Scalable Manufacturing of Metal Micro/Nano Wires and Particles by Thermal Fiber Drawing from a Preform

Permalink
https://escholarship.org/uc/item/2417f2xj

Author
Zhao, Jingzhou

Publication Date
2017

Peer reviewed|Thesis/dissertation
Scalable Manufacturing of Metal Micro/Nano Wires and Particles by Thermal Fiber Drawing from a Preform

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Mechanical Engineering

by

Jingzhou Zhao

2017
ABSTRACT OF THE DISSERTATION

Scalable Manufacturing of Metal Micro/Nano Wires and Particles by Thermal Fiber Drawing from a Preform

by

Jingzhou Zhao

Doctor of Philosophy in Mechanical Engineering

University of California, Los Angeles, 2017

Professor Xiaochun Li, Chair

The objective of this study is to significantly advance the fundamental understanding of the process of metal-core thermal drawing from a preform for the scalable manufacturing of metal micro/nano-particles and wires. Metal micro/nano-wires and particles, with controlled size, aspect ratio and spatial distribution, exhibit unusual mechanical, electrical, magnetic, thermal, and optical properties that are desirable for numerous applications in industry as well as for fundamental research. Thermal fibre drawing from a preform, capable of mass production of continuous and uniform glass and polymer fibers, has emerged as an advanced scalable manufacturing tool for
such metal micro/nano-wires and particles. It is of tremendous scientific and technical interest to gain fundamental knowledge through theoretical and experimental studies and to explore and break the fundamental limits of the metal-core thermal drawing process.

Throughout this study, material combinations of the metal Tin (Sn) core and thermoplastic Polyethersulfone (PES) cladding are used as a model system. Because the viscosity ratio between molten metal and polymer (or glass) melt is much smaller than one during normal process conditions, results obtained in this study based on Sn/PES system are expected to have useful implications for other metal/glass or metal/polymer combinations as well.

Despite the fact that thermal drawing from a preform is capable of the high volume production of continuous metal microwires for numerous applications, no theoretical model can yet satisfactorily provide effective predictions of core diameter and continuity from process parameters and material properties. A long wavelength model is therefore derived aiming to fill this gap and describe the dynamics of a molten metal micro-jet entrained within an immiscible, viscous, nonlinear free-surface extensional flow. The model requires numerical data (e.g. drawing force and cladding profile) be measured in real-time. Examination of the boundary conditions reveals that the diameter control mechanism is essentially volume conservation. The flow rate of molten metal is controlled upstream while the flow velocity is controlled downstream realized by solidification of the molten metal. The dynamics of the molten metal jet is dominated by interfacial tension, stress in the cladding, and pressure in the molten metal. Taylor’s conical fluid interface solution (Taylor 1966) can be considered as a special case in this model. A dimensionless capillary number $Ca = \frac{2Fa}{\gamma A(0)}$ is suggested to be used as the indicator for the transition from continuous mode (i.e. viscous stress dominating) to dripping mode (i.e. interfacial tension dominating).
Experimental results showed the existence of a critical capillary number $Ca_{cr}$, above which continuous metal microwires can be produced, providing the first ever quantitative predictor of the core continuity during preform drawing of metal micro wires.

With the new understanding obtained through the fundamental studies on single-core preform drawing, experimental design and analysis on thermal drawing of micro metal wires are carried out to optimize the drawing conditions for multi-core preforms. To minimize the experimental cost and time, we made an unreplicated $2^3$ factorial design and evaluated the effects and interactions of drawing parameters (e.g. draw-down ratio, stress at melt front, and aspect ratio) on the capillary instability and core continuity. Two numerical indicators, namely Relative Standard Deviation (RSD) and Deviation from Draw-down Ratio (DDR), were proposed as measures of the extent of growth of capillary instability and the core continuity respectively. The results indicate that all main factors considered significantly affect the RSD and DDR and the interactions between main factors are not negligible. Comparison between models fitted respectively based on RSD and DDR suggests that capillary instability may not be the only cause of core break-up, which led to the discovery of solid-state break-up. Empirical rules for optimizing parameters are derived based on the surface plots of RSD and DDR. At least at microscale domain, maximizing the stress at the melt front is believed to minimize the growth of capillary instability while maximizing the draw-down ratio tends to maximize the chance of obtaining a continuous core, given all other parameters unchanged.

While previous studies focus on maintaining the continuity of the metal core during preform drawing, i.e. preventing fluid instabilities, exploratory studies were also conducted to control the wavelength of break-up by electric fields and to harness the fluid instabilities for the
production of metal nanoparticles. We conducted a feasibility study on utilizing a radial electric field to control the break-up wavelength of an initially continuous microwire during preform drawing. It was hypothesized that the radial electric field significantly affects the break-up wavelength of the metal core during preform drawing. The result of an unpaired two-sample t-test confirmed the effect thus shed new light on the controlled emulsification of molten metal in a viscous dielectric medium. We then experimentally show the scalable manufacturing of metal Sn nanoparticles (<100 nm) in Polyethersulfone (PES) fibers. The underlying mechanism for the particle formation is revealed, and a strategy for the particle diameter control is proposed. This process opens a new pathway for scalable manufacturing of metal nanoparticles from liquid state facilitated solely by hydrodynamic forces, which may find exciting photonic, electrical, or energy applications.
The dissertation of Jingzhou Zhao is approved.

Chih-Ming Ho

Pei-Yu Chiou

Hossein Pirouz Kavehpour

Xiaochun Li, Committee Chair

University of California, Los Angeles

2017
To my family.
# TABLE OF CONTENTS

Table of Contents.............................................................................................................. viii

Acknowledgements........................................................................................................... xii

Vita........................................................................................................................................ xiii

Book Chapter ....................................................................................................................... xiii

Journal Articles ................................................................................................................... xiii

Peer-Reviewed Conference Proceedings ............................................................................ xiv

Patents ................................................................................................................................... xiv

Chapter 1. Introduction ....................................................................................................... 1

  1.1 Background and Motivation......................................................................................... 1

  1.2 Overarching Goals and Specific Research Objectives............................................... 4

  1.3 Outline ........................................................................................................................... 4

Chapter 2. Literature Review ............................................................................................... 5

  2.1 Metal-core fiber drawing from a preform ................................................................. 5

  2.1.1 Applications of metal wires in drawn multi-material multi-functional fibers  7

  2.1.2 Summary on metal core fiber drawing from a preform ......................................... 10

  2.2 Scalable manufacturing of metal micro- and nanowires and particles by thermal
drawing .................................................................................................................................. 10

  2.2.1 Micro/nano-particles .............................................................................................. 11
2.2.2 Metal microwires

2.2.3 Metal nanowires

2.2.4 Toward the continuum limit

2.2.5 Summary on scalable manufacturing of metal micro/nanowires and particles by thermal drawing

2.3 Theoretical and experimental studies on metal core thermal fiber drawing

2.3.1 Tomotika dispersion relation

2.3.2 Comparison with nonmetals

2.3.3 Beyond the Tomotika model

2.3.4 Modeling and simulations

2.3.5 Summary of theoretical and experimental studies

2.4 Literature review summary

Chapter 3. Experimental apparatus

3.1 Fiber drawing tower

3.1.1 Preform Feeding System

3.1.2 Wire Drawing and Winding System

3.1.3 Tension Monitoring System

3.1.4 Motor Control

3.1.5 Temperature Control System
3.2 Preform consolidation tower ................................................................. 34

Chapter 4. Theoretical study on the manufacturing of continuous microwires by thermal fiber drawing from a preform ................................................................. 36

4.1 Problem formulation ........................................................................... 36

4.2 Boundary conditions and diameter control mechanism ...................... 42

4.3 Steady state core shape ..................................................................... 44

4.3.1 A. Isothermal drawing with constant cladding velocity and zero core flow rate

\[(Uz = U(0), \mu z = \mu, Qz, t = 0)\] ............................................................................. 44

4.3.2 B. Isothermal drawing with exponential cladding velocity

\[(Uz = U(0)U(L)U(0)zL, \mu z = \mu)\] ............................................................................. 45

4.4 Measurement of interfacial energy ...................................................... 47

4.5 Mode transition and critical capillary number .................................... 50

4.6 Summary ............................................................................................. 52

Chapter 5. Use of Factorial Designs for thermal fiber drawing .................. 54

5.1 Fiber drawing experiment and experimental design ............................ 54

5.1.1 Experimental design ....................................................................... 55

5.1.2 Capillary instability and core continuity ......................................... 56

5.2 Data analysis and results .................................................................... 58

5.2.1 Model fitting .................................................................................... 58

5.2.2 Results ............................................................................................. 60
5.3 Summary .......................................................................................................................... 63

Chapter 6. Nanomanufacturing by thermal fiber drawing ................................................. 65

6.1 Scalable Manufacturing of Metal Nanoparticles by Thermal Fiber Drawing..... 65

6.1.1 Materials and Methods ............................................................................................ 66

6.1.2 Results and Discussion ............................................................................................ 71

6.2 Break-up control by electric field.................................................................................. 79

6.3 Summary .................................................................................................................... 82

Chapter 7. Conclusions ....................................................................................................... 84

Chapter 8. Recommendations for future work ............................................................... 87

8.1 Scalable manufacturing of metal nanomaterials ......................................................... 87

8.2 Integrated nanomanufacturing....................................................................................... 87

8.3 Advanced composite materIAls .................................................................................... 89

References .......................................................................................................................... 90
ACKNOWLEDGEMENTS

I would like to thank Professor Xiaochun Li for his continuous support and guidance, without which the accomplishment of this work would not be possible.

I would also like to acknowledge Professors Chih-ming Ho, Pei-Yu Chiou and Pirouz Kavehpour for serving on my doctoral committee. Their insights and inputs have shaped and benefited my research greatly.

I am also very grateful to all of my colleagues in the research group, for being my friends, collaborators, and comrades.

Special thanks go to Professor Gan-ce Dai and Professor Bob Bird for being my role models.

I will always be indebted to my family for their unconditional support throughout this endeavour.
VITA

2013, M.S., Mechanical Engineering, University of Wisconsin–Madison
2011, B.S., Mechanical Engineering & Automation, Shanghai Jiao Tong University, China

BOOK CHAPTER


JOURNAL ARTICLES


• Mutyala, M. S. K., Zhao, J., Li, J., Pan, H., Yuan, C., and Li, X., 2014, "In-situ Temperature Measurement in Lithium Ion Battery by Transferable Flexible Thin Film Thermocouples," Journal of Power Sources, 260(0), pp. 43-49.


PEER-REVIEWED CONFERENCE PROCEEDINGS


• Lin, T.C., Zhao, J. Li, X., 2016, "Feasibility Study on Thermal Drawing of Polymer Fibers Containing Micro/Nano Metal Wires," Proceedings of International Symposium on Flexible Automation, Cleveland, Ohio, 1 - 3 August, in press.


PATENTS

• Xiaochun Li, Jingzhou Zhao, Injoo Hwang, Method for thermally drawing nanocomposite-enabled multifunctional fibers, International Patent, Publication No.: WO 2016/122958 A1


• Wayne Cai, Jeff Abell, Xiaochun Li, Hongseok Choi, Hang Li, Jingzhou Zhao, Vibration welding system with thin film sensor, US Patent, Publication No.: US8672211 B2

• Chengliang Liu, Xuyong Wang, Jingzhou Zhao, Chen Chen, Jianfeng Tao, Oil absorption optimized device for oil cooler having gradient side slot oil suction pipe, CN Patent, Publication No.: CN 101900151 A
CHAPTER 1. INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Thermal drawing from a preform is a scalable manufacturing method for the high volume production of continuous and uniform metal microwires, in a way very similar to continuous casting, but at a much smaller length scale. Indefinitely long metal microwires are produced from bulk metal in the sequence of melting, liquid state forming, and then solidifying directly within an amorphous cladding material (e.g. usually made of thermoplastics or glass).

During a typical fiber drawing process, as shown in Fig. 1.1, the metal embedded preform is aligned and fixed under a preform chuck, which is then slowly lowered into a furnace which temperature is carefully controlled and stabilized at a designated value. After the heated preform in the furnace necks down under its weight (or under external pulling forces sometimes), the bottom portion of the preform is cut away and the fiber is fed through a pinch wheel. The produced fiber filament is ultimately wound onto a spool. The diameter of the fiber $D_f$ is usually measured by a laser diameter gauge. The draw-down ratio $D_r$ is defined as the ratio between the fiber pulling speed $U(L)$ and preform feeding speed $U(0)$. At steady-state, the law of mass conservation requires $D_r \equiv \frac{U(L)}{U(0)} = \left(\frac{D_p}{D_f}\right)^2$, where $D_p$ is the preform diameter. The drawing force or fiber tension, often monitored by a load cell, is also an important control parameter and measures the tensile stress along the fiber.
Figure 1.1 Schematic and process parameters of fiber drawing from a preform with a metal core

In addition to metal microwires manufacturing, preform drawing is also used for the manufacturing of long fibers with embedded functionalities of great potential for numerous applications. Ongoing research on ultra-long functional fibers include, but are not limited to, microstructured photonic crystal fibers (Russell 2007), optical micro/nanofibers (Wang, Wang et al. 2013), electronics in fibers (Wang, Wang et al. 2013), fiber-based metamaterials (Argyros 2013), fibers as a novel platform for sensing devices (Ricciardi, Consales et al. 2013), studying chemical reactions (Sparks, Sazio et al. 2013), and multi-material functional fibers (Abouraddy, Bayindir et al. 2007, Tao, Stolyarov et al. 2012, Stolyarov, Wei et al. 2013). The trend of combining a multitude of functionalities into a single long fiber demands the incorporation of a multiplicity of solid materials with disparate physical properties. Significant progress has been made along this direction by thermal drawing of macroscopic multi-material preforms. Materials that have distinctively different electrical and optical properties are integrated into a single fiber.
Various electronic and optoelectronic devices were realized in kilometre-long fibers. Large-scale fabrics woven from such fibers were also demonstrated.

While numerous research utilize thermal drawing from a multi-material preform for various applications, fundamental understanding of the underlying physics of the process is still lacking, especially those that concern the dynamics of molten metals at micro/nanoscale during preform drawing, such as what are the dominating physical forces that govern the dynamics of the molten metal (e.g. viscous stress, interfacial tension, etc.), and how the liquid-state break-up of the metal core is quantitatively related to the material properties and drawing parameters. The knowledge is not only valuable for the existing applications of preform drawing that contain metals but also suggests pathways to break existing limit of the process. For example, the literature review revealed that the continuous manufacturing of indefinitely long and uniform crystalline metal nanowires is not yet achievable by preform drawing, while arrays of such long metal nanowires hold promise for new devices with unprecedented capabilities in areas of energy, electronics, and photonics. In addition to nanowires, the application of thermal drawing for the scalable manufacturing of nanoparticles has recently been demonstrated with mixed success (Kaufman, Tao et al. 2011, Yaman, Khudiyev et al. 2011, Kaufman, Tao et al. 2012, Kaufman, Ottman et al. 2013). Great potential and difficulties lie in the low-cost mass production of micro- and nanowires and particles, especially those crystalline metal ones formed at liquid state, with controlled size, aspect ratio, and assembly for functional/structural applications as well as fundamental studies, which motivates this study.
1.2 OVERARCHING GOALS AND SPECIFIC RESEARCH OBJECTIVES

The overarching goals of this study is to establish the foundation for scalable manufacturing of metal micro- and nanoparticles and wires at molten state by preform drawing, with the specific objectives: (a) to significantly advance the fundamental understanding of the single core thermal fiber drawing process from a preform at microscale, (b) to establish empirical rules for process optimization of multicore preform drawing through experimental design, (c) to explore and extend the capability of metal core preform drawing into nanoscale.

1.3 OUTLINE

The dissertation will be organized as follows.

- Chapter 2 reviews the literature that is relevant to this study
- Chapter 3 describes a custom-built experimental apparatus that are used to conduct the fiber drawing experiments
- Chapter 4 conducts fundamental studies to understand the manufacturing of continuous microwires by thermal fiber drawing from a preform
- In Chapter 5, the method of factorial experimental design is employed based on the new findings obtained from Chapter 4 for process optimization
- Chapter 6 explores the feasibility of utilizing thermal fiber drawing for nanomanufacturing
- The conclusions of this work and recommendations for future work are made in Chapter 7.
CHAPTER 2. LITERATURE REVIEW

The literature review begins with a brief introduction to thermal fiber drawing from a metal-core preform and its applications, followed by a thorough examination on the state-of-art of the scalable manufacturing of metal micro- and nanowires and particles by thermal drawing broadly defined, including but are not limited to preform drawing. Research needs are then identified through an extensive review of existing theoretical studies for process physics understanding and experimental studies for process optimization.

2.1 METAL-CORE FIBER DRAWING FROM A PREFORM

Since the first report of the formation of metal microwires by thermal drawing (Taylor 1924), the technology has evolved tremendously from its original form, as shown in Fig. 2.1.

---

Figure 2.1. Evolution of technologies that produce metal micro/nano-wires from melt
Among all variants of the modern fiber drawing processes that are documented either as patents or research articles, fiber drawing from a preform has received tremendous interest due to its potential for the scalable manufacturing of multi-material and multifunctional fibers, as well as nanoparticles and continuous nanowires. The minimal requirements (or the material selection criteria) that need to be met for the preform drawing to be successful, can be found in the literature (Ma, Hong et al. 2011, Tao, Stolyarov et al. 2012) and are summarized here:

1) The viscosity of the most viscous constituent material (i.e. the cladding) should fall between $10^{3.5}$ and $10^7$ Poise at the drawing temperature for the process to be controllable. Amorphous materials, such as glass and polymers, are typically used as the support (cladding).

2) The melting temperature of the core metal ($T_m$) should be lower than or at least overlap with the drawing temperature ($T$). Low vapor pressure of the metal is desired and its boiling should be avoided.

3) Chemical reactions between the cladding and core materials should be prevented unless intentionally designed, e.g. for in-fiber synthesis purposes (Orf, Shapira et al. 2011).

4) It is desired that cladding and core materials exhibit excellent adhesion/wetting with each other during and after drawing to avoid cracks, bubbles and fluid instability of the core material(s).
5) The cladding and core materials should have relatively compatible thermal expansion coefficients in the temperature range up to the drawing temperature.

2.1.1 Applications of metal wires in drawn multi-material multi-functional fibers

Continuous metal wires play essential roles in multi-material multi-functional fibers drawn from a preform. They are structurally supported by the cladding material (e.g. a thermoplastic or Pyrex glass), and their spatial arrangements are determined by design in the macroscopic preform. The mechanical, electrical, thermal, optical, and magnetic properties of the metal wires along with the spatial arrangement give rise to exotic functionalities that are reviewed in the section.

2.1.1.1 Metamaterial fibers

Metamaterials are defined as materials artificially structured to exhibit properties that rely more on the unit structure than on the constituent materials (Cai, Shalaev et al. 2010, Yang 2016). Wire array metamaterials with plasmonic response at THz and Mid-IR can be fabricated using preform drawing technique (Argyros 2013, Naman, New-Tolley et al. 2013). By adjusting the size and spacing between the microwires, which can be easily realized for preform drawing, the permittivity at a particular frequency can be tuned. Such fibers behave as high-pass filters and have potential applications in THz imaging and thermal detection. Subdiffraction imaging and focusing at terahertz frequencies using the drawn wire array metamaterial fibers has been demonstrated (Tuniz, Kaltenecker et al. 2013). It is theoretically predicted that fibers invisible to visible light can be realized in a hexagonal nanowire array structure of 361 silver nanowires with diameters of 27 nm and spacing of 100 nm in a silica cladding of 1 µm radius (Tuniz, Kuhlmey et al. 2010).
Challenges lie in the fabrication of such fine wires over a long distance while still maintaining their continuity.

### 2.1.1.2 Conductive electrodes for fiber device

The high conductivity of metal microwires renders them indispensable components in multifunctional fiber devices. Polymer-metal multielectrode fiber probes were fabricated by preform drawing as neural probes for the simultaneous stimulation, recording, and delivery in behaving mammals with high resolution (Canales, Jia et al. 2015). Arrays of up to 36 tin electrodes (each having a diameter of ~5\( \mu \)m) with poly(etherimide) and poly(phenylsulfone) claddings were produced through a two-step thermal drawing process for single-neuron recordings with average signal-to-noise ratios (SNR) of 13. Other applications of metal wires as conductive electrodes include: fibrous 1D photodetectors (Bayindir, Sorin et al. 2004), thermal sensors (Bayindir, Shapira et al. 2005, Bayindir, Abouraddy et al. 2006), piezoelectric transducers (Egusa, Wang et al. 2010, Chocat, Lestoquoy et al. 2012), chemical sensors (Gumennik, Stolyarov et al. 2012), and capacitors (Lestoquoy, Chocat et al. 2013).

### 2.1.1.3 Plasmonic Photonic Crystal Fibers

Strong photon-electron interactions occur when light encounters metal at a metal-dielectric interface. Surface-plasmon polaritons form at these interfaces to result in strong field enhancements(Schmidt, Sempere et al. 2008). As the wire size is reduced to the nanoscale, Surface Plasmonic Resonances (SPRs) occur and can be utilized for waveguiding. By arranging the metal wires in the same way air holes are arranged in Photonic Crystal Fibers (PCFs), a new class of
fiber called Plasmonic Photonic Crystal Fibers emerged offering enhanced sensitivity to optical fiber based sensors (Hu and Ho 2017). Numerous research focus on the fundamentals and applications of the SPR for improved sensor performance or new sensing principles (Chen, Li et al. 2016, Jiang, Zheng et al. 2016, Tuniz and Schmidt 2016, Ando, Tuniz et al. 2017, Johns, Beane et al. 2017, Santos, Guerreiro et al. 2017, Santos, Guerreiro et al. 2017). Challenges again lie in the manufacturing of arrays of long nanowires (such as Au and Ag) over an extended distance while still maintaining their continuity.

2.1.1.4 Thermoelectric fibers

It has been long known that nanowires have improved thermoelectric performance than their bulk counterpart due to the enhanced phonon scattering in their confined 1D structures (Caballero-Calero and Martín-González 2016). Arrays of long nanowires made of thermoelectric materials are thus expected to exhibit higher thermoelectric power (Badinter, Huber et al. 2004). High-sensitivity micro-thermocouples and micro-coolers are produced as nanowire bundles for medical applications. The micro-thermocouples offer high spatial and temporal resolution measurement of local temperature with the accuracy of 0.1 ~ 0.01 °C, an order of magnitude greater than conventional thermocouples (Ioisher, Badinter et al. 2012).

2.1.1.5 Magnetic wires

Amorphous or nanocrystalline metal microwires made of magnetic materials find numerous applications as essential components in sensors based on their magnetic properties, such as bistability, high magnetic susceptibility, giant magneto-impedance, and ferromagnetic
resonance, etc (Zhukov, González et al. 2000, Marin, Hernando et al. 2004, Aleinicov, Ioisher et al. 2016). How these properties change as the wire diameters shrink to less than 100 nm is currently under investigation (Ioisher, Badinter et al. 2012). Magnetic bistability is observed in nanowire arrays made of Fe based alloys with the width of the response during the magnetic remagnetization increased by a factor of 2–2.5 as compared to microwires.

2.1.2 Summary on metal core fiber drawing from a preform

Preform drawing of metal wires from melt possess the unique characteristics that allow for the simultaneous fabrication and massive assembly of metal microwire arrays inside a dielectric cladding. Numerous existing and emerging applications are reviewed that utilize the mechanical, electrical, thermal, optical, and magnetic properties of metals. Manufacturing challenges exist in the scalable manufacturing of such metal wire arrays at a smaller scale that will find unprecedented applications in the areas of energy, biomedical device, electronics, and photonics.

2.2 SCALABLE MANUFACTURING OF METAL MICRO- AND NANOWIRES AND PARTICLES BY THERMAL DRAWING

This section provides a thorough review on the state-of-art of the scalable manufacturing of metal micro- and nanowires and particles by thermal drawing broadly defined, including but are not limited to preform drawing. The aim is to identify the limit of the current thermal drawing processes regarding the capability to control the size and aspect ratio of the particles and wires produced.
2.2.1 Micro/nano-particles

Metal nanoparticles possess unique mechanical, physical and chemical properties that are of great significance to both technologies and fundamental science. The making of such nanoscale entities has been an active research field for the last two decades. While bottom-up (Xia, Xiong et al. 2009) and top-down (Jaworek 2007) methods for metal nanoparticle manufacturing exist, there is always need to produce them inexpensively at high volume.

Thermal fiber drawing process has recently emerged as a novel top-down process for the continuous manufacturing of non-metallic nanoparticles. In-fiber fabrication of semiconductor and polymer nanoparticles was successfully demonstrated (Kaufman, Tao et al. 2012, Gumennik, Wei et al. 2013, Kaufman, Ottman et al. 2013). However, a scalable production of metal nanoparticles by thermal drawing is not yet reported. The formation of metal microparticles during thermal fiber drawing relies on the emulsification of immiscible glass/metal systems facilitated by capillary fluid instability. Traditional thermal fiber drawing requires that cladding being viscous during drawing, which casts stringent requirements on the material properties. It is believed that the cladding should have a high viscosity which changes gradually with temperature for the process to be controllable. Amorphous materials, such as fused silica, Pyrex glass, and thermoplastic polymers, are typically used. The particle forming core materials should have melting points or glass transition temperatures lower than the glass transition temperature of the cladding material to allow for emulsification during heating. Two in-fiber particle generation mechanisms have been reported so far, namely, particle generation by Plateau-Rayleigh (PR) Instability (Shabahang, Kaufman et al. 2011), and by in-fiber thermal gradient (Gumennik, Wei et al. 2013). The PR Instability driven particle generation is observed for core materials with high viscosity and low interfacial energy.
with cladding such as polymers and viscous semiconductors inside a polymer cladding. The thermal gradient driven particle generation is observed for core materials with low viscosity and high interfacial energy with the cladding such as silicon inside fused silica cladding. For the scalable in-fiber manufacturing of metal nanoparticles utilizing either of the two mechanisms reported, long metal wires with sub-micrometer diameters need to be fabricated first before they are subjected to capillary instability to break up to form metal nanoparticles, which is extremely difficult to obtain, due to the low viscosity and high surface tension of molten metals.

2.2.2 Metal microwires

Fibers with metal microwires are routinely produced by thermal drawing. The softening temperature of the cladding determines the types of metals that can be drawn within. Low melting temperature metals such as tin (Sn), bismuth (Bi), indium (In), and their alloys have been thermally drawn in polymer cladding (e.g. polyethersulphone (PES), polysulfone (PSU), and (polyethylenimine) PEI which softening temperature is below 300 °C). The resulting metal fibers with rectangular or circular cross sections have critical dimensions ranging from tens to hundreds of micrometers. The smallest diameter reported for crystalline metal wires that can be reliably drawn into infinitely long arrays is 4 μm and is achieved from Sn0.95Ag0.05 alloy with PES cladding (Yaman, Khudiyev et al. 2011). Beads, discontinuities and structural deformation would be observed upon further size reduction. Nevertheless, thermally drawn functional fibers embedding In wires with diameters approaching 1 μm has been demonstrated (Tuniz, Lwin et al. 2012). In arrays were thermally drawn in PMMA cladding to yield a metamaterial fiber that exhibits electric and magnetic responses for terahertz and far-infrared spectrum.
Higher melting temperature metals such as gold (Au), copper (Cu), zinc (Zn), and their alloys, require cladding materials with higher softening temperature. Pyrex glass (with a softening point of ~800 °C) and fused silica (with a softening point of ~1700 °C) are the materials of choice in this temperature regime, though not excluding their usage to draw metals with low melting temperatures. In fact, metal microwire fabrication by thermal drawing in a glass cladding, known as the Taylor-wire process, has been in practice for almost a century (Donald 1987). Thermally drawn continuous Cu microwire of 4 μm in diameter has been demonstrated which enables single-mode visible light guidance by metallic reflection in a photonic crystal fiber (Hou, Bird et al. 2008).

2.2.3 Metal nanowires

After the invention of the novel stack-and-draw approach, there have been significant efforts in the fabrication of metal nanowires. Au microwires of 4 μm diameter were fabricated over a length of several centimeters and, however, this continuous length shrank to ~20 μm as their diameter reduced to 260 nm (Tyagi, Lee et al. 2010). Pb-Sn alloys and Bi nanowires (drawn in glass cladding) with diameter down to 150 nm were reported with a length reaching 1 m; however, no experimental evidence was provided to support their continuity over the claimed drawn length (Badinter, Ioisher et al. 2010), and no repeatable results are reported. Similarly, fabrication of discontinuous Cu$_{0.93}$P$_{0.07}$ with a diameter of 500 nm has been reported using Pyrex glass cladding (Zhang, Ma et al. 2008).

Up to now, to the best of our knowledge, indefinitely long crystalline metal nanowires (<100 nm) has not yet been achieved, whereas indefinitely long amorphous semiconductor and air hole smaller than 100 nm were demonstrated, as shown in Table 2.1.
<table>
<thead>
<tr>
<th>Date published</th>
<th>Cladding Material</th>
<th>Core Material</th>
<th>Core diameter</th>
<th>Max. Length</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jun-10</td>
<td>Borosilicate glass</td>
<td>Bi</td>
<td>150 nm</td>
<td>1 m</td>
<td>(Badinter, Ioisher et al. 2010)</td>
</tr>
<tr>
<td>Jun-10</td>
<td>Borosilicate glass</td>
<td>PbSn</td>
<td>150 nm</td>
<td>1 m</td>
<td>(Badinter, Ioisher et al. 2010)</td>
</tr>
<tr>
<td>Dec-10</td>
<td>Vycor</td>
<td>Ge</td>
<td>150 nm</td>
<td>1 m</td>
<td>(Ioisher, Badinter et al. 2011)</td>
</tr>
<tr>
<td>Jul-11</td>
<td>Borosilicate glass</td>
<td>Cu</td>
<td>200~300 nm</td>
<td>N/A</td>
<td>(Ioisher, Badinter et al. 2011)</td>
</tr>
<tr>
<td>Apr-08</td>
<td>Fused silica</td>
<td>Cu</td>
<td>4 μm</td>
<td>N/A</td>
<td>(Hou, Bird et al. 2008)</td>
</tr>
<tr>
<td>Oct-12</td>
<td>PMMA</td>
<td>In</td>
<td>~5 μm</td>
<td>Indefinite</td>
<td>(Kuhlmey, Tuniz et al. 2012)</td>
</tr>
<tr>
<td>Oct-08</td>
<td>PSu</td>
<td>Se</td>
<td>&lt;100 nm</td>
<td>N/A</td>
<td>(Deng, Orf et al. 2008)</td>
</tr>
<tr>
<td>Jan-10</td>
<td>PSu</td>
<td>Se</td>
<td>200 nm</td>
<td>2 cm</td>
<td>(Deng, Orf et al. 2010)</td>
</tr>
<tr>
<td>Jan-09</td>
<td>Borosilicate glass</td>
<td>PbTe</td>
<td>400 nm</td>
<td>N/A</td>
<td>(Hong, Ma et al. 2009)</td>
</tr>
<tr>
<td>Jun-11</td>
<td>PSu</td>
<td>PVDF</td>
<td>20 nm</td>
<td>Indefinite</td>
<td>(Yaman, Khudiyev et al. 2011)</td>
</tr>
<tr>
<td>Jun-11</td>
<td>PES</td>
<td>PVDF, As$_2$Se$_3$</td>
<td>14 nm</td>
<td>Indefinite</td>
<td>(Yaman, Khudiyev et al. 2011)</td>
</tr>
</tbody>
</table>
2.2.4 Toward the continuum limit

While we search for the longest yet thinnest metal nanowire already achieved by thermal drawing, one fundamental question naturally arises: In theory, does an ultimate lower bound exist regarding the diameter of nanowires made by deformation at liquid state followed by quenching? As the length scale approaches tens of nanometers, we enter a regime where the continuum hypothesis on which the classical theories are based can be questioned.

From a purely hydrodynamic analysis, flow focusing toward the continuum limit is possible (Zhang 2004, Eggers and Villermaux 2008). On the experimental side, Ioisher et al.
demonstrated that Cu nanowire down to 300nm could be continuously produced by just one single cast from bulk (Ioisher, Badinter et al. 2011). The flow condition which led to the 300 nm continuous production of Cu nanowire is very close, though not identical, to that described in (Zhang 2004).

Via tapering, a method slightly different but can be viewed as a consecutive sequence of steady-state thermal drawing with minimal draw-down ratio, people have achieved Pt wire with a 10 nm tip (Cox and Zhang 2012, Percival, Vartanian et al. 2014) and semiconductor wire down to 5 nm (Kaufman, Tao et al. 2011), over a short length. A solid-state room temperature wire drawing process called Gallaston process can produce Pt wires as thin as 8 nm (Sacharoff, Westervelt et al. 1985), though the Pt nanowire does not go through the liquid state in this process.

These earlier studies suggest that the capability of the thermal drawing method may go beyond what continuum mechanics can explain and predict. In searching for the ultimate theoretical lower bound, one may need to resort to theories that deal with individual atoms or molecules.

2.2.5 Summary on scalable manufacturing of metal micro/nanowires and particles by thermal drawing

An extensive literature survey revealed that, using thermal fiber drawing, controlled manufacturing of metal micro/nanoparticles and wires are not yet achievable and there exists a fundamental size limit to the diameter of thermally drawn crystalline metal wires below which the metal wires become inherently unstable and extremely difficult to control, if not impossible, by
current manufacturing techniques. The studies that focus on the underlying mechanisms that prohibit the control of particle sizes and further scale down of the wire sizes will be reviewed in the next section.

2.3 THEORETICAL AND EXPERIMENTAL STUDIES ON METAL CORE THERMAL FIBER DRAWING

For fibers that are subject to capillary instability during drawing, the Tomotika model (Tomotika 1935) is almost ubiquitously used. Based on the instability growth time calculated from Tomotika model, Deng et al. first proposed a quantitative material selection method to ensure continuous drawing of semiconductor core nanowires (Deng, Nave et al. 2011). Observation of the development of capillary fluid instability in a polymer fiber with a low-temperature semiconductor core further confirms the validity of the theory (Shabahang, Kaufman et al. 2011). Structured semiconductor spheres, achieved by using the fluid instability were also demonstrated (Kaufman, Tao et al. 2012, Gumennik, Wei et al. 2013).

2.3.1 Tomotika dispersion relation

Tomotika model is essentially the dispersion relation of a viscous thread surrounded by another infinite viscous medium. Fiber drawing with a molten core falls into this regime as the molten metal thread is embedded in the viscous cladding as shown in Fig. 2.2. The assumptions that were made during the derivation of this dispersion relation are: 1. Small motion (the system is linear). 2. The cladding is infinitely thick. 3. The absence of general flow. 4. Uniform core
diameter. Fluid inertia is neglected. The validity of these assumptions for this study is discussed in the later section (see: beyond Tomotika model).

![Figure 2.2. Model configuration of Tomotika dispersion relation](image)

The dispersion relation

\[-i\omega = \frac{\gamma_{sl}G(x, \eta_{core}/\eta_{clad})}{D_{core}\eta_{clad}}, \quad \chi = \frac{\pi D_{core}}{\lambda} = \frac{kD_{core}}{2}\]

(2)

where \(\omega\) is the angular frequency, \(k\) the wavenumber, \(\lambda\) the wavelength of perturbation, \(D_{core}\) the diameter of metal core, \(\gamma_{sl}\) the interfacial energy between core and cladding, \(\eta_{clad}\) and \(\eta_{core}\) the viscosity of cladding and core respectively, includes an expression \(G(x, \eta_{core}/\eta_{clad})\) which is a function of the dimensionless wavenumber \(x\) and viscosity ratio between core and cladding.

\(G(x, \eta_{core}/\eta_{clad})\) reaches its maximum at the most amplified wavenumber \(k_m\)

\[G\left(\frac{k_mD_{core}}{2}, \frac{\eta_{core}}{\eta_{clad}}\right) = \max\{G(x, \eta_{core}/\eta_{clad})\}\]

(3)

As \(\eta_{core}/\eta_{clad}\) changes from \(2 \times 10^{-8}\) to 1, \(\max\{G(x, \eta_{core}/\eta_{clad})\}\) changes from 1 to approximately 0.07, as shown in Fig. 2.3.
Figure 2.3. Plot of (a) \( G(x, \eta_{core}/\eta_{clad} = 2 \times 10^{-8}) \), (b) \( G(x, \eta_{core}/\eta_{clad} = 2 \times 10^{-4}) \), (c) \( G(x, \eta_{core}/\eta_{clad} = 1) \).

The associated time of growth \( \tau(k_m) \equiv \Re[-\ii \omega(k_m)]^{-1} \) is thus

\[
\tau(k_m) = \frac{D_{core} \eta_{clad}}{\gamma_s \max[G(x, \eta_{core}/\eta_{clad})]} \tag{4}
\]

The associated time of growth \( \tau(k_m) \) can be defined as the instability time \( \tau \) for simplicity.

2.3.2 Comparison with nonmetals

Tomotika dispersion relation allows us to compare the instability time of molten metal threads with other materials. Experiments from previous section show that indefinitely long amorphous semiconductor nanowire (<100 nm) and air holes (<100 nm) has been achieved, whereas the same for crystalline metal has not. In principle, the instability behavior of metal, semiconductor or even air holes can all be interpreted by Tomotika dispersion relation because no assumption was made regarding the interfacial energy and viscosities which may exclude the use of Tomotika model for any of these materials. A comparison is thus made in an attempt to find the
limiting factors that prohibit the successful drawing of metal nanowires down to less than 100 nm continuously. A list of material properties either obtained from literature or estimated is shown below in Table 2.2. The interfacial energies are calculated from Young’s equation

\[ \gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos \theta \]  

(5)

**Table 2.2. Relevant physical properties of materials for thermal drawing**

<table>
<thead>
<tr>
<th>Cladding</th>
<th>Core</th>
<th>Cladding surface tension ( \gamma_{sv} ) [mJ/m(^2)]</th>
<th>Core viscosity [Pa-s]</th>
<th>Core surface tension ( \gamma_{lv} ) [mJ/m(^2)]</th>
<th>Contact angle ( \theta^0 )</th>
<th>Interfacial energy ( \gamma_{sl} ) [mJ/m(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>air</td>
<td>30.3</td>
<td>2.78E-07</td>
<td>0.00E+00</td>
<td>0</td>
<td>3.03E+01</td>
</tr>
<tr>
<td>Silica</td>
<td>air</td>
<td>300</td>
<td>5.60E-07</td>
<td>0.00E+00</td>
<td>0</td>
<td>3.00E+02</td>
</tr>
<tr>
<td>PES</td>
<td>As(_2)Se(_3)</td>
<td>47</td>
<td>1.00E+05</td>
<td>1.13E+02</td>
<td>126.6</td>
<td>1.14E+02</td>
</tr>
<tr>
<td>PES</td>
<td>Se</td>
<td>47</td>
<td>2.48E-02</td>
<td>1.00E+02</td>
<td>120*</td>
<td>9.70E+01*</td>
</tr>
<tr>
<td>PES</td>
<td>Sn</td>
<td>47</td>
<td>1.88E-03</td>
<td>570</td>
<td>120*</td>
<td>3.32E+02*</td>
</tr>
<tr>
<td>Pyrex</td>
<td>Bi</td>
<td>300*</td>
<td>1.80E-03</td>
<td>285</td>
<td>120*</td>
<td>4.43E+02*</td>
</tr>
<tr>
<td>Pyrex</td>
<td>Cu</td>
<td>300*</td>
<td>4.00E-03</td>
<td>1355</td>
<td>120*</td>
<td>9.78E+02*</td>
</tr>
<tr>
<td>Silica</td>
<td>Au</td>
<td>300</td>
<td>5.00E-03</td>
<td>1138</td>
<td>139</td>
<td>1.16E+03</td>
</tr>
</tbody>
</table>

*Estimated

The plot in Fig. 2.4 shows the dependence of the instability time on interfacial energy and core viscosity at constant cladding viscosity \(10^6 \) Pa-s and core diameter (200 nm). Each of the established drawing processes in Table 2.2 is represented by a data point. The relative height of each data point on the plotted surface tells the likelihood of such material combination to suffer from capillary fluid instability compared with another under same process conditions. The higher a material combination is on the surface, the less likely the core breaks during thermal drawing and thus easier to achieve smaller diameter wires continuously.
Figure 2.4. Surface plot of instability time as a function of interfacial energy and core viscosity at constant cladding viscosity ($10^6$ Pa-s) and core diameter (200 nm) for different cladding/core combinations.

It is not surprising to see that the material combinations that have the largest instability time are those that have been drawn to indefinitely long wires with a diameter of less than 100 nm. Combinations of polymer core and cladding generally have higher instability times due to the low surface tension of polymers, as can be seen in Table 2.2.

As evidenced from the plot, the limiting factors that prevent metals from being drawn continuously down to a diameter of less than 100 nm are the high interfacial energy with the glass and quartz cladding and their low viscosity.
One promising material combination is the PES/Sn as it has a larger instability time than the Pyrex/Bi combination which so far holds the record for the longest metal nanowire drawn (about 1.0 m). Errors in estimation of the interfacial energy may be present as the exact type of glass used for the record length Pyrex/Bi combination is unknown.

Although same process conditions are assumed a priori in this plot, the actual experiments for the Pyrex/Bi and Pyrex/Cu combinations are experimented with distinctly different drawing speeds, indicating the two possible directions of process optimization to push the limit further down.

2.3.3 Beyond the Tomotika model

Tomotika model assumes infinite cladding thickness, which is not true for the real drawing process. Recent studies regarding the instability of multilayer fiber drawing can be found in (Liang, Deng et al. 2011) and (Suman and Tandon 2010).

Tomotika model does not take into account of the general flow pattern of the viscous cladding. In fact, the molten metal core in the neck-down region experiences stretching and accelerates with the cladding. The effect of an extending surrounding was recognized by Tomotika himself (Tomotika 1936), stating that fluid instability is suppressed in an extending surrounding. However, as soon as the extension stops, the fluid tread breaks immediately. Effect of longitudinal stretching is discussed in (Eggers and Villermaux 2008). The subject of droplet deformation in extensional flow (Stone 1994) is also of high relevance.
2.3.4 Modeling and simulations

Literature survey above suggests that there exists a fundamental size limit to the diameter of thermally drawn crystalline metal wires below which the metal wires become inherently unstable and extremely difficult to control, if not impossible, by current manufacturing techniques. The physical forces that dominate the break-up, however, is still in dispute. Some attribute the break-up to Plateau-Rayleigh instability (Alchalaby, Lwin et al. 2016) while others suggest metal cannot withstand shear stress (Yaman, Khudiyev et al. 2011). Resolution of this challenge meets roadblocks both theoretically and experimentally. No model can yet satisfactorily describe the dynamics of the molten metal core during preform fiber drawing, as pointed out by Zhao et al. (Zhao, Javadi et al. 2016), although numerous works concerning the modeling and simulation of compound and microstructured fiber drawing processes exist (Pone, Dubois et al. 2006, Suman and Tandon 2010, Stokes, Buchak et al. 2014, Jasion, Shrimpton et al. 2015). Recent attempt made is based on Tomotika’s model that was established nearly a century ago (Tomotika 1936, Alchalaby, Lwin et al. 2016), which considered the break-up of a cylindrical thread in a surrounding flow that is extending uniformly. Quantitative comparisons between simulation and experiments are emerging (Xue, Barton et al. , Alchalaby, Lwin et al. 2016, Xue, Barton et al. 2017, Xue, Barton et al. 2017), yet far from being applicable for real-time control. Experimental investigation of the core dynamics, on the other hand, is equally challenging, which require high-speed, high-resolution characterization of high-aspect-ratio objects embedded in a thick glass/polymer material under high temperature. A simple yet useful model is called for to elucidate the underlying mechanism of diameter control and to predict in real-time the core continuity from measurable process parameters and material properties.
In addition to its implication in manufacturing of continuous metal microwires, the model also leads us to believe that metal core fiber drawing from a preform may provide a new way for study and control of fluid interfaces in addition to the existing flow fields such as entrainment problems (Zhang 2004), flow focusing (Ganan-Calvo, Gonzalez-Prieto et al. 2007), and microfluidic devices (Christopher and Anna 2007). With the various studies pointing out the possibility of obtaining nanoscale droplets by hydrodynamic forces, further advancement of knowledge is hindered by the lack of methods for experimental observation and in-line metrology. The fact that the shape of the metal wires is formed at liquid state while can be observed at solid state provides an unexpected yet new way for the study of the complex nonlinear dynamics of fluid flows at micro/nanoscale.

2.3.5 Summary of theoretical and experimental studies

Almost all literature that concerns the theoretical and experimental study on the metal core thermal fiber drawing process aims at obtaining a more accurate prediction of the break-up time of the molten metal cure during drawing due to the capillary instability. Yet the actual physical forces that govern the break-up dynamics is still in dispute, which cast major doubt onto the applicability of the results obtained from instability analysis due to single driving force (interfacial tension) alone. Moreover, a quantitative predictive method that can correlate the core continuity with process parameters and material properties is still missing, which will be the key that links the theoretical studies with the experimental observations.
2.4 LITERATURE REVIEW SUMMARY

In summary, metal-core fiber drawing from a preform is a potentially disruptive technology for the scalable manufacturing of micro/nano-particles and wires that has numerous existing and emerging applications. The limitations and challenges of this process have been identified as fluid instabilities of molten metals, which has high surface tension, high interfacial energy, and low viscosity, rendering the control of their size, geometry, and spatial arrangement by the external viscous cladding flow very difficult. Fundamental understanding of the process down to nanoscale is severely lacking which calls for further theoretical and experimental study.
CHAPTER 3. EXPERIMENTAL APPARATUS

This chapter introduces the necessary experimental apparatus that are used in this work for the manufacturing of metal core fibers from a preform, which includes a custom built fiber drawing tower, and a custom built consolidation system for preform fabrication. The focus will be on the description of components, working mechanisms and functionalities.

3.1 FIBER DRAWING TOWER

Successful thermal drawing of uniform and continuous metal fibers from a preform require simultaneous control of the feeding speed, pulling speed, and furnace temperature. A thermal fiber drawing tower should be capable of performing all these functions with high precision and reliability. A schematic of a custom built tower is shown in Fig. 3.1. If divide based on functionalities, the tower consists of five subsystems, namely, preform feeding system, wire drawing and winding system, tension monitoring system, motor control system, and temperature control system. Each of the subsystems is described in the following sections.
Figure 3.1 Schematic of a fiber drawing tower
3.1.1 Preform Feeding System

![Preform feeding system diagram]

The preform feeding system provides the preform with a steady and slow linear motion in the vertical direction, typically on the order of tens of micrometer per second. A power screw system, a preform chuck, a stepper motor with a gearbox and an optical encoder are the essential elements that construct a working preform feeding system that meets this requirement, as shown in Figure 3.2.

Figure 3.2. Preform feeding system
in Fig. 3.2. A linear bearing platform is implemented to ensure linear and vertical motion of the preform. The overall length of the power screw determines the maximum length of the preform drawable by this system and the minimum step of the stepper motor, and the gearbox determines the resolution of the feeding speed.

3.1.2 Wire Drawing and Winding System

![Figure 3.3 Wire drawing and winding system](image)

The wire drawing and winding system is responsible for providing a constant pulling speed to the drawn fiber and subsequently wind it onto a bobbin as shown in Fig. 3.3. A guide wheel is a fixed pulley which makes sure the fiber is being pulled down perfectly perpendicular to the ground to prevent any asymmetry caused by misalignment. The capstan wheel is driven by a stepper motor mounted on the back of the panel thus not visible in the figure. The wire is pressed
against the capstan wheel during drawing by a belt thus follows the wheel through friction force. A second belt transmits the line speed of the pulleys to the bobbin so that the drawn fibers can be wounded and collected.

3.1.3 Tension Monitoring System

![Custom made tension meter](image)

Figure 3.4. Custom made tension meter

Although not used as a control input in this study, the drawing force or the tension in the wire is a highly important indicator of the quality and continuity of the drawn wires. A tension meter is, therefore, custom designed and made. A strain gage is attached to the middle wheel as shown in Fig. 3.4. Moreover, the resistance of the gauge is monitored in real time through a bridge circuit. Calibration is done by measuring the tension of a rope with a known weight hanged below.
3.1.4 Motor Control

The control of the two motors used respectively in the feeding and pulling systems are realized by a data acquisition system from National Instrument. Fig. 3.5 shows the front panel of the Labview interface which monitors and controls the speed of tow motors and monitors the wire tension. Microstepping is used to improve the resolution and enhance the low-speed performance of the two stepper motors.

Figure 3.5. Labview interface for motor control
3.1.5 Temperature Control System

The temperature control system serves to maintain the drawing furnace at a constant preset temperature. It is composed of the following components labelled and connected according to the diagram shown in Fig. 3.7. The completed control box is shown in Fig. 3.6.

1. Heating element (Furnace)
2. Controller
3. Relay
4. Thermocouples
5. Fuses

Figure 3.7. Connection diagram of the temperature control system from Omega Engineering
The preform consolidation system is used for the preparation of high-quality preforms through a zone melting process conducted in a vacuum. The preform is slowly fed downward through a tube furnace at a temperature higher than the melting point of the core but lower than the softening temperature of the cladding. This process ensures the seamless contact between the metal core and the cladding which is essential for the success of the drawing. The mechanism that realizes the downward motion is the same as that for the preform feeding system. Instead of feeding
the preform through an open furnace, it is fed through a sealed quartz tube which is connected to a vacuum pump to minimize the oxidation of the core metal during melting. Fig. 3.8. shows a picture and a schematic of the preform consolidation furnace.
CHAPTER 4. THEORETICAL STUDY ON THE MANUFACTURING OF CONTINUOUS MICROWIRES BY THERMAL FIBER DRAWING FROM A PREFORM

Thermal drawing from a preform recently emerges as a scalable manufacturing method for the high volume production of continuous metal microwires for numerous applications. However, no model can yet satisfactorily provide an effective understanding of core diameter and continuity from process parameters and material properties during thermal drawing. In this chapter, a long wavelength model is derived to describe the dynamics of a molten metal micro-jet entrained within an immiscible, viscous, nonlinear free-surface extensional flow.

4.1 PROBLEM FORMULATION

During a typical thermal drawing process, as the preform is slowly fed into the furnace at a constant speed and uniform fibers being pulled from below, a steady-state in Eulerian frame is soon reached such that the temperature and velocity of the cladding vary along the axis of symmetry but do not change with time, if viewed from a fixed laboratory position. We focus on the dynamics of the molten metal core under the condition that the cladding flow is steady, requiring that the diameter of cladding be much larger than the core $A(z) \gg \pi R^2(z, t)$, so that the molten metal core is assumed to have negligible effect on the cladding flow except for the region in the vicinity of the centerline. We further assume that the velocity and temperature of cladding
along the axis of symmetry do not vary in the radial direction, suggesting that the molten thread line is much longer than the diameter of the preform.

We consider preform drawing of Sn microwire in Pyrex cladding. For the exterior cladding flow, inertia, gravity, and surface tension are assumed to be negligible as compared to the viscous term in the cladding flow following Yarin et al. (Yarin, Gospodinov et al. 1999). For the interior metal flow, the corresponding values of the Reynolds, Weber, and Bond numbers of the molten core under the parameters given in Table 4.1 are calculated as follows: $Re = \frac{2 \rho \bar{U} R}{\mu_0} = 0.4$, $We = \frac{2 \rho \bar{U}^2 R}{\gamma} = 2 \times 10^{-5}$, $Bo = \frac{4 \Delta \rho g a^2}{\gamma} = 9 \times 10^{-4}$, all of which are much smaller than 1, allowing us to neglect the core inertia and gravity effects.

Effect of the thermal gradient needs further consideration. The viscosity of the cladding is very sensitive to temperature and undergoes orders of magnitude variations along the thread line, thus cannot be neglected. Viscosity change of the molten metal core due to thermal gradient is neglected since $\mu_0 \ll \mu(z)$. Thermal gradient also introduces interfacial tension gradient along the thread line, which may result in Marangoni flow that can be approximated by

$$\frac{-d\gamma}{dT} \frac{d\bar{u}_z}{dz} = \frac{\partial u_z}{\partial r}$$

where $u_z$ is the surface velocity due to Marangoni flow in the axial direction, assuming a cylindrical interface. A dimensionless number can therefore be defined to gauge the strength of the Marangoni flow $Ma = -\frac{d\gamma}{dT} \frac{4 \Delta T R}{\mu \bar{u} \bar{L}} = 1.64 \times 10^{-8}$ compared to the cladding flow, which in this case is small, allowing us to neglect the Marangoni flow induced by thermal gradient.
### Table 4.1. Material properties and process parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Approximate value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of PES melt [83][83][83][83]</td>
<td>( \rho_{PES} )</td>
<td>1212.6</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>Density of molten Sn at melting point (Wang, Wang et al. 2003)</td>
<td>( \rho_{Sn} )</td>
<td>6990</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>Sn/PES interfacial energy</td>
<td>( \gamma )</td>
<td>0.319</td>
<td>J m(^{-2})</td>
</tr>
<tr>
<td>Temperature dependency of interfacial energy (Eustathopoulos, Nicholas et al. 1999)</td>
<td>( d\gamma/dT )</td>
<td>-0.1</td>
<td>mJ m(^{-2}) K(^{-1})</td>
</tr>
<tr>
<td>Length of thread line</td>
<td>( L )</td>
<td>4.129</td>
<td>cm</td>
</tr>
<tr>
<td>Feeding speed</td>
<td>( U(0) )</td>
<td>20</td>
<td>( \mu )m s(^{-1})</td>
</tr>
<tr>
<td>Pulling speed</td>
<td>( U(L) )</td>
<td>10</td>
<td>mm s(^{-1})</td>
</tr>
<tr>
<td>Average speed</td>
<td>( \bar{U} )</td>
<td>5</td>
<td>mm s(^{-1})</td>
</tr>
<tr>
<td>Viscosity of core (Gancarz, Moser et al. 2011)</td>
<td>( \mu_0 )</td>
<td>0.003</td>
<td>Pa s</td>
</tr>
<tr>
<td>Initial core radius</td>
<td>( a )</td>
<td>35.7</td>
<td>( \mu )m</td>
</tr>
<tr>
<td>Average core radius</td>
<td>( \bar{R} )</td>
<td>17.85</td>
<td>( \mu )m</td>
</tr>
<tr>
<td>Tensile stress at ( z = L )</td>
<td>( T_{zz} )</td>
<td>1.65</td>
<td>MPa</td>
</tr>
<tr>
<td>Temperature rise above melting point of metal</td>
<td>( \Delta T )</td>
<td>(~100)</td>
<td>K</td>
</tr>
<tr>
<td>Viscosity of cladding under isothermal condition</td>
<td>( \mu )</td>
<td>( 2.115 \times 10^5 )</td>
<td>Pa s</td>
</tr>
</tbody>
</table>

The steady-state cladding flow without core is modelled as a quasi-one-dimensional free surface extensional flow with velocity \(-\frac{r}{2} \frac{dU(z)}{dz}, 0, U(z)\). We let molten metal of viscosity \( \mu_0 \) be entrained from a nozzle or melt front with radius \( a \) by the extensional cladding flow with position dependent viscosity \( \mu(z) \), and solidifies downstream at \( z = L \) with radius \( R(L, t) \). Focusing on the limit \( \mu_0 \ll \mu(z) \) following Taylor, Acrivos, Sherwood, and others' works (Taylor 1934, Acrivos...
and Lo 1978, Sherwood 1984), the coupling between the interior metal flow and the exterior cladding flow simplifies to a balance between the interior pressure and the exterior stress, and the entrainment dynamics can be accurately described by a long-wavelength model provided that the slope of the spout is everywhere small.

Extruded Polyethersulfone (PES, BASF Ultrason E3010) rods (extruded and distributed by Port Plastics, Inc.) with an outer diameter (OD) of 19.05 mm and length of 10 cm were first dehydrated at 150 °C for 5 days under vacuum (2 Torr) to remove moisture. A through hole was then drilled to allow insertion of a Sn metal wire (SRA Soldering Products). The PES preform was then slowly fed into a vertical tube furnace at 250 °C at a speed of 50 μm/s under a vacuum of 40 mTorr to consolidate the preform and ensure seamless contact between the metal core and the cladding. The consolidated preform was used either for thermal drawing or interfacial energy measurement (see Section V).
Figure 4.1. Image of the neck-down region (a) and the schematic (b) corresponding to an axisymmetric free surface extensional flow in the cladding entraining an immiscible molten metal from a nozzle (or melt front) located at \( z = 0 \). The entrained molten metal core has radius \( R(z, t) \). Downstream at \( z = L \), the metal solidifies with diameter \( R(L, t) \).

Unsteady volume conservation inside the spout gives

\[
\frac{\pi \partial R^2(z, t)}{\partial t} + \frac{\partial Q(z, t)}{\partial z} = 0
\]  

(2)

where \( Q(z, t) \) is the flow rate of core.

The velocity inside the molten metal core is nearly unidirectional and is composed of a plug flow induced by the cladding flow and a pressure driven flow, which has the form

\[
\bar{u}_{\text{core}} = u(z, r, t)\bar{e}_z = \left[ U(z) - \frac{1}{4\mu_0} \frac{\partial P_0(z, t)}{\partial z} \left( R^2(z, t) - r^2 \right) \right] \bar{e}_z
\]  

(3)

where \( P_0(z, t) \) is the interior pressure, and \( R(z, t) \) is the radius of the metal core.
At \( z = 0 \), the molten metal comes out from the melt front or a nozzle connected to a large reservoir, so the pressure in the metal is determined by the local stress at the core/cladding interface.

We thus obtain an expression for \( P_0(z, t) \)

\[
P_0(z, t) = 2\mu(z)\left(\frac{dU(z)}{dz} + \frac{1}{R(z, t)} \frac{\partial R(z, t)}{\partial t} + \frac{U(z)}{R(z, t)} \frac{\partial R(z, t)}{\partial z}\right) + P_{\text{clad}}(r, z) + \gamma \kappa
\]

(3)

, which contains contributions from surface tension due to the full curvature \( \kappa = \frac{1}{R(z, t)} \left(\frac{\partial R(z, t)}{\partial z}\right)^2 \approx \frac{1}{R(z, t)} - \frac{\partial^2 R(z, t)}{\partial z^2} \), pressure and viscous stress in the cladding.

Flow rate of core is therefore

\[
Q(z, t) = \int_S u(z, r, t) dS = 2\pi \left[ \frac{U(z)R^2(z, t)}{2} - R^4(z) \frac{d}{dz} P_0(z, t) \right] = \pi U(z)R^2(z, t) - \frac{\pi R^4(z, t)}{8\mu_0} \left( \frac{\partial}{\partial z} \left( 3\mu(z) \left( \frac{dU(z)}{dz} + \frac{2}{3R(z, t)} \frac{\partial R(z, t)}{\partial t} + \frac{2U(z)}{3R(z, t)} \frac{\partial R(z, t)}{\partial z} \right) + \gamma \kappa \right) + \frac{d\mu(z)}{dz} \frac{dU(z)}{dz} \right)
\]

(4)

, where \( u(z, r, t) \) is the core velocity, \( S(z, t) \) the cross-sectional area of the core.

The unknown quasi-one-dimensional velocity field can be obtained by volume conservation to give \( U(z) = \frac{A(0)U(0)}{A(z)} \), where the cross-sectional area of the cladding \( A(z) \) can be easily measured. The unknown position dependent viscosity can be approximated by \( \mu(z) = -\frac{A(z)F}{3A(0)U(0)} \left( \frac{dA(z)}{dz} \right)^{-1} \) (Taroni, Breward et al. 2013), knowing draw force \( F = 3A(z)\mu(z) \frac{dU(z)}{dz} \).

Plugging (4) into (2) yields a fourth-order nonlinear differential equation to be solved given \( A(z) \) and \( F \), both being measureable. While previous works focus on the zero flow rate limit \( Q(0, t) \to 0 \) in a linear straining flow (Zhang 2004) or pressure driven flow(Castro-Hernández, 2004).
Campo-Cortés et al. 2012, Gordillo, Sevilla et al. 2014), this work focus on $Q(0, t) = \pi a^2 U(0)$ in a nonlinear free surface extensional flow with position dependent viscosity.

### 4.2 BOUNDARY CONDITIONS AND DIAMETER CONTROL MECHANISM

At the nozzle opening or melt front under steady-state drawing, the flow rate of molten metal is controlled at $Q(0, t) = Q_{\text{core}}$. Downstream, due to the fact that the solidified metal core has same velocity as the cladding assuming no slip between solidified core and cladding, the radius of the solidified metal $R(L, t)$ is therefore determined by the drawing speed $U(L)$ of the cladding and the flow rate $Q(L, t)$ of molten metal at the solidification front to give $R(L, t) = \sqrt{\frac{Q(L, t)}{\pi U(L)}}$, neglecting the density change of the metal due to solidification. These constitute the boundary conditions $R(0, t) = a$, $Q(0, t) = Q_{\text{core}}$, and $R(L, t) = \sqrt{\frac{Q(L, t)}{\pi U(L)}}$.

**Table 4.2. Process parameters for experimental validation of the diameter control mechanism**

<table>
<thead>
<tr>
<th>Run</th>
<th>$Q_{\text{core}}$ [m$^3$/s]</th>
<th>$U(0)$ [m/s]</th>
<th>$U(L)$ [m/s]</th>
<th>$\sqrt{\frac{Q_{\text{core}}}{\pi U(L)}}$ [m]</th>
<th>$R(L)$ [m]</th>
<th>Std. Dev. [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.74 \times 10^{-13}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$1.41 \times 10^{-3}$</td>
<td>$6.27 \times 10^{-6}$</td>
<td>$6.82 \times 10^{-6}$</td>
<td>$5 \times 10^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>$1.61 \times 10^{-11}$</td>
<td>$8 \times 10^{-6}$</td>
<td>$1 \times 10^{-2}$</td>
<td>$2.26 \times 10^{-5}$</td>
<td>$2.43 \times 10^{-5}$</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>$2.01 \times 10^{-11}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$1.41 \times 10^{-3}$</td>
<td>$6.74 \times 10^{-5}$</td>
<td>$6.79 \times 10^{-5}$</td>
<td>$8 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Figure 4.2. Cross-sectional images of the metal core fibers obtained from process parameters given in Table 4.2.

Under a steady state drawing, metal wire produced being continuous and uniform requires the flow rate of metal core at the solidification front to be independent of time, thus $Q(L, t) = Q(L)$. Volume conservation inside the metal jet further require that the amount of molten metal enters at $z = 0$ equals to the amount exits at $z = L$, yielding $Q(L) = Q(0) = Q_{\text{core}}$. The third boundary condition $R(L, t) = \sqrt{\frac{Q(L)}{\pi U(L)}}$ is thus turned into $R(L) = \sqrt{\frac{Q_{\text{core}}}{\pi U(L)}}$ under steady state drawing. Recognizing that $Q_{\text{core}} = \pi a^2 U(0)$ for preform drawing, and plugging in the third boundary condition to give $R(L) = a \sqrt{\frac{U(0)}{U(L)}} = a \sqrt{\frac{1}{D_r}}$, we have shown that the diameter control mechanism for continuous metal microwire production manufacturing by preform drawing is essentially volume conservation and the metal core diameter does follow the draw-down ratio, if a steady state can be reached.

Steady state drawings were done under the parameters listed in Table 4.2 and cross sections of the resultant metal core fibers shown in Fig. 4.2. to validate the proposed diameter control mechanism. A linear fit of $R(L)$ with $\sqrt{\frac{Q_{\text{core}}}{\pi U(L)}}$ is plotted in Fig. 4.3. The slope is 0.9945 with the
coefficient of determination equals to 0.9996, suggesting $R(L) = \frac{Q_{\text{core}}}{\sqrt{\pi U(L)}}$. We can thus conclude that the diameter of the metal produced indeed follow draw down ratio $Dr = \frac{U(L)}{U(0)}$, provided that the flow rate is controlled at the nozzle or melt front so that the feeding speed of the metal is the same as the feeding speed of the cladding, a diameter control mechanism that potentially holds valid down to nanoscale in principle but never explicitly stated in the literature.

![Graph](image)

Figure 4.3. Experimental result supporting the proposed diameter control mechanism

4.3 STEADY STATE CORE SHAPE

4.3.1 A. Isothermal drawing with constant cladding velocity and zero core flow rate

$$(U(z) = U(0), \mu(z) = \mu, Q(z, t) = 0)$$

In the simplest case, when $U(z) = U(0), \mu(z) = \mu$, and $Q(z, t) = 0$, Eq. 4 is reduced to
\[ Q(z, t) = \pi U(0) R^2(z, t) - \frac{\pi R^4(z)}{8 \mu_0} \left\{ \frac{d}{dz} \left[ 2 \mu \left( \frac{1}{R(z, t)} \frac{\partial R(z, t)}{\partial t} + \frac{U(0)}{R(z, t)} \frac{\partial R(z, t)}{\partial z} \right) + \frac{\gamma d^2 R(z, t)}{dz^2} \right] \right\} \] (5)

Rescaling all radial length scales by \( a \), axial length scales by \( a \sqrt{\mu/4 \mu_0} \), pressure by \( \frac{\gamma}{a} \), and solve for steady state solution, we obtain

\[ R^*(z^*) = \frac{1 + \sqrt{\left(\frac{1}{U^*}\right)^2 - 4}}{2} z^* + 1 \] (6)

, where \( U^* = \frac{4 \sqrt{\mu \mu_0} U_0}{\gamma} \). We have thus shown that our model includes the conical fluid interface solution first derived by Taylor (Taylor 1966) as a special case.

4.3.2 B. Isothermal drawing with exponential cladding velocity \( (U(z) = U(0) \left( \frac{U(L)}{U(0)} \right)^z, \mu(z) = \mu) \)

The cladding profile is available in an exponential form for isothermal drawing of Newtonian fluid (Middleman 1977) with \( U(z) = U(0) \left( \frac{U(L)}{U(0)} \right)^z \). In Fig. 4.4, the analytical cladding profile is plotted against the actual cladding profile drawn under the conditions listed in Table 4.1.
Figure 4.4. Measured and analytical cladding profile

Plugging the analytical profile into Eq. 4 assuming both cladding and core are at steady state, and negligible axial pressure gradient in the cladding gives the expression for flow rate

$$Q = 2\pi \frac{z}{2} \frac{U_0 D_r^{1/2} R^2(z)}{z} - \frac{R^4(z)}{16 \mu_0} \frac{d}{dz} \left[ 2\mu U_0 D_r^{1/2} \left( \frac{\ln D_r}{L} + \frac{1}{R(z)} \frac{dR(z)}{dz} \right) + \gamma \left( \frac{1}{R(z)} - \frac{d^2 R(z)}{dz^2} \right) \right]$$

(7)

If we scale \(z\) by \(L\), and \(R\) by \(a\), \(Q\) by \(\pi a^2 U(0)\), we obtain Eq. 7 in the dimensionless form

$$Q^* U^* = U^* D_r^{1/2} R^4(z^*) - R^4(z^*) \frac{d}{dz^*} \left[ Ca D_r^{1/2} \left( 1 + \frac{1}{\ln D_r} \frac{1}{R^2(z^*)} \frac{dR^2(z^*)}{dz^*} \right) + \frac{1}{R^2(z^*)} - \frac{1}{AR^2} \frac{d^2 R^2(z^*)}{dz^*} \right]$$

(8)

where \(Ca = \frac{2a \mu u_0 \ln D_r}{\gamma L}\) is the dimensionless strain rate at the nozzle opening; \(U^* = 4\lambda AR^2 Ca/\ln D_r\), where \(\lambda = \frac{\mu_0}{\mu}\), \(AR = \frac{L}{a}\); \(Q^*\) is the dimensionless flow rate of metal with \(Q^* = 1\) meaning metal is flowing at the same average velocity as the cladding at the melt front. This scaling allows the domain of \(z^*\) be fixed as [0,1] with \(R^*(0) = 1\) and \(R^*(1) = \sqrt{\frac{Q^*}{D_r}}\).

Numerical solution of Eq.8 is obtained using bvp4c function in Matlab with parameters listed in Table 4.1., under a third boundary condition \(\frac{dR^2(z^*)}{dz^*} |_{z^*=1} = 0\).
The shape of the entrance and exit areas match the theoretical calculations very well. However, the shape of the calculated metal core during steady state drawing appears similar to the “die swelling” phenomenon due to the viscoelasticity of the polymer melt typically encountered in melt spinning of polymeric fibers. Here, our theory predicts that “die swelling” may also occur during preform drawing of a Newtonian molten metal within a Newtonian cladding as shown in Fig. 4.5. Yet, such swelling behavior is not observed in the measured core profile, possibly because the calculation was based on isothermal cladding profile while the actual profile is obtained under non-isothermal drawing. Study based on actual numerical data measured from the cladding will be conducted to verify the theoretical prediction in the future.

4.4 MEASUREMENT OF INTERFACEAL ENERGY

In the previous calculation, the data of interfacial energy between PES and Sn was needed. However, interfacial energy data for liquid-liquid interfaces between metals and polymers are almost nonexistence in the literature. There are increasing needs (Alchalaby, Lwin et al. 2016) for such data for the manufacturing of metal micro/nanowires as well as functional multi-material
fibers. Here, the interfacial energy $\gamma$ between the molten Sn and PES was measured by sessile drop method using the following equation derived by Birdi et al. (Birdi, Vu et al. 1988)

$$
\gamma = \frac{\Delta \rho g H^2}{2(1 - \cos \theta)}
$$

, where $\Delta \rho$ is the density difference between the drop and its surrounding, $g$ is the gravitational force of acceleration, $H$ the limiting drop height, $\theta$ the contact angle.

A dripping method was designed and employed as shown in Fig. 4.6. to avoid exposure of molten metal to ambient air thus minimising oxidation of the molten metal at high temperature. A consolidated preform was subjected to furnace heating at 350 °C with an alumina crucible placed below. The lower portion of the preform softened and dripped down into the crucible. A single drop of molten Sn surrounded by PES was thus obtained.

![Figure 4.6. Schematic of the procedure to obtain a Sn sessile drop surrounded by PES](image)

Eight droplets with increasing volume were made, whose drop height are plotted against their volume to make sure that the height of the largest droplets does reach the limiting height $H$
as shown in Fig. 4.7. Droplets with heights within 5% of the limiting height are used for the measurement of the interfacial energy.

![Graph showing drop height vs drop volume](image)

**Figure 4.7. Drop height vs drop volume**

Measurement of contact angles and drop heights were done on the images of the solidified droplet, which is routinely applied for the estimation of the surface tension of molten metals (Eustathopoulos, Nicholas et al. 1999). Fig. 4.8. shows optical images of the Sn droplet after removal of the PES by dissolving in Dichloromethane for contact angle measurement.

![Solidified Sn droplet](image)

**Figure 4.8. A solidified Sn droplet after removing the PES for contact angle measurements**
Images for three droplets were taken using APPR® B/W digital camera and FTA video software. Drop heights were measured by a calliper and contact angles measured by ImageJ (Schneider, Rasband et al. 2012) with the drop shape analysis plugin developed by Stalder et al. (Stalder, Kulik et al. 2006).

Measurement results are summarized in Table 4.3. The interfacial energy between Sn and PES at around the melting point of Sn was determined to be \(0.319 \pm 0.010 \text{ J/m}^2\), which was listed in Table 4.1 earlier.

<table>
<thead>
<tr>
<th>No.</th>
<th>(\theta) [deg]</th>
<th>(H) [mm]</th>
<th>(\Delta\rho) [kg/m(^3)]</th>
<th>(g) [m/s(^2)]</th>
<th>(\gamma) [J/m(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>163.2</td>
<td>4.7</td>
<td>5777.4</td>
<td>9.8</td>
<td>0.319</td>
</tr>
<tr>
<td>2</td>
<td>164.9</td>
<td>4.78</td>
<td>5777.4</td>
<td>9.8</td>
<td>0.329</td>
</tr>
<tr>
<td>3</td>
<td>165.5</td>
<td>4.64</td>
<td>5777.4</td>
<td>9.8</td>
<td>0.309</td>
</tr>
</tbody>
</table>

4.5 MODE TRANSITION AND CRITICAL CAPILLARY NUMBER

We suggest a dimensionless capillary number \(Ca = \frac{2Fa}{\gamma A(0)}\) to be used as the indicator of the mode transition from continuous entrainment (i.e. viscous stress dominating) to capillary break-up (interfacial tension dominating). There exists a critical capillary number \(Ca_{cr}\) below which the metal core breaks due to capillary instability and forms a train of stretched droplets that translate downstream as they are deformed in the cladding flow when \(Ca = 0.20\) as shown in Fig. 4.9 (b), while Fig. 4.9 (a) shows an optical micrograph of the solidified metal core that is continuous and
drawn under a capillary number $Ca = 0.78$. The critical capillary number, in this case, falls between 0.2–0.78.

![Image](a)

$Ca = 0.78$

500 μm

(b)

$Ca = 0.20$

500 μm

**Figure 4.9. Continuous mode (a) and dripping mode (b)**

More experiments using preforms with different aspect ratios (ratio of preform diameter to thread length) show that the critical capillary number is on the order of 0.5 in the parameter ranges studied as shown in Fig. 4.10.

![Image](4.10)

**Figure 4.10. Capillary number vs aspect ratio**
4.6 SUMMARY

We have extended previous authors’ theoretical work on viscously entrained jet dynamics and derived a long wavelength model that may be used to solve for the dynamics of the molten metal core during the production of continuous metal microwires by thermal fiber drawing from a preform. Examination of the boundary conditions revealed that the diameter control mechanism for continuous microwire production by preform drawing is essentially volume conservation. The flow rate of molten metal is controlled upstream while the flow velocity is controlled downstream realized by solidification of the molten metal. This mechanism works for the diameter control of nanowire in principle as well. Scaling analysis revealed that the dominant physical forces that govern the dynamics of the metal jet are interfacial tension, stress in the cladding, and pressure in the metal. The accuracy of the model can be improved by replacing the cladding flow with a more accurate profile, either obtained analytically (Taroni, Breward et al. 2013), by simulation (Reeve and Mescher 2003) or measurements (Zaporojan, Plotnic et al. 2011). Although derived for metal drawing, semiconductor core is applicable as well, as long as it is molten during drawing. Steady state solution of the model is compared with experiments and discrepancies attributed to the fact that the process is non-isothermal. A general and simple method to measure the liquid-liquid interfacial energy between the molten metal and viscous claddings was designed and implemented for Sn/PES interface. A dimensionless capillary number \( Ca = \frac{2Fa}{\gamma A(0)} \) is suggested to be used as the indicator for the transition from continuous mode (i.e. viscous stress dominating) to dripping mode (i.e. interfacial tension dominating). Experiments suggests the existence of a critical capillary number above which continuous metal microwires can be produced, providing the first ever
quantitative measure of the core continuity during preform drawing of metal microwires based on process parameters and material properties.
CHAPTER 5. USE OF FACTORIAL DESIGNS FOR THERMAL FIBER DRAWING

Experimental design is a standard tool that has numerous applications in science and engineering. Yet, there has been no report on the use of factorial design for the study of metal core fiber drawing. The goal of this chapter is to utilize this tool and find the optimal drawing conditions for multi-core preform drawing and to learn what effects the drawing parameters have on the growth of capillary instability and continuity of the cores.

This chapter is organized as follows. In section 5.1, we describe the background of the fiber drawing experiment and experimental design. In section 5.2, we analyze the data from the experiment and discuss the results. Section 5.3 gives a summary.

5.1 FIBER DRAWING EXPERIMENT AND EXPERIMENTAL DESIGN

As described in previous chapters and shown in Fig. 5.1, numerous process parameters and material properties may affect the continuity of the metal core in the fiber produced by thermal drawing. Testing the significance of all of them by experiments is expensive and time-consuming. To minimize the experimental cost and time, we conducted an unreplicated $2^3$ factorial design to evaluate the effects and interactions of three carefully chosen process parameters on the capillary instability and core continuity. These three factors are draw-down ratio ($D_r = \frac{V_2}{V_1}$), normal stress in the cladding at melt front ($\tau = \frac{4F}{\pi D^2}$), and aspect ratio ($AR = \frac{D}{L}$), where $V_1$ and $V_2$ are the feeding
and pulling speed respectively, $F$ the drawing force, $D$ the preform diameter, and $L$ the length of the furnace.

![Diagram of metal core fiber drawing process]

**Figure 5.1. Schematic and parameters for metal core fiber drawing process**

5.1.1 Experimental design

The value ranges of each factor, as shown in Table 5.1, are determined based on the equipment dimension and capabilities, and to make sure the parameter space spread evenly to include the points with $Ca = 0.5$ so that both continuous and discontinuous cores can be obtained in the experiments. The specific drawing parameters for each of the 8 runs are listed in Table 5.2.

**Table 5.1. Factors and levels of the fiber drawing experiment**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>A = Draw-down ratio</td>
<td>200, 1000</td>
</tr>
<tr>
<td>B = Stress at melt front</td>
<td>1 KPa, 10 KPa</td>
</tr>
</tbody>
</table>
\[ C = \text{Aspect ratio} \quad 0.2 \quad 0.38 \]

**Table 5.2. Process parameters of the fiber drawing experiment**

<table>
<thead>
<tr>
<th>Run</th>
<th>Feeding speed [μm/s]</th>
<th>Pulling speed [mm/s]</th>
<th>Stress [KPa]</th>
<th>Ca</th>
<th>Initial core diameter [mm/s]</th>
<th>Final core diameter [μm/s]</th>
<th>Initial preform diameter [mm]</th>
<th>Fiber diameter [mm]</th>
<th>Dr</th>
<th>Target draw force [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>4.00</td>
<td>1</td>
<td>0.22</td>
<td>70.71</td>
<td>5.00</td>
<td>19.05</td>
<td>1.35</td>
<td>200</td>
<td>29.08</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>20.00</td>
<td>1</td>
<td>0.50</td>
<td>158.11</td>
<td>5.00</td>
<td>19.05</td>
<td>0.60</td>
<td>1000</td>
<td>29.08</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>4.00</td>
<td>10</td>
<td>2.22</td>
<td>70.71</td>
<td>5.00</td>
<td>19.05</td>
<td>1.35</td>
<td>200</td>
<td>290.84</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>20.00</td>
<td>10</td>
<td>4.96</td>
<td>158.11</td>
<td>5.00</td>
<td>19.05</td>
<td>0.60</td>
<td>1000</td>
<td>290.84</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>4.00</td>
<td>10</td>
<td>2.22</td>
<td>70.71</td>
<td>5.00</td>
<td>10.00</td>
<td>0.71</td>
<td>200</td>
<td>8.01</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>20.00</td>
<td>1</td>
<td>0.50</td>
<td>158.11</td>
<td>5.00</td>
<td>10.00</td>
<td>0.32</td>
<td>1000</td>
<td>8.01</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>4.00</td>
<td>10</td>
<td>4.96</td>
<td>158.11</td>
<td>5.00</td>
<td>10.00</td>
<td>0.71</td>
<td>200</td>
<td>80.14</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>20.00</td>
<td>10</td>
<td>4.96</td>
<td>158.11</td>
<td>5.00</td>
<td>10.00</td>
<td>0.32</td>
<td>1000</td>
<td>80.14</td>
</tr>
</tbody>
</table>

### 5.1.2 Capillary instability and core continuity

Numerous factors may cause the metal cores to break during drawing. Breakage may occur either at liquid state or solid state. Capillary instability accounts for the break-up at liquid state. Solid state break-up may occur due to the stretching of the solidified core by the cladding either due to the mismatch between their thermal expansion coefficients or when core solidifies before the cladding does. While it is easy to test the continuity of the metal cores after drawing by various methods, there has not yet been any published methods that can distinguish whether the break-up occurred at solid state or liquid state, which is of paramount importance to the process understanding and optimization.

In order to tackle this challenge, we propose two numerical indicators, namely Relative Standard Deviation (RSD) and Deviation from Draw-down Ratio (DDR), as measures of the extent
of growth of capillary instability and the core continuity respectively. RSD is defined as the ratio between the standard deviation of core diameters ($s$) and the mean core diameter ($\bar{x}$) to give $RSD = \frac{s}{\bar{x}}$. Using the relative standard deviation instead of just the standard deviation without dividing the mean core diameter allows for comparison between drawings that target at different core diameters. In the limiting condition when the capillary instability is completely suppressed, there is no sinuous or varicose growth of core diameter along the centerline which will give $RSD = 0$, and the diameter of the metal core will be uniform. Any sign of instability growth will result in $RSD > 0$. RSD therefore provides a good measure of the magnitude of the growth of capillary instability. However, as pointed out above, since core break-up results not only from capillary instability, $RSD = 0$ is not the sufficient condition for the core being continuous. The second numerical indicator, Deviation from Draw-down Ratio (DDR), is then defined as $DDR = \frac{|ARR - Dr|}{Dr}$ to provide a direct measurement of core continuity, where $ARR$ is the Area Reduction Ratio and $Dr$ the draw-down ratio. Studies presented in chapter 4 show that if the metal core is continuous after drawing, the area reduction ratio must equal the draw-down ratio. In other words, the amount the measured $ARR$ deviates from the $Dr$ measures the likelihood of the core being discontinuous. With the two newly defined numerical indicators, we can express our objective to achieve continuous and uniform core in a quantitative manner as requiring $RSD \to 0$ and $DDR \to 0$.

**Table 5.3. Design and data of the fiber drawing experiment**

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor</th>
<th>Readout</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>
5.2 DATA ANALYSIS AND RESULTS

5.2.1 Model fitting

The purpose of the model is to evaluate and validate the effect of the selected process parameters on the continuity of the drawn metal wires and to detect any interactions among them. We fit a linear model with three factors, $x_1$, $x_2$, and $x_3$,

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i<j}^{3} \beta_{ij} x_i x_j + \varepsilon, \quad (1)$$

where $y$ is the response, $x_1$, $x_2$, and $x_3$ are the three process parameters (coded as $-1, 1$), $\beta_i$, $\beta_j$, and $\beta_{ij}$ are the intercept, linear, and interaction (or bilinear) terms, respectively, and $\varepsilon \sim N(0, \sigma^2)$ is the error term.

We fit the linear model (1) using RSD and DDR respectively as the response and performed variable selection via stepwise regression. The estimate of the parameters is given in Table 5.4. The model fits the data quite well with an $R^2$ value of 98.8% for RSD and 96.5% for DDR. Table 5.4 shows that the linear effects A, B, and C are all significant at the 5% level for both RSD and DDR; interaction AC and BC are significant for RSD and interaction BC is significant for DDR. The residual analysis indicates reasonable assumptions made on the error. The models are

$$RSD = 0.40 - 0.06A - 0.16B - 0.11C - 0.11AC + 0.14BC \quad (2)$$
$DDR = 0.40 - 0.15A - 0.05B - 0.10C + 0.15 BC$  \hspace{1cm} (3)

We keep the linear effect A in RSD because AC is significant, and B in DDR because BC is significant.

**Table 5.4. Estimate of parameters for the fiber drawing experiment**

<table>
<thead>
<tr>
<th></th>
<th>RSD</th>
<th>DDR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.39*</td>
<td>0.4*</td>
</tr>
<tr>
<td>A</td>
<td>0.06</td>
<td>0.15*</td>
</tr>
<tr>
<td>B</td>
<td>0.16*</td>
<td>0.05</td>
</tr>
<tr>
<td>C</td>
<td>0.11*</td>
<td>0.1*</td>
</tr>
<tr>
<td>AC</td>
<td>0.11*</td>
<td>0.03</td>
</tr>
<tr>
<td>BC</td>
<td>0.14*</td>
<td>0.15*</td>
</tr>
<tr>
<td>$\hat{\sigma}$</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.988</td>
<td>0.965</td>
</tr>
</tbody>
</table>

*significant at level 0.05
5.2.2 Results

The data analysis identifies that stress at melt front (B) and aspect ratio (C) have significant effects on the growth of capillary instability; the draw-down ratio (A) and aspect ratio (C) have significant effects on the core continuity. To further understand the system, we examine the contour plot RSD and DDR from the model (2) and (3). Fig. 5.2 shows the contour plots of the predicted responses of A and B, A and C, and B and C, respectively, when the other factor is held at the middle level 0. Strong interactions can be observed between draw-down ratio (A) and aspect ratio (C), and between stress at melt front (B) and aspect ratio (C) on the growth of capillary instability; and also strong interaction between melt front (B) and aspect ratio (C) on the core continuity.
The RSD readout is optimal when all three factors are at high level, while DDR is optimal when A and C are at high level, and B is at low level. The fact that RSD and DDR reach optimal at different conditions is a clear indication that capillary break-up is not the sole reason for the discontinuity because the process conditions that result in the most continuous cores are not those that lead to the minimum growth of capillary instability. Optical microscope images further provide evidence of solid state break-up as shown in Fig. 5.3, since the blow-up cross-sectional view obtained under an optimal condition for RSD indicates an empty hole which cannot form due to capillary instability.

![Figure 5.3. Optical micrographs of cross sections obtained under (a) process conditions for optimal RSD, and (b) process conditions for optimal DDR.](image)

\( A = 1, B = 1, C = 1 \)

\[ RSD = 7.84\% \]

\[ DDR = 29.6\% \]

\( A = 1, B = -1, C = 1 \)

\[ RSD = 13.81\% \]

\[ DDR = 4.07\% \]
Empirical rules useful for process optimization can be derived after examination of the response surface plots of the model (2) and (3), as shown in Fig. 5.4. The fact that RSD surface at high B is not coinciding with that at low B regardless of the level of A and C, as shown in the middle plot of Fig. 5.4(a), leads us to the conclusion that if everything else is held the same, increasing the stress at the melt front always tend to suppress the capillary instability. This can be easily understood by drawing a vertical line from any point on the low B surface, and its intersection with the high B surface is always below. The same conclusion, however, cannot be made for the other two factors to suppress capillary instability. On the other hand, it can be anticipated that increasing the draw-down ratio with all other factors kept the same will surely reduce DDR, i.e. improve continuity of the core because surfaces of DDR with factor A maintained at high and low do not intersect.
5.3 SUMMARY

We present the design and analysis of an experiment that studies the metal core fiber drawing processes. This study experimentally confirmed that the three most important process parameters (i.e. drawing down ratio, stress at melt front, and aspect ratio) significantly affect the growth of capillary instability and core continuity during drawing. Empirical models identify multiple interactions between these three main factors and may provide insights to the validation of the analytical model derived in chapter 4. Two important numerical indicators (i.e. relative standard deviation and deviation from draw-down ratio) are proposed and used in this study, which allows experimental determination of multiple break-up mechanisms for the first time.
Experimental results show evidence that there exist other mechanisms in addition to capillary instability, such as solid-state core break-up, that may lead to the core being discontinuous, at least for the PES/Sn material pair in this study.
CHAPTER 6. NANOMANUFACTURING BY THERMAL FIBER DRAWING

Metal core thermal fiber drawing process holds great promise as a nanomanufacturing tool for the scalable production of nanomaterials and nanocomposites. The scalability of the process can be attributed to the fact that the formation of the nanoscale elements happens at liquid state, which on the other hand renders the process extremely difficult to control. The key lies in the capability to control the dynamics of the deformation and break-up of the liquid-fluid interfaces between the molten metal core and the viscous cladding down to the nanoscale. In this chapter, feasibility studies are conducted to explore the potential of thermal fiber drawing process for the production of nanoelements and identify possible pathways and physical forces that can be utilized to realize the control of the liquid-fluid interfaces. In section 6.1, we explore the feasibility of utilizing hydrodynamic force alone for the scalable production of metal nanoparticles. In section 6.2, we test the effect of electric field on the break-up of a molten metal thread surrounded by viscous cladding. Section 6.3 summarizes the new findings.

6.1 SCALABLE MANUFACTURING OF METAL NANOPARTICLES BY THERMAL FIBER DRAWING

Thermal fiber drawing has emerged as a novel process for the continuous manufacturing of semiconductor and polymer nanoparticles. Yet a scalable production of metal nanoparticles by thermal drawing is not reported due to the low viscosity and high surface tension of molten metals. Here we present a generic method for the scalable nanomanufacturing of metal nanoparticles via
thermal drawing based on droplet break-up emulsification of immiscible polymer/metal systems. We experimentally show the scalable manufacturing of metal Sn nanoparticles (<100 nm) in Polyethersulfone (PES) fibers as a model system. The underlying mechanism for the particle formation is revealed, and a strategy for the particle diameter control is proposed. This process opens a new pathway for scalable manufacturing of metal nanoparticles from liquid state facilitated solely by hydrodynamic forces, which may find exciting photonic, electrical, or energy applications.

6.1.1 Materials and Methods

In this proposed method, the metal nanoparticles are formed at liquid state, as a result of the break-up of an initially slender droplet surrounded by a viscous elongational flow created by the drawing process. The material selection criteria are as follows:

1. Controllable cladding viscosity (10^{2.5}~10^6 Pa-s)
2. Metal is molten at the processing temperature
3. Metal does not react with the cladding

Polyethersulfone (PES) and crystalline metal Tin (Sn) were chosen for the experimental validation of the proposed method. The glass transition temperature of PES is 225 °C and the melting point of Sn is 232 °C, which is close enough for the metal to be molten during the drawing process. While most metals require high glass transition point glasses such as Pyrex glass and fused silica as cladding, the selection of a thermoplastic material allows for a relatively low-temperature processing.
6.1.1.1  **Preform Fabrication**

Extruded Polyethersulfone (PES, BASF Ultrason E3010) rods (extruded and distributed by Port Plastics, Inc.) with an outer diameter (OD) of 19.05 mm and length of 10 cm were first dried at 150°C for 5 days under vacuum (2 Torr) to remove moisture. A through hole was then drilled to allow insertion of a Sn metal wire (SRA Soldering Products). The PES preform was then consolidated in a vertical tube furnace at 250°C for 30 mins under a vacuum of 40 mTorr before the first cycle of thermal fiber drawing. The consolidation has to be conducted at a temperature higher than the melting point of the metal but lower than the softening point of the polymer to ensure seamless contact between the metal core and the cladding.

6.1.1.2  **Iterative Thermal Fiber Drawing**

During a typical fiber drawing process, as shown in Fig. 6.1, the metal embedded preform is slowly lowered into a furnace, where the temperature is carefully controlled and stabilized at a designated value. After the heated preform in the furnace necks down under its weight, the bottom portion of the preform is cut away, and the fiber is pulled at a constant speed while the preform continues to be fed into the furnace. The diameter of the fiber \( D_f \) is controlled by varying the fiber pulling speed \( v_f \). The draw-down ratio \( D_r \) is defined as the ratio between the fiber pulling speed and preform feeding speed \( v_p \). At steady-state, the law of mass conservation requires \( D_r \equiv \frac{v_f}{v_p} = \left( \frac{D_p}{D_f} \right)^2 \), where \( D_p \) is the preform diameter, and \( v_p \) the preform feeding speed.
Figure 6.1. Schematic of thermal fiber drawing process

The fibers obtained from the first drawing cycle are cut into equal lengths and bundled, as shown in Fig 6.2, to serve as the core for a new preform, which is again thermally drawn to thin fibers. All drawings were done in a furnace with a graphite liner resistively heated. The liner has an inner diameter of 36 mm and length 35 mm. The temperature of the furnace is measured with a K type thermocouple inserted horizontally into the furnace with the tip of thermocouple aligned with the inner wall of the graphite. Table 6.1 lists the preform/fiber dimensions and the process parameters for each drawing cycle. The fibers achieved in one cycle (iteration) are bundled and inserted into the inner hole of a new preform for the next drawing cycle (iteration).
Figure 6.2. Schematic of bundle-and-draw method for the iterative size reduction to achieve nanoparticles

Table 6.1. Thermal drawing process parameters

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Preform OD [mm]</th>
<th>Preform ID [mm]</th>
<th>Drawing temperature [°C]</th>
<th>Feeding speed [μm/s]</th>
<th>Pulling speed [mm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.05</td>
<td>3.2</td>
<td>320</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>5</td>
<td>355</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>19.05</td>
<td>5</td>
<td>305</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>19.05</td>
<td>5</td>
<td>305</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

6.1.1.3 Particle Formation Mechanism and Size Control

The nanoparticles from at liquid state as a result of the break-up and deformation of the initially slender metal wires under the physical forces of interfacial tension and viscous stress.

Long microwires are first produced after the first and second iterations, which then start to break in the third iteration.
Various break-up events then follow. The formation of the smallest particles may be attributed to the satellites drops or a phenomenon known as tip-streaming, during which the droplet becomes slender with a pointed end where tiny droplets may eject, first documented by G.I. Taylor (Taylor 1934). Recent theoretical studies suggest that, at the nanoscale, thermal fluctuation may dominate (Eggers and Villermaux 2008).

The largest particles are those that survive the flow without further break up after sufficient times of iterations. A theoretical estimation of the size of the largest particle is given in the discussion.

6.1.1.4 Particle Production Rate

The upper bound of the volume production rate of the nanoparticles can be estimated as \( Q = \frac{\pi d_0^2 v_p}{4} \), where \( d_0 \) is the initial metal wire diameter in the preform and \( v_p \) the preform feeding speed, assuming the metal wire being completely converted to nanoparticles after enough number of iterations. Plugging in the preform inner diameter (ID) and feeding speed of iteration 1 from Table 6.1 yields a theoretical volume production rate of 0.064 mm\(^3\)/s. The actual production rate is much lower than this value considering the material loss during the production and collection.

6.1.1.5 Sample Preparation and Characterization Methods

Samples for characterization by Scanning Electron Microscope (SEM) are prepared by laying down multiple fibers on a silicon wafer submerged in Dimethylacetamide (DMA, Sigma Aldrich) at room temperature for 4 hours until all polymer claddings are dissolved. Samples for
characterization by Transmission Electron Microscope (TEM) are obtained by dissolving the fibers in DMA followed by centrifuging. The sediments are dispersed in ethanol from which one drop is cast onto the TEM grid.

### 6.1.2 Results and Discussion

Slender and long metal microwires were achieved after two drawing cycles as shown in Fig 6.3. The measured diameter is close to the thinnest continuous metal wires reported that was drawn in a polymer cladding (Yaman, Khudiyev et al. 2011).

![SEM image of Sn microwires](image_url)

Figure 6.3. SEM image of Sn microwires (3.4 ± 0.6 μm in diameter) after two iterations of drawing (cladding dissolved by solvent)

Nanoparticles were successfully produced as shown in Fig 6.4, with diameters ranging randomly from 100 nm to 500 nm. TEM image (Fig 6.5) with Selected Area Electron Diffraction

71
(SAED) patterns (Table 6.2.) further show that Sn nanoparticles smaller than 20 nm could be achieved. While it is confirmed that Sn nanoparticles can be produced as shown in Fig. 6.5., it is possible that the particles shown in Fig. 6.4. are still encapsulated in polymers that are not entirely dissolved away.

Figure 6.4. SEM image of nanoparticles obtained after 4 iterations of bundle-and-draw.
Figure 6.5. Atomic resolution TEM image of a twinned β-Sn nanoparticle with polygonal shapes showing many facets as confirmed by their ring patterns (insets)

Table 6.2. Interplanar spacing, d, determined by indexing the SAEDs, indicates β-Sn with a tetragonal crystal structure

<table>
<thead>
<tr>
<th>Spot #</th>
<th>d-spacing (nm)</th>
<th>β-Sn hkl</th>
<th>Intensity ( % )</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.6</td>
<td>110</td>
<td>55</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>101</td>
<td>100</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>1.9</td>
<td>200</td>
<td>20</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>211</td>
<td>35</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>220</td>
<td>10</td>
<td>0.7</td>
</tr>
</tbody>
</table>

To the best of the author’s knowledge, there is no published model yet that can satisfactorily describe the dynamics of the metal core during thermal drawing process from a preform. In an attempt to fill this gap, we start with a heuristic way and recognize that in addition to the breakup
of a cylindrical thread or layers of concentric cylindrical shells with various ratios of the material properties for which a wealth of literature exists (Papageorgiou 1995, Wang 2013), attentions must also be brought to the deformation of the metal droplets inside an elongational flow which we believe is the leading cause of the formation of the nanoparticles.

During a typical run of thermal drawing, as the preform is slowly fed into the furnace at a constant speed and uniform fibers being pulled from below, a steady-state in the Eulerian frame is soon reached such that the temperature and velocity profile in the preform remains constant with time if viewed from a fixed laboratory position. We assume the flow is one-dimensional recognizing that the length of the preform is much larger than its diameter. The molten metals embedded in different locations in the preform thus experience an almost identical flow history as they melt, deform and solidify under the influence of the energy and momentum input from the surrounding viscous cladding under thermal drawing.

A complete mathematical description of the dynamics of the shape evolution from a cylindrical metal rod to the final nanoparticle products is a formidable task, which involves multiple length scales spanning from millimeters to nanometers, and requires taking into account all relevant physical forces from interfacial tension, viscous stresses, inertia, and gravity. Fortunately, since we focus on small droplet sizes at micro/nanoscale, gravity and inertia effects are negligible due to small Reynolds number and body force. This greatly simplifies the problem by allowing us to consider only the surface forces that are the interfacial tension, and viscous stresses in the cladding, neglecting the viscous stress of the molten metal because the viscosity ratio ($\lambda$) between molten crystalline metal and the viscous cladding is close to zero (typically $<10^{-7}$). The ratio of these two
forces defines the dimensionless capillary number \( Ca = \frac{\tau a}{\gamma} \), where \( \tau \) is the first normal stress difference in the cladding flow (Bird, Stewart et al. 2007), \( a \) the radius of the droplet retracted to a perfect sphere, and \( \gamma \) the interfacial energy between the viscous cladding and the droplet. \( \tau \) measures the external viscous stress and \( \frac{\gamma}{a} \) scales with the interfacial-tension pressure. A low capillary number (\( Ca \ll 1 \)) indicates that the dynamics of the droplet deformation is governed by the interfacial tension alone while a high capillary number (\( Ca \gg 1 \)) suggests the viscous force is dominating.

Under steady state drawing, the \( \tau \) increases in the direction of pulling and scales with the inverse of the area of the circular cross sections because the fiber tension \( (T) \) is the same everywhere along the axis. The corresponding capillary number increases from \( Ca_{min} = \frac{\tau a}{A_0 \gamma} \) to \( Ca_{max} = \frac{\tau a}{A_L \gamma} \), where \( A_0 \) is the area of the cladding on the cross section of the preform, and \( A_L \) the area of the cladding on the cross section of the fiber.

In the low capillary number limit, when \( Ca_{min} \ll 1 \), corresponding to the case of a small pulling force or when the metal wires or droplets just enters the heating zone and are just melted, its dynamics is governed solely by interfacial tension.

Two modes of break-up may result in this case, namely capillary break-up and end pinching. An unconstrained slender molten metal thread is inherently unstable. It flows spontaneously to minimize its surface energy by reducing its surface area. An unperturbed slender thread would shrink and eventually become one single sphere. In the presence of any disturbances from the
surrounding, which is always the case, the disturbances can be decoupled into the superposition of sinusoidal perturbations along its three axes as shown in Fig 6.6.

![A slender thread of molten metal](image)

Figure 6.6. Perturbations in the forms of (a) centerline undulation (b) modulation of radius along azimuthal angle (c) distortion of radius along centerline

Since the volume of the thread keeps constant, sinusoidal undulation of centerline does not change its surface area; the fluid thread would not break under such perturbations alone. Azimuthal modulation increases its surface area, and therefore the thread will not grow in this direction either. However, when the radius of the thread is perturbed along its symmetric axis as shown in Fig 6.6(c), one can calculate and see that its surface area is reduced if the wavelength of the perturbation is larger than a critical value (Eggers and Villermaux 2008), meaning the perturbed state has lower surface energy and thus is more stable than the unperturbed state. It is for this reason that the small initial perturbation grows spontaneously and quickly leads to breakage of the fluid thread into droplets along its centerline. In the case of end pinching, droplet break-up does not happen simultaneously but sequentially from the two ends of the slender thread as it retracts to the spherical shape to minimize its surface energy (Eggers and Villermaux 2008), which
typically happens when the viscosity of the droplet is much lower than its surrounding as in the molten metal/viscous cladding case. Studies show that there exists a critical aspect ratio \( AR_{cr} \) above which either end pinching or capillary break-up may happen. Experiments and numerical simulations indicate that moderately stretched droplets with an aspect ratio \( AR < AR_{cr} (\lambda) \) can retract back to the spherical shape without fragmentation (Tjahjadi, Ottino et al. 1994) and the critical aspect ratio \( AR_{cr} (\lambda) \) is a function of viscosity ratio. Here we again utilize the fact that \( \lambda \) is close to zero, therefore assuming that \( AR_{cr} \) is a constant not sensitive to the viscosity changes of the metal and polymer arising from the spatial temperature and velocity profile.

As the capillary number increases along the fiber axis, the metal droplets or wires experience stronger flow. Studies show that there exists a critical capillary number \( Ca_{cr} \) above which the droplet may disintegrate due to the viscous shearing as well, and the break-up may assume more than one mechanism, namely, center pinching, indefinite elongation, or tip streaming (Favelukis, Lavrenteva et al. 2012), among which indefinite elongation and tip streaming are believed to be able to produce nanoscale droplets which we do observe in this study.

With the knowledge of the possible break-up mechanisms, it is now feasible to estimate the size of the largest droplet that can survive the fiber drawing flow without further break-up after multiple iterations of bundle-and-draw.

We argue that, for a droplet with radius \( a \) to survive the fiber drawing flow without breaking up, it may neither break due to interfacial tension, nor viscous shearing. This essentially requires that the aspect ratio and the capillary number corresponding to the droplet exceeds neither the critical aspect ratio \( AR_{cr} \), nor the critical capillary number \( Ca_{cr} \).
We further argue that the capillary number needed to stretch a droplet to its critical aspect ratio is always smaller than the critical capillary number that may give rise to its disintegration by shearing, which is self-evident as break-up can only happen when the shearing is too strong such that a stationary shape, which assumes a finite aspect ratio, can no longer exist.

Now we define a new critical capillary number \( a_{\text{crit}}(a) = \frac{\tau a}{\gamma} \), above which a droplet with initial radius \( a \) will be stretched to an aspect ratio larger than \( AR_{cr} \). Equivalently, if the maximum stress \( (\tau_{\text{max}}) \) in the flow is known, any droplets with radius larger than \( a_{\text{max}} = \frac{\gamma a_{\text{crit}}}{\tau_{\text{max}}} \) is subject to break-up thus will not survive.

In the fiber drawing, the maximum axial stress in the flow \( (\tau_{\text{max}}) \) is proportional to the fiber tension force \( (T) \) divided by the area of the fiber cross section \( (A_L) \). We therefore reach the following expression:

\[
a_{\text{max}} = f\left(\frac{\gamma A_L}{T}\right)
\]

The proposed functional relationship captures the key process parameters as well as material properties that govern the metal particle size. The suggested mechanism has general implications for metal particle size design and control. The validity of this relationship should be experimentally tested in future.

Several assumptions are inherent in the above analysis which needs to be noted here:

1. The effect of temperature gradient on the interfacial tension is neglected, which can be justified when the Marangoni number is much smaller than 1.
2. It is assumed that the droplets are small enough so that the flow around it can be considered as linear, although the actual flow is nonlinear at larger length scale.

3. It is assumed that there is no interaction between droplets.

4. The continuum hypothesis is assumed to be valid, neglecting the molecular effects.

6.2 BREAK-UP CONTROL BY ELECTRIC FIELD

The previous section focus on the formation of metal nanoparticles by hydrodynamic forces only. In this section, a feasibility study is conducted to use electric field as an alternative method for the controlled break-up of molten metal threads. As shown in Fig. 6.7, a single core fiber is surrounded by a graphite liner which serves as both the heater and the ground electrode. The metal core serves as the positive electrode, thus creates a radial electric field pointing outward from the center of the heating zone where the graphite liner is located.
The metal core fiber used in this study has an inner diameter of 12 μm as shown in Fig. 6.8. The fiber is slowly fed into the resistive heater with graphite liner at 300 °C. The feeding speed is 40 μm/s and pulling speed 50 μm/s.

An unpaired two-sample t-test is conducted to test the null hypothesis $H_0$ that the break-up wavelength of the molten metal core is not significantly affected by the radial electric field, which can be expressed as, $\bar{\lambda}_{0V} = \bar{\lambda}_{2kV}$, where $\bar{\lambda}_{0V}$ is the mean break-up wavelength of the metal core without the electric field and $\bar{\lambda}_{2kV}$ the mean break-up wavelength of the metal core with electric field. Fig. 6.9. shows the typical optical microscope images of the broken core at different voltages.
Figure 6.9. Optical microscope images of the thermally drawn fiber after break-up (a) without electric field, and (b) with electric field.

The experimental data presented in Table 6.3. are measured by the image processing software ImageJ (Schneider, Rasband et al. 2012). The mean break-up wavelength were calculated from the lengths of 97 metal segments formed without electric field and lengths of 146 segments formed under the influence of electric field, as listed in Table 6.3 and plotted in Fig. 6.10., together with their standard deviation.

Table. 6.3. Measured data for the hypothesis test.

<table>
<thead>
<tr>
<th>Group</th>
<th>0V</th>
<th>2kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>548 μm</td>
<td>379 μm</td>
</tr>
<tr>
<td>SD</td>
<td>168 μm</td>
<td>139 μm</td>
</tr>
<tr>
<td>N</td>
<td>97</td>
<td>146</td>
</tr>
</tbody>
</table>

With a p-value of $4.63 \times 10^{-14}$, it suggests that electric field does significantly affect the break-up wavelength and hold the promise as a facile tool for the controlled emulsification of molten metal inside a viscous medium.
6.3 SUMMARY

In this chapter, a feasibility study of using thermal fiber drawing as a scalable nanomanufacturing tool is conducted. It is first proposed that metal nanoparticles can be produced in a scalable manner by thermal fiber drawing utilizing the iterative size reduction method. Sn metal nanoparticles smaller than 100 nm were successfully produced by drawing inside a thermoplastic (PES) cladding. The successful manufacturing of metal nanoparticles in liquid state from long and slender metal filaments is attributed to the physical forces of interfacial tension and viscous stress. The diameter of the particles produced is predicted to be a function of the maximum stress in the fiber and the interfacial tension between the molten metal and the viscous cladding. In addition to hydrodynamic forces, experiments are also conducted to test the hypothesis that an electric field can significantly affect the break-up wavelength of the molten metal. The presence of a radial electric field reduces the break-up wavelength by 30.8% under the experimental conditions studied, which shed new light on the controlled emulsification of molten metals in a viscous medium. Both methods studied are generic and can be readily extended to other material
systems, following the given material selection criteria, to control size and geometry of metals with higher melting points for many exciting photonic, electrical, or energy applications.
CHAPTER 7. CONCLUSIONS

As thermal fiber drawing emerges as a powerful tool for the scalable manufacturing of metal micro/nanowires and particles for novel applications, strong needs for fundamental understanding motivates this work. The specific research objectives are to significantly advance the basic understanding of the single core thermal fiber drawing process from a preform at the microscale, to establish empirical rules for process optimization of multicore preform drawing through experimental design, and to explore and extend the capability of metal core preform drawing into nanoscale.

The analytical study revealed that the underlying physics of the process concerns the dynamics of a molten metal jet viscously entrained in a free surface flow. A long wavelength model is derived to solve for the dynamics of the molten metal core during the production of continuous metal microwires by thermal fiber drawing from a preform. The analysis confirms volume conservation as the diameter control mechanism for continuous microwire production by preform drawing. The dominant physical forces that govern the dynamics of the metal jet are interfacial tension, stress in the cladding, and pressure in the metal. Steady state solution of the model is obtained through a numerical study which qualitatively agrees with experiments. The analytical and numerical studies also identify a lack of interfacial energy data in the literature which stimulates the development of a general and simple method to measure the liquid-liquid interfacial energy between the molten metal and viscous claddings, which is applied to the Sn/PES interface. During a stable drawing condition, a dimensionless capillary number $Ca = \frac{2Fa}{\gamma A(0)}$ is suggested to be used as the quantitative indicator for the prediction of process conditions that
produce continuous metal wires (i.e. continuous mode) as opposed to broken wires (i.e. dripping mode). A critical capillary number about 0.5 has been identified. Process conditions with capillary number above the critical capillary numbers yield continuous metal microwires. This provides the first ever quantitative measure of the core continuity during preform drawing of metal microwires based on process parameters and material properties.

We further performed a factorial experimental design that studies the fiber drawing processes with multiple metal cores. Draw-down ratio, stress at the melt front, and aspect ratios are experimentally confirmed to have a significant effect on the growth of capillary instability and core continuity during drawing. Multiple interactions between these three factors have been identified as well. Two important numerical indicators, namely relative standard deviation and deviation from the draw-down ratio, are proposed as measures of core continuities which enables the experimental determination of multiple break-up mechanisms in addition to the commonly accepted capillary instability. Experimental results show that suppressing capillary instability may not always improve core continuity, which is against the common belief reported in the literature, at least not for the PES/Sn material pair in this study.

Finally, feasibility studies were conducted to explore the potential of using thermal fiber drawing as a scalable nanomanufacturing tool. It was first hypothesized that metal nanoparticles could be produced in a scalable manner by thermal fiber drawing utilizing only hydrodynamics forces. Sn metal nanoparticles smaller than 100 nm were successfully produced by drawing inside a thermoplastic cladding (PES). In addition to hydrodynamic forces, electrical forces were also hypothesized to significantly affect the break-up wavelength of the molten metal. An unpaired t-
test was conducted and compared the break-up wavelength of metal cores with and without an electric field. The presence of an electric field reduced the break-up wavelength by 30.8%. These findings opens new avenues toward the dimensional control at nanoscale which will be the focus of future study.

In summary, analytical, numerical and experimental methods have been employed to advance the fundamental understanding of the metal thermal fiber drawing process. The new findings obtained in this study lays the groundwork for the control of micro/nanoscale fluid interfaces of molten metals inside a viscous, free-surface flow by parameters accessible at macroscales, which is the key element to a successful scalable micro/nano-manufacturing process.
CHAPTER 8. RECOMMENDATIONS FOR FUTURE WORK

The full potential of thermal fiber drawing is far from being explored. The new findings discovered in this work opens up more possibilities for research and development.

8.1 SCALABLE MANUFACTURING OF METAL NANOMATERIALS

Future research should continue to focus on the fundamental and applied research for high-throughput and low-cost production of metal nanomaterials by thermal fiber drawing. Key research issues will be addressed (1) to increase throughputs and variety of materials, (2) to control size and aspect ratio by external forces (e.g. shear force, thermal gradient, nanoparticles, surfactants, and electromagnetic fields, etc.), (3) to implement online metrology for close-loop control, (4) to conduct modelling and simulation for fundamental understanding as well as process control, (5) and to assess throughput, environmental footprint, and sustainability. The outcome of this research will lead to the low-cost manufacture of various nanoscale building blocks (e.g. metal nanoparticles, ultra-long metal nanowires, polymer/metal and glass/metal nanocomposite fibers, nanocomposite microparticles and microwires, etc.), which contribute to the overarching goal of scalable nanomanufacturing to create new applications and accelerate market penetration of nanomaterials.

8.2 INTEGRATED NANOMANUFACTURING

With the rapid increase of availability and variety of nanomaterials, research needs are gradually shifting from scalable production of nanoelements toward the large-scale assembly and
system level integration of them to retain nanoscale properties in macroscale systems. Conventional wisdom seeks solutions combining top-down and bottom-up processes to achieve a multiscale product, which meets severe roadblocks regarding scalability. There are strong needs for intrinsically multiscale processes with “scale invariant” properties that allow control of dimensional precision over wide length scales, which solves the nano-to-macro interfacing challenges in a seminal way. The goal of this research is to discover and utilize such processes for the scalable manufacturing of useful multi-material and multi-scale structures that have broad applications in energy, electronics, medical device, and communication industries.

Thermal fiber drawing exhibits such “scale invariant” properties. Challenges will be overcome in materials selection and process control to meet geometrical (e.g. length and size of electrodes, distances between electrodes) and material requirements (e.g. biocompatibility, resistivity, thermal conductivity, dielectric constant, etc.). Potential applications include but are not limited to (1) 3D optical metamaterials for nonlinear optics and subwavelength imaging, (2) 3D thermal metamaterials for microscale heat manipulation, (3) wearable fibers for waste heat recovery (4) individually addressable electrode arrays for nanoscale electromagnetic and thermal sensing/stimulation, (5) 3D nano-to-macro electronic interfacing unit, (6) high strength bundled micro/nanowires, (7) nerve/electronic interfaces. In the long run, more of such scale invariant processes will be sought and developed. Special focus will be laid on complex natural phenomena that show strong nonlinearity or fractal behaviors, such as biological systems, electric discharge, and phase transition.
8.3 ADVANCED COMPOSITE MATERIALS

This future research will focus on the study of processing, properties and physics of (1) non-Newtonian metals, and (2) metal/polymer and metal/glass interfaces and their emulsions for the scalable manufacturing of advanced composite materials. Molten metals are known as Newtonian fluids with low viscosity and high surface tensions in general. The first goal of this research aims to utilize nanoelements to engineer molten metals to exhibit viscous, plastic, and even elastic behavior, which will bring about transformational changes in the metals processing industry. The experimental and theoretical research will be conducted including the selection, incorporation, and dispersion of nanoelements, design and manufacture of rheometers for measurement at high temperatures, and constitutive modelling and simulation. The second goal of this research is to achieve nano-emulsification and stabilization of molten metals in polymers and glasses by experimentation and modelling. Measurement of interfacial properties between molten metal/polymer and metal/glass will be conducted with custom-made equipment. The effect of interfacial modifiers such as nanoparticles, surfactants, and electric fields will be studied as well. The highly disparate physical properties between metals and polymers/glasses with engineered interfaces will bring about unusual and useful properties (e.g. ductile glass, thermally conductive but electrically insulating polymer, transparent but conductive polymer), which may find applications in energy, manufacturing, communication and defence industries.
REFERENCES

- Datasheet from manufacturer (BASF).


