CONTROL OF THERMAL EXPANSION COEFFICIENT OF A METAL POWDER COMPOSITE VIA CERAMIC NANOFIBER REINFORCEMENT

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ABSTRACT

Solder is used in nearly all electronic packages to provide mechanical, electrical and thermal contact between various components. The mismatch between the components’ coefficient of thermal expansion results in thermal stresses which can damage components or connections and render the circuit board useless. In order to reduce this mismatch, a novel fabrication method was developed to produce composites of solder and ceramic reinforcement are presented. Composites were prepared by uniaxial compression of 63Sn/37Pb solder powder and various morphologies of titania reinforcement. A solution of poly(vinyl pyrrolidone), ethanol and tetraisopropyl titanate was used to produce beaded nanofibers; acetic acid was added to the solution in order to lower the dielectric constant of the solution and produce smooth nanofibers. Ultrasonication was used to cut the calcined, electrospun nanofibers to consistent lengths of about 6μm. Optical microscopy, electron microscopy and x-ray mixture of 80wt% spherical beaded titania (3.5μm diameter) with 20wt% cylindrical nanofibers (400nm diameter). A 25% reduction in the coefficient of thermal expansion of the composite
was achieved regardless of the shape, size or quantity of reinforcement. The melting and freezing points of the composite samples were not statistically different from that of pure solder but the specific gravity was lowered by about 1.5%.

During reflow it was observed that the majority of the filler was expelled from the molten solder core. The differences in density between the filler and solder provide a buoyant force that tends to expel the less dense titania from the more dense molten solder. A force balance on a rigid cylinder floating at a liquid-gas interface revealed that the filler is dominated by surface tension forces; once the filler reaches the surface of the molten solder its equilibrium position is located primarily in the surrounding gas. Therefore a novel recommendation is presented to investigate neutrally buoyant filler in order to prevent filler expulsion during reflow.
DEDICATION

For Tosh.
I wish to thank Mr. Mathew Isenberg for his valued support and numerous suggestions throughout the development of this thesis, as well as for lending me the use of his motto. To Dr. George Chase, I thank you for putting up with my frequent and occasionally random inquiries. I would further like to thank Mr. Dan Scheiman at NASA for graciously volunteering his time for sample analysis. Finally, I offer my thanks to my advisor, Dr. Edward Evans. I appreciate the support and suggestions, but most of all the trust inherent in allowing an atmosphere of friendship and equality rather than simply teacher and student.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
</tr>
</tbody>
</table>

## CHAPTER

I. FUNDAMENTAL QUESTIONS .................................................................................. 1

II. MOTIVATION ........................................................................................................ 6

2.1 Joint Munitions Technology Support Program (JMP) ........................................ 7

2.2 Joint NASA/DoD Pb-Free Electronics .................................................................. 8

2.3 Nvidia GE84 Graphics Processor Unit .............................................................. 9

2.4 Microsoft Xbox 360™ ....................................................................................... 10

III. CIRCUIT BOARD BASICS ................................................................................... 12

3.1 The Printed Circuit Board .................................................................................. 12

3.2 Lead Connections ............................................................................................. 16

3.3 Methods of Soldering .......................................................................................... 22

3.4 Solder Composition and Properties ..................................................................... 36

IV. LITERATURE SURVEY ......................................................................................... 44

4.1 Aluminum Composites ....................................................................................... 45
4.2 Solder Composites ................................................................. 49
4.3 Summary of Findings ............................................................. 56

V. EXPERIMENTAL PROCEDURES .................................................. 58
  5.1 Titania Nanofiber Electrospinning ........................................ 58
  5.2 Ultrasonication of Calcined Titania Nanofibers ..................... 65
  5.3 Powder Composite Preparation ........................................... 68
  5.4 Determination of Coefficient of Thermal Expansion .......... 72
  5.5 Reflow of Composite Samples ............................................ 73

VI. RESULTS AND DISCUSSION ..................................................... 78
  6.1 Titania Characterization ..................................................... 78
  6.2 Specific Gravity Measurements .......................................... 93
  6.3 Optical Microscopy .......................................................... 95
  6.4 Thermomechanical Analysis .............................................. 99
  6.5 Reflow .......................................................... 120
  6.6 Filler Expulsion ............................................................ 127

VII. SUMMARY AND CONCLUSIONS ............................................. 144

REFERENCES ........................................................................... 148

APPENDICES ............................................................................. 159
  APPENDIX A. ARCHIMEDEAN DENSITY MEASUREMENTS .......... 160
  APPENDIX B. ULTRASONICATION OF TITANIA NANOFIBERS .... 163
APPENDIX C. DERIVATION OF $F'_\text{net}$ .............................................. 170

APPENDIX D. COPYRIGHT PERMISSIONS............................................. 180
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.1</td>
<td>Viscosity of solder paste as it varies with weight percentage of metal loading [89H1, pg61]</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Pb-free alloys and their advantages and disadvantages, arranged by melting point. Collected from [06G1, pg84-91]</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Summary of aluminum composites reviewed in this text. The methods are representative of the primary composite fabrication methods and are generally performed with only slight modification; descriptions of each method are provided in the text.</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Summary of solder composites reviewed in this text. The composites are arranged by the type of solder matrix.</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Parameters for titania nanofiber electrospinning process. Asterisked values represent standard observations of uncontrolled parameters; non-asterisked values are equipment settings.</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Titania nanopowder and nanofiber concentrations used in this study. Filler amounts are weight percentages</td>
</tr>
<tr>
<td>6.4.1</td>
<td>Material properties used for Figure 6.4.3 and their references</td>
</tr>
</tbody>
</table>
6.6.1 Densities of commonly encountered materials. Densities determined in this work were measured via Archimedes’ Method.................................................................134

6.6.2 Surface tensions of various solders and ceramic materials. The last four entries are for solid ceramic materials whereas the others are for molten solder alloys. ........................................139

6.6.3 Commercially available ceramics sorted by density which may be used to match the density of the filler to that of the metal alloy. Values in italics are from [00A1]; all others are from [02E2]. .................................................................142
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Decision hierarchy for nanocomposite study. The performance branch is associated with those parameters affecting long-term performance; the processing branch is associated with those parameters affecting the industrial processing of the composite.</td>
</tr>
<tr>
<td>2.3.1</td>
<td>NVIDIA’s GeForce 8500M-GT graphics processor unit [08L1]. The image on the right is the mounting surface; each point represents a soldered connection.</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Standard printed circuit board (PCB) layers and features. Labels: (a) solder mask, (b) copper surface pads, (c) core material, (d) blind via, (e) buried via, (f) prepreg material, (g) subsurface printed copper path, (h) through via.</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Optical micrograph (100x) of a through-via and surface pad cross-section on a PCB. This via was not needed for the desired product and so was filled with solder; the inner copper via coating is clearly visible.</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Typical pin-through-hole (PTH) components (b). Perspective (a) reveals the increased height of the components and exposure of the pins; perspective (c) is the underside of the PCB revealing the exposed pins on the opposite side of the board.</td>
</tr>
</tbody>
</table>
3.2.2 A typical gull-wing SMT device. The larger component (a) is raised slightly from the surface of the PCB whereas the smaller components (b) are nearly flush. The inset is a profile of a gull-wing lead.................................19

3.2.3 An example of a lead-less SMT device. The inset profile indicates that the devices rests smoothly on the PCB. In the image, solder has been applied to the metallic end-caps. .................20

3.2.4 A component utilizing a BGA for attachment, separated into the PCB and chip components. Note the significantly higher connection density compared to PTH or gull-wing attachments..............................................................22

3.3.1 Diagram of wave soldering for PTH components. The pump (a) supplies a continuous fountain of molten solder (b) to coat the underside of the PCB (c). The PCB is moved through the fountain to solder all PTH components leaving a conical cap of solder (d). .................................................................23

3.3.2 Chemical structure of abietic acid, the primary component of rosin. The condensed ring structure, carboxylic group and double bonds within are characteristic of the carboxylic acids found in solder flux.........................................................28

3.3.4 Conceptual diagram depicting stresses and shear arising from CTE mismatch between components. When heat is applied to a composite with materials of different CTE’s the composite exhibits the bending shown above (exaggerated). The stresses and shear are referred to as thermal stresses. 31

3.3.5 Basic vapor phase reflow setup. (With permission, from Hinch, Handbook of Surface Mount Technology, Pearson Education, Harlow, Essex 1988, pg314.) 34

3.3.6 General structure of a fluorinated hydrocarbon used in vapor phase reflow. The molecular structure typically varies in the number of carbons present due to variations in manufacturing. 35

3.4.1 Phase diagram for the Sn/Pb system [06S2, pg326]. Note the eutectic composition (Alloy 1 line) with a melting point of 183°C and a composition of 61.9wt% Sn and 38.1wt% Pb. At the eutectic point three phases can coexist: liquid (61.9wt%Sn), α (19.2wt%Sn) and β (97.5wt%Sn). (With permission, from Smith, Hashemi, Foundations of Materials Science and Engineering, 4th Ed, New York, NY: McGraw-Hill, 2006.) 38

4.2.1 Publication history for search terms solder and composite as reported by the ISI Web of Knowledge [09T1] in June 2009. Highlighted in green are increases that may be correlated with the establishment of RoHS in 2002 [03E1] and its enactment in 2006 [05R2]. 50

4.2.2 Microhardness data from Lin et al. [03L2] for a titania-solder composite. The F-test (P-value = 0.61) and Tukey’s HSD procedure (red line) show no significant difference between the reported results. This is likely due to filler expulsion during reflow as described in Section 6.6. 54
5.1.1 Electrospinning apparatus for titania nanofiber electrospinning. (a) Syringe (b) Syringe pump (c) Support structure (d) Rotary power supply (e) DC high-voltage supply (f) Needle tip. ................................................................. 60

5.2.1 Ultrasonication setup used for sonication of titania nanofibers in ethanol. (a) Coolant outlet (b) Coolant inlet (c) Coolant water bath (d) Sonication vessel (e) Sonication horn (f) Ultrasonic converter. The solution to be sonicated is dyed green here to provide contrast to the coolant bath. .................................................. 67

5.3.1 100x magnification of the eutectic solder powder used for composite fabrication. Mesh size for this solder is -300/+525, or about 25-50μm. ................................................................. 70

5.3.2 Typical pressed composite sample and dimensions. All measurements are in inches. .............. 71

5.5.1 Low temperature reflow oven for reflowing composite samples. (a) Exterior view of oven, DAQ and SSR; the grey metal box in the upper-left corner is a Variac to reduce wall voltage to 30V. (b) Interior view of oven. The white cylinder extending from the top of the image is the sample thermocouple; the sample is resting underneath the thermocouple on the glass/aluminum support. Two oven thermocouples can be seen at the rear of the oven. ................................................................. 75
5.5.2 One-quarter (~0.5g) of a composite sample ready to be reflowed. The sample is covered with liquid rosin flux to prevent oxidation during reflow and rests on a disposable aluminum sheet to facilitate removal and analysis via optical microscopy.

6.1.1 Typical SEM micrograph of the titania powder. The average particle size as determined by measurements on eighty four different particles was $6.5 \pm 1 \mu m$, where the error represents the 95% confidence interval on the mean. Agglomerations greater than 25μm were assumed to have been broken apart during the ball milling process.

6.1.2 X-ray pattern of powdered titania. Blue text and arrows denote anatase (A) peaks; red denotes rutile (R) peaks. From top to bottom, each label lists the phase, reflectance angle and relative intensity of the peak. Equation (6.1-1) estimates that the powder is 81.2wt% anatase titania, based on the anatase and rutile peaks at 25.43° and 27.55°, respectively.

6.1.3 Optical micrographs of as-spun titania nanofibers using the titania solution described in Section 5.1. A bead-on-string structure is clearly visible at both 100x magnification (left column) and 500x magnification (right column). The scale bar at 500x magnification is 50μm.

6.1.4 SEM micrograph of calcined, ultrasonicated beaded titania nanofibers from Figure 6.1.3. Notice that the beads have generally been smoothly separated from the fiber, leaving a mixture of beads and fibers. The average bead diameter is $3.5 \pm 1.5 \mu m$. 
6.1.5 Optical micrographs of electrospun titania solution with acetic acid added prior to spinning. The top, middle and bottom rows are 100x, 500x and 1000x magnification, respectively. The scale bars in each are 100, 20 and 10μm, respectively. There are no visible beads as opposed to the highly beaded structure observed in Figure 6.1.3.

6.1.6 SEM micrograph of calcined electrospun titania nanofibers; the spinning solution contained acetic acid. The beads observed in Figure 6.1.4 have been eliminated by the addition of acetic acid to the spinning solution.

6.1.7 FESEM micrograph of calcined, ultrasonicated beadless titania nanofibers at increased magnification. The average diameter of the fibers is 164±12nm, where the error is the 95% confidence interval about the mean.

6.1.8 X-ray pattern of beaded, electrospun titania. Blue text and arrows denote anatase (A) peaks; red denotes rutile (R) peaks. From top to bottom, each label lists the phase, reflectance angle and relative intensity of the peak. Equation (6.1-1) estimates that the powder is 68.9wt% anatase titania, based on the anatase and rutile peaks at 25.35° and 27.5°, respectively.

6.1.9 X-ray pattern of beadless, electrospun titania. Red text and arrows denote rutile (R) peaks. From top to bottom, each label lists the phase, reflectance angle and relative intensity of the peak. The lack of reflectance peaks for the anatase phase implies a purely rutile titania.
6.1.10 Average, to-scale sizes of titania reinforcement. Dotted lines represent 95% confidence intervals about the mean. From left to right is (a) titania powder, (b) calcined, beaded titania and (c) calcined smooth nanofibers prepared by using acetic acid in the spinning solution.

6.2.1 Summary of specific gravity measurements on compressed sample pellets. Solid colors are measurements made on samples before sintering at 150°C for 24hrs; gradient colors are data collected after sintering. Except for the powder samples there is no statistical difference between the specific gravities before and after sintering. However, each composite has a specific gravity less than or statistically equivalent to pure solder, which is expected when reinforcing with a less dense material. Error bars are 95% confidence intervals.

6.3.1 Optical micrographs (100x, scale bar is 200μm) of the inside of compressed, sintered samples. (a) Pure solder (b) Titania powder (c) Beaded titania (d) Titania nanofibers. All composite sample images are at 1wt%. Clearly the titania has agglomerated in but the agglomerations are even distributed throughout the composite. The green arrows point to area of white which represent titania filler; these areas are not present in the pure solder.

6.3.2 Optical micrographs (500x, scale bar is 50μm) of the inside of compressed, sintered samples. (a) Pure solder (b) Titania powder (c) Beaded titania (d) Titania nanofibers. All images of composite samples are with 1wt% filler. The secondary phase of titania reinforcement is visible in (b)-(d).
6.4.1  Typical thermomechanical data output for CTE calculation. The CTE is determined (via software) by dividing the slope of the plot by the original height of the sample. .................................................. 99

6.4.2  Grand composite CTE comparison. Error bars represent 95% confidence intervals. Detailed statistical comparisons of the various fillers to pure solder are offered in Figure 6.4.6, Figure 6.4.7 and Figure 6.4.8. ............................................................. 101

6.4.3  Plots of the ROM, Kerner, Turner and Schapery CTE models. The equations were originally stated in terms of volume fraction; transformation to mass fraction results in a slightly increased curvature. Only Schapery’s lower bound on composite CTE is plotted; the upper bound corresponds exactly with Kerner’s model. The ROM and Kerner models predict gradual transitions of the CTE whereas Turner and Schapery predict large decreases in CTE at low titania mass fractions and diminishing returns beyond about 20wt%.......................... 105

6.4.4  Experimental data plotted with the model estimates from Figure 6.4.3. The scale has been adjusted to 0-5wt% titania reinforcement since experimental measurements were made at 1.0wt% or less. Error bars for experimental data were omitted for clarity................................................................. 108

6.4.5  Upper and lower CTE bounds for a titania/solder composite based on Turner’s model. The lower bound uses experimental data from Low et al. [91C1]; the upper bound is from Dasgupta et al. [92D1]. The variation may be due to the high homologous temperature of solder at room temperature....................... 112
6.4.6 Summary table, ANOVA and bar graph of titania nanopowder composite CTE measurements. The low $P$-value (0.00088) indicates that the variation observed between groups is greater than could be expected by random variation. The bar graph shows the results of Tukey's HSD test ($\alpha=0.05$): the red line indicates that all titania composites have statistically equivalent CTE's but are all different from pure solder. Error bars are 95% confidence intervals. ........................................ 117

6.4.7 Summary table, ANOVA and bar graph of beaded titania nanofiber composite CTE measurements. The low $P$-value (0.00049) indicates that the variation observed between groups is greater than could be expected by random variation. The bar graph shows the results of Tukey's HSD test ($\alpha=0.05$): the red line indicates that all titania composites have statistically equivalent CTE's but are all different from pure solder. Error bars are 95% confidence intervals. ........................................ 118

6.4.8 Summary table, ANOVA and bar graph of titania beadless titania nanofiber composite CTE measurements. The acceptable $P$-value (0.04079) indicates that the variation observed between groups is greater than could be expected by random variation. The bar graph shows the results of Tukey's HSD test ($\alpha=0.05$): the absence of a red line indicates that the titania composites are different from pure solder. Error bars are 95% confidence intervals. ........................................ 119
6.5.1 Typical reflow plot of a compacted solder pellet. The melting point is determined as the temperature of the well on the left of the plot; the freezing point is the plateau on the right. A slight rise over and the sharp decrease to the melting point is due a thin layer of oxidation on the solder spheres inside the pellet. Melt undercooling, a phenomena related to homogeneous nucleation in many materials, is observed around the freezing point.

6.5.2 Detail of the melt transition for the reflow profile in Figure 6.5.1. The gradual leveling and sharp drop in temperature was attributed to oxidation of the interior portions of the solder sample during sintering and thermomechanical analysis. The melting temperature is taken as the bottom of the well.

6.5.3 Detail of the crystalline transition for the reflow profile in Figure 6.5.1. The slight drop before the plateau is a standard melt undercooling feature. The freezing temperature is taken as the plateau.

6.5.4 Melting and freezing points of pure solder and composite samples. Error bars are 95% confidence intervals; there is no statistical difference between composite melting points and pure solder's melting point, or between composite freezing points and pure solder's freezing point.

6.6.1 Reflowed samples as seen by the human eye. (a) No filler, (b) 0.25wt% titania fiber, (c) 0.25wt% beaded titania fibers, (d) 1.00wt% non-beaded titania fibers. Note the obvious opaqueness of (b)-(d) contrasting the clarity of (a).
6.6.2 Optical micrograph of pure solder flux at 100x magnification. The lined pattern is the underlying aluminum foil which indicates that there is no appreciable foreign material in the crystallized flux. ................................................................. 130

6.6.3 Optical micrograph of beaded and non-beaded composite samples at 100x magnification. The blue is the solder sample and the white, which is not seen in pure sample micrographs, is assumed to be titania filler....................... 131

6.6.4 Optical micrographs at 500x magnification of ultrasonicated beaded titania fibers before incorporation into composite and after expulsion from composite during reflow. The distinctive bead shape confirms that the titania filler is morphologically unaltered during reflow and is expelled during the process................................................................. 133

6.6.5 Geometry for the problem of a solid, rigid cylinder floating at the interface between two fluids, a liquid and gas. The inset is a perspective view of the problem. Definitions of symbols are provided in the text................................. 135

6.6.6 A plot of $F'_{net}$ for two different contact angles: 109° by Good and Girifalco, and 147° by Nikolopoulus. The intercepts represent equilibrium values of $\varphi$ and confirm that the cylinder is expected to rest atop the molten solder................................................................. 141
CHAPTER I
FUNDAMENTAL QUESTIONS

It is important at the outset of any investigation to determine a question or set of questions that, when answered, will produce a meaningful result. While new questions will certainly arise during the investigation, the overall aim of the project will remain consistent if these new questions are answered in the context of the larger study. Reason would then suggest that presenting these questions immediately is most appropriate to provide context for the following report sections. While the questions may at first seem abrupt or even arbitrary, they will become clearer upon further reading and will also serve to clarify that same reading by providing contextual landmarks.

The latter portion of this thesis title, “...of a metal powder composite via ceramic nanofiber reinforcement”, presents an implicit question: Can a ceramic nanofiber be incorporated into a metal matrix? Certainly this represents the most fundamental of questions, in that failing to satisfactorily incorporate nanofibers into the metal matrix would result in a premature end to the study. The first portion
of the title, “Control of thermal expansion coefficient...”, identifies the second question: Do ceramic nanofibers have an effect on the thermal expansion coefficient in a metal matrix? At this point an underlying assumption must be made, namely that there is a suitable reason for investigating these two questions; this assumption will be expanded upon further in Chapter I.

The remaining two questions are designed to expand the applicability of the investigation, first in a theoretical manner and second in an industrial manner. Since the title proclaimed the use of “nanofibers” as opposed to some other nanoscaled-geometry the obvious question would be: Does the thermal expansion coefficient depend upon the shape of the filler? Nanofibers themselves can be synthesized in a variety of geometries, with the primary variation being fiber radius, but nanoparticles were also investigated to provide information on dimensional effects. In this case nanofibers, regardless of diameter, represent a two-dimensional nanomaterial since two dimensions, x- and y- in Cartesian coordinates, are on the nanoscale. Nanoparticles are appropriately three-dimensional nanomaterials since all three dimensions are on the nanoscale.

The final question requires some knowledge of the composite’s end-use: Does the addition of such nanomaterials have an effect on the melting temperature of the resulting composite? The metal investigated was a eutectic solder that is primarily used for electronic package
assemblies, colloquially known as circuit boards. 0 will expand upon processing parameter restrictions during circuit board manufacturing. Briefly, too low of a melting temperature is characteristic of a solder too weak to provide sufficient mechanical connection while too high of a melting temperature will require processing temperatures high enough to damage surrounding components.

The hierarchy of this decision structure, as illustrated by Figure 1-1, can be grouped by effect type: processing effects, which are those effects that influence the processing steps in circuit board manufacturing, and performance effects, which are those effects important to normal operation of circuit boards. Changes in the coefficient of thermal expansion are considered a performance effect since it is primarily of interest in a completed circuit board. Melting temperature, on the other hand, is a processing effect because it is most important during the manufacturing of the circuit board.
Figure 1.1. Decision hierarchy for nanocomposite study. The performance branch is associated with those parameters affecting long-term performance; the processing branch is associated with those parameters affecting the industrial processing of the composite.
A note regarding homographic clarity: the unfortunate pairing of the term “lead” (pronounced lēd) and the 82\textsuperscript{nd} element in the periodic table (pronounced lĕd) occurs quite frequently in electronics; for example, it is entirely possible to have a “lead lead”. In order to make clear the desired usage of each term, this document will use the elemental symbol “Pb” when referring to the element and the term “lead” when referring to an electrical or mechanical contact. Hence, the confusing expression “lead lead” becomes “Pb lead”.

An additional note regarding the reference style of this document: all in-text references are presented in the form of two numbers, followed by a letter and finally one additional number. The first two numbers are the last two digits of the reference’s year of publication. The letter is the first letter of the last name of the lead author, and the last number is to distinguish multiple references published in the same year by authors with the same first letter in their last name. For example, this document would be referenced as [09D1] since it was authored in 2009 by Aaron Drews. References at the end of this document are arranged first chronologically and then alphabetically.
CHAPTER II

MOTIVATION

With ever-increasing demand for smaller and faster electronic devices there is typically little mention of the solder interconnects that provide mechanical and electrical connection between chip and board. Despite their less glamorous public image, solder interconnects remain an area of research and investment for government and private industry. It is the failure of these interconnects, typically due to cyclic thermal stresses, that causes failure in a wide variety of electronic devices. This chapter provides recent examples of investment, research and consequences surrounding solder interconnects in an attempt to highlight their central role in electronic devices.

The first two examples document a portion of the ongoing efforts of the United States government to understand, manipulate and adapt to new problems in soldering technology. The two additional examples are of the costs associated in poor design or consideration of solder interconnects in commercial electronic devices. Decreases in size along with increases in performance and power consumption in
modern electronic devices have magnified the importance of heat dissipation. Thermal cycles result in stresses between components due to variations in the coefficient of thermal expansion (CTE); hence heat dissipation and CTE’s are intrinsically linked. Device failure in the third and fourth examples is due in part to poor heat dissipation, or at a more basic level because of CTE mismatch.

2.1 Joint Munitions Technology Support Program (JMTP)

With the first successful, large-scale deployment of the Tomahawk cruise missile in 1991 [07N1] the United States Armed Forces shifted its focus from unguided weaponry to “smart” weapons. The evolution of such weaponry has lead to advances such as the Predator unmanned aircraft system, costing $30 million per vehicle [08A1]. Incorporating computer guidance and control technology into lethal weaponry presents an ultimatum to insure optimum performance and reliability. Obviously, the circuitry’s physical and electrical reliability is closely tied to an understanding of solder performance.

Unclassified documents indicate the interest of both the U.S. Department of Defense (DoD) and Department of Energy (DoE) in solder technology beginning as early as 1998. Budget evaluations in 1999 [99J1] indicate a total expenditure of $16 million towards the development of non-nuclear munitions. Approximately 14% of this
budget was directed towards investigation of electronic components in aging munitions stockpiles with an emphasis on solder interconnect reliability. Additional budget evaluations in 2003 [03J1] and 2007 [07J1] confirm the ongoing process of understanding and modeling solder interconnects. Given the projected budgets provided in these reports the cumulative sum of governmental funding for this solder interconnect study will total at least $25 million by 2009.

2.2 Joint NASA/DoD Pb-Free Electronics

In 2006 the European Union enacted the Restriction of the Use of Hazardous Substances (RoHS) in order to reduce or eliminate certain hazardous materials in consumer products [05R2]. Anticipating the restriction on Pb-based solders, the National Aeronautics and Space Administration (NASA) and U.S. DoD jointly began investigation Pb-free solders in 2001. This first study, conducted from 2001-2005, investigated the performance of three Pb-free solders in comparison to eutectic Pb/Sn solder [07N2]. In collaboration with over twenty commercial organizations tests were performed to evaluate solder performance under a variety of conditions, though particular attention was paid to thermal fatigue of solder joints. A follow-up study, planned for 2006-2010, aims replicate many of the original thermal fatigue studies but for reworked and mixed solders [08N2]. With a span of nearly ten
years this joint program not only illustrates the importance of solder interconnects but also emphasizes the complexity of making a seemingly simple substitution of Pb-free solders in existing manufacturing techniques.

2.3 Nvidia GE84 Graphics Processor Unit

In July 2008 computer chip manufacturer Nvidia announced a charge of $150-$200 million to their revenue to cover the replacement of defective graphics processor units [08N1]. The graphics processor unit (GPU) is responsible for a variety of functions in computer, hand-held and console applications but is generally responsible for rendering graphic elements [08Y1]. Clearly, since most applications require a display, the performance and reliability of the GPU is critical to a variety of systems. Complicated soldering patterns, such as in GPUs, are typically achieved via ball grid arrays (BGA’s): solder pads are placed on both the substrate material and chip, spheres of solder are placed between the two pads and the entire system is heated to fuse the individual connections. A more detailed explanation of soldering techniques is provided in Section 3.3; Figure 2.3.1 shows a ball grid array used for Nvidia’s GeForce 8500m GT chip.
A primary source of Nvidia’s defective GPUs, the G84 and G86 series, was failure due to a mismatch between the thermal expansion coefficients of the solder, chip and substrate [08D2, 08G1, 08G2]. The resulting thermal stresses arising from this mismatch were sufficient to break the physical connection between the chip and substrate, effectively rendering the chip useless. The ability to manipulate the coefficient of thermal expansion in the solder joints could have reduced mismatch and perhaps made unnecessary the extensive replacement plan.

2.4 Microsoft Xbox 360™

Microsoft’s Xbox 360™ is an electronic gaming console released in 2005 [08S1] and originally featured a GPU known as Xenos. In July 2007

![NVIDIA’s GeForce 8500M-GT graphics processor unit](image.png)

Figure 2.3.1. NVIDIA’s GeForce 8500M-GT graphics processor unit [08L1]. The image on the right is the mounting surface; each point represents a soldered connection.
Microsoft announced a charge of $1.01-$1.15 billion for its quarter ending in June 2007 to cover a replacement plan initiated in response to increasingly common hardware failures [07M2]. The failure, indicated by a “General Hardware Failure” message during system operation, was not well-described by Microsoft but can be easily traced to poor heat dissipation. Most obvious is an interview conducted with a system designer citing “excessive heat on the GPU” as the main design flaw [08M1], a claim supported by subsequent hardware alterations performed by Microsoft. The Xenos GPU was replaced with a smaller, second-generation GPU known as Falcon that featured additional mechanical reinforcement between the GPU and motherboard [08S1]. Eventually Falcon was replaced by Jasper, a still smaller GPU with a redesigned heat sink to provide improved cooling [08J1].

While an official explanation of the hardware failures has not been released by Microsoft it is reasonable to assume that thermal stresses, as with Nvidia’s GE84, caused at least a portion of the solder interconnects to fail. Certainly improved heat dissipation would help to mitigate the failures; however, carefully engineered solder and surrounding components could be designed to minimize CTE mismatch and thereby also reduce failure rates.
CHAPTER III
CIRCUIT BOARD BASICS

Unique vocabularies often develop in order to make fine distinctions when examining any topic in detail. These vocabularies also generally draw on colloquial terminology and are therefore susceptible to misunderstanding. In addition to providing the common terminology associated with electronic package assemblies the following sections will highlight the materials and manufacturing methods involved in circuit board production. Where applicable, reference will be made to the examples described in Chapter I to provide greater insight and understanding of this interconnectedness.

3.1 The Printed Circuit Board

The backbone of any electronic package assembly is the printed circuit board (PCB), occasionally referred to as a printed wiring board (PWB). A PCB is a sandwich of several different materials; a simple schematic of this construction can be seen in Figure 3.1.1. Starting
from at the center, a PCB is constructed by coating a core material (c) with a conductive layer such as copper foil. The core material is woven fiberglass impregnated with epoxy resin and cured to harden, the most common of which is known as FR-4 [97H1]. The term “printed” in PCB refers to the photolithographic method used to etch a wiring diagram into the copper foil. The copper foil is coated with a photoresist, a pattern is transferred via exposure to light and the excess copper and photoresist is removed by chemical treatment [05R1]. Prepreg material (f) is woven fiberglass with varying amounts of uncured epoxy resin and serves to both control the thickness of the PCB and electrically insulate adjacent layers [05R1]. Layers of core and prepreg are pressed and heated to form a standard, multilayer PCB. In order to connect multiple layers, holes known as vias (d, e, h) are machined at various points in production [08L2]. A through-via (h) or blind-via (e) can be used as a component attachment point for components requiring pin leads. If not needed, vias are filled with solder as in Figure 3.1.2. Finally the outer layers are coated by a photosensitive solder mask. Solder masks are typically acrylic or methacrylic oligomers and serve a dual purpose: to protect the outermost layer of copper wiring and to resist solder wetting [95M1]. Pigment is often added to the solder mask to provide the characteristic green coloring of a PCB.
Figure 3.1.1. Standard printed circuit board (PCB) layers and features. Labels: (a) solder mask, (b) copper surface pads, (c) core material, (d) blind via, (e) buried via, (f) prepreg material, (g) subsurface printed copper path, (h) through via.
Figure 3.1.2. Optical micrograph (100x) of a through-via and surface pad cross-section on a PCB. This via was not needed for the desired product and so was filled with solder; the inner copper via coating is clearly visible.
3.2 Lead Connections

Of course the PCB is nearly useless without peripheral connectors, chips and terminals that provide the desired functionality of a device. A variety of connection styles have been developed to address the myriad needs associated with PCB’s; the major styles will be presented along with a critique of common failure points and mechanisms. Necessarily these various lead connectors each have their own appropriate soldering techniques; these techniques are addressed in Section 3.3.

The previous section introduced the concept of vias and their role as an electrical connection between multiple layers in a PCB. Vias also provide mechanical connection for the first lead connector: the pin-through-hole (PTH) lead. As the name implies a hole must be machined in the PCB to accept both the pin of the component and the solder required to anchor the pin in place. Furthermore the pins of such components typically pass entirely through the PCB to emerge on the underside of the PCB. Figure 3.2.1 details several additional aspects of PTH design. In perspective (a) it is demonstrated that not only are the pins partially exposed but that the pins are responsible for increasing the dimension normal to the plane of the board. Obviously this characteristic presents a drawback when considering PTH connectors for low-profile or compact designs. However, this additional clearance makes post-solder cleaning more effective because the cleaning solvent can more easily
access the solder joints [87K1, pg341]. Perspective (c) details the pin exposure on the opposite side of the PCB. The large contact area between the pin and solder provides sufficient mechanical reinforcement to make PTH the primary method of attachment for components that require physical connections such as cable or USB ports, or components intended to be serviced by the user such as random access memory (RAM) slots in Figure 3.2.1.

The next type of lead attachment, J-leads and gull-wings, are a subset of the larger surface mount technology (SMT) designation. SMT, as implied by the acronym, limits the type of attachment to those placed only on the surface on the PCB as opposed to those such as PTH components which pass into or through the board. SMT components are also soldered in a different manner compared to PTH components which will be covered in more detail in Section 3.3. Usually the terms gull-wing and J-lead are interchangeable: most characteristics apply to both J-leads and gull-wings, the only difference being whether the lead is curled at the end (J-lead) or flat (gull-wing). Gull-wings are metallic connectors usually made from either Kovar, an iron-nickel-cobalt alloy [02E1], or an iron-nickel alloy known as Alloy 42 [03N1]. Furthermore the shape of the gull-wing, as shown in inset of Figure 3.2.2, can serve to slightly raise the component from the PCB as in (a) or, for smaller components as in (b), have little or no effect on the profile of the board.
Figure 3.2.1. Typical pin-through-hole (PTH) components (b). Perspective (a) reveals the increased height of the components and exposure of the pins; perspective (c) is the underside of the PCB revealing the exposed pins on the opposite side of the board.
Figure 3.2.2. A typical gull-wing SMT device. The larger component (a) is raised slightly from the surface of the PCB whereas the smaller components (b) are nearly flush. The inset is a profile of a gull-wing lead.
Figure 3.2.3. An example of a lead-less SMT device. The inset profile indicates that the device rests smoothly on the PCB. In the image, solder has been applied to the metallic end-caps.
The remaining subset of SMT components consists of so-called “lead-less” components: unlike PTH or gull-wing devices the mechanical and electrical connections of these components are part of the component itself. The simplest versions can be found in resistor packages such as those shown in Figure 3.2.3. The leads in this case are the metallic end-caps detailed as the light-grey ends of the inset image; solder is applied directly to the end-caps to mount the device on the PCB. Clearly the number of leads is limited to fewer than that possible by gull-wing attachment but the simplicity and ubiquitous nature of small devices such as resistors lends itself to the lead-less assembly.

The other lead-less method is by far the most common for attaching components requiring a high density of connections: the ball-grid array, or BGA. The term “ball” in BGA refers to the small sphere of solder that forms the primary connection between the PCB pads and the component; “grid array” refers to pattern of the spheres. In Figure 3.2.4 a component attached using a BGA has been removed to reveal the pattern of soldering attachments. Note that the BGA allows for the highest connection density for a given area of PCB; this is advantageous as the physical size of most devices is required to be smaller and smaller. It is not unexpected that since the highest density of connections exists in BGA’s the majority of circuit failures arise from failures of the BGA, as was determined for the aforementioned cases of Nvidia and Microsoft.
3.3 Methods of Soldering

Obviously hand-soldering components to a PCB with a soldering iron and solder coil is unrealistic on a production scale, although the method is occasionally used as a quality control repair procedure. Instead, a variety of methods, each suited to a particular type of connection introduced in Section 3.2, has been developed to provide consistent and reliable soldering of components. Not only will this section introduce these methods but it will also elaborate on which soldering method is used for which lead connection. The goal of such a discussion is to illustrate the primary industrial methods of soldering PCB’s. Following this section will
be a summary of the types of solder common to industry along with important processing properties.

3.3.1 Wave Soldering

For attaching PTH components and some leadless components a method called wave-soldering is employed. A continuous wave of molten solder flows vertically by means of a submerged pump and contacts the exposed pins of each PTH component as depicted in Figure 3.3.1. Wetting and capillary forces transport the molten solder into the annular space created by the pin and via. Because the pump and molten solder reservoir are stationary, the entire PCB must be moved through the solder stream in order to solder each component.

Figure 3.3.1. Diagram of wave soldering for PTH components. The pump (a) supplies a continuous fountain of molten solder (b) to coat the underside of the PCB (c). The PCB is moved through the fountain to solder all PTH components leaving a conical cap of solder (d).
Several drawbacks of wave soldering serve to limit its applicability. Many modern PCB’s have components mounted on both sides of the PCB and yet wave soldering can only be performed on a single side of the PCB; otherwise the existing components will be coated with an undesirable layer of solder [88H1, pg207]. Similarly, the solder used in wave soldering must be capable of maintaining its mechanical and electrical integrity while the SMT components are attached and soldered. Common industrial solders have a contact angle of about 30-50° [00A1] on most metallic substrates and so will tend to remain in place when inverted but cannot support a significant load while molten. Furthermore the process of wave soldering can introduce significant thermal gradients as the PCB moves over the molten solder fountain [88H1, pg313]. Such a gradient can result in the failure of some ceramic lead-less SMT devices such as capacitors or plastic-encapsulated semi-conductors [88H1, pg352; 86M1, pg131]. Finally, wave soldering lacks the precision necessary to solder components with a high density of contacts. If the proximity of the nearest neighboring lead is closer than the natural radius of curvature of the solder, the molten solder will tend to form bridges between the two leads [00A1; 86M1, pg166]. The radius of curvature for eutectic Sn/Pb solder, a common industrial solder, is approximately 2mm [93V1]; therefore placing PTH leads closer than 2mm risks bridging the contacts. Clearly, the components in Figure 3.2.2 or Figure 3.2.4 have leads closer than 2mm and so alternative methods must be employed to
achieve such close spacing and, in general, reduce the problematic nature of wave soldering.

3.3.2 Solder Paste and Screen Printing

One alternative solder placement method employs a procedure not unlike silkscreen printing to apply a solder paste to the PCB in a precise manner. Solder paste consists of two parts: solder powder and flux. Solder powder is free-flowing powder consisting of solder spheres ranging from 5-75μm [05Q1]. Powder sizes are typically reported as mesh ranges: the solder powder shown in Figure 5.3.1 on pg70 is referred to as a -300/+525 mesh solder meaning that the powder will pass through a 300 mesh screen but not a 525 mesh screen. Particle size will have an effect on the viscosity and total metallic loading of the final paste and so the equipment and application of the paste must be considered when choosing particle size [89H1 pg59]. Nearly spherical particles can be produced in a number of ways, such as gas or centrifugal atomization [88H1, pg233]. In gas atomization a stream of inert gas is flowed over molten solder to produce small spheres of solder whereas centrifugal atomization functions by dropping molten solder onto a rapidly spinning wheel to produce the small spheres.

The liquid flux used in solder pastes can be quite complicated and offers a number of opportunities for application-specific design. At the
most general level the role of the liquid flux in solder pastes is to remove oxides and other contaminants to facilitate solder wetting [88H1, pg124; 89H1, pg38]. Fluxes typically contain at least three components: solvents, rosins and activators [90C1, pg157]. The rosin is perhaps the most central component because it performs the chemical removal of oxide layers on the solder and contact pads. Furthermore the rosin serves as an oxygen barrier to limit oxidation during melting and further processing. A naturally occurring viscous resin obtained from pine trees, rosin is composed primarily of abietic acid and related carboxylic acids [89H1, pg44]. These carboxylic acids share structures similar to the abietic acid structure shown in Figure 3.3.2: a condensed three-ring structure, a carboxylic group and one or more double bonds within the three-ring structure. It is the carboxylic group that provides the majority of the oxide removal power [89H1, pg49] but such power may be augmented with the use of an activator. Fluxes are loosely categorized based on the level of activation: R-type for non-activated pure resins, RMA-type for mildly activated rosins, RA-type for activated rosins, and SRA-type for superactivated rosins [86M1, pg95]. The role of the solvent, typically an alcohol such as ethanol or n-butanol, is to act as a vehicle for the activator and to improve the shelf life of the paste [88H1, pg238].

Combination of the solder powder and flux results in a viscous paste or slurry able to be printed, pumped or injected. For any of these processes a particularly important physical property of the paste is its
viscosity. While the viscosity of the paste is certainly a function of the type and composition of the flux, the amount of metal loading also has a pronounced effect on viscosity as seen in Table 3.3.1 [89H1, pg61]. Moreover, it can be seen that smaller particle sizes (i.e., higher meshes) result in increased paste viscosity. These two parameters, weight fraction and size, must be selected to optimize the paste for the anticipated application method.

For small production runs a syringe dispenser may be most economical and efficient; such a device utilizes a peristaltic or air-driven pump to apply small amounts of paste via needle tip [88H1, pg254]. Larger commercial production runs typically employ a screen printing method whereby a flexible screen or rigid metal stencil is machined so that holes are present where solder paste needs to be applied [88H1, pg244; 90C1, pg167]. The screen is placed directly and carefully atop the PCB to be soldered, the screen is covered with solder paste and a squeegee passes over the screen. The purpose of the squeegee, a rigid rubber blade, is to force the solder paste into the voids of the screen.
Figure 3.3.2. Chemical structure of abietic acid, the primary component of rosin. The condensed ring structure, carboxylic group and double bonds within are characteristic of the carboxylic acids found in solder flux.

Table 3.3.1. Viscosity of solder paste as it varies with weight percentage of metal loading [89H1, pg61].

<table>
<thead>
<tr>
<th>Metal Loading (wt%)</th>
<th>-200/+325 Mesh</th>
<th>-325 Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>240,000</td>
<td>280,000</td>
</tr>
<tr>
<td>87</td>
<td>300,000</td>
<td>350,000</td>
</tr>
<tr>
<td>89</td>
<td>390,000</td>
<td>510,000</td>
</tr>
<tr>
<td>90</td>
<td>460,000</td>
<td>660,000</td>
</tr>
<tr>
<td>91</td>
<td>690,000</td>
<td>880,000</td>
</tr>
<tr>
<td>92</td>
<td>1,020,000</td>
<td>1,450,000</td>
</tr>
</tbody>
</table>
The solder is thus deposited in precisely the location and amount required. The height of the deposit is controlled by the thickness of the screen or stencil while the dimensions of the deposit are controlled by the dimensions of the opening.

3.3.3 Reflow Methods

Finally, the screen printing method requires application of heat to form pure molten solder joints free of flux materials. This melting step is generally referred to as ‘reflow’, a slightly ambiguous term in that the first melting (flow) was employed to create the solder powder and now that same powder is again melted (reflowed) to create solder joints. However, ‘flow’ soldering has historically been synonymous with wave soldering and so the process for melting SMT solder joints is simply referred to as ‘reflow’ soldering [88H1, pg314]. As with virtually every other aspect of PCB manufacturing, a variety of methods has been developed to achieve efficient reflow. These methods can be divided according to their method of heat transfer be it through convection, radiation or phase change. The goal of each method is to develop a temperature profile similar to that depicted by Figure 3.3.3; it is left as a design consideration to choose which method is most effective at providing such a temperature profile.
Convection reflow utilizes hot air or inert gases to transfer heat to the solder joints. Since various temperature, heating and cooling profiles are necessary, the PCB’s travel on a conveyor through zones of different temperature. The initial drying stage removes volatiles such as the ethanol or \textit{n}-butanol solvents in the flux; the maximum temperature must be chosen carefully to avoid boiling the solvents too quickly. Rapid boiling of the solvents results in paste spattering whereby small amounts of solder paste are ejected from the mass of solder paste to land elsewhere on the PCB [89H1, pg317]. The preheat zone that follows the drying stage is designed to slowly raise the temperature of the PCB in

![Figure 3.3.3. Standard temperature profile for reflow soldering of SMT solder joints. (With permission, from Hinch, \textit{Handbook of Surface Mount Technology}, Pearson Education, Harlow, Essex 1988, pg314.)](image)

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order to avoid component or board damage at the elevated temperatures necessary to reflow the solder.

This preheat zone is the first instance where CTE mismatch can cause board failure, mainly in the form of component and board warping. As described in Section 3.1 the PCB is a composite material containing fiberglass, copper, adhesive materials and other components, all of which have unique CTE’s. Furthermore, SMT devices such as capacitors, which are usually ceramic leadless devices, are composites made of as many as fifty alternating layers of dielectric and electrode layers [88H1, pg48]. The mismatch of CTE between the layers in composite materials results in bending stresses and shear forces as shown in Figure 3.3.4, which are generally referred to as thermal stress or thermal shock.

![Conceptual diagram depicting stresses and shear arising from CTE mismatch between components. When heat is applied to a composite with materials of different CTE’s the composite exhibits the bending shown above (exaggerated). The stresses and shear are referred to as thermal stresses.](image)

Figure 3.3.4. Conceptual diagram depicting stresses and shear arising from CTE mismatch between components. When heat is applied to a composite with materials of different CTE’s the composite exhibits the bending shown above (exaggerated). The stresses and shear are referred to as thermal stresses.
However, at this stage the CTE of the solder is unimportant because the solder remains as solder particles suspended in the “dried” flux.

Once the PCB has passed through the preheat section it enters the reflow section where the actual soldering of the component to the substrate occurs. The maximum temperature of the reflow section is dictated by the melting point of the chosen solder; Section 3.4 explores the properties and types of solders most commonly employed. Similarly, the dwell time in the reflow zone is dictated by the amount of solder present in the various joints. During this time the resin in the flux serves as a barrier to prevent oxidation, which can be rapid at the elevated temperatures of the reflow section [90C1, pg61]. Just as the preheat section serves to mitigate thermal shock so too does the cooling period after reflow. Figure 3.3.3 indicates that both the preheat and cooling period have lower rates of temperature change compared to the reflow section; simply removing the reflowed PCB to atmospheric temperature would risk rapid temperature changes resulting in damage to the board or components.

Radiative heat transfer can be used in a similar manner by conceptually substituting hot gas sources with infrared (IR) sources. Conveyor systems and zones of various temperatures, as in convective reflow, are employed to produce the desired temperature profile. Two common IR arrangements are lamp and panel systems which vary primarily by utilization of reradiation [88H1, pg337]. Both systems
employ tungsten as an IR source, but whereas the lamp system uses a reflective surface to redirect off-target radiation, panel systems use a ceramic backplane to absorb and reradiate off-target radiation. Adjustments to the temperature profile are generally controlled by conveyor speed, voltage applied to the lamps and distance between the lamps and PCB’s. Addition of inert gases such as nitrogen to the reflow atmosphere can be used to blanket the PCB’s and maintain the activity of the fluxes although this process adds significant processing costs [88H1, pg341].

The final form of heat transfer to be presented is heat transfer by phase change, specifically the condensation of saturated vapor on the PCB. Heat transfer by phase change is somewhat more complicated than either conduction or convection: in addition to having characteristics of both conduction and convection, consideration of mass transfer effects and radiation must also be given to develop an accurate model [73P1, pg10-18]. Condensation heat transfer is subdivided according to the wetting behavior of the vapor on the substrate [01W1, pg345]. Film condensation occurs when the condensed vapor wets the substrate to form a film; dropwise condensation occurs when the condensed vapor does not wet the surface and instead forms droplets of liquid that fall off the surface under the influence of gravity. Generally film condensation is less efficient because of the additional heat transfer barrier once the film is established.
When used as a soldering method, condensation heat transfer is referred to as vapor phase reflow. Figure 3.3.5 shows the basic vapor phase reflow setup: a heater vaporizes the process liquid, the saturated vapor condenses on the part to be soldered, and the condensed liquid returns to the liquid reservoir. A condenser above the chamber prevents the saturated liquid from escaping. The requirements of the vapor/liquid system to be used are stringent: a boiling point above the reflow temperature but not so high to cause thermal degradation of components, chemical stability, non-flammable and a density ideally heavier than air so as to facilitate confinement [90C1, pg208]. The most commonly chosen process fluids are fluorinated hydrocarbons [88H1, pg328] with structures similar to that of Figure 3.3.6. Such fluids typically have a range

![Figure 3.3.5. Basic vapor phase reflow setup. (With permission, from Hinch, Handbook of Surface Mount Technology, Pearson Education, Harlow, Essex 1988, pg314.)](image-url)
of molecular weights due to variations in the manufacturing process, hence the indeterminate structure. Because of the various wetted materials possible in a vapor phase reflow system it is difficult to determine if the unit will achieve heat transfer as film or dropwise condensation; however it is generally assumed that film condensation is predominant [90C1, pg208].

Vapor phase reflow offers a number of processing advantages over convective or radiative reflow [88H1, pg 325; 90C1, pg207; 89H1, pg209]. The temperature profile can be well controlled by choosing appropriate molecular weight ranges for each heating zone. Despite the possible variations in boiling point due to the range of molecular weights, the temperature of the saturated vapor is generally a much smaller range than could be achieved using either radiative or convective reflow techniques. Furthermore, the atmosphere within the chamber is generally oxygen-free save for small amounts entering with the conveyor.

\[
\begin{array}{cccccc}
F & F & F & F \\
| & | & | & | \\
... & -C-C-C-C-C- & ... \\
| & | & | & | \\
F & F & F & F
\end{array}
\]

Figure 3.3.6. General structure of a fluorinated hydrocarbon used in vapor phase reflow. The molecular structure typically varies in the number of carbons present due to variations in manufacturing.
system, thus reducing the risk of oxidation. Finally, the heating of the component is relatively insensitive to lead geometry: lead or leadless, J-lead or BGA, the saturated vapor is equally capable of accessing, condensing, and thus reflowing all types of solder joints.

3.4 Solder Composition and Properties

With a history of use in electronic packages dating back over thirty years, the eutectic Sn/Pb alloy has the greatest depth of background information and technical understanding of all solders. Commonly referred to as 63Sn/37Pb, where the numerical values represent weight percentages, the actual eutectic composition is 61.9Sn/38.1Pb. Slightly off-eutectic compositions such as 60Sn/40Pb and 63Sn/37Pb are referred to as hypoeutectic and hypereutectic, respectively. The eutectic mix has a melting point (mp) of 183°C as shown by the Alloy 1 line in Figure 3.4.1, the phase diagram for the Sn/Pb system. At the eutectic point three phases may coexist: liquid (61.9wt%Sn), α (19.2wt%Sn) and β (97.5wt%Sn). Off-eutectic compositions, such as the hypoeutectic composition denoted by the Alloy 2 line, have a temperature range where both solid and liquid can coexist. This temperature range, as opposed to the single point of the eutectic composition, is also known as the “pasty range” and can be useful in applications. It offers a larger window of time for manipulation during the soldering process which is particularly
beneficial for non-machine soldering of copper pipes in water systems. Some BGA’s use a 10Sn/90Pb spherical solder core as the primary support which is attached to the leads via eutectic Sn/Pb. As can be seen in Figure 3.4.1 the solidus of the 10Sn/90Pb is not reached until well over 250°C; thus the spherical core remains solid and can provide mechanical support to the chip during the soldering process.

Despite its versatility and history in electronic packages Pb-based solder is rapidly being phased out of use due to environmental and health concerns. Pb is a cumulative poison that can result in a variety of developmental disorders in fetuses and infants in addition to being a carcinogen in adults [89S2]. In its elemental (inorganic) form Pb presents the least danger. Ingestion does not result in significant absorption into the body with the majority of Pb excreted via the digestive system or removed by the liver. Inhalation of elemental Pb is far more destructive due to easy absorption through the lungs. Pb can become airborne by careless handling of fine powders such as the +325/-500 powder used in this work. Similarly the wave soldering process can produce an accumulation of oxidized material, or dross, on the wave pool surface which can release Pb and Pb oxides into the atmosphere. Fortunately inorganic Pb will not easily absorb through the skin, which is not the case with organic Pb compounds.
Figure 3.4.1. Phase diagram for the Sn/Pb system [06S2, pg326]. Note the eutectic composition (Alloy 1 line) with a melting point of 183°C and a composition of 61.9wt% Sn and 38.1wt%Pb. At the eutectic point three phases can coexist: liquid (61.9wt%Sn), $\alpha$ (19.2wt%Sn) and $\beta$ (97.5wt%Sn). (With permission, from Smith, Hashemi, Foundations of Materials Science and Engineering, 4th Ed, New York, NY: McGraw-Hill, 2006.).
Organic Pb compounds are the cause for most concern and legislation because they are easily absorbed through the skin and lungs. In the past, a variety of Pb-containing compounds were routinely used in unregulated ways, even on food products. Pb arsenate was once a common insecticide for fruits; amazingly the combination of Pb and arsenic in a single compound wasn’t a source of worry and it was used for nearly half a century [98P1]. Unfortunately it was replaced by an insecticide no less dangerous, dichlorodiphenyltrichloroethane (DDT). Tetraethyl Pb was an anti-knock agent for internal combustion engines and its removal from the petroleum industry was marked by the advent of “lead-free” gasolines. With such a history of health hazards it is not surprising that a number of legislative bodies have limited the use of Pb regardless of form or application.

Perhaps the most widely known restriction on Pb is the Restriction of Certain Hazardous Substances, or RoHS. In addition to restricting the atomic percentage of Pb of any form in RoHS also limits the distribution of products containing cadmium, mercury, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated dipheny ether (PBDE). Effective July 1, 2006 RoHS bans the placement of any new electrical or electronic equipment containing the aforementioned compounds on the UK market [05R2]. The majority of violations as of 2008 were in hand-soldered reworks and Pb used as a pigment in plastics; the majority of machined solder joints were considered Pb-free
However, there are at least 27 products or industries exempt from the ban, notably eight concerning soldering and solder alloys. In particular, the automotive, avionics, medical and military applications of Pb in solders are generally exempt from RoHS restrictions [06G1, pg55]. Moreover, the U.S. Environmental Protection Agency (EPA) does not have an explicit ban on Pb-based solders in electronics but instead relies on economic pressure to reduce the amount of Pb in products [05G2]. The emphasis on going Pb-free has been generally successful in that a majority of large corporations have adopted Pb-free policies, and as a result a number of Pb-free solder alloys have been developed to replace the once-ubiquitous eutectic Sn/Pb solder.

Nearly all Pb-free solder alloys consist of a majority of Sn because it wets a variety of substrates and does not require corrosive or aggressive fluxing agents [00A1]. The first requirement for solders to be used in electrical packages is to be at a eutectic composition; the aforementioned pasty range of off-eutectic compositions is detrimental to soldering because it allows a greater opportunity for the components to shift or dislodge during cooling. After composition comes melting point which is directly related to energy costs and can potentially impact other PCB components. Ganesan and Pecht [06G1, pg84-91] offer an extensive summary of Pb-free solders along with their advantages and disadvantages; these findings are summarized in Table 3.4.1. When discussing Sn-based alloys, the weight percent of Sn is generally omitted.
and only the other compound percentages are reported; thus 63Sn/37Pb would become Sn/37Pb.

An alloy with a particularly low melting point of 138°C, Sn/58Bi is also one of the few alloys that do not have a majority Sn component. Despite the economic advantages of such a low melting point it also precludes applications in electronics because of the operating temperature of the electronic package can occasionally exceed 140°C; the solder joint would thus melt and likely fail to provide adequate mechanical support to the component. Sn/9Zn has a melting temperature comparable to eutectic Sn/Pb, 199°C, and also exhibits generally higher tensile strength, ductility and fatigue resistance. The rapid oxidation of Zn at reflow temperatures can lead to embrittlement and poor wetting; such oxidation leads to considerable reaction with fluxing agents.

Silver and copper have been alloyed with tin to good effect. The low material cost of Sn/0.7Cu (mp 227°C) makes an argument for the alloy but the high reflow temperatures, usually about 35°C higher than the melting point, are cause for concern regarding thermal damage to PCB components. Moreover the alloy tends to form bridges between SMT leads resulting in short-circuiting. Another majority-Sn alloy is Sn/3.5Ag (mp 221°C) which again has a high reflow temperature but has favorable mechanical properties compared to Sn/0.7Cu. The high reflow temperatures of Sn/3.5Ag and Sn/0.7Cu can be tolerated and are in fact preferable in certain applications such as the automotive
industry where operating temperatures are generally higher than in other electronic applications.

A popular ternary alloy developed as a drop-in replacement for Sn/37Pb solder is Sn/3.5Ag/0.7Cu (mp 217-218°C). Its advantages include fatigue strength 3-4 times greater than Sn/37Pb as well as good wetting characteristics, albeit with the requirement of careful flux selection. Similarly Sn/2.5Ag/0.8Cu/0.5Sb (mp 217°C) has nearly identical thermal and electrical conductivities to Sn/37Pb and better fatigue resistance. Addition of antimony is somewhat controversial in that it can thermally degrade and release toxic compounds [06G1, pg91] but

Table 3.4.1. Pb-free alloys and their advantages and disadvantages, arranged by melting point. Collected from [06G1, pg84-91].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Melt Point (°C)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/58Bi</td>
<td>138</td>
<td>• Decent fatigue resistance</td>
<td>• Low mp precludes use in electronics</td>
</tr>
<tr>
<td>Sn/9Zn</td>
<td>199</td>
<td>• Comparable MP to Sn/37Pb</td>
<td>• Rapid Zn oxidation leads to embrittlement, poor wetting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Higher tensile strength, ductility and fatigue resistance compared to Sn/37Pb</td>
<td>• Reaction with flux</td>
</tr>
<tr>
<td>Sn/2.5Ag/0.8Cu/0.5Sb</td>
<td>217</td>
<td>• Comparable thermal and electrical conductivities</td>
<td>• Antimony can be toxic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Improved fatigue strength</td>
<td>• Quaternary alloys can present quality control issues</td>
</tr>
<tr>
<td>Sn/3.5Ag/0.7Cu</td>
<td>217-218</td>
<td>• 3-4x greater fatigue strength</td>
<td>• Fatigue strength deteriorates quickly</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Decent wetting</td>
<td></td>
</tr>
<tr>
<td>Sn/3.5Ag</td>
<td>221</td>
<td>• Longest history of use of all Pb-free alloys</td>
<td>• High reflow temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Good mechanical properties</td>
<td>• High silver requirement for wave soldering applications</td>
</tr>
<tr>
<td>Sn/0.7Cu</td>
<td>227</td>
<td>• Adequate wetting</td>
<td>• High reflow temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Lowest cost of Pb-free solders</td>
<td>• Tends to bridge leads on SMT components</td>
</tr>
</tbody>
</table>
is generally considered safe at reflow temperatures. Finally, quaternary alloys may present quality control issues because of their carefully defined component percentages; small variations in composition can decrease the reliability of the soldered joints.

Despite the variety of solder alloys commercially available each has their own disadvantages as briefly summarized in Table 3.4.1. Moreover the average coefficient of thermal expansion of a solder is between 20 and 30 ppm/°C [00A1] whereas that of a Kovar or Alloy 42 lead is about 5 ppm/°C [02E1, 03N1]. There is therefore a demand for solders with improved mechanical and thermal properties. In the interest of developing such a solder, a number of researchers have investigated additives to serve as reinforcements; a solder with a secondary reinforcement phase is termed a “solder composite”. The types and methods of reinforcement have been developed in the field of metal matrix composites alongside a variety of non-solder composites, which will be covered in the next section.
Producing a metal matrix composite can be accomplished by combining various fillers and metals by an assortment of different methods. The purpose of this review is to highlight the recent direction of filler choice, namely towards nano-scaled materials, and to present the common methods of composite fabrication. While the thrust of this thesis concerns solder and solder composites a more complete image of composite technology can be afforded by first reviewing progress in non-solder metals. Consequently there are two sections to follow, the first on aluminum composites and the second on solder composites. Aluminum was chosen as the reference metal because it is one of the more common metals used in composites, likely because of its low cost and relatively low melting point. No solders were excluded from this survey because generally all solders have the same operating requirements in that they are rarely used outside electronic packages.
4.1 Aluminum Composites

Aluminum is a popular metal for metal matrix composites because it is often chosen as a light-weight, electrically conductive material for high-performance applications such as aircraft fuselages or electronic packages. Fillers can be added to aluminum in order to improve the mechanical and thermal properties of bulk aluminum, such as ultimate tensile strength or the coefficient of thermal expansion (CTE). Fabrication methods can be grouped into the categories listed in Table 4.1.1 which summarizes the fillers, loading levels, methods and testing results from recent publications. Each is described in detail in the following passage.

Perhaps the most obvious method of producing a metal matrix composite is to melt the metal, add filler and allow the metal to cool and crystallize. These steps are the premise of squeeze casting, whereby a

Table 4.1.1. Summary of aluminum composites reviewed in this text. The methods are representative of the primary composite fabrication methods and are generally performed with only slight modification; descriptions of each method are provided in the text.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Loading</th>
<th>Method</th>
<th>Result</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC particles</td>
<td>55vol% (3,10,20,40um)</td>
<td>Squeeze casting</td>
<td>CTE decrease</td>
<td>[98E1]</td>
</tr>
<tr>
<td>SiC particles</td>
<td>0-40vol%</td>
<td>Duralcan®</td>
<td>CTE decrease</td>
<td>[98L1]</td>
</tr>
<tr>
<td>SWCNT</td>
<td>5wt%</td>
<td>Powder compaction</td>
<td>Hardness increase</td>
<td>[03Z1]</td>
</tr>
<tr>
<td>SWCNT</td>
<td>0-15vol%</td>
<td>Powder metallurgy</td>
<td>CTE decrease</td>
<td>[04T1]</td>
</tr>
<tr>
<td>SWCNT, MWCNT</td>
<td>0-2vol%</td>
<td>Powder metallurgy</td>
<td>Young’s modulus, yield strength, UTS</td>
<td>[05G1]</td>
</tr>
<tr>
<td>MWCNT</td>
<td>1wt%</td>
<td>Squeeze casting</td>
<td>CTE decrease</td>
<td>[08D1]</td>
</tr>
<tr>
<td>AlN</td>
<td>4-40vol%</td>
<td>PVD</td>
<td>CTE decrease</td>
<td>[09L1]</td>
</tr>
</tbody>
</table>
molten metal is poured into a mold containing the filler and pressure is applied to force the metal to fill the voids between the filler particles. Elomari et al. [98E1] used such a technique to fabricate silicon carbide (SiC) aluminum composites. The volume fraction of filler was kept at a constant 55% while the size of the filler was varied from 3-40 μm and it was observed that the CTE decreased with decreasing particle size. This result was attributed to an increase in the ratio of surface area to volume which promoted greater interfacial contact and restricted the thermal expansion of the aluminum. More recently Zhang and Gu [06Z1] used squeeze casting on aluminum with silicon (Si) microparticles and found that not only did the CTE decrease but so too did the flexural strength and density of the composite. These last two results are reasonable since Si is more brittle and less dense than aluminum.

Similarly Lemieux et al. [98L1] varied the volumetric percentage of 10 μm SiC particles in aluminum from 0-40% by using the Duralcan® method. The Duralcan® technique involves stirring the molten metal, usually with a graphite mixer, under an inert gas shroud as filler is slowly added; the composite is crystallized by pouring the molten composite into a mold. Measurements of the composite CTE showed a decrease with increasing volume percentage of filler, a result that can be interpreted through the results from Elomari et al.: the greater volume percentage results in greater interfacial contact and therefore a lower CTE. Recently Deng et al. [08D1] developed a modified squeeze casting process in
which 1wt% of multi-walled carbon nanotubes (MWCNTs) were combined with aluminum particles by room temperature isostatic pressing followed by compression above aluminum’s melting point. An 11-12% decrease in the composite’s CTE was attributed to “the restriction on aluminum”, referring to the large interfacial area of the MWCNTs inhibiting the thermal expansion of the aluminum matrix.

An alternative to working with molten metal is the technique of powder metallurgy whereby the filler is mechanically mixed with a powdered metal, compressed into pellets, sintered and extruded. Mixing can be performed with either dry materials or by suspending the powdered metal and filler in a liquid to form a slurry. Compression can be carried out under controlled atmosphere (vacuum, air, inert) and temperature. The extrusion can take place under hot or cold conditions but is always performed below the melting temperature of the metal. Using such a process without the extrusion step, Tang et al. [04T1] fabricated single-walled carbon nanotube (SWCNT) composites. As the volume percentage varied from 0-15% it was observed that the CTE was reduced by a maximum of about 65%. Carbon nanotubes are generally accepted to have a CTE of nearly zero [04T1, 06S1, 08D1, 09L1] in addition to exceptionally high Young’s moduli, between 1 and 5 TPa [05G1]. Combined with their low density of about 1-2 g/cm³ [00C1, 07D1] carbon nanotubes present themselves as excellent candidates for composite fillers. George et al. [05G1] used powder metallurgy with hot
extrusion to observe improved mechanical properties in aluminum composites of both SWCNTs and MWCNTs fillers at low concentrations, 0-2vol%. The properties investigated did not include CTE but instead focused on Young’s modulus, yield strength and ultimate tensile strength (UTS); all increased with increasing concentration.

In addition to the above methods several groups have their own fabrication techniques. Ultrasonication was utilized by Zhong, Cong and Hou [03Z1] to disperse 0.5wt% SWCNT in a solution of ethanol and aluminum nanopowder. After drying the composite was compacted first at room temperature and then again at temperatures ranging from 260 to 480°C; an increase of 78% in hardness over the non-composite aluminum nanopowder was reported. Most recently Liu, Cong and Cheng [09L1] fabricated the initial powder composite via arc-discharge plasma evaporation of aluminum. By controlling the amount of nitrogen in the atmosphere, the amount of aluminum nitride nanoparticles could also be controlled; hot pressing consolidated the powder into pellets for testing. Varying the volume percentage of aluminum nitride from 4-40% had negligible effect on the composite’s thermal conductivity but resulted in up to a 48% decrease in CTE.
4.2 Solder Composites

Before detailing pertinent examples of solder composites, a review of relevant publication rates may be beneficial in understanding the driving force behind composite development. The Institute for Scientific Information (ISI) Web of Knowledge [09T1, Figure 4.2.1] shows less than four publications per year from 1991-1998 containing the keywords **solder** and **composite**. In 2002, however, European Union (EU) Directive 95 established the RoHS directive to remove Pb-based solders from the European market [03E1]; see Section 3.4 for more details on RoHS and the hazards of Pb. In the same year the number of publications increased by nearly 60% over the previous year and nearly surpassed the sum of publications from the aforementioned eight year time frame. Similarly when RoHS was enacted in 2006 [05R2] the publication count saw a full 100% increase over the previous year and a 72% increase over the previous high in 2002. A corollary in materials selection was observed as well; the solder chosen prior to 2002 were primarily eutectic Sn/Pb whereas starting in 2002 non-Pb eutectics such as Sn/Cu and Sn/Ag were far more popular choices. Accordingly, the following literature survey is grouped by the metal used for composite fabrication; Pb-based solders will be followed by Pb-free solders. A summary table is again provided in Table 4.2.1.
Figure 4.2.1. Publication history for search terms SOLDER and COMPOSITE as reported by the ISI Web of Knowledge [09T1] in June 2009. Highlighted in green are increases that may be correlated with the establishment of RoHS in 2002 [03E1] and its enactment in 2006 [05R2].
Table 4.2.1. Summary of solder composites reviewed in this text. The composites are arranged by the type of solder matrix.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Filler</th>
<th>Method</th>
<th>Result</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/Pb</td>
<td>Cu-coated carbon fiber</td>
<td>Squeeze casting</td>
<td>CTE, ductility decrease; thermal fatigue, tensile increase</td>
<td>[90H1]</td>
</tr>
<tr>
<td>Sn/Pb</td>
<td>Al2O3, TiO2 nanoparticles</td>
<td>Repeated hot press</td>
<td>Generally increased strength</td>
<td>[98M1]</td>
</tr>
<tr>
<td>Sn/Pb</td>
<td>Cu nanoparticles</td>
<td>Mech. mix w/ solder paste</td>
<td>Increased intermetallic growth</td>
<td>[02L1]</td>
</tr>
<tr>
<td>Sn/Pb</td>
<td>Cu, TiO2 nanoparticles</td>
<td>Mech. mix w/ solder paste</td>
<td>Refined microstructure</td>
<td>[03L1]</td>
</tr>
<tr>
<td>Sn/Pb</td>
<td>TiO2 nanoparticles</td>
<td>Mech. mix w/ solder paste</td>
<td>Refined microstructure</td>
<td>[03L2]</td>
</tr>
<tr>
<td>Sn/Pb</td>
<td>SWCNT</td>
<td>Powder metallurgy</td>
<td>CTE, MP decrease; mech. prop. improved</td>
<td>[08K1]</td>
</tr>
<tr>
<td>Sn/Cu</td>
<td>Ag nanoparticles</td>
<td>Mech. mix w/ solder paste</td>
<td>Improved wettability, mechanical properties</td>
<td>[05T1]</td>
</tr>
<tr>
<td>Sn/In/Cu/Ga, Sn/Ag/Cu/In</td>
<td>Al2O3 nanoparticles</td>
<td>Powder metallurgy</td>
<td>CTE reduction, UTS increase, duct. decrease MP decrease, improved mech. properties</td>
<td>[05Z1]</td>
</tr>
<tr>
<td>Sn/Pb, Sn/Ag/Cu</td>
<td>SWCNT</td>
<td>Powder metallurgy</td>
<td>CTE , contact angle decrease; MP unchanged</td>
<td>[06K1]</td>
</tr>
<tr>
<td>Sn/Ag/Cu</td>
<td>MWCNT</td>
<td>Powder metallurgy</td>
<td>Nano does not change electrical res.; micro does</td>
<td>[06N1]</td>
</tr>
<tr>
<td>Sn/Ag, Sn/Ag/Cu</td>
<td>SnO2, TiB2, Cu, Y2O3 nanoparticles</td>
<td>Powder metallurgy</td>
<td></td>
<td>[09B1]</td>
</tr>
</tbody>
</table>
In 1990 Ho and Chung [90H1] coated 10μm carbon fibers with copper and incorporated them into near-eutectic 60Sn/40Pb solder via squeeze casting. With a filler content of 0-45vol%, increases in tensile strength and thermal fatigue life were observed as well as decreases in CTE and ductility; the Cu-coated fibers generally performed better than the uncoated fibers. For soldering applications an increase in thermal fatigue life is desirable because electronic packages are frequently exposed to temperature cycles as the components are powered on and off. Mavoori and Jin [98M1] developed a unique hot pressing method whereby a pellet of pressed solder and alumina or titania nanopowders is repeatedly cut, stacked and pressed again to one-sixth of the pellet’s initial size. Decreases in ductility were accompanied by increases in tensile strength and were attributed to grain boundary pinning by the nanoparticles. Lin et al. [02L1, 03L1, 03L2] mechanically mixed copper and titania nanoparticles with solder paste and then reflowed the paste under an argon atmosphere. Hardness testing on the titania composites reportedly revealed an increase but the data fail to show statistical significance according to a standard F-test (P-value = 0.61) or Tukey’s HSD procedure. Figure 4.2.2 shows the considerable overlap of 95% confidence intervals in Lin’s titania data; the implication is that there is no statistical difference between pure solder and that with titania nanoparticles. A reasonable explanation is filler expulsion during reflow, as described in Section 6.6.
Departing from Pb-based solders, silver nanoparticles were combined with eutectic Sn/Cu solder by Tai et al. in 2005 [05T1]. Instead of a standard powder metallurgy method the composites were fabricated via mechanical mixing with the solder paste, as with Lin et al. [02L1]. Slight increases with filler concentration in the contact angle between the molten solder composite and a copper substrate were noticeable but considered acceptable. Generally increases in contact angle imply a reduction in wetting performance but the observed increase was only about 3°, from a contact angle of 11° to 14°. Improvements in shear strength and creep performance were observed as well. Zhong and Gupta [05Z1] investigated the effects of alumina nanoparticles in a patented quaternary alloy, Viromet 349, which is an alloy containing unknown ratios of Sn/In/Cu/Ga or Sn/In/Cu/Ag. Varying the weight percent of alumina from 0-2.74% via powder metallurgy resulted in CTE reduction, increases in hardness, 0.2% yield strength and UTS, as well as a reduction in ductility.
Figure 4.2.2. Microhardness data from Lin et al. [03L2] for a titania-solder composite. The $F$-test ($P$-value = 0.61) and Tukey’s HSD procedure (red line) show no significant difference between the reported results. This is likely due to filler expulsion during reflow as described in Section 6.6.
However these results were generally invariant with respect to the amount of filler: so long as any amount of alumina nanoparticles was present there was a change in the mechanical property. Increasing the extrusion temperature resulted in a decrease in CTE, yield strength and UTS compared to room temperature extrusion. Recently Bagahorbani, Nai and Gupta [09B1] used powder metallurgy with binary (Sn/Ag) and ternary (Sn/Ag/Cu) solders to fabricate composites of a variety of nanoparticle fillers including SnO$_2$, TiB$_2$, Cu and Y$_2$O$_3$. While improved mechanical properties were reported the emphasis was that nanometer-scaled reinforcements do not change the electrical resistivity of the composite whereas micron-scaled reinforcements show a marked increase in resistivity. Electrical resistivity plays a role in heat generation during operation and can therefore exacerbate related thermal problems in electronic packages such as CTE mismatch or poor thermal fatigue resistance.

As was the case with aluminum composites, attention has recently turned to solder composites using SWCNTs and MWCNTs as fillers. Kumar et al. [06K1], using powder metallurgy with SWCNTs at 0.05 and 0.5wt%, observed decreases in melting point and ductility as well as increases in UTS and Young’s modulus. Both eutectic Sn/Pb and Sn/Ag/Cu solders were investigated and offered similar results. Later, Kumar and Kripesh [08K1] again investigated SWCNTs in only eutectic Sn/Pb but varied the filler content from 0-0.5wt% in seven steps and
observed a smooth transition in CTE from 25.8ppm/°C to 19.2ppm/°C. Mechanical properties such as microhardness, yield strength, UTS and Young’s modulus again showed continuous increase although UTS exhibited a maximum at 0.3wt% due to agglomeration. Nai, Wei and Gupta [06N1] investigated a ternary (Sn/Ag/Cu) solder composite via powder metallurgy with MWCNTs from 0-0.07wt%. However the results were considerably different from Kumar’s group: the melting point was unchanged, the CTE was decreased by the same amount regardless of filler quantity and both the microhardness and tensile measurements showed maximums at 0.04wt%. Decreases beyond 0.04wt% were attributed to the formation of micropores due to the high filler concentrations; the pores then served as crack nucleation sites and regions of high stress concentration.

4.3 Summary of Findings

Clearly it is possible to improve mechanical properties such as CTE, hardness and yield strength of metal matrix composites with the addition of a filler materials; methods have been presented to incorporate ceramic, metallic and carbon-based (i.e. SWCNTs, MWCNTs) fillers. However, the most important conclusion is that regardless of method, be it powder metallurgy, squeeze casting, or any variant thereof, the composite is almost universally tested before reflow. The products of
powder metallurgy, typically cm- or mm-sized rods, are frequently cited as a product for soldering applications; this is true but the rods are melted to form pools for wave soldering as described in Section 3.3.1. Squeeze casting is not practical for the high density of contacts typical of surface mount technology and is not feasible for ball-grid arrays as in Section 3.2. In the few cases where reflow was performed on the composite sample, there was either no analysis of filler agglomeration or expulsion [05T1], or the results exhibited error beyond acceptable limits [02L1, 03L1, 03L2]. Therefore the need to understand the effects of reflow on solder composites should be clear if one is to develop a practical application of such a composite.
The goal of the experimental procedures was to reliably produce ceramic nanofiber-reinforced metal powder composites to be tested for the coefficient of thermal expansion. In order to produce such a composite the fabrication steps were broken into four distinct areas: electrospinning, ultrasonication, composite formation and testing. This section seeks to elaborate upon each of these areas to the extent that the results could be reproduced in an independent laboratory. Where appropriate, comment regarding especially important or critical steps will be provided.

5.1 Titania Nanofiber Electrospinning

The process of electrospinning utilizes a high-voltage electric field to elongate polymeric solutions and thereby reduce their diameter to the nanoscale. As shown in Figure 5.1.1 the electrospinning apparatus consisted of a variable DC high-voltage source (Gamma High Voltage
ES30P-5W), electronic syringe pump (WPI SP101I), rotating drum for fiber collection and plastic sheet enclosure. The positive lead of the high voltage supply was connected to a modified syringe needle; the negative lead was connected to the collection drum. Plastic fittings and tubing connected the needle to the syringe and allowed the needle to be placed above the collection drum while the syringe pump was located to the side. The plastic sheet enclosure, in addition to protective eyewear and face masks, limited exposure to airborne nanofibers.

A titania precursor solution, described in greater detail shortly, was loaded into a disposable 5mL disposable syringe (BD 21G1). The needle tip was modified to remove the bevel in order to allow a more symmetric distribution of solution at the needle tip during spinning. The collection drum was set to rotate at approximately 5RPM and was covered in aluminum foil to facilitate collection and removal of fiber mats. The syringe pump was set to dispense solution at 15μL/min and an electric field of 19kV was applied between the needle tip and collection drum. A gap of approximately 19cm separated the needle tip and collection drum which resulted in an electric potential of about 1kV/cm. Relative humidity (RH) and temperature were monitored.
Figure 5.1.1. Electrospinning apparatus for titania nanofiber electrospinning. (a) Syringe (b) Syringe pump (c) Support structure (d) Rotary power supply (e) DC high-voltage supply (f) Needle tip.
during electrospinning via digital hygrometer (Control Company, 4185) which allowed humidity resolution down to 10%RH ± 4% and temperature resolution to ± 1°F. Table 5.1.1 summarizes these electrospinning parameters.

The aforementioned titania precursor solution resulted from a two-step process. In the first step a 5.5wt% solution of poly(vinyl pyrrolidone) (PVP, Sigma-Aldrich, MW 1.3E06) in ethanol (Pharmco, 200 proof) was mixed at room temperature for twenty-four hours to ensure complete dissolution of PVP into the ethanol. Mixing was performed in 60mL narrow-neck amber glass bottles with a Teflon-coated magnetic stir bar providing agitation. Absolute values (i.e. RPMs) were not available but stirrer speed was consistently set at a dial reading of 6 on the magnetic stir plate (Corning PC-420). 99.9% tetraisopropyl titanate (TPT, Table 5.1.1. Parameters for titania nanofiber electrospinning process. Asterisked values represent standard observations of uncontrolled parameters; non-asterisked values are equipment settings.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>23*</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>%</td>
<td>&lt; 10*</td>
</tr>
<tr>
<td>Syringe Pump Rate</td>
<td>µL/min</td>
<td>15</td>
</tr>
<tr>
<td>Collector Rotation Speed</td>
<td>RPM</td>
<td>5</td>
</tr>
<tr>
<td>Gap Distance</td>
<td>cm</td>
<td>19</td>
</tr>
<tr>
<td>DC Voltage Potential</td>
<td>kV</td>
<td>19</td>
</tr>
<tr>
<td>DC Voltage Field</td>
<td>kV/cm</td>
<td>1</td>
</tr>
</tbody>
</table>
Dupont Tyzor TPT) was then added to the polymer solution at a ratio of 1:0.56 by weight solution:TPT. The resulting mixture was stirred for three hours in the same manner as the PVP solution but was additionally jacketed in cooling water to maintain a temperature of approximately 22°C. The solution was allowed to age for seven days after which electrospinning was performed.

The duration of this aging period was intended to allow a number of in-solution processes to equilibrate and is consequently an important step in the preparation of electrospun nanofibers. The effects of viscosity on electrospun fibers have been shown to include fiber diameter [07T1] and bead formation [99F1] and so the potential variations in viscosity must be considered in order to achieve reproducible results. The addition of TPT to the 5.5% PVP solution was observed to alter the viscosity much as the addition of any liquid to a solution could be expected to do, and so ample time was provided to allow the solution to achieve homogeneous viscosity. Similarly, since viscosity is a function of temperature, the heat of mixing that resulted from the introduction of TPT into the PVP solution was another source of non-homogeneity that was countered by a seven day aging period. Furthermore TPT, a relatively large molecule of about 12Å [04T2], would be more susceptible to steric hindrance during diffusion processes. Therefore, the even distribution of TPT into PVP chain cavities by diffusion was encouraged by the aging period. Finally the aging period allowed gas pockets that had developed during mixing
via magnetic stir plate to dissipate. Obviously the presence of gas pockets would produce discontinuous fiber segments if they were to reach the needle tip of the electrospinning apparatus (see Figure 5.1.1, detail f).

The solution and method above resulted in a bead-on-string structure of electrospun material which is elaborated upon in Section 6.1. In order to spin smooth titania nanofibers a method of removing the beads is necessary. One method of bead formation occurs when the capillary forces of the fiber are greater than the elongational forces of the applied electric field [99F1, 08R1]. The capillary forces act to minimize surface area by creating spherical drops of solution while the electric charge on the solution, concentrated mostly on surface of the fiber, provides a counteracting force due to the repulsion between particles of the same charge. Thus, one possible way of spinning smooth nanofibers is to increase the net charge density in the fiber by adding a material with lower dielectric constant.

The dielectric constant of a material is the ratio of the material’s electrical permittivity to that of empty space. Generally, a high permittivity reduces the strength of an electric field; therefore low permittivities, and hence low dielectric constants, should be beneficial for electrospinning smooth fibers. The solution described above used primarily ethanol as a liquid carrier; ethanol has a dielectric constant of 24.3. Acetic acid, used in several titania solutions in literature [08C1, 08T1], has a dielectric constant of 6.2 and so its addition to the solution
would be expected to lower the overall dielectric constant of the solution. To add acetic acid to the existing solution, a volume of the solution was drawn into a 5 cm$^3$ syringe and the mass determined via electronic balance. A mass of acetic acid approximately equal to the calculated mass of TPT in the solution was added to the syringe via pipet; this mass provides a concentration of acetic acid slightly higher than reported in literature. Scanning electron microscopy (SEM, Quanta 200, FEI Corporation), field emission SEM (FESEM, JEOL JSM 7501 Scanning Electron Microscope) and x-ray diffraction (XRD, XRG 3100, Philips) were used to characterize the shape and titania phase of the reinforcement. Any measurements of SEM micrograph features were performed with ImageJ software (Version 1.04o, NIH) using the scale bar provided on each micrograph. CuKα radiation with a wavelength of 1.54Å was used for the XRD analysis on all titania samples after ultrasonication and drying.

A hydrolysis reaction is responsible for converting TPT to titanium dioxide (titania) and isopropyl alcohol (IPA). During electrospinning the TPT in the solution undergoes hydrolysis after exiting the needle tip to form titania particles entrapped in a polymer matrix and IPA. Once spun, the fibers were collected from the aluminum foil and placed in alumina crucibles for calcining. Calcining at 700°C in air (Thermolyne 2100 Tube Furnace) for 2 hours removed organics such as PVP and IPA and sintered the titania particles into a continuous fiber.
5.2 Ultrasonication of Calcined Titania Nanofibers

Ultrasonication is a process in which a piezoelectric crystal expands and contracts at high frequencies to create intense cavitation in a liquid sample. An ultrasonicating system (Misonix XL2020, 600W) was equipped with a ½” titanium resonator horn tuned to 20kHz; the apparatus is depicted in Figure 5.2.1. Ultrasonication served two purposes: to evenly disperse the fibers and provide a degree of control over the length of fibers. Calcined fibers were immersed in 140mL of ethanol; the horn tip was then submerged 1.5in below the surface of the ethanol. The sonication chamber was immersed in a cooling water bath to dissipate heat generated during ultrasonication. Water at 20°C was passed through the coolant bath at 900mL/min; the titania/ethanol solution temperature at the end of mixing was typically around 35°C. The sonication power setting was 7 based on manufacturer recommendations for solution viscosity and volume; the duration was 10 minutes. Appendix B details the effects of sonication intensity and duration on fiber length as determined by optical microscopy. Accordingly, the 10 minute duration was chosen to ensure that fiber lengths were approximately equal to the diameters of the titania powder (6.5μm). The resulting slurry was dried under vacuum at 150°C (VWR 1410D) with a standard rough pump (Edwards E2M2) providing vacuum of around 30inHg for 24 hours. It was observed that drying under ambient conditions for the same time period
did not sufficiently remove the ethanol and resulted in uneven surfaces and porosity in sintered composite samples. This additional drying step therefore represents a critical portion of the fabrication process in that failure to perform this step will result in inconsistent samples. Moreover the inconsistency will not be observed until after the processed fibers are incorporated into the final pressed form as in Section 5.3; consequences include a loss of material and not insignificant amounts of time and effort. The dried fibers were collected from the borosilicate glass dish used for drying and stored in sealed plastic containers for incorporation into powder composites.

Commercially available titania nanopowder (Nanomyte TiO$_2$, Nanopowder Enterprises, Inc) was subjected to the same process to provide information on shape effects of composite fillers. The powder was subject to SEM analysis to determine the average size of the particles; results are presented in Section 6.1.
Figure 5.2.1. Ultrasonication setup used for sonication of titania nanofibers in ethanol. (a) Coolant outlet (b) Coolant inlet (c) Coolant water bath (d) Sonication vessel (e) Sonication horn (f) Ultrasonic converter. The solution to be sonicated is dyed green here to provide contrast to the coolant bath.
5.3 Powder Composite Preparation

A eutectic Sn/Pb (63/37wt%) solder powder (Amtech 219x18) with a mesh size of -300/+525, or about 25-50μm, was used as the matrix material. Figure 5.3.1 shows the powder with a contrasted background. Various weight percentages of titania nanofibers and nanopowders were added to the solder powder; these combinations are detailed in Table 5.3.1. The powder mixtures were ball-milled with tin shot (99.999%, A.D. Mackay) for 2 hours in borosilicate glass bottles at 25RPM to provide even distribution of the filler. 2g samples of the composite powder were uniaxially compressed (Dake 44-226) at 70MPa for three minutes to form green sample pellets. The pressure applied to the die lowered of its own accord to about 50MPa during the three minute period as the sample compressed. A cross-section of a typical pellet is shown in Figure 3.3.2. Pellet density was determined using Archimedes’ method in deionized water at room temperature and Appendix A provides a description of this method.

Sintering was employed in an attempt to increase the density of the green pellets to nearly the density of reflowed samples. The samples were sintered at 150°C under vacuum for 24 hours in the same apparatus described in Section 5.2. An evacuated chamber was used to prevent oxidation of the samples for a number of reasons: a liquid flux coating proved difficult to remove after sintering; a nitrogen or other inert gas
atmosphere would require a separate unit. Sintering times longer than 24 hours (i.e. 36, 48 hours) resulted in a decrease in sample density, likely due to the imperfect vacuum allowing small amounts of oxidation. Densities were again measured by Archimedes’ method after sintering.

Table 5.3.1. Titania nanopowder and nanofiber concentrations used in this study. Filler amounts are weight percentages.

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Samples in set</th>
<th>Wt% Filler Nanopowder</th>
<th>Nanofiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.50</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.75</td>
<td>0</td>
</tr>
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<td>1.00</td>
<td>0</td>
</tr>
<tr>
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<td>5</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>0</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>0</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 5.3.1. 100x magnification of the eutectic solder powder used for composite fabrication. Mesh size for this solder is -300/+525, or about 25-50μm.
Figure 5.3.2. Typical pressed composite sample and dimensions. All measurements are in inches.
5.4 Determination of Coefficient of Thermal Expansion

Sintered samples were sent to NASA-Glenn Research Center (Cleveland, OH, U.S.A) for thermomechanical analysis. A dilatometer (TA Instruments Q-Series) with 0.01μm resolution was used to determine sample expansion from 0-100°C. Before each set of measurements an aluminum standard was measured to confirm that the equipment was operating properly and consistently. A quartz sample holder supported the compressed solder sample in air while a quartz probe rested on the top of the sample. Good mechanical contact between the quartz and sample was necessary to avoid spikes in measurements due to sample movement. Such contact was achieved after several iterations by preparing the samples via uniaxial compression in a die with smooth, parallel surfaces. Samples were initially cooled to around -50°C and then heated at 2.5°C/min to compensate for unavoidable noise in initial measurement values. Noise during the initial warm-up period, from -50°C to 0°C, was attributed to thermal gradients within the sample causing uneven expansion of the sample. The coefficient of thermal expansion (CTE) was determined by software analysis (TA Universal Analysis software package).
5.5 Reflow of Composite Samples

As described in Section 3.3.3 a variety of methods exist for obtaining a desired reflow profile. Since no equipment was available that could both control the temperature profile and withstand the frequent expulsions of gases and material a low-temperature oven was constructed to fill this need. A control system was designed to offer appropriate flexibility and data collection, and was implemented with LabVIEW software (National Instruments, LabVIEW 8.6).

The finished oven is shown in Figure 5.5:1: (a) is an exterior view and (b) an interior showing the sample support structure and thermocouple contact point. The primary structure of the oven was a 4” OD tube constructed of 1/16” aluminum. Four 1/8” internal protrusions run the length of the tube (1’) and were located at 90° intervals; these protrusions served to support standard glass slides as sample supports. The aluminum tube was coated with an approximately 3/16” layer of thermally conductive ceramic material (Omegabond 400, Omega Engineering Inc) which served as an electrical insulator for the heating element. The heating element was five feet of 19 AWG nichrome (nickel/chromium/iron alloy) resistance heating wire (Mor Electric Heating Associates Inc) wrapped around the ceramic-coated aluminum tube. Additional ceramic material was placed directly atop the nichrome to prevent shifting and direct contact with any other materials. The entire
structure was then covered with 1” thick fiberglass insulation and wrapped in steel mesh to maintain good thermal contact. The end caps were cylinders of the same fiberglass insulation.

For temperature monitoring three exposed J-type thermocouples (0.005”, Omega Engineering Inc) were inserted through the end caps at varying lengths. One additional thermocouple was inserted through the cylinder such that it could rest on the sample during reflow. All four thermocouples were sheathed in double-bore ceramic tubes to prevent electrical contact with surrounding materials. A data acquisition unit (Personal DAQ/55, IOTech) was used to acquire temperature signals and route them to a computer via USB connection. After a variety of analysis by means of a unique LabVIEW virtual instrument (VI) a digital signal was sent to the DAQ to trigger a solid state relay (SSR, SSRL240DC25, Omega Engineering Inc).

The digital signal was based on a manner of control known as Pulse Width Modulation (PWM) where the time spent in the “on” position is the duty cycle of a square wave period. A variety of heating rates could be achieved by adjusting the duty cycle; larger duty cycles meant greater amounts of time in the “on” position and thus higher heating rates. While no explicit control system such as Proportional-Integral-Derivative (PID) was implemented, the system was able to achieve constant temperatures to about ±1% of the set point, with some degree of sinusoidal variation.
Figure 5.5.1. Low temperature reflow oven for reflowing composite samples. (a) Exterior view of oven, DAQ and SSR; the grey metal box in the upper-left corner is a Variac to reduce wall voltage to 30V. (b) Interior view of oven. The white cylinder extending from the top of the image is the sample thermocouple; the sample is resting underneath the thermocouple on the glass/aluminum support. Two oven thermocouples can be seen at the rear of the oven.
The data collected were the three oven temperatures and one sample temperature as well as the time the temperature was collected. The sample was covered with liquid flux (Liquid Rosin Soldering Flux 980063, Craftsman) to prevent oxidation during reflow; such a prepared sample is shown in Figure 5.5.2. The oven was set to ramp at a 40% duty cycle until the sample reached 100°C; this corresponded to a sample heating rate of about 6.5°C/min. After 100°C the temperature was ramped at 80% duty cycle until the sample reached 210°C; the 80% duty cycle was approximately 11°C/min. The initial slow heating rate was to prevent ejection of solder material as the volatile components of the flux

Figure 5.5.2. One-quarter (~0.5g) of a composite sample ready to be reflowed. The sample is covered with liquid rosin flux to prevent oxidation during reflow and rests on a disposable aluminum sheet to facilitate removal and analysis via optical microscopy.
boiled off; this corresponds to the “Paste Drying” section of Figure 3.3.3.

Note that the heating rate in this figure is approximately 120°C/min; the generally slower heating rate of the oven was simply a limitation of the unit, which had a maximum rate of about 20°C/min. After the sample reached 210°C the power was turned off and the sample cooled at about 5°C/min which was the natural, unforced cooling rate of the oven. Once the sample cooled to 150°C data collection ceased in the interest of maintaining reasonable file sizes. The oven was allowed to cool to at least 40°C before the next sample was reflowed. Samples were retained for examination via optical microscope (Mitutoyo 378 Finescope).
CHAPTER VI
RESULTS AND DISCUSSION

This chapter will present the results and analysis of the experimental work performed in Chapter I. The general order of this chapter parallels that of the experimental work: titania characterization, specific gravity measurements, optical microscopy, thermomechanical analysis and reflow analysis. An additional section regarding filler expulsion is included to further explore observations made during and after reflow. Suggestions for future work are included at the end of the chapter and focus on neutrally buoyant and scaffold-type fillers to overcome or eliminate the tendency of the filler to be expelled during reflow.

6.1 Titania Characterization

Three types of titania filler were incorporated into solder composites to observe morphological and size effects. Scanning electron microscopy (SEM) and x-ray diffraction (XRD) were used to
characterize the size and phase of each filler type. Here, phase refers to one of the three phases of crystalline titania: anatase (A), rutile (R), or brookite (B), or some combination thereof. For electrospun ultrasonication was used to ensure consistent fiber lengths as described in Appendix B. This section will summarize the results of SEM, XRD and optical microscopy performed on the three fillers, beginning with powdered titania followed by beaded and then non-beaded titania nanofibers. For clarity and because of the quantity of figures necessary for such an analysis, all figures will be presented at the end of the section.

As noted in Section 5.2 powdered TiO$_2$ (Nanomyte TiO$_2$, NEI) was used as an approximately spherical reinforcing material. Despite the size implied by the name, the powdered titania was generally not in the nanometer scale. Figure 6.1.1 illustrates a typical SEM micrograph of the powdered titania; agglomerations on the order of microns in diameter are clearly visible. While there may indeed have been nanoscale titania particles in the powder it was assumed that the majority of the titania mass was due to these micron-sized particles. Measurements of 84 different particles from a variety of SEM micrographs resulted in an average particle size of about 6.5±1μm where the error represents a 95% confidence interval. Agglomerations greater than 25μm were assumed to have been broken apart during ball milling.
A mix of anatase and rutile titania was reported by the manufacturer and was confirmed by XRD analysis. Work by Spurr and Myers [57S1] established a relationship between the intensities of rutile ($I_R$) to anatase ($I_A$) reflections at $25.4^\circ$ and $27.5^\circ$, respectively, and the weight fraction of anatase titania ($f$):

$$f = \frac{1}{1 + 1.26 \frac{I_R}{I_A}} \quad (6.1-1)$$

The XRD pattern for the titania powder is provided in Figure 6.1.2. Equation (6.1-1) estimated an average of 81.2wt% anatase titania in the titania powder. It was assumed that the remainder is entirely rutile titania.

Electrospun nanofibers were prepared according to the process described in Section 5.1. Samples collected during electrospinning were analyzed via optical microscopy at 100x and 500x magnification. The titania solution as described in the beginning of Section 5.1 produced the fibers shown in the micrographs of Figure 6.1.3. An obvious bead-on-string structure is visible at only 100x magnification; increasing the magnification provides slightly more detail of the beads. Originally this structure was considered a detriment since smooth nanofibers are generally the desired product from electrospinning. However, it was observed that after ultrasonication in ethanol the beads were separated from the fiber leaving a bead with small protrusions where the fiber was once connected. Such a mixture of separated beads and fiber segments
was confirmed by the SEM micrograph in Figure 6.1.4. Diameters of 30 beads were measured from SEM micrographs and showed an average of 3.5±1.5μm, where the error is the 95% confidence interval about the mean. The average diameter of the fiber segments, based on 47 measurements, was 0.36±0.18μm; the average length was about 6±0.2μm. Based on the average spacing between beads (48±7μm), the size of beads and fibers, and assuming that beads and fibers were spherical or cylindrical respectively, it was estimated that the fraction of beads in the mix was about 80wt%.

The effect of acetic acid, which was added to the spinning solution as described in the latter portion of Section 5.1 on fiber morphology is illustrated by Figure 6.1.5. From top to bottom, each row contains micrographs of as-spun fibers at 100x, 500x and 1000x magnification, respectively. Clearly the bead-on-string structure observed in Figure 6.1.3 has been eliminated by the addition of acetic acid to the electrospinning solution. The fibers remain smooth after calcination and ultrasonication as shown by Figure 6.1.6, an SEM micrograph. Figure 6.1.7 is an FESEM micrograph of the calcined, ultrasonicated nanofibers; measurement of 51 fibers estimates the average diameter as 164±12nm where the error is given as the 95% confidence interval about the mean.

The transition from anatase to rutile can begin between 610°C and 720°C [58C1]. The XRD pattern of beaded nanofibers (Figure 6.1.8) revealed a mix of 68.9wt% anatase with rutile, typical of a polycrystalline
titania sample calcined at 700°C [05W4]. However, non-beaded samples calcined at the same temperature were determined to be entirely rutile because of the lack of the primary anatase peak at 25.4° coupled with all three primary rutile reflections (Figure 6.1.9). The rapid formation of rutile titania at low temperatures (100°C) has been observed in literature [01W2] and was attributed to interactions between the acetic acid, ethanol and the growing surface groups of titanium dioxide. Therefore the presence of acetic acid in the electrospinning solution for beadless fibers also contributes to the formation of purely rutile titania nanofibers.

A scaled illustration in Figure 6.1.10 provides some indication of the relative filler sizes; the dotted outlines represent 95% confidence intervals about the mean. The titania powder is the largest filler followed by the beaded titania, and finally the smooth titania nanofibers. Error lines for smooth titania nanofibers were omitted for clarity. In addition to this variation in size a variation in morphology was also achieved. Approximately spherical reinforcement was available in the form of titania powder, cylindrical reinforcement was produced from the smooth titania nanofibers and a mix of spherical and cylindrical reinforcement was prepared from the beaded titania fibers.
Figure 6.1.1. Typical SEM micrograph of the titania powder. The average particle size as determined by measurements on eighty four different particles was $6.5 \pm 1 \mu m$, where the error represents the 95% confidence interval on the mean. Agglomerations greater than $25 \mu m$ were assumed to have been broken apart during the ball milling process.
Figure 6.1.2. X-ray pattern of powdered titania. Blue text and arrows denote anatase (A) peaks; red denotes rutile (R) peaks. From top to bottom, each label lists the phase, reflectance angle and relative intensity of the peak. Equation (6.1-1) estimates that the powder is 81.2wt% anatase titania, based on the anatase and rutile peaks at 25.43° and 27.55°, respectively.
Figure 6.1.3. Optical micrographs of as-spun titania nanofibers using the titania solution described in Section 5.1. A bead-on-string structure is clearly visible at both 100x magnification (left column) and 500x magnification (right column). The scale bar at 500x magnification is 50μm.
Figure 6.1.4. SEM micrograph of calcined, ultrasonicated beaded titania nanofibers from Figure 6.1.3. Notice that the beads have generally been smoothly separated from the fiber, leaving a mixture of beads and fibers. The average bead diameter is $3.5 \pm 1.5 \mu m$. 

86
Figure 6.1.5. Optical micrographs of electrospun titania solution with acetic acid added prior to spinning. The top, middle and bottom rows are 100x, 500x and 1000x magnification, respectively. The scale bars in each are 100, 20 and 10μm, respectively. There are no visible beads as opposed to the highly beaded structure observed in Figure 6.1.3.
Figure 6.1.6. SEM micrograph of calcined electrospun titania nanofibers; the spinning solution contained acetic acid. The beads observed in Figure 6.1.4 have been eliminated by the addition of acetic acid to the spinning solution.
Figure 6.1.7. FESEM micrograph of calcined, ultrasonicated beadless titania nanofibers at increased magnification. The average diameter of the fibers is 164±12nm, where the error is the 95% confidence interval about the mean.
Figure 6.1.8. X-ray pattern of beaded, electrospun titania. Blue text and arrows denote anatase (A) peaks; red denotes rutile (R) peaks. From top to bottom, each label lists the phase, reflectance angle and relative intensity of the peak. Equation (6.1-1) estimates that the powder is 68.9wt% anatase titania, based on the anatase and rutile peaks at $25.35^\circ$ and $27.5^\circ$, respectively.
Figure 6.1.9. X-ray pattern of beadless, electrospun titania. Red text and arrows denote rutile (R) peaks. From top to bottom, each label lists the phase, reflectance angle and relative intensity of the peak. The lack of reflectance peaks for the anatase phase implies a purely rutile titania.
Figure 6.1.10. Average, to-scale sizes of titania reinforcement. Dotted lines represent 95% confidence intervals about the mean. From left to right is (a) titania powder, (b) calcined, beaded titania and (c) calcined smooth nanofibers prepared by using acetic acid in the spinning solution.
6.2 Specific Gravity Measurements

As described in Section 5.3 and Appendix A, compressed solder pellets were subjected to Archimedean density measurements before and after sintering. The average specific gravities are presented in Figure 6.2.1; results have been reported as specific gravity rather than density for convenience and error bars are 95% confidence intervals. The average specific gravity of the pure solder samples was about 5% lower than the 8.9 reported in literature [00A1]. This is not unexpected since the samples were prepared via uniaxial compression as opposed to reflow. Prior to sintering the average specific gravity of all composite samples is less than, or for 0.50wt% and 0.75wt% powder statistically equivalent to, pure solder. This trend is understandable since the density of titania is about half that of solder as described in further detail in Section 6.6. With the exception of the powdered samples there was no statistical difference between sintered and un-sintered specific gravities. Considering the thermomechanical analysis offered in Section 6.4 this result implies that sintering is unnecessary for fabricating uniform specimens.
Figure 6.2.1. Summary of specific gravity measurements on compressed sample pellets. Solid colors are measurements made on samples before sintering at 150°C for 24hrs; gradient colors are data collected after sintering. Except for the powder samples there is no statistical difference between the specific gravities before and after sintering. However, each composite has a specific gravity less than or statistically equivalent to pure solder, which is expected when reinforcing with a less dense material. Error bars are 95% confidence intervals.
The case of titania powder composites presents an interesting trend because there was an average reduction in specific gravities of about 2.5% after sintering. This may be attributable to the entrapment of air in large agglomerations of the powder which can contribute to the formation of less-dense metallic oxides on the surface of the solder spheres during sintering or thermomechanical analysis. As discussed in the previous section, the titania particles had diameters twice as large as the beaded titania and more than twenty times that of the non-beaded titania fibers and therefore cannot pack as tightly. Such poor packing could contribute to oxidation by allowing oxygen to reach the solder spheres even when in the vacuum conditions employed for sintering.

6.3 Optical Microscopy

Powdered composite samples were ball-milled as described in Section 5.3, and in order to confirm that the titania reinforcement was uniformly dispersed, optical microscopy was used. A filtering lens on the microscope allowed for high contrast between the ceramic filler and metallic matrix. Optical micrographs at 100x magnification of 1wt% composites and pure solder, as in Figure 6.3.1, reveal that the ceramic reinforcement has agglomerated in the spaces between solder spheres but is evenly distributed throughout the matrix. The green arrows indicate these regions of agglomerations. Figure 6.3.2 shows the same
samples at 500x magnification. The small depth-of-field of the optical microscope results in small areas that are in focus but there is clearly a white material observable in the spaces between the solder spheres.
Figure 6.3.1. Optical micrographs (100x, scale bar is 200 μm) of the inside of compressed, sintered samples. (a) Pure solder (b) Titania powder (c) Beaded titania (d) Titania nanofibers. All composite sample images are at 1wt%. Clearly the titania has agglomerated in but the agglomerations are even distributed throughout the composite. The green arrows point to area of white which represent titania filler; these areas are not present in the pure solder.
Figure 6.3.2. Optical micrographs (500x, scale bar is 50μm) of the inside of compressed, sintered samples. (a) Pure solder (b) Titania powder (c) Beaded titania (d) Titania nanofibers. All images of composite samples are with 1wt% filler. The secondary phase of titania reinforcement is visible in (b)-(d).
6.4 Thermomechanical Analysis

In order to determine the coefficient of thermal expansion (CTE) a thermomechanical analyzer (TMA) was used as described in Section 5.4. A typical data output, as shown in Figure 6.4.1, was a plot of temperature versus dimension change. In order to determine the CTE from such a plot the slope of the curve was divided by the original height of the sample. Such a calculation was performed by software (Universal Analysis 4.2E, TA Instruments) and the resulting units of CTE were μm/mm/°C, which were then converted to standard units of ppm/°C. Initially the sample was cooled to about -50°C and then heated at 2.5°C/min. The probe of the TMA rested on the sample with a force equivalent to 0.5g and

![Graph of CTE calculation](image)

Figure 6.4.1. Typical thermomechanical data output for CTE calculation. The CTE is determined (via software) by dividing the slope of the plot by the original height of the sample.
typically showed one to several sharp variations up to 0°C; this was attributed to the probe tip settling on the sample. As such slope measurements were only made on smooth curves from 0-100°C as exhibited by Figure 6.4.1. Statistical analysis included analysis of variance (ANOVA) and Tukey’s HSD procedure to determine statistical significance; all analyses were performed at the 0.05 level. Figures of the ANOVA and Tukey results for each are summarized at the end of the chapter.

For pure solder the measured CTE was about 20 ppm/°C, which is in agreement with published values [00A1, 04H1, 08K1]. The influence of titania on the CTE was statistically equivalent regardless of weight percent or morphology: the CTE was reduced to around 15 ppm/°C, which represents an approximately 25% reduction compared to unreinforced solder. Figure 6.4.6, Figure 6.4.7 and Figure 6.4.8 at the end of the chapter summarize these findings. Figure 6.4.2 is a bar graph of all CTE results where the error bars represent 95% confidence intervals. Each of the composite CTE’s was statistically different from pure solder according to Tukey’s HSD procedure at the
Figure 6.4.2. Grand composite CTE comparison. Error bars represent 95% confidence intervals. Detailed statistical comparisons of the various fillers to pure solder are offered in Figure 6.4.6, Figure 6.4.7 and Figure 6.4.8.
0.05 level. In an attempt to provide rationale to these results several models including those of Kerner, Schapery and Turner were investigated for their applicability to the solder/titania composite system. These models are popular in literature [98E1, 98L1, 01C1, 06Z1, 09L1] likely because of their simplicity and broad applicability to composite materials.

Kerner’s model [57K1] assumes that a spherical reinforcing particle is perfectly wetted by a uniform layer of matrix; the composite CTE is predicted to be equivalent to such a system where the volume fractions of the particle and shell are the same as the bulk composite. The CTE is predicted as

$$\alpha_C = \alpha_{ROM} + V_p(1 - V_p)(\alpha_p - \alpha_M) \frac{K_p - K_M}{(1 - V_p)K_M + V_pK_p + \frac{3K_pK_M}{4G_M}}$$

(6.4-1)

where $\alpha_{ROM}$ denotes the composite CTE as predicted by the rule-of-mixtures and subscripts $P$, $M$, and $C$ denote properties of the reinforcing particle, matrix and composite, respectively. Volume fraction in the bulk composite is given by $V$ while $K$ and $\mathcal{G}$ represent the bulk and shear moduli, respectively. It can be difficult to locate experimental data on the bulk modulus but it is related to the shear and Young’s moduli through the standard relation

$$K = \frac{E}{3(3 - \frac{E}{\mathcal{G}})}$$

(6.4-2)
where $E$ is Young’s modulus, also referred to as the elastic modulus. The rule-of-mixtures (ROM) for a two component system by volume fraction is given by

$$\alpha_{ROM} = V_P \alpha_P + V_M \alpha_M = V_P \alpha_P + (1 - V_P) \alpha_M \quad (6.4-3)$$

Schapery’s model [68S1] attempts to establish upper and lower bounds on composite CTE’s by assuming isotropic composites and applying extremum principles of crystallographic thermoelasticity. The composite CTE is

$$\alpha_c = \alpha_p + (\alpha_M - \alpha_P) \frac{1/K_C - 1/K_P}{1/K_M - 1/K_P} \quad (6.4-4)$$

where $K_C$ is the bulk modulus of the composite. Hashin and Shtrikman [63H1] proposed the following estimate for the lower bound of the composite bulk modulus:

$$K_{C,\text{LOWER}} = K_M + \frac{V_P}{K_P - K_M + \frac{3V_M}{3K_M + 4G_M}} \quad (6.4-5)$$

Thus by using the lower bulk modulus in Equation (6.4-4) an upper bound on the CTE can be established. The upper bound on the bulk modulus is obtained simply by interchanging the subscripts $P$ and $M$ in Equation (6.4-5); substitution into Equation (6.4-4) will then yield the lower bound on the CTE.
Turner’s model [46T1] is the most broadly applicable of the presented models because it is not limited to particle-matrix interactions; it can be applied to a composite consisting of any number of components. It assumes homogeneous strain throughout the composite and then balances the internal forces, noting that at equilibrium the sum of internal forces must be equal to zero. The CTE of a composite of \( n \) components is

\[
\alpha_C = \frac{\sum_{i=1}^{n} \frac{\alpha_i x_i K_i}{\rho_i} / \sum_{i=1}^{n} \frac{x_i K_i}{\rho_i}}{n}
\]

(6.4-6)

where \( x_i \) and \( \rho_i \) are the weight fraction and density of component \( i \). For a two component system in terms of volume fraction Turner’s model becomes

\[
\alpha_C = \frac{\alpha_V V_P K_P + \alpha_M V_M K_M}{V_P K_P + V_M K_M}
\]

(6.4-7)

where terms and subscripts are the same as previously defined. Unlike Kerner’s model, which assumes spherical reinforcements, and Schapery’s model, which assumes isotropic composites, Turner’s
Figure 6.4.3. Plots of the ROM, Kerner, Turner and Schapery CTE models. The equations were originally stated in terms of volume fraction; transformation to mass fraction results in a slightly increased curvature. Only Schapery’s lower bound on composite CTE is plotted; the upper bound corresponds exactly with Kerner’s model. The ROM and Kerner models predict gradual transitions of the CTE whereas Turner and Schapery predict large decreases in CTE at low titania mass fractions and diminishing returns beyond about 20wt%.
model makes no assumptions regarding the shape of the filler. Its simple formula can accommodate any number of components and was not derived for a particular system such as polymer, metal or ceramic matrix composites.

The ROM, Kerner, Schapery and Turner are plotted for the 63Sn/37Pb solder and titania system in Figure 6.4.3. A slight curvature is introduced, as exemplified by the ROM curve, because the above equations were all developed in terms of volume fraction but the x-axis in Figure 6.4.3 is the mass fraction of titania. This is because the volume fractions in each of the preceding equations were converted to mass fraction for comparison to experimental data, which was collected in terms of mass fraction. Inherent is the assumption that the nanofibers, nanopowders and beads were solid titania so that densities available in literature for bulk titania are appropriate. Only the lower CTE bound of Schapery’s model has been plotted because the upper bound corresponds exactly to Kerner’s model. Kerner’s model and the ROM predict gradual

Table 6.4.1. Material properties used for Figure 6.4.3 and their references.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>CTE (ppm/°C)</th>
<th>E (MPa)</th>
<th>K (MPa)</th>
<th>G (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>3.89</td>
<td>8.5</td>
<td>287</td>
<td>206</td>
<td>113</td>
</tr>
<tr>
<td>Sn/Pb</td>
<td>8.9</td>
<td>20.26</td>
<td>20</td>
<td>12.21</td>
<td>8.15</td>
</tr>
<tr>
<td>Ref (TiO₂)</td>
<td>[09S1]</td>
<td>[07C1,pg 629]</td>
<td>[07C1,pg 293]</td>
<td>[07C1,pg 293]</td>
<td></td>
</tr>
<tr>
<td>Ref (Sn/Pb)</td>
<td>[00A1]</td>
<td>This work</td>
<td>Avg of [91L1, 92D1]</td>
<td>Equation (6.4-2)</td>
<td>Avg of [91L1, 92D1]</td>
</tr>
</tbody>
</table>
transitions of the CTE as the titania mass fraction is increased. This parity is not unexpected: examining Equation (6.4-1) reveals that Kerner’s model is essentially a modification of the ROM prediction. Conversely, both Turner’s and Schapery’s models predict a steeper transition; large decreases can be obtained from 0-5wt% with diminishing returns beyond about 20wt%. Table 6.4.1 summarizes the material properties used in Figure 6.4.3.

Including the experimental data and focusing on the 0-5wt% range is shown in Figure 6.4.4; error bars on the experimental data were omitted for clarity. Turner’s model most closely estimates the experimental data but all models underestimate the observed decrease in CTE via titania reinforcement. The ROM is generally not expected to predict composite properties because of its simplicity. Similarly Kerner’s model, by assuming a spherical reinforcement and being a modification of the ROM, is also not expected to accurately portray a system of non-spherical reinforcements. Kerner’s model further requires perfect wetting of the matrix around the reinforcement; however samples were tested after uniaxial compression and sintering but not after reflow. Therefore the reinforcement may not be surrounded on all surfaces by a uniform layer of matrix. Moreover, as will be shown in Section 6.6, even if the reinforcements were added to
Figure 6.4.4. Experimental data plotted with the model estimates from Figure 6.4.3. The scale has been adjusted to 0-5wt% titania reinforcement since experimental measurements were made at 1.0wt% or less. Error bars for experimental data were omitted for clarity.
molten solder, the respective surface energies of the solder and titania would inhibit perfect wetting.

Schapery’s model provides a slightly better estimate to experimental reality because the model was derived in an attempt to establish a lower limit for the composite CTE; by definition this is expected to be lower than most other estimates. However, assuming isotropic composite properties may lead to deviations in the predicted CTE because samples prepared by uniaxial compression may perform differently depending on the axis of measurement, be it radial or axial. Turner’s model makes no assumptions regarding isotropy or reinforcement morphology and the reasonable accuracy of its prediction implies that the composite samples behave as homogeneous composites. Examining Turner’s equation more closely reveals that because of the low titania concentration CTE predictions are highly dependent upon the properties of the solder and not the titania. This warrants an evaluation of the elastic constants in Table 6.4.1.

As noted in the caption of Table 6.4.1 the elastic ($E$) and shear ($G$) moduli are averages from different sources. Since Turner’s model relies on the bulk modulus $K$, which is in turn dependent upon $E$ and $G$ as in Equation (6.4-2), accurate estimates of $E$ and $G$ are crucial to CTE predictions. The homologous temperature is a ratio of operating temperature to a material’s melting point and can offer insight into variations in measurements of a material’s elastic constants. At room
temperature the homologous temperature of eutectic Sn/Pb solder is about 0.85T_M implying that elastic constants are strongly dependent on temperature and strain rate [09T2]. Despite having been originally determined by the same industrial corporation (Westinghouse, [68W1]), the variation in $K$ for eutectic Sn/Pb solder in Low et al. [91L1] and Dasgupta et al. [92D1] highlight the difficulty of determining elastic constants at high homologous temperatures. With a melting point of 1850°C titania has a homologous temperature of 0.14T_M at room temperature; the elastic constants are therefore not expected to vary significantly.

Since investigating elastic constants of solder was not within the scope of this investigation the maximum and minimum published values of $K_M$ were used to estimate a range of possible composite CTE’s according to Turner’s model. The result is provided in Figure 6.4.5 where the lower and upper bounds are calculated for a bulk modulus of 5.14 GPa [91L1] and 46.63 GPa [92D1], respectively. The lower bound intersects the experimental data scatter plot at a titania concentration of about 0.05-0.1wt% whereas the upper bound predicts significantly higher composite CTE’s. Only by using the lowest published value for the solder’s bulk modulus does the model prediction coincide with experimental results.

In order to merge together the results presented thus far, consider a summary of the major points presented in Chapter 6 up to and
including thermomechanical analysis. First, characterization of the titania filler in Section 6.1 revealed that no two fillers were exactly alike. The size of the powder agglomerations was about 6.5μm, the beads 3.5μm and the fibers, whether from beaded or bead-free electrospinning, were less than 400nm. X-ray diffraction determined primarily anatase titania in the beaded and powdered samples but nearly pure rutile in the bead-free fibers. In Section 6.3, optical microscopy of the composites revealed aggregations of filler in the spaces around the solder spheres, as exemplified by Figure 6.3.1 (c). Despite the variety of fillers the CTE’s of all the composite samples were equally 25% lower than that of pure solder. Comparison of four different theoretical CTE models showed that only Turner’s model provided a prediction that even partially coincided with experimental data. Moreover, investigation deeper into Turner’s predictions revealed that the low filler concentration placed a theoretical emphasis on the bulk modulus of the solder. By working backwards through such a summary a mechanism can be established that accounts for each of the observations.
Figure 6.4.5. Upper and lower CTE bounds for a titania/solder composite based on Turner’s model. The lower bound uses experimental data from Low et al. [91C1]; the upper bound is from Dasgupta et al. [92D1]. The variation may be due to the high homologous temperature of solder at room temperature.
The bulk modulus can be understood as defining how a material’s volume responds to applied pressure. Similarly, the coefficient of thermal expansion defines the linear expansion of a material in response to a change in temperature. While the TMA used to determine CTE’s in this work was only capable of observing one-dimensional changes it is intuitive that the sample must be expanding in all three dimensions; only cases of severe anisotropy would allow truly one-dimensional thermal expansion. Thus there is a connection between the bulk modulus and the CTE: both describe how the volume of a material responds to a stimulus. This is evidenced by the presence of only the bulk modulus and CTE as material properties in Turner’s model, Equation (6.4-6). Thus Turner’s model can be understood as making no assumption regarding mechanical contact between reinforcement and matrix but instead approximating the overall effect of volume changes. However, Kerner and Schapery both assume that the filler has rigid mechanical contact with the matrix: the lower CTE of the filler coupled with mechanical contact serve to restrict the expansion of the metal.

An analogy may be useful: consider a spherical, sealed balloon with a single wire loop fitted snugly around its equator. This represents a filler (the wire) perfectly wetted to a matrix (the balloon). As the temperature of this single balloon-and-wire unit increases, the volumes of the balloon and wire also increase but at different rates. The wire restricts the expansion of the balloon’s equator and such that the expanded volume of
the balloon-and-wire unit is slightly less than an unrestricted balloon. If millions of balloon-and-wire units were combined in a random fashion, the result would be a new material with an overall CTE lower than the same number of unreinforced balloons. This is essentially how Kerner and Schapery account the change in CTE of a metal matrix composite.

Turner’s model, on the other hand, does not necessitate such contact between the filler and matrix. Instead, the composite can be visualized as millions of sealed balloons, each placed within a box slightly larger than a single balloon. As the balloon expands in response to a temperature change it is free to expand without deforming the box. If the boxes are combined in a random fashion as before, the result will again be a material with an overall CTE lower than the same number of unreinforced balloons but utilizes a different mechanism. Perfect wetting between the balloons and the box is not necessary because the balloon is simply encased in a structure that is free to compress as the balloon expands. The effect of enclosing the balloons in boxes is not to restrict the thermal expansion of the balloons but rather to accommodate it.

With the description of a so-called “accommodating” filler in mind, the optical micrographs of the composite are now reconsidered. Assuming that the agglomerations noted in Figure 6.3.1 have not been compressed to the density of pure titania, the filler can be further compressed in response to a volume change of the solder spheres. This presents a situation similar to the balloon-in-a-box analogy presented
earlier: the solder spheres are free to expand and that expansion is accommodated by the “box” of filler enclosing each solder sphere. The notion of an accommodating filler also explains why no variation in composite CTE with filler type or concentration was observed. Regarding the size of the filler, as long as the characteristic size of the filler is significantly smaller than the solder the filler will form regions of compressible agglomerates around the spheres. Similar reasoning can be extended to the shape of the filler: spheres and short cylinders of the sizes reported are not expected to pack an ordered, structural manner so as to resist compression. The phase of the titania, be it anatase or rutile, has no observed effect because no rigid connection is created between the metal and filler; the filler is free to move as the agglomerate packs more tightly. In general the microscopic properties of the reinforcement such as particle size, particle shape or crystallographic structure have been overshadowed by the macroscopic properties of the filler agglomerations.

While the experimental evidence indicates that the concentration of filler has no effect on the composite CTE the mechanism developed above suggests that at some point the amount of filler surrounding the solder spheres will be incapable of accommodating the solder’s expansion. Therefore a reasonable extension of this work is to further reduce the filler concentration until an increase in composite CTE is observed. At this point the filler concentration could be considered the minimum necessary
to accommodate the solder expansion. However the models of Kerner and Schapery have been utilized since their development in 1957 and 1968, respectively, through modern research regarding metal matrix composites [09L1]. The implication is that the models must accurately capture various aspects of composite thermal properties or else the models would no longer be in use. Consequently an investigation into the effects of rigid mechanical contact between filler and solder is recommended. As described in Section 4.2, rigid mechanical contact can be achieved by a variety of methods such as powder metallurgy with extrusion or mixing of the filler with molten solder. However, bearing in mind the standard industrial methods of creating solder joints offered in Section 3.3, any solder composite must be capable of maintaining its performance level after reflow. As will be described in subsequent sections a significant challenge in fabricating practical solder composites has been identified as the reflow process.
Figure 6.4.6. Summary table, ANOVA and bar graph of titania nanopowder composite CTE measurements. The low P-value (0.00088) indicates that the variation observed between groups is greater than could be expected by random variation. The bar graph shows the results of Tukey’s HSD test (α=0.05): the red line indicates that all titania composites have statistically equivalent CTE’s but are all different from pure solder. Error bars are 95% confidence intervals.
Figure 6.4.7. Summary table, ANOVA and bar graph of beaded titania nanofiber composite CTE measurements. The low $P$-value (0.00049) indicates that the variation observed between groups is greater than could be expected by random variation. The bar graph shows the results of Tukey’s HSD test ($\alpha=0.05$): the red line indicates that all titania composites have statistically equivalent CTE’s but are all different from pure solder. Error bars are 95% confidence intervals.
Figure 6.4.8. Summary table, ANOVA and bar graph of titania beadless titania nanofiber composite CTE measurements. The acceptable P-value (0.04079) indicates that the variation observed between groups is greater than could be expected by random variation. The bar graph shows the results of Tukey’s HSD test (α=0.05): the absence of a red line indicates that the titania composites are different from pure solder. Error bars are 95% confidence intervals.
6.5 Reflow

Temperature data of the sample during reflow were collected with the oven described in Section 5.5 to compare the melting point of composite samples to pure solder. Such a collection of data, with temperature plotted as a function of time, is referred to as a “reflow profile.” A reflow profile typical of any sample in this work is provided in Figure 6.5.1; in this case the profile is for a sample with 1.00wt% beaded fibers. The sample first undergoes melting at 183°C after about twenty three minutes, as detailed in Figure 6.5.2. The slow heating rate of about 10°C/min was designed to simulate the paste drying and preheat profiles of Figure 3.3.3; it was also necessary because a system capable of achieving the rates suggested by the aforementioned figure (120-240°C/min) was unavailable. Shortly after the melting temperature is reached, a peak reflow temperature of 210°C is achieved. Finally a cooling rate of 5°C/min cools the sample to room temperature; the freezing point is around 181°C as detailed in Figure 6.5.3.

An unexpected feature around the melting point can be observed in Figure 6.5.2. First, during the melt transition the sample initially heats to about 186°C for about thirty seconds and then sharply drops to 183°C. After the sample has completely melted the temperature of the molten sample rises quickly but continuously. The discontinuous drop can be attributed to a combination of the fabrication method used to prepare the
samples and the conditions of thermomechanical analysis. After uniaxial compression a thin layer of highly deformed solder was observed to form on the faces of the sample where the die made physical contact with the metallic powder. This surface is observed in Figure 5.3.2 where the reflective surface is distinctly different from the interior of the sample as pictured in Figure 6.3.1. It is thought that a layer of oxidized metal (SnO$_2$ or PbO) is present on the metallic spheres throughout the composite and that the highly deformed surface of the compacted pellet prohibits contact of the flux and the oxidized spheres on the interior of the sample. This oxide layer may be produced during thermomechanical analysis, which is performed up to 100°C in air, or as a consequence of sintering at 150°C in an imperfect vacuum. However, the reducing action of the flux is sufficient to remove the oxide layers on the surface of the pellet which allows a layer of molten solder to form on the pellet. This accounts for the initial slowing and plateau observed in the melting portion of Figure 6.5.1.
Figure 6.5.1. Typical reflow plot of a compacted solder pellet. The melting point is determined as the temperature of the well on the left of the plot; the freezing point is the plateau on the right. A slight rise over and the sharp decrease to the melting point is due a thin layer of oxidation on the solder spheres inside the pellet. Melt undercooling, a phenomena related to homogeneous nucleation in many materials, is observed around the freezing point.
Figure 6.5.2. Detail of the melt transition for the reflow profile in Figure 6.5.1. The gradual leveling and sharp drop in temperature was attributed to oxidation of the interior portions of the solder sample during sintering and thermomechanical analysis. The melting temperature is taken as the bottom of the well.
Figure 6.5.3. Detail of the crystalline transition for the reflow profile in Figure 6.5.1. The slight drop before the plateau is a standard melt undercooling feature. The freezing temperature is taken as the plateau.
Since the bare-wire thermocouple rests on the surface of the sample under its own weight the temperature-sensing junction immediately passes through this layer of molten solder to rest on the solid mass of partially oxidized compressed solder spheres. The mass continues to heat until the temperature is sufficient to overcome the restraining effects of the oxidized layer; the sharp drop represents the point where the interior solder spheres coalesce into a molten state.

Average melting and freezing points of all samples are summarized in Figure 6.5.4 except for the beadless nanofiber data, which were omitted from the figure but had melting and freezing points of 183.4°C and 181.9°C, respectively. None of the melting or freezing points of the composites were statistically different from that of pure solder.

Regarding the melting point, a constant 183°C despite filler implies that the ceramic reinforcement is not present in sufficient quantities to affect the reflow profile. This is important when considering modifications to manufacturing equipment; an unchanged melting temperature means no modifications are necessary. The uniformity of freezing points was expected because the ceramic reinforcement was expelled during the melt transition, as will be described in Section 6.6. Thus the solder was essentially pure eutectic Sn/Pb solder during the cooling process.
Figure 6.5.4. Melting and freezing points of pure solder and composite samples. Error bars are 95% confidence intervals; there is no statistical difference between composite melting points and pure solder’s melting point, or between composite freezing points and pure solder’s freezing point.
6.6 Filler Expulsion

After thermomechanical analysis to determine the coefficient of thermal expansion, the composite samples were reflowed by the system described in Section 5.5. For all samples it was observed that some of the flux tended to remain in a relatively thin coating on the solder sample but primarily formed a pool around the sample’s base. In non-composite samples, that is, pure solder samples, the flux pool was a translucent amber color. However in composite samples the flux pool was an opaque orange with what appeared to be a white material; this phenomenon occurred regardless of the weight percentage of added titania. Moreover some samples appeared to have white material in the thin coating of flux that remained on the solder sample itself. The morphology of the titania, be it powder, beaded fibers or non-beaded fibers, did not seem to be relevant; all composites were noted by this white material in the flux pool regardless of filler shape. This naked-eye-level discrepancy between composite and non-composite flux pools is illustrated in Figure 6.6.1.

There are four images in Figure 6.6.1: (a) no filler, (b) 0.25wt% titania powder, (c) 0.25wt% beaded titania fibers and (d) 1.00wt% non-beaded titania nanofibers. The amber material present in each of the figures is crystallized solder flux, the metallic hemispheres are the solder samples and the underlying material is aluminum foil that has been shaped in the center into square depressions. Image (a) exhibits
transparent flux in the square depression as well as in the area directly surrounding the sample. Furthermore the amber material on the sample itself appears to be transparent. These features are what one would expect from a typical solder reflow: one primary solder mass and no foreign material in the flux pool. Contrast this with (b) which does have a single solder mass but also has a distinctly colored flux pool. The flux at the outer edges of the square depression appears to be less contaminated compared to the center but still lacks the clarity of (a). A nearly identical result is observed in (c) and (d) where again a material has clouded the flux pool. While these observations present rather strong evidence that the filler is being expelled from the solder during reflow it cannot be determined from this resolution that the material expelled is indeed the filler and not a by-product of a reaction between the filler and flux or solder.
Figure 6.6.1. Reflowed samples as seen by the human eye. (a) No filler, (b) 0.25wt% titania fiber, (c) 0.25wt% beaded titania fibers, (d) 1.00wt% non-beaded titania fibers. Note the obvious opaqueness of (b)-(d) contrasting the clarity of (a).
When observed at 100x magnification, as in Figure 6.6.2, the flux from the pure samples is clean enough to reveal the line patterns in the underlying aluminum foil. However the flux is sufficiently clouded for the composite samples that only by moving the focus onto the sample itself can any meaningful detail be resolved. Figure 6.6.3 is two 100x magnification images of beaded (top) and non-beaded (bottom) composite samples. By using a filtering lens on the microscope a stark contrast between the metallic sample and the expelled material can be achieved.

Figure 6.6.2. Optical micrograph of pure solder flux at 100x magnification. The lined pattern is the underlying aluminum foil which indicates that there is no appreciable foreign material in the crystallized flux.
Figure 6.6.3. Optical micrograph of beaded and non-beaded composite samples at 100x magnification. The blue is the solder sample and the white, which is not seen in pure sample micrographs, is assumed to be titania filler.
The blue is the solder sample while the white is supposedly the titania filler. Other than the color, though, there is still not definitive proof that it is precisely the titania filler that has been expelled from the sample. However, much as was the case with naked-eye resolution, 100x magnification presents further evidence that the filler is being expelled from the samples.

With increased magnification the evidence for filler expulsion only becomes more conclusive. As was noted in Section 5.2 and expanded upon in Appendix B all electrospun fibers were ultrasonicated to provide control over the length of the nanofibers. Consequently a number of optical micrographs were collected and analyzed that reveal the shape of the fillers before incorporation into the composite. It is through comparison of these images and those of the reflowed solder composites that it becomes obvious that the material used to make the composite is the same material that is being expelled during reflow. Since the beaded fibers had the most conspicuous shape under the microscope they were chosen to illustrate the before-and-after in Figure 6.6.4 where (a) is the beaded fibers just after sonication in ethanol and (b) is the material expelled during reflow. Both optical micrographs are at 500x magnification and reveal the distinctive bead structure of the electrospun titania nanofibers.
Figure 6.6.4. Optical micrographs at 500x magnification of ultrasonicated beaded titania fibers before incorporation into composite and after expulsion from composite during reflow. The distinctive bead shape confirms that the titania filler is morphologically unaltered during reflow and is expelled during the process.
With strong evidence for the expulsion of filler during reflow the underlying mechanism should prove critical to creating composites that can be successfully reflowed using standard techniques.

The most obvious reason for filler expulsion is buoyancy. Typical densities of soldering materials and titania are provided in Table 6.6.1. The ratio of solder to anatase titania density is about the same as water to bamboo wood. Thus an appropriate comparison is that the solder composite is essentially bamboo packed in ice cubes: when the ice cubes melt and coalesce the bamboo would be expected to float to the water surface. Similarly when the solder particles are reflowed the titania would be expected to float to the molten solder surface, which is precisely what is observed in Figure 6.6.3. Furthermore buoyancy effects must

Table 6.6.1. Densities of commonly encountered materials. Densities determined in this work were measured via Archimedes’ Method.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (elemental)</td>
<td>11.35</td>
<td>[08G3]</td>
</tr>
<tr>
<td>Sn (elemental)</td>
<td>7.28</td>
<td>[08G3]</td>
</tr>
<tr>
<td>60Sn/40Pb solder</td>
<td>8.90</td>
<td>[00A1]</td>
</tr>
<tr>
<td>Pressed 63Sn/37Pb</td>
<td>8.32</td>
<td>This work</td>
</tr>
<tr>
<td>Ti (elemental)</td>
<td>4.5</td>
<td>[08G3]</td>
</tr>
<tr>
<td>TiO2 (rutile)</td>
<td>4.27</td>
<td>[09S1]</td>
</tr>
<tr>
<td>TiO2 (anatase)</td>
<td>3.89</td>
<td>[09S1]</td>
</tr>
<tr>
<td>Crystallized flux</td>
<td>1.07</td>
<td>This work</td>
</tr>
<tr>
<td>Bamboo (wood)</td>
<td>0.40</td>
<td>[05U1]</td>
</tr>
<tr>
<td>Water</td>
<td>0.999</td>
<td>[01W1]</td>
</tr>
</tbody>
</table>
overcome the surface tension of the molten solder in order to pass through the interface; otherwise the fibers would be located underneath the molten solder surface and not in the flux pool.

Force balances on floating particles can be used as a way of predicting where particles are located at two-phase boundaries by accounting for buoyancy and surface effects [69P1, 77R1]. Generally one begins with the setup described by the inset in Figure 6.6.5 where a cylinder rests at the fluid interface; the geometry of interest is denoted in the primary figure. The interfacial and surface tensions $\gamma_{SL}$, $\gamma_{LV}$ and $\gamma_{SV}$ are characterized at the three-phase boundary by the contact angle $\theta$. The length and radius of the cylinder are $L$ and $R$, respectively. Densities $\rho_s$,

Figure 6.6.5. Geometry for the problem of a solid, rigid cylinder floating at the interface between two fluids, a liquid and gas. The inset is a perspective view of the problem. Definitions of symbols are provided in the text.
\( \rho_s, \) and \( \rho_v \) are the densities of solid, liquid and vapor, respectively. The distance \( z_0 \) measures the amount of depression of the fluid interface relative to its undistorted state; note that a positive value for \( z_0 \) would indicate a sinking direction. Angle \( \phi \) describes the location of the cylinder center line relative to the three-phase boundary while angle \( \beta \) describes the slope of the meniscus.

With the appropriate geometry defined as above one can perform a careful accounting of all forces acting on the cylinder. A detailed explanation of such a balance is provided in Appendix C but the general considerations are given by

\[
F_{\text{net}} = F_{\text{buoyancy}} + F_{\text{surface tension}} + F_{\text{gravity}}
\]

where \( F_{\text{net}} \) is the net force per unit length acting on the cylinder and the other forces are described by their subscripts. As implied by the convention for \( z_0 \), sinking forces are positive, upward forces are negative and the cylinder is at rest when \( F_{\text{net}} = 0 \). Following Appendix C the net force acting on the cylinder can be expressed in dimensionless form \( F'_{\text{net}} \) by

\[
F'_{\text{net}} = 2 \sin(\theta + \varphi) + C\{\pi D - [\varphi - \sin(\varphi) \cos(\varphi)] - 2 \left(\frac{z_0}{R}\right) \sin(\varphi)\}
\]

where

\[
C = A^2 R^2 \quad \text{(6.6-3)}
\]

\[
D = \frac{B}{\pi A^2} = \frac{\rho_s - \rho_v}{\rho_L - \rho_v} \quad \text{(6.6-4)}
\]

\[
A^2 = (\rho_L - \rho_V) g / \gamma_{LV} \quad \text{(6.6-5)}
\]
\[ B = \pi (\rho_S - \rho_V) g / \gamma_{LV} \quad (6.6-6) \]

Note that \( C \) and \( D \) are dimensionless values reflecting the radial size and relative density of the cylinder, respectively. The quantity \( (z_0/R) \) can be expressed in dimensionless form by means of the Laplace Equation [69P1], which after rearranging becomes:

\[
\left( \frac{z_0}{R} \right) = \pm \left( \frac{2}{R} \right)^{\frac{1}{2}} \left[ 1 + \cos(\varphi + \theta) \right]^{\frac{1}{2}} \quad (6.6-7)
\]

where the sign is determined by the angle \( \beta \): negative \( \beta \) results in a positive \( z_0 \) and vice versa. Equations (6.6-2) through (6.6-7) fully describe the forces acting on the cylinder at the interface; the equilibrium position can be determined by varying the angle \( \varphi \) until \( F'_{\text{net}} = 0 \).

Fortunately the solder system has been well-studied and a majority of the characteristic values such as surface energy and density are available but several assumptions are nonetheless required. First, the titania cylinder is assumed to be rigid, solid and possess the same density as bulk anatase titania. Second the nanoscale of the filler does not affect the behavior as described by Equations (6.6-2) through (6.6-7) which were derived for macroscopic bodies. Third, the system is operating under atmospheric pressure but flux is not present and oxidation effects are negligible. This requirement stems from the manner in which surface tension data are collected for molten solder, namely that an inert gas such as nitrogen or helium is usually used to prevent oxidation. Measurements of surface energies under flux at elevated temperatures
would prove considerably difficult due to degradation and variation of the flux; thus a final assumption arises wherein the action predicted under inert gases is equivalent to what could be expected under liquid flux conditions. Table 6.6.2 summarizes a variety of solder and ceramic surface energies.

Since the titania/solder/air system has not been reported in literature, it remains to estimate the contact angle at the three phase interface. A typical method is to employ the Good-Girifalco estimation [90A1, pg114] for the work of adhesion, \( \text{viz} \)

\[
W_{SL} = 2\Phi(\gamma_{SV}\gamma_{LV})^{1/2}
\]

and combine it with the Young-Dupre’ equation [90A1, pg386] to yield

\[
\gamma_{LV}(1 + \cos(\theta)) = 2\Phi(\gamma_{SV}\gamma_{LV})^{1/2}
\]

which can be used to estimate the contact angle \( \theta \). In the original work of Good and Girifalco [57G1] the parameter \( \Phi \), which is not to be confused with \( \phi \), was a ratio of molar volumes. The ratio of molar volumes, given by

\[
\Phi = \frac{4V_A^{1/3}V_B^{1/3}}{(V_A^{1/3} + V_B^{1/3})^2}
\]

where \( V_A \) and \( V_B \) represent the molar volumes of two different phases, is approximately unity for the solder/titania system; this is because the molar volume of titania is nearly equivalent to that of titania. Work by Nikolopoulos and Agathopoulos [92N1] suggested an alternative expression specifically for molten metals atop ceramic substrates:
\[ \gamma_{SL} = \left( \psi \frac{V_{METAL}}{V_{OXIDE}} + 1 \right)^{2/3} (\gamma_{SV} \gamma_{LV})^{1/2} \]  

(6.6-11)

where \( V_{METAL} \) and \( V_{OXIDE} \) are the molar volumes of the metal and ceramic, respectively. The constant \( \psi \) is the ratio of the ion radii in the oxide multiplied by the stoichiometric ratio of oxygen to metal in the oxide, \( \text{viz:} \)

\[ \frac{x}{y} \frac{R_{OXYGEN}}{R_{METAL}} \]  

(6.6-12)

For titania (\( \text{TiO}_2 \)), \( x/y = 2/1 \) and \( R_{OXYGEN}/R_{METAL} = 137/60.5 \) [99D1] and so \( \psi = 4.53 \). The contact angle can then be determined by combining Equation (6.6-11) with Young’s Equation [90A1, pg385]:

\[ \gamma_{LV} \cos(\theta) = \gamma_{SV} - \gamma_{SL} \]  

(6.6-13)

These two different methods of estimating contact angles, the Good-Girifalco method and the Nikolopoulos method, give significantly

Table 6.6.2. Surface tensions of various solders and ceramic materials. The last four entries are for solid ceramic materials whereas the others are for molten solder alloys.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \gamma_{LV} ) or ( \gamma_{SV} ) (mN/m)</th>
<th>Atmosphere</th>
<th>Temp (°C)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>60Sn/40Pb</td>
<td>480</td>
<td>air</td>
<td>200</td>
<td>[05K1]</td>
</tr>
<tr>
<td>60Sn/40Pb</td>
<td>417</td>
<td>air</td>
<td>241</td>
<td>[00A1]</td>
</tr>
<tr>
<td>73.2Sn/26.8Pb (at%)</td>
<td>500.4</td>
<td>helium</td>
<td>300</td>
<td>[78S1]</td>
</tr>
<tr>
<td>60.4Sn/39.6Pb (at%)</td>
<td>484.6</td>
<td>helium</td>
<td>300</td>
<td>[78S1]</td>
</tr>
<tr>
<td>43.4Sn/56.6Pb (at%)</td>
<td>469.4</td>
<td>helium</td>
<td>300</td>
<td>[78S1]</td>
</tr>
<tr>
<td>30Sn/70Pb (at%)</td>
<td>458.9</td>
<td>helium</td>
<td>300</td>
<td>[78S1]</td>
</tr>
<tr>
<td>61.9Sn/38.1Pb (wt%)</td>
<td>473.5</td>
<td>air</td>
<td>300</td>
<td>[92N1]</td>
</tr>
<tr>
<td>( \text{TiO}_2 ) (bulk)</td>
<td>68.2</td>
<td>air</td>
<td>unk</td>
<td>[06P1]</td>
</tr>
<tr>
<td>( \text{TiO}_2 ) (nanoparticle, 35nm)</td>
<td>53.12</td>
<td>air</td>
<td>unk</td>
<td>[05H1]</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 ) (bulk)</td>
<td>41.1</td>
<td>air</td>
<td>unk</td>
<td>[06K2]</td>
</tr>
<tr>
<td>( \text{ZrO}_2 ) (bulk)</td>
<td>45.6</td>
<td>air</td>
<td>unk</td>
<td>[06K2]</td>
</tr>
</tbody>
</table>

139
different values for $\theta$: 109° and 147°, respectively. Generally one should consider the method of Nikolopoulos more appropriate than the generalized method originally offered by Good and Girifalco. The former was derived specifically for molten metal and ceramic systems and although the ceramic investigated was aluminum oxide ($\text{Al}_2\text{O}_3$) the metals investigated included a variety of Sn/Pb compounds including the eutectic mix. However both the Nikolopoulos and Good/Girifalco estimates share the similarity that the molten solder is not expected to wet the titania filler.

Both values have been used to plot $F'_{\text{net}}$ against values for $\phi$ in Figure 6.6.6. The vertical lines mark the value for $\phi$ that results in equilibrium as determined by fitting a 3rd order polynomial to Equation (6.6-2) and employing the Newton-Raphson method to find the zero point. The equation for $F'_{\text{NET}}$ was fit to a polynomial simply to facilitate finding the zero point via Microsoft Excel. The solid line indicates an estimate using Equation (6.6-11) to determine the contact angle; the dashed line is for Equation (6.6-9). Regardless of the method chosen to estimate the contact angle $\theta$ the resulting value of $\phi$ for equilibrium is always less than 90° which by referring to Figure 6.6.5 indicates that the cylinders are primarily located in the less dense fluid, i.e., outside the molten solder.

Interestingly the equilibrium position of the cylinder is insensitive to density because radius was assumed to be 25μm and so the coefficient $C$ controlling buoyancy contributions in Equation (6.6-2) is also quite small.
Thus in the region of the two phase interface it is primarily the surface tension forces that decide where the cylinder will be located at equilibrium. It follows then that for the actual titania cylinders, which were estimated to have diameters of less than 200nm, will also be dominated by surface effects.

Figure 6.6.6. A plot of $F'_{net}$ for two different contact angles: 109° by Good and Girifalco, and 147° by Nikolopoulus. The intercepts represent equilibrium values of $\phi$ and confirm that the cylinder is expected to rest atop the molten solder.
Two methods are suggested to overcome the filler expulsion problem. First, increasing the density of the filler to the point of neutral buoyancy may be sufficient to keep the filler a safe distance from the surface. There are of course fluid dynamics to consider during the phase transition experienced during reflow but the more dense filler, having greater inertia, would be more resistant to motion. A variety of ceramic materials are available that can match or nearly match the density of common solders; an incomplete list is provided in Table 6.6.3. Since ceramics generally exhibit lower CTE’s when compared to metals [07C1 pg629] a reduction in composite CTE’s could be expected from most

Table 6.6.3. Commercially available ceramics sorted by density which may be used to match the density of the filler to that of the metal alloy. Values in italics are from [00A1]; all others are from [02E2].

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>4.25</td>
</tr>
<tr>
<td>Titanium carbide</td>
<td>TiC</td>
<td>4.93</td>
</tr>
<tr>
<td>Titanium nitride</td>
<td>TiN</td>
<td>5.22</td>
</tr>
<tr>
<td>Zirconium dioxide</td>
<td>ZrO₂</td>
<td>5.89</td>
</tr>
<tr>
<td>Nickel oxide</td>
<td>NiO</td>
<td>6.57</td>
</tr>
<tr>
<td>Tin dioxide</td>
<td>SnO₂</td>
<td>6.9</td>
</tr>
<tr>
<td>Iron boride</td>
<td>FeB</td>
<td>7.15</td>
</tr>
<tr>
<td>Tungsten oxide</td>
<td>WO₃</td>
<td>7.16</td>
</tr>
<tr>
<td>96.5Sn/3.5Ag solder</td>
<td>Sn/Ag</td>
<td>7.39</td>
</tr>
<tr>
<td>Erbium oxide</td>
<td>Er₂O₃</td>
<td>8.64</td>
</tr>
<tr>
<td>60Sn/40Pb solder</td>
<td>Sn/Pb</td>
<td>8.9</td>
</tr>
<tr>
<td>Bismuth oxide</td>
<td>Bi₂O₃</td>
<td>8.9</td>
</tr>
<tr>
<td>Lead oxide</td>
<td>PbO</td>
<td>9.53</td>
</tr>
<tr>
<td>Hafnium nitride</td>
<td>HfN</td>
<td>11.3</td>
</tr>
<tr>
<td>Hafnium carbide</td>
<td>HfC</td>
<td>12.2</td>
</tr>
<tr>
<td>Tungsten carbide</td>
<td>WC</td>
<td>13.6</td>
</tr>
</tbody>
</table>
ceramic fillers. Erbium oxide and bismuth oxide both have densities comparable to Sn/Pb solder and are therefore candidates for neutrally buoyant fillers.

Second, employing a scaffold to “lock” the filler into a predetermined position would not only prevent filler expulsion but would also lend itself to modeling scenarios. The scaffold structure must be strong enough to endure the aforementioned fluid dynamics during phase change but also flexible enough to be deployed on a mass scale. Ceramic foams have been investigated for a variety of uses including molten metal filtration [06S3] but would need to be developed on the microscale in order to prove viable in soldering applications. Sol-gel processing, as employed for ceramic aerogels [09A1] and xerogels [09S2], may allow for the low filler percentages dictated by expensive ceramic materials.
CHAPTER VII
SUMMARY AND CONCLUSIONS

The effects of CTE mismatch in electronic packages have been shown to warrant multi-million dollar investments from the federal government. In the private sector failure to properly consider CTE mismatches has required companies to reserve hundreds of millions of dollars to cover potential repair costs. Soldered connections are particularly sensitive to CTE mismatches because they must frequently serve as thermal, mechanical and electrical contact between dissimilar materials. Moreover the wide variety of soldering methods necessitates a versatile solder, one that can perform effectively in the bulk quantities needed for wave soldering as well as the minute amounts necessary for ultra-fine pitch surface mount components or ball grid arrays. The trend towards ever more miniaturization places only higher demands on the soldered connections as they must perform in more confined spaces with no compromise in performance or reliability. Combined with recent legislation in Europe restricting the use of Pb-based solders, and thereby creating economic pressure to quickly develop Pb-free solders, the thrust of academic research has turned to composite solders in order to
preserve the wide range of performance capabilities of the once-ubiquitous eutectic 63Sn/37Pb solder. However, Pb-based solders still serve as the performance standard in electronic packages and so are included in nearly all efforts to research and develop new solder composites.

It was in an attempt to provide a novel addition to the small list of thoroughly analyzed Pb-based solder composites that titania was chosen as a reinforcement material. While powdered titania is currently available for purchase with a size of about 6.5μm, a wider variety of shapes and sizes can be formed investigated in the laboratory environment. Electrospinning a solution of ethanol, poly(vinyl pyrrolidone) and tetraisopropyl titanate resulted in a bead-on-string morphology; calcining the fibers yielded 3.5μm diameter beads connected by fiber segments measuring 0.36μm in diameter. By adding acetic acid to the solution before electrospinning was performed smooth titania nanofibers were produced with diameters of less than 150nm. Ultrasonication of the calcined fibers in ethanol, whether beaded or bead-free, resulted in fiber segments about 6μm in length. Thus three distinct morphologies were available for composite fabrication: micron-size spherical powders, nano-sized cylindrical fibers, and a mixture of spherical beads and cylindrical fibers with sizes intermediate of other two morphologies.

The titania reinforcement, after ultrasonication and drying, was incorporated into solder powder via ball milling. In a modified form of
powder metallurgy, the composite powder was uniaxially compressed and then sintered to provide uniform samples. By means of thermomechanical analysis the CTE’s of all composites, regardless of filler, was found to be on average 25% lower than that of pure solder. Theoretical predictions generally underestimated such a reduction but since the reinforcement concentrations were less than 1wt% the predictions were highly sensitive to the elastic properties of bulk solder. Additional parameters such as melting point and density of the composites did not vary significantly from pure solder. If the composites could be used as-prepared they could prove superior to existing solder connections but, in addition to the adverse opinion towards Pb-based solders, the composites must overcome an additional barrier during the soldering process: reflow.

The critical role of reflow and the quantities of relative density and surface tension are often neglected in literature despite their importance to successful electronic package manufacturing. During reflow the crystalline solder’s temperature is raised above its melting point and held there for several minutes to allow adequate wetting between the solder and connecting components. When the composite samples from this work were reflowed it was observed that the titania reinforcement was expelled from the molten core. A force balance on a hypothetical rigid cylinder indicated that once buoyancy brought the less-dense titania to the surface of the more-dense solder, the small size of the reinforcement
ensured that surface tension forces dominated the behavior of the cylinder at the interface. Because no application of force is reasonable to overcome the surface effects and place the reinforcement in the molten solder, it is instead suggested that a reinforcement of neutral buoyancy be investigated. The hypothesis is that neutrally dense filler will stay sufficiently distant from the surface during reflow so as to remain in the composite upon reflow and subsequent crystallization. Several ceramic reinforcements, such as erbia or bismuth oxide, have densities approximately equivalent to that of eutectic Sn/Pb solder as well as low CTE’s.

In conclusion, the connection of materials with dissimilar thermal expansion coefficients can be costly and represents a reliability concern. A straightforward method for fabricating solder composites was developed as a modified powder metallurgy technique. Incorporation of a variety of micron- and nano-sized titania reinforcement into eutectic Sn/Pb solder was observed to decrease the CTE of the overall composite by 25% at concentrations as low as 0.25wt%. Research into neutrally buoyant fillers may overcome the problem of filler expulsion during reflow but a ceramic reinforcement has been shown as a promising candidate for improved solder connections.
REFERENCES


[92N1] Nikolopoulos, Agathopoulos. "Interfacial phenomena in Al\textsubscript{2}O\textsubscript{3}-liquid metal and Al\textsubscript{2}O\textsubscript{3}-liquid alloy systems." J. European Ceramic Society 10 (1992) 415-424


[03L3] Li, Xia. "Fabrication of Titania Nanofibers by Electrospinning." Nano Letters. 3 (2003): 555-560


[07T1] Thompson, Chase, Yarin, Reneker. "Effects of parameters on nanofiber diameter determined from electrospinning model." Polymer. 48 (2007): 6913-6922


NASA. "NASA-DOD Lead-Free Electronics (Project 2)". NASA Technology Evaluation for Environmental Risk Mitigation Principal Center. 12/31/08. NASA. 1/31/09. 

Reneker, Yarin. "Electrospinning jets and polymer nanofibers". Polymer 49 (2008): 2387-2425


APPENDICES
APPENDIX A
ARCHIMEDEAN DENSITY MEASUREMENTS

Archimedes’ principle states that the weight of a submerged object is equal to the object’s weight in air less the buoyant force on the object and furthermore that the buoyant force of a submerged object is equal to the weight of the fluid displaced by the object [05F1]. Assuming the buoyant force of air is negligible, this statement can be expressed as:

\[ W_{\text{submerged}} = W_{\text{dry}} - W_{\text{buoyant}} \]  \hspace{1cm} (A-1)

where \( W_{\text{submerged}} \) is the weight of the object when submerged, \( W_{\text{dry}} \) is the weight of the object in air, and \( W_{\text{buoyant}} \) is the buoyant force (weight). Using water as the fluid the buoyant force can be written in terms of the mass of water displaced by

\[ W_{\text{buoyant}} = m_{\text{water}} g \]  \hspace{1cm} (A-2)

where \( m_{\text{water}} \) is the mass of water displaced by the object and \( g \) is gravitational acceleration. The volume of water displaced must be equal to the volume of the submerged object and so Equation (A-2)
can be expressed in terms of fluid (water) density and object volume as described by

\[ W_{buoyant} = \rho_{water} V_{object} g \]  \hspace{1cm} (A- 3)

Combining Equations (A- 1) through (A- 3) and rearranging gives

\[ V_{object} = \frac{W_{dry} - W_{submerged}}{\rho_{water} g} \]  \hspace{1cm} (A- 4)

Eliminating gravitational acceleration and rewriting in terms of object density gives

\[ \rho_{object} = \frac{m_{dry}}{m_{dry} - m_{submerged}} \rho_{water} \]  \hspace{1cm} (A- 5)

Equation (A- 5) is the working equation for Archimedean density measurements. Figure A.1 illustrates the apparatus used for determining submerged object masses. An overhead support rests on a balance; the object is suspended from the support via fine wire. The fluid container, supported by aluminum plate, does not contact the balance. The effects of the wire, which is partially submerged, must be accounted for by subtracting its mass from that of the submerged object mass.
Figure A.1. Archimedean density measurement system using water as the working fluid. (a) Support structure to transfer sample load directly to balance (b) Fluid container (c) Fluid level (d) Sample, (e) Fluid container support which does not contact support structure (f) Balance plate (g) Wire suspending sample.
APPENDIX B
ULTRASONICATION OF TITANIA NANOFIBERS

The ultrasonication system described by Figure 5.1.1 in Section 5.2 served two roles: to disperse the fibers in ethanol and provide control over the length of fiber. Dispersion in ethanol aided mixing during the ball mill process by providing a powdered, flowing material rather than the non-woven mat produced by electrospinning. While only a single length for composites was chosen to reduce the complexity of this study, the ability to control the length of the fiber will prove beneficial in further studies.

After calcining (see Section 5.1), masses of 1-2g were placed in 150mL borosilicate glass square-bottom beakers. Studies with and without eutectic solder added to the mixing vessel were performed; a weight ratio of approximately 10:1 solder powder to fiber was the maximum amount able to be fluidized by the sonicator. Figure B.1 (a) and (b) show as-spun and calcined fibers, respectively, at 500x magnification (Mitutoyo 378 Finescope). Figure B.2 shows calcined titania fibers after sonication for 10 minutes at an intensity of 7
without solder in the solution. The fibers were then dried under vacuum at 150°C for 24 hours, as described in Section 5.2.

Fiber length measurements were performed at 500x magnification using ImageJ software (ImageJ v1.41o, NIH). Pixel calibration was performed on 0.05mm standards supplied by the microscope manufacturer. Measurements were performed on fibers in ethanol rather than dried fibers because of the increased dispersion offered by the ethanol solution. At least 100 measurements were made for each processing technique with statistical analysis (ANOVA) performed using the Data Analysis Toolpack in Microsoft Excel 2007. It was assumed that the data conform to the requirements of F-test analyses: constant error variance within groups, uncorrelated errors and normally distributed errors. The Student’s t-statistic [06N2] was used to determine 95% confidence intervals (95% CI); error bars on the following graphs represent these confidence intervals.

The ANOVA and summary statistics of as-spun and calcined fibers sonicated without solder in the solution are presented in Table B.1 and Table B.2, respectively. An alpha value of less than 0.0001 in each indicates a clear distinction between groups; that is, sonication duration has a larger impact on fiber length than the error inherent in the process. Figure B.3 and Figure B.4 indicate that the average fiber length behaves asymptotically and approaches a length of 5-6μm. The red tie bars in
each figure represent statistically equivalent averages using Tukey’s HSD procedure at 95% confidence [05M1, pg95].

Similarly the ANOVA and summary statistics of fibers sonicated with solder powder are presented in Table B.3. Again the approximately zero value for the p-value indicates that the differences between treatments are considerably greater than those within treatments. Note that the asymptotic minimum again appears to be around 6μm in Figure B.5. Error bars are 95%CI; red bars indicate no statistical difference via Tukey’s HSD procedure at 95% confidence.

The decision to use sonication without solder powder was based on consideration of processing requirements and final product. Samples sonicated without solder powder were easier to transfer and separate: the high density of the solder powder resulted in rapid settling and hence required additional ethanol to dislodge. Furthermore it was necessary to separate the solder from the powder so that accurate measurements of composite compositions were possible. Given that sonication with or without solder powder gave approximately equivalent fiber lengths, the method of sonication without solder powder was chosen as the most efficient for composite preparation. Finally, since both methods resulted in approximately equivalent fiber lengths after 9 minutes of sonication, the method employing powder-free sonication was chosen as the most efficient.
Figure B.1. 500x magnification of beaded titania nanofibers. (a) As-spun (b) Calcined. Spinning and calcining parameters are summarized in Table 5.1.1 and Section 0, respectively.

Figure B.2. 500x magnification of sonicated titania fibers after 10 minutes at an intensity of 7.
Table B.1. Summary and ANOVA results of as-spun, sonicated titania fibers at a sonication intensity of 7. The “Count” column refers to the number of fibers measured; “Sum” refers to the total sum of fiber lengths and has units of microns. The units of average fiber length and variance are also microns.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Count</th>
<th>Sum</th>
<th>Average</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5min</td>
<td>200</td>
<td>1735.3</td>
<td>8.677</td>
<td>7.463</td>
</tr>
<tr>
<td>3min</td>
<td>200</td>
<td>1408.0</td>
<td>7.040</td>
<td>4.934</td>
</tr>
<tr>
<td>6min</td>
<td>200</td>
<td>1317.8</td>
<td>6.589</td>
<td>2.787</td>
</tr>
<tr>
<td>9min</td>
<td>200</td>
<td>1095.9</td>
<td>5.480</td>
<td>2.387</td>
</tr>
<tr>
<td>15min</td>
<td>200</td>
<td>1113.9</td>
<td>5.570</td>
<td>2.585</td>
</tr>
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</table>

ANOVA

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>1359.6</td>
<td>4</td>
<td>339.90</td>
<td>84.317</td>
<td>1.087E-61</td>
<td>2.381</td>
</tr>
<tr>
<td>Within Groups</td>
<td>4011.0</td>
<td>995</td>
<td>4.031</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>5370.6</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Figure B.3. The effect of sonication duration on as-spun titania fiber lengths at a sonication intensity of 7. Error bars are 95% confidence intervals; red bars indicate no statistical difference via Tukey’s HSD procedure at 95% confidence.
Table B.2. Summary and ANOVA results of calcined, sonicated titania fibers at a sonication intensity of 7; no solder was included during sonication. The “Count” column refers to the number of fibers measured; “Sum” refers to the total sum of fiber lengths and has units of microns. The units of average fiber length and variance are also microns.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Count</th>
<th>Sum</th>
<th>Average</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 min</td>
<td>104</td>
<td>759.15</td>
<td>7.300</td>
<td>7.924</td>
</tr>
<tr>
<td>6 min</td>
<td>163</td>
<td>1009.6</td>
<td>6.194</td>
<td>4.727</td>
</tr>
<tr>
<td>9 min</td>
<td>197</td>
<td>1200</td>
<td>6.091</td>
<td>5.401</td>
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ANOVA

<table>
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<tr>
<th>Source of Variation</th>
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<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>109.86</td>
<td>2</td>
<td>54.932</td>
<td>9.590</td>
<td>8.3E-05</td>
</tr>
<tr>
<td>Within Groups</td>
<td>2640.5</td>
<td>461</td>
<td>5.728</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2750.3</td>
<td>463</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure B.4. The effect of sonication duration of calcined titania fiber lengths at a sonication intensity of 7 without solder powder in the solution. Error bars are 95% confidence intervals; red bars indicate no statistical difference via Tukey’s HSD procedure at 95% confidence.
Table B.3. Summary and ANOVA results of calcined, sonicated titania fibers at a sonication intensity of 7. Solder powder was included at a 10:1 weight ratio of powder to fibers. The “Count” column refers to the number of fibers measured; “Sum” refers to the total sum of fiber lengths and has units of microns. The units of average fiber length and variance are also microns.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Count</th>
<th>Sum</th>
<th>Average</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 min</td>
<td>158</td>
<td>1421.9</td>
<td>9</td>
<td>14.843</td>
</tr>
<tr>
<td>3 min</td>
<td>115</td>
<td>787.64</td>
<td>7</td>
<td>7.292</td>
</tr>
<tr>
<td>6 min</td>
<td>181</td>
<td>1077.3</td>
<td>6</td>
<td>5.171</td>
</tr>
<tr>
<td>9 min</td>
<td>222</td>
<td>1210</td>
<td>5</td>
<td>4.327</td>
</tr>
<tr>
<td>15 min</td>
<td>268</td>
<td>1524.2</td>
<td>6</td>
<td>3.883</td>
</tr>
</tbody>
</table>

ANOVA

<table>
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<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
</tr>
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<tbody>
<tr>
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<td>365.806</td>
<td>56.445</td>
<td>1.068E-42</td>
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<tr>
<td>Within Groups</td>
<td>6085.4</td>
<td>939</td>
<td>6.481</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>7548.6</td>
<td>943</td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

Figure B.5. The effect of sonication duration on calcined titania fiber lengths at a sonication intensity of 7 with solder powder added at a 10:1 powder to fiber ratio. Error bars are 95% confidence intervals; red bars indicate no statistical difference via Tukey’s HSD procedure at 95% confidence.
In light of the observation that all forms of filler are expelled from the molten matrix it is enlightening to consider equilibrium position of the fillers. There are several possibilities given that there are three fluids of interest: a thin layer of flux separates the molten solder core from the atmosphere. Buoyancy forces should ensure that the filler will be located at an interface but which interface requires further investigation. The filler should be located at either the solder-flux interface or the flux-atmosphere interface as determined by the density of the materials and, once at a particular interface, should take on an equilibrium position with greater volume in one phase or the other.

Consideration will be given to a cylinder floating on the interface between two fluids, which for clarity will be a liquid and vapor. Such an analysis has been offered several times in different forms ([69P1, pg1-84], [77R1], [05V1]); this analysis will be a force balance on the cylinder. The general setup is depicted in Figure C.1, where a solid, rigid cylinder
in red floats atop a liquid volume outlined in blue; the vapor is to be considered everywhere the fluid or cylinder is not. The Cartesian coordinate system in this figure has been carefully chosen and merits a brief summary. First, note that the center-line of the cylinder, which would extend from \( O \), is not defined as the \( y \)-axis. Second, the \( x \)-axis is located along the undisturbed liquid level. Third, and perhaps most important, the \( z \)-axis is measured such that positions below the \( x \)-axis are positive and those above are negative. It follows that forces acting in the positive \( z \)-direction are sinking forces whereas those acting in the negative \( z \)-direction are lifting forces. Similarly, angles measured counterclockwise from the \( x \)-axis are positive and those measured clockwise are negative.

Figure C.1. Cartesian coordinate system for a rigid, solid cylinder floating at the interface between two fluids. Note that the \( z \)-coordinate is measured downward from the undisturbed fluid level, which is not constrained to be at the same level as the center of the cylinder.
A detailed description of the setup of interest is given by Figure C.2, the x-z perspective. Densities of the liquid, vapor and solid are denoted by $\rho_L$, $\rho_V$ and $\rho_S$, respectively. Similarly $\gamma_{SL}$, $\gamma_{SV}$ and $\gamma_{LV}$ denote the solid-liquid, solid-vapor and liquid-vapor surface tensions; angle $\theta$ denotes the contact angle as measured through the liquid. Line $AC$ defines the three-phase contact line; thus segment $ABC$ is submerged in the liquid and segment $ADC$ is within the vapor. Angle $\varphi$ defines the angle $BOC$ and denotes the position of the cylinder’s center relative to the three-phase contact line. The distance between the undisturbed liquid level and the contact line ($AC$) is denoted as $z_0$. Although not shown the length of the cylinder is to be $L$, line $OC$ is the radius $R$ of the cylinder. Finally, angle $\beta$ is the angle of the line tangent to the meniscus;

Figure C.2. Relevant quantities and geometry for the derivation of $F_{net}$. Definitions for each are noted in the text.
this definition will be refined at a later point. The most important point to remember about $\beta$ is that it is zero at $B$ (i.e., at $x=0$).

Three vertical forces act on the cylinder: surface tension, cylinder weight and buoyancy. For simplicity, cylinder weight and buoyancy will be combined into a single force $F_B$; the vertical component of the surface tension will be $F_{ST}$. The force due to surface tension acts along the entire wetted perimeter of the cylinder but for mathematical simplicity the caps of the cylinder will be neglected; the analysis offered in Section 6.6 confirms this assumption. In order to determine the vertical component of the surface tension the angle between $\gamma_{LV}$ and the horizontal must first be determined geometrically in terms of $\varphi$ and $\theta$.

While the answer is already supplied in Figure C.2, this angle will for the moment be denoted as $\delta$. Magnification at point $C$ in Figure C.2 allows one to draw Figure C.3, where the extraneous symbols have been removed for clarity. Two useful identifications have been made: line $(OC)$ is perpendicular to $\gamma_{SL}$, and line $(OC)$ has been extended to identify angle $\varphi$ again. Since the angle between $\gamma_{SL}$ and $\gamma_{LV}$ is defined as the contact angle $\theta$, simple addition of terms gives

$$\theta = \left(\frac{\pi}{2} - \varphi\right) + \varphi + \left(\frac{\pi}{2} - \varphi\right) + \delta,$$  \hspace{1cm} (C-1)
\[ \delta = \theta + \varphi - \pi. \] \hspace{1cm} (C-2)

Recalling that upward forces are negative, one can then write
\[ F_{ST} = -2L\gamma_{LV} \sin(\delta) \]
\[ = -2L\gamma_{LV} \sin(\theta + \varphi - \pi). \] \hspace{1cm} (C-3)

Finally, noting the two trigonometric identities
\[ \sin(-x) = -\sin(x) \] \hspace{1cm} (C-4)
and
\[ \sin(\pi - x) = \sin(x), \] \hspace{1cm} (C-5)

one can write \( F_{ST} \) as
\[ F_{ST} = 2L\gamma_{LV} \sin(\theta + \varphi). \] \hspace{1cm} (C-6)

It should again be emphasized that Equation (C-6) is the vertical component of the surface tension, an upward force, and is positive only

Figure C.3. Magnification at point \( C \) of Figure C.2 for determining the angle of \( \gamma_{LV} \) with the horizontal, i.e. \( \delta \).
by careful application of the above trigonometric identities. Moreover the contribution to this force from the caps of the cylinders has been neglected for mathematical simplicity, an assumption affirmed in Section 6.6.

In order to express the buoyant force in a compact manner it is useful to divide the cylinder into two sections as in Figure C.4. Volume $ABC$ is subjected to the buoyant forces from the liquid whereas volume $ACD$ is subjected to those of the vapor. Using Archimedes’ principle as in Appendix A, the buoyant force of each section is proportional to the volume of fluid displaced by that section, or

$$F_{\text{buoyant}} = -[V_{ACD}\rho_V g + V_{ABC}\rho_L g]. \quad (C\text{-}7)$$

Again, the sign is negative because the buoyant forces act to lift the cylinder. As mentioned previously the weight of the cylinder will be

$$V_{ABCD} = V_{ABC} + V_{ACD}$$

Figure C.4. Portions of the total cylinder used for writing the buoyant force.
incorporated into the buoyant force in the interest of simplification; the weight of the cylinder is simply
\[ F_{\text{WEIGHT}} = V_{ABCD} \rho_S g. \] (C- 8)
This can be rewritten in terms of Figure C.4’s cylinder segments which allows for an expression analogous to that of Equation (C- 7), or
\[ F_{\text{WEIGHT}} = V_{ACD} \rho_S g + V_{ABC} \rho_S g. \] (C- 9)
Adding Equations (C- 7) and (C- 9) results in the total buoyant force:
\[ F_B = V_{ACD} (\rho_S - \rho_V) g + V_{ABC} (\rho_S - \rho_L) g. \] (C- 10)
Equation (C- 10) can be rewritten to a simpler form if
\[ (V_{ABC} \rho_3 g - V_{ABC} \rho_2 g) + (V_{ABC} \rho_1 g - V_{ABC} \rho_1 g) = 0 \] (C- 11)
is added to both sides, which after rearrangement results in
\[ F_B = V_{ABCD} (\rho_S - \rho_V) g - V_{ABC} (\rho_L - \rho_V) g, \] (C- 12)
where \( V_{ABCD} \) is the total volume of the cylinder \( \pi R^2 L \), and \( V_{ABC} \) is the volume of the cylindrical segment \( ABC \). The latter volume can be visualized as in Figure C.5 and then expressed as
\[ V_{ABC} = V_{ABCD} - V_{AOC} \] (C- 13)
\[ = LR^2 \phi - LR^2 \sin(\phi) \cos(\phi) \] (C- 14)
\[ V_{ABC} = LR^2 [\phi - \sin(\phi) \cos(\phi)]. \] (C- 15)
However, there is an additional buoyancy force due the depression of the liquid-vapor interface. This force depends on the amount of depression as denoted by \( z_0 \) and acts along the area of the three-phase contact line, and can be written as
\[ F_{\text{depression}} = -2RL \sin(\phi) z_0 (\rho_L - \rho_V) g. \] (C- 16)
Therefore the total force due to buoyancy effects is

\[ F_B = \pi LR^2(\rho_S - \rho_V)g \]

\[-LR^2[\varphi - \sin(\varphi) \cos(\varphi)](\rho_L - \rho_V)g \quad (C-17)\]

\[-2RL \sin(\varphi) z_0(\rho_L - \rho_V)g. \]

The net upward force \( F_{\text{net}} \) could now be written by summing \( F_B \) and \( F_{ST} \).

However, if two system constants are defined as

\[ A^2 = (\rho_L - \rho_V)g/\gamma_{LV} \quad (C-18) \]

\[ B = \pi(\rho_S - \rho_V)g/\gamma_{LV}. \quad (C-19) \]

then \( F_{\text{net}} \) can be written in terms of the two dimensionless constants

\[ C = A^2 R^2 \quad (C-20) \]

\[ D = \frac{B}{\pi A^2} = \frac{\rho_S - \rho_V}{\rho_L - \rho_V}. \quad (C-21) \]

Dividing the sum of Equations (C-6) and (C-17) by \( L \gamma_{LV} \) and applying

\[ V_{ABC} = \quad V_{ABCO} = \quad V_{AOC} \]

Figure C.5. Volume segments used to determine the volume of the submerged cylindrical segment, \( V_{ABC} \).
Equations (C-18) through (C-21) results in

\[ F'_{\text{net}} = \frac{F_{\text{net}}}{LY_{LV}} = 2 \sin(\theta + \varphi) + C \left\{ \pi D - [\varphi - \sin(\varphi) \cos(\varphi)] - 2 \left( \frac{z_0}{R} \right) \sin(\varphi) \right\}, \]  

(C-22)

where \( F'_{\text{net}} \) is the dimensionless net force on the cylinder. Equilibrium is achieved when \( F'_{\text{net}} \) is equal to zero; positive and negative values indicate that the cylinder is being subjected to sinking and lifting forces, respectively. Alternatively, if \( F'_{\text{net}} \) is positive the cylinder is too far into the vapor phase, whereas it is too far in the liquid if the sign is negative. Except for \( (z_0/R) \) Equation (C-22) is a function solely of the system properties as denoted by \( D, C \) and \( \theta \). The Laplace Equation [69P1] can be used to describe the shape of the meniscus, viz

\[ \Delta P = \gamma_{LV} \left( \frac{1}{R} \right) = -\frac{d \cos(\beta)}{dz}, \]  

(C-23)

which upon substitution for \( \Delta P \) becomes

\[ A^2 dz = -d \cos(\beta). \]  

(C-24)

This differential can be solved analytically with the constant of integration determined by the aforementioned condition that at \( z=0, \beta=\theta \).

Recognizing that \( \beta=\delta=\varphi+\theta-\pi \) at the interface, the solution is

\[ \left( \frac{z_0}{R} \right) = \pm \left( \frac{2}{C} \right)^{\frac{1}{2}} \left[ 1 + \cos(\varphi + \theta) \right]^{\frac{1}{2}}. \]  

(C-25)

The sign can be determined by careful inspection of Figure C.2: if \( \beta>\theta \) the meniscus must be above the center line of the cylinder and so \( z_0 \) is negative, with the reverse also being true. Equations (C-22) and (C-25) will predict where the cylinder rests on the interface at equilibrium. In
practice, this can be achieved by determining the value of $\varphi$ which results in $F_{\text{net}} = 0$, as in Section 6.6.
APPENDIX D

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