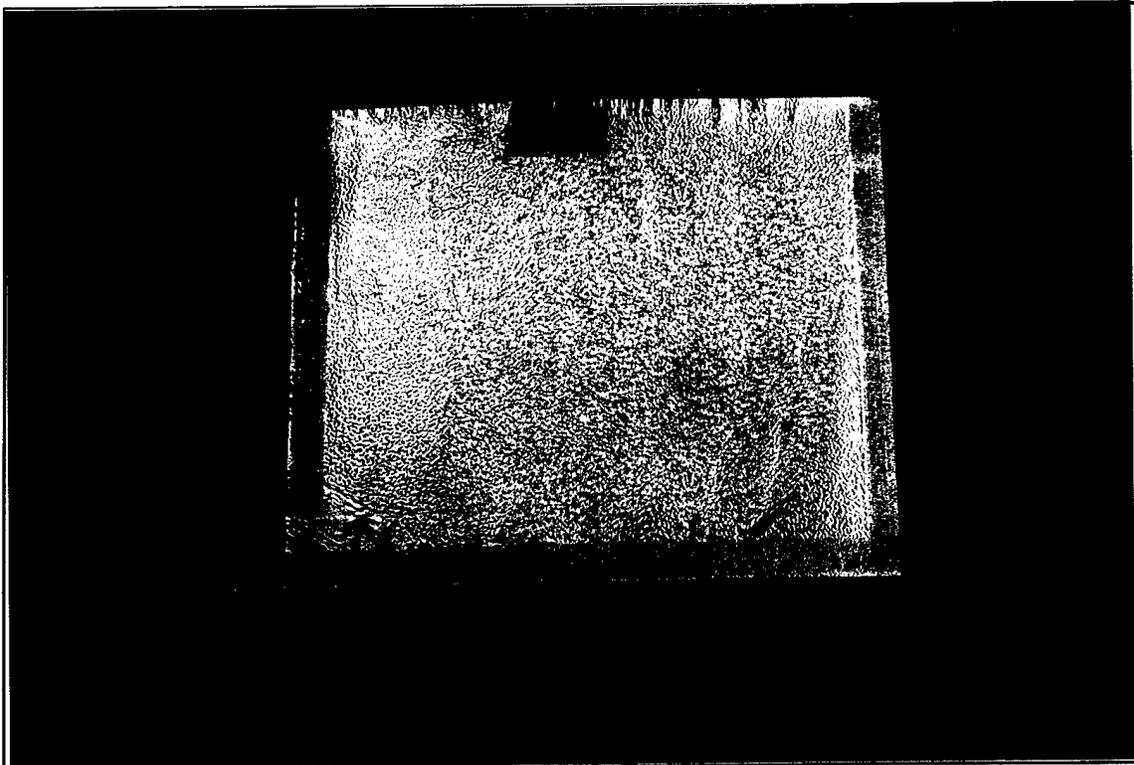
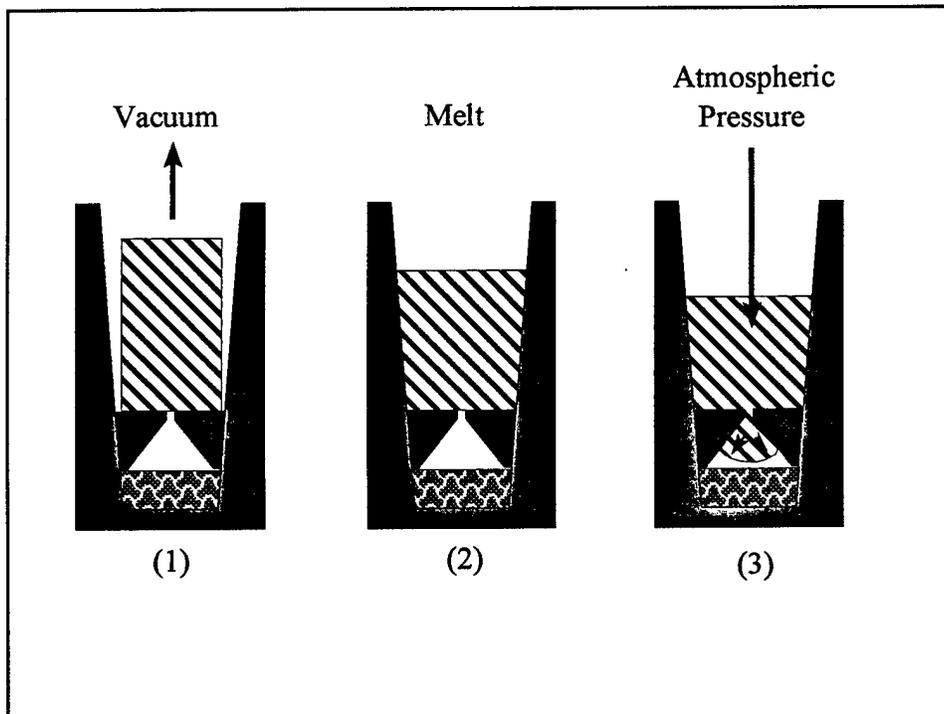


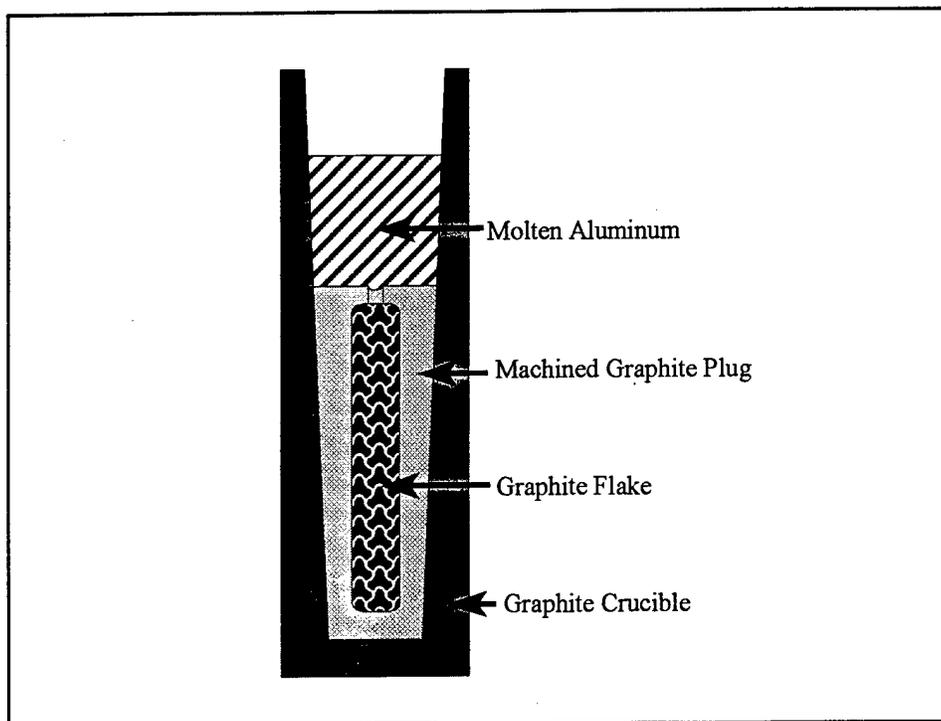
Figure 4- Close-up of Molybdenum-Coated Graphite Flake



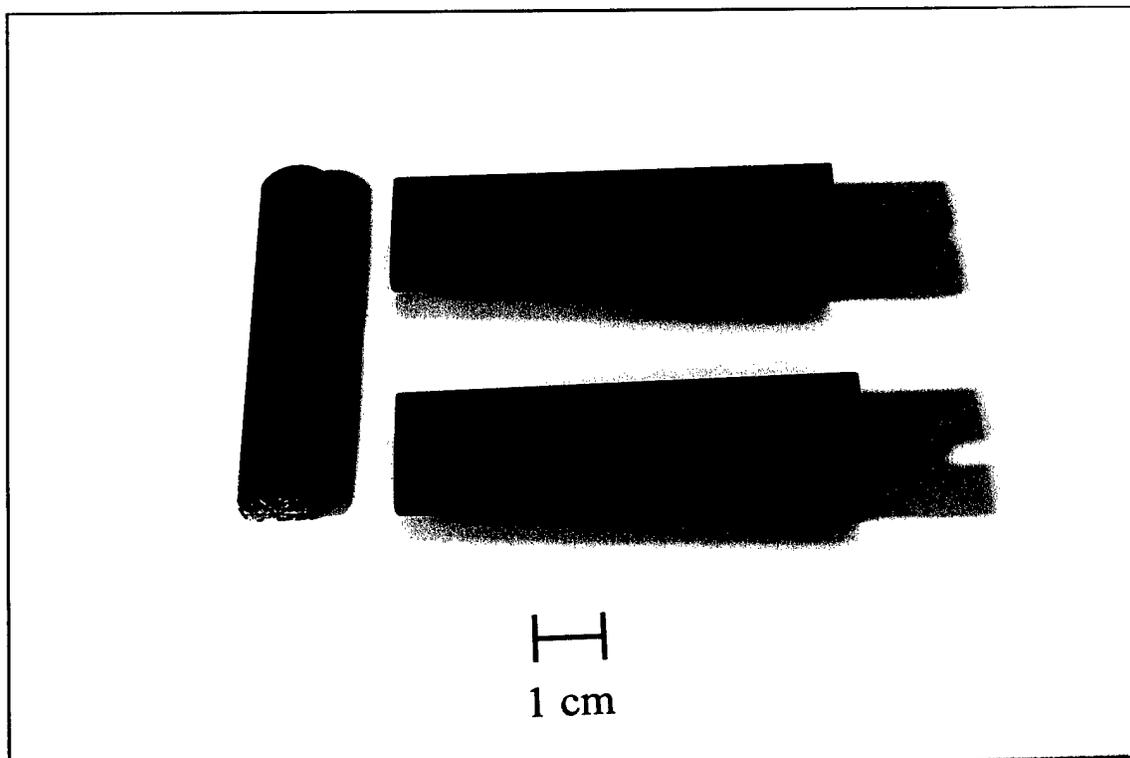
**Figure 5-** Aluminum Foil Vacuum Bag Ultrasonically Welded on Three Sides.



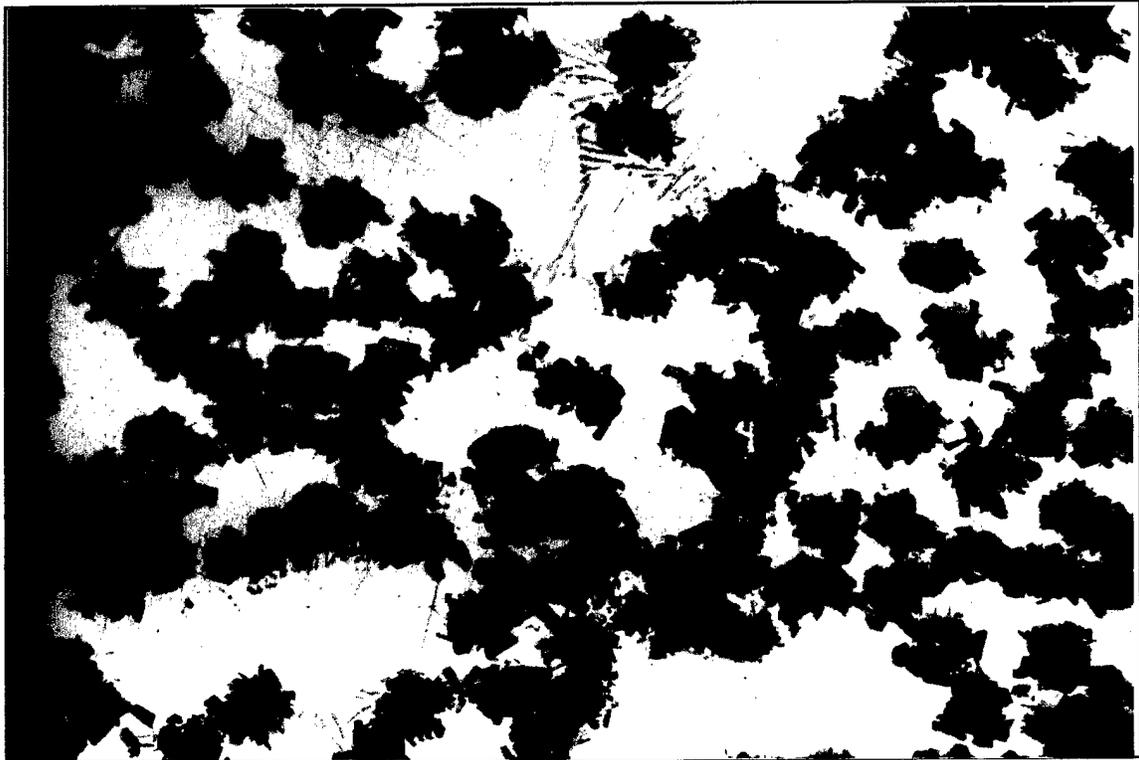
**Figure 6-** Process used to Vacuum Infiltrate Coated Flakes with Molten Aluminum Alloy.



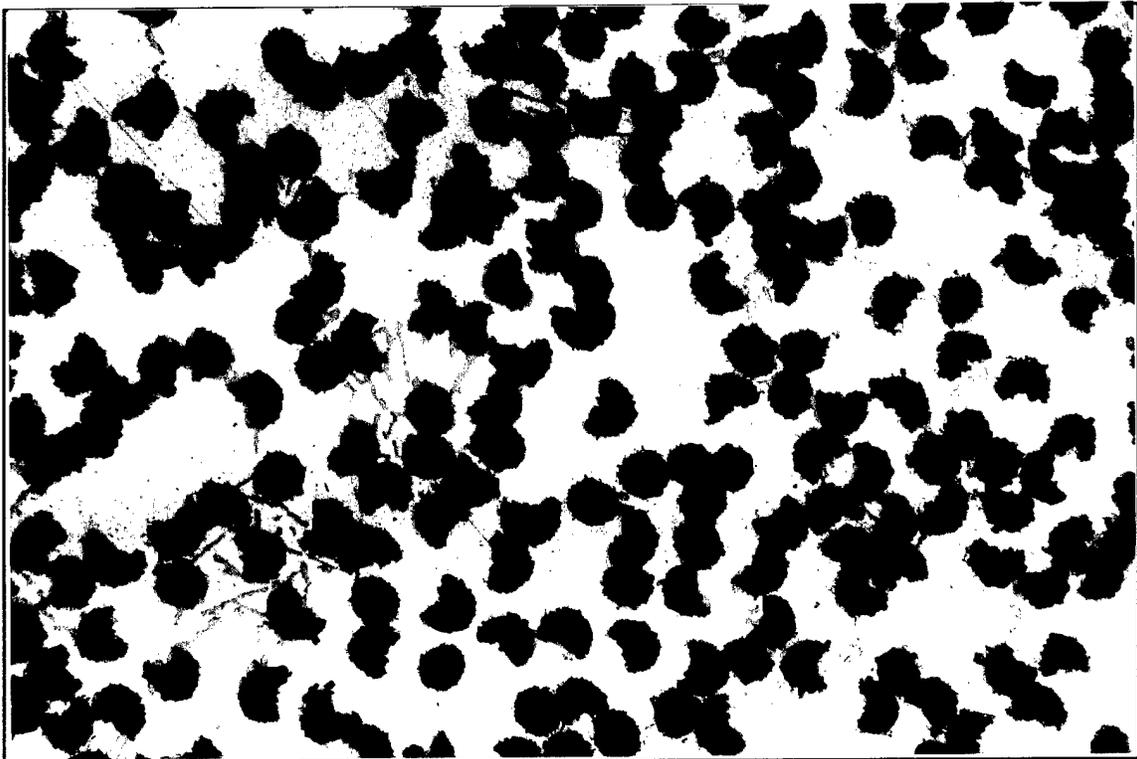
**Figure 7-** Configuration Used to Make Long CTE Specimens



**Figure 8-** Al/Gr Composite (2.0" long) with Tapered Graphite Die.



**Figure 9-** Uncoated EWC-600 Graphite Cloth Infiltrated with 443 Aluminum-Silicon Alloy and Held for 20 Minutes at Temperature. Uncoated Graphite Cloth Severely Reacted with Aluminum Matrix. (Scale: 1 cm = 20 $\mu$ m).



**Figure 10-** Molybdenum-Coated Graphite Fiber Cloth Infiltrated with 443 Al-Si Alloy at 1000°C and Held for 20 Minutes. Graphite Fibers Remain Virtually Unreacted. (Scale: 1 cm = 20 $\mu$ m).

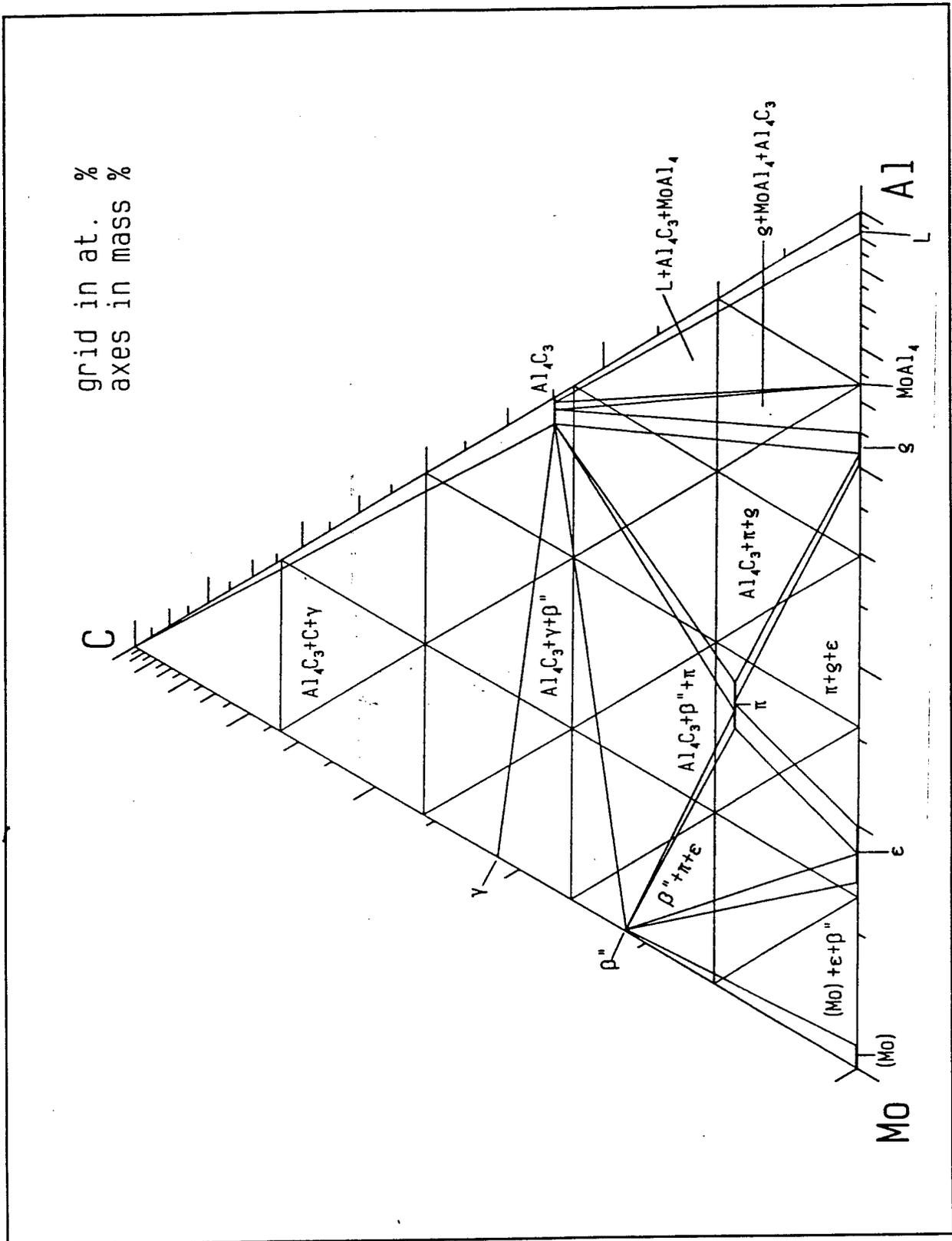


Figure 11- Mo-Al-C Ternary Phase Diagram at 1000°C



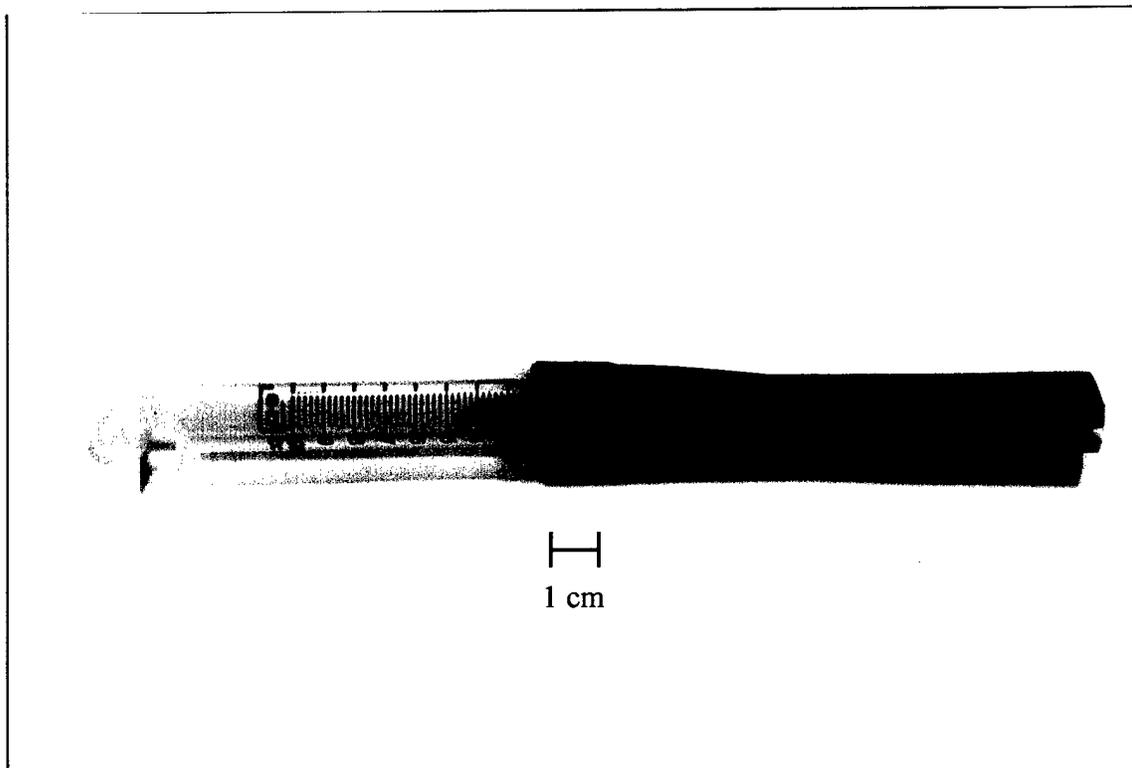
**Figure 12-** Composite Containing Molybdenum-Coated Graphite Flake in 443 Alloy Matrix. Protective Molybdenum-Coating Prevented Graphite Flake Reaction with Matrix. (Scale: 1 cm = 40 $\mu$ m).



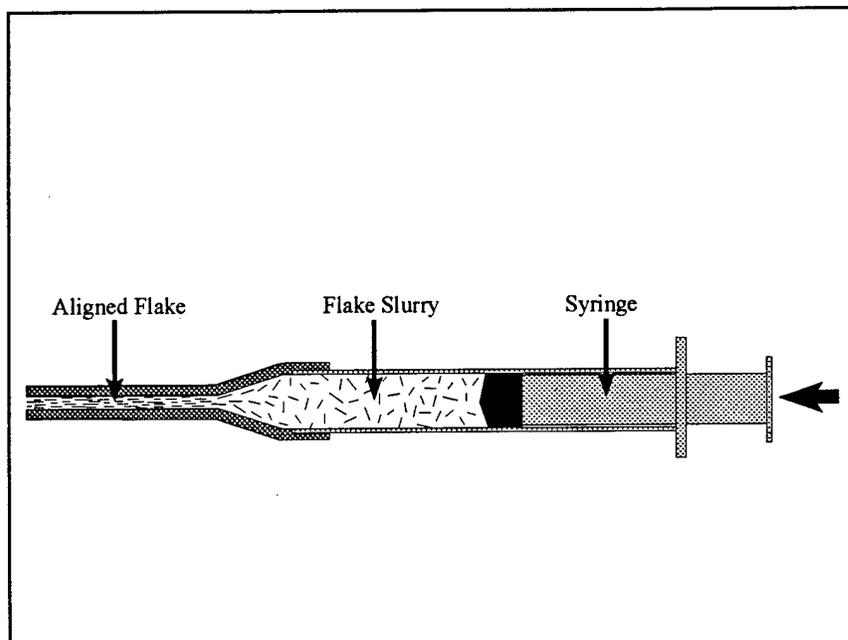
**Figure 13-** Micrograph of Al/Gr Composite (Sample B). Significant Flake Reaction Occurred Because of Defective Molybdenum Coating. (Scale: 1cm = 40 $\mu$ m)



**Figure 14-** Microstructure of Al/Gr Composite (Sample D). Less Reaction with Flake Resulted in Higher Thermal Conductivity and Lower CTE. (Scale: 1cm = 80 $\mu$ m).

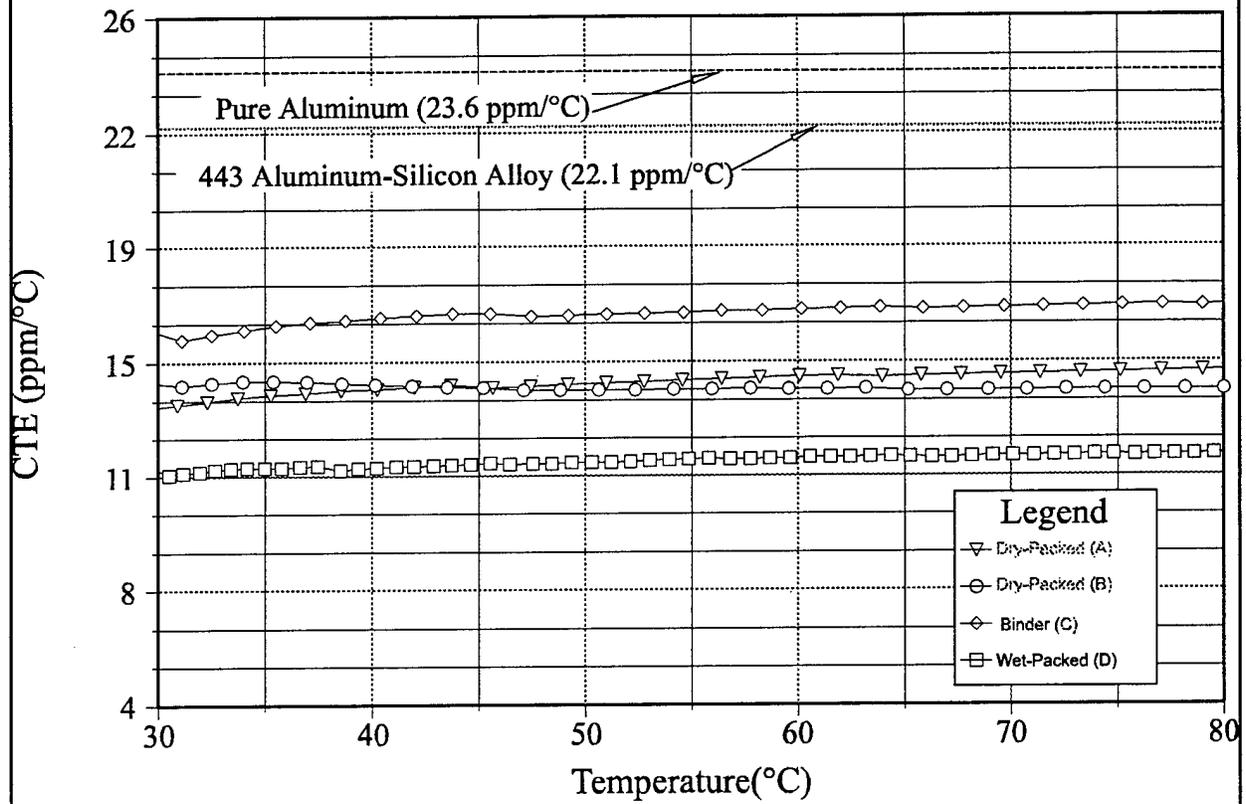


**Figure 15-** Extrusion Device Used to Align Graphite Fibers.

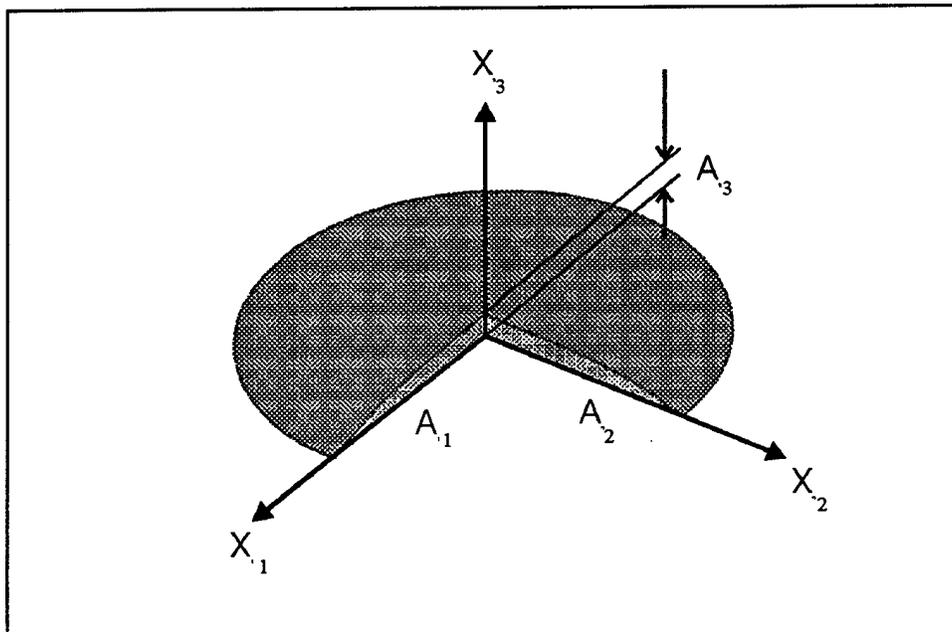


**Figure 16-** Alignment of Graphite Flakes By Extrusion Process

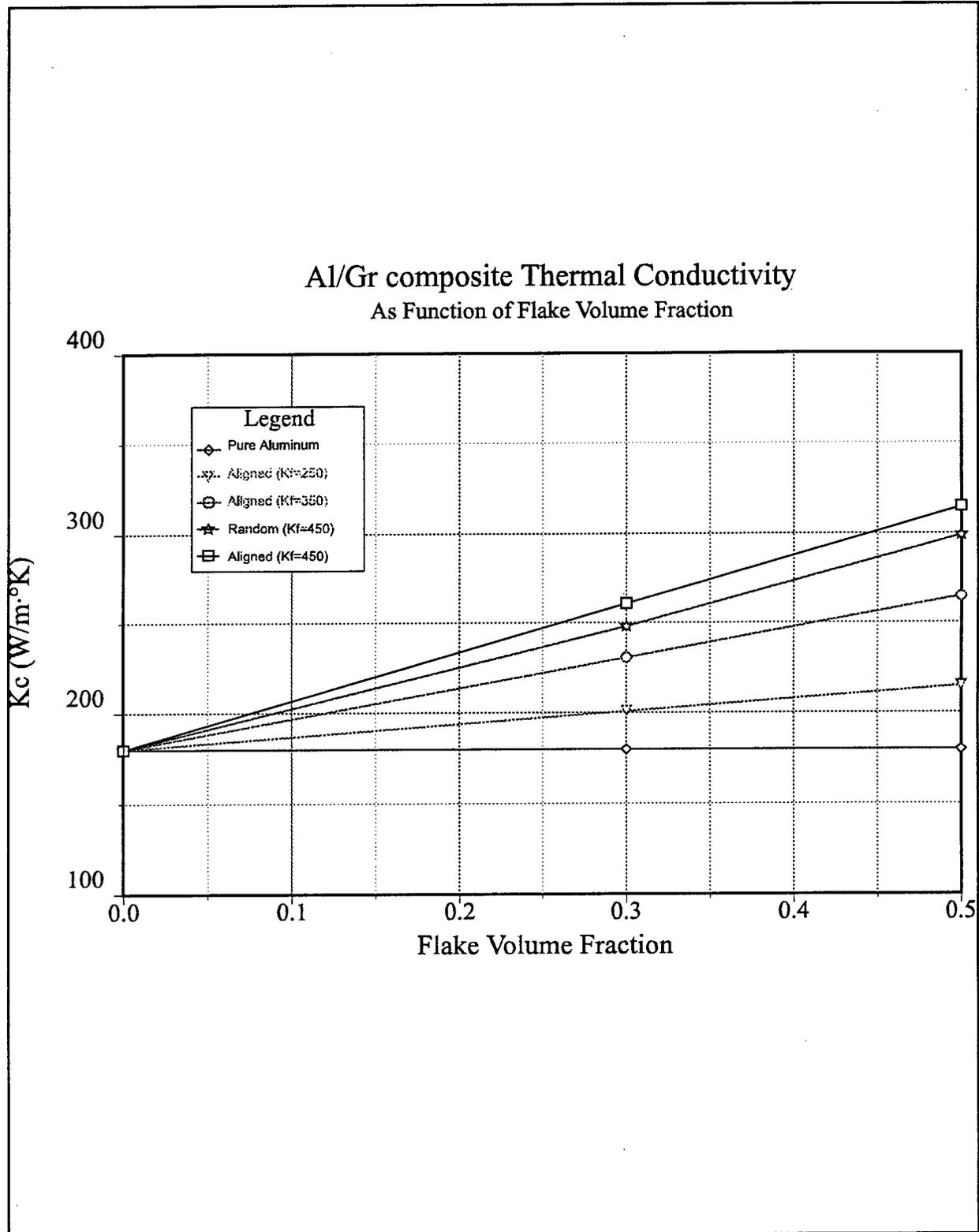
### CTE of Al/Gr Flake Composite Samples



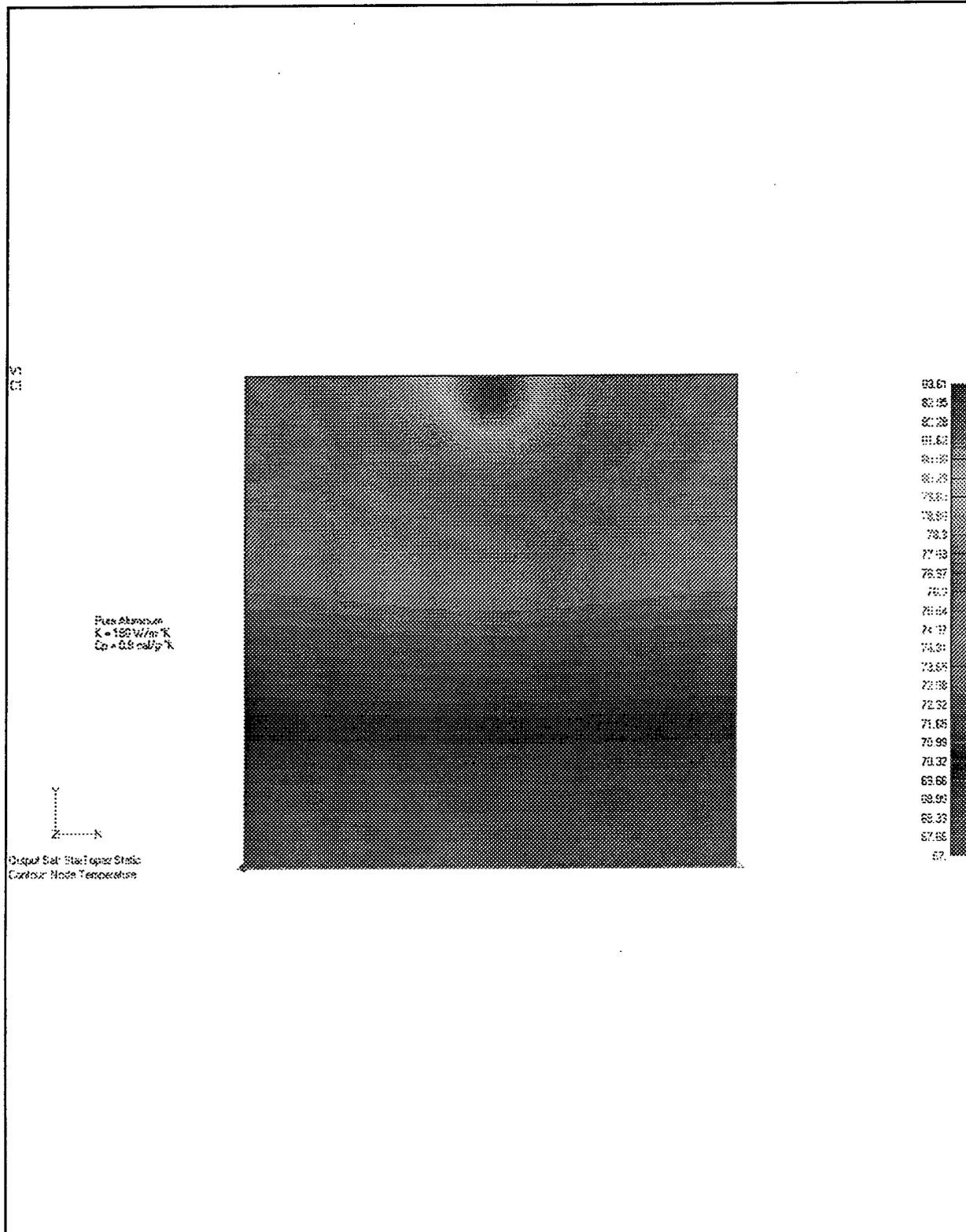
**Figure 17-** Experimental Thermal Expansion Coefficient of Al/Gr Composites Compared to Alloy 443 and Pure Al as a Function of Time.



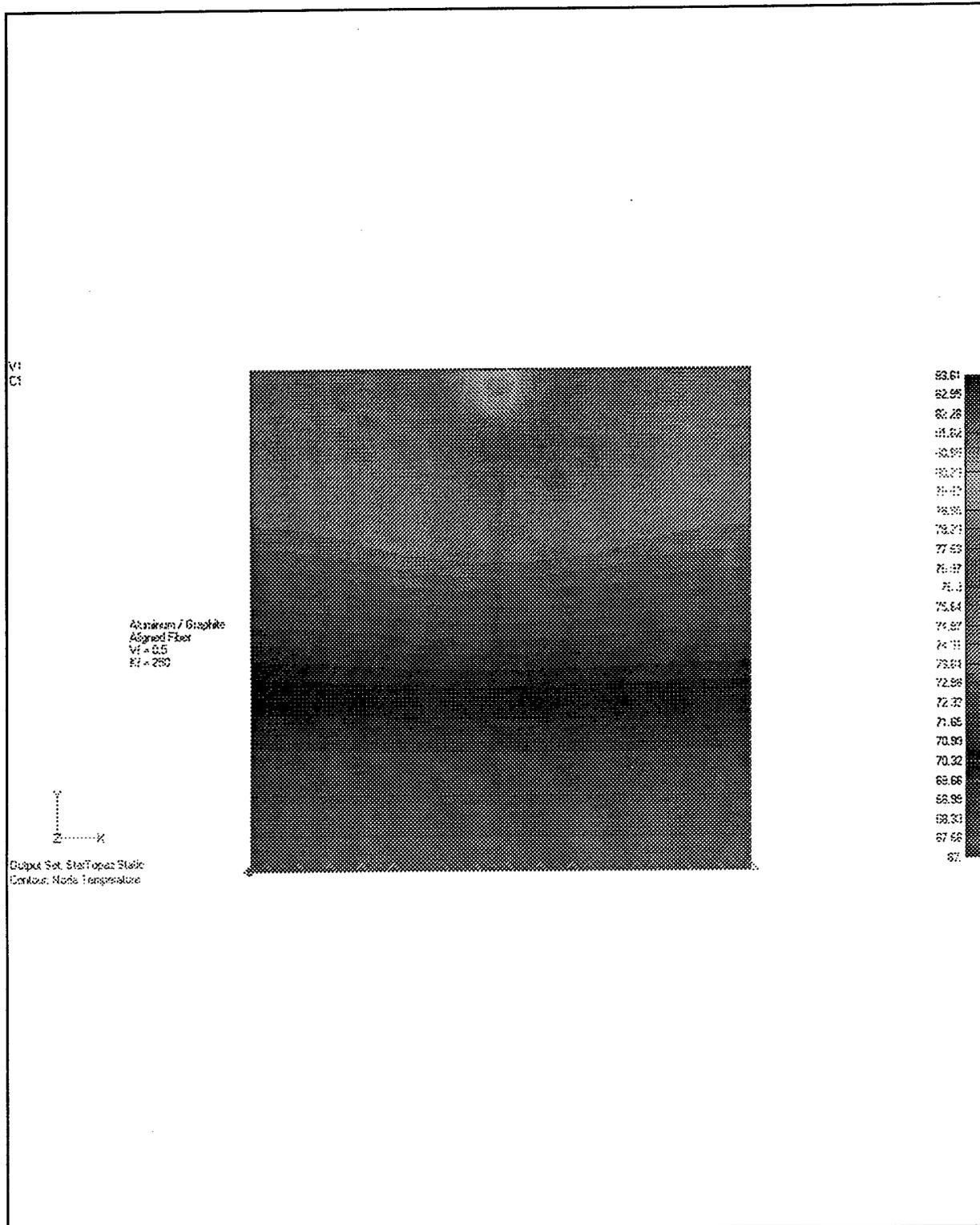
**Figure 18-** Dimensions of “Penny-Shaped” Inclusion used in Modeling Composite Randomly-Oriented Graphite Flake.



**Figure 19-** Calculated Thermal Conductivity of Al/Gr Composites for Randomly Packed and Aligned Flakes as a Function of Flake Volume Fraction and Thermal Conductivity.



**Figure 20-** Steady-State Temperature Distribution for Aluminum Plate with  $20 \text{ W/cm}^2$  Heat Source on Surface and Bottom Edge Maintained at  $20^\circ\text{C}$ . ( $K_x = 180 \text{ W/mK}$ ).



**Figure 21-** Steady-state Temperature Distribution of Al/Gr Composite Plate with  $20 \text{ W/cm}^2$  Heat Source and Bottom Edge Maintained at  $20^\circ\text{C}$ . ( $V_f = 0.5$ ,  $K_{\text{flake}} = 250 \text{ W/mK}$ , and  $K_{\text{comp}} = 215 \text{ W/mK}$ ).

