THROUGH THIN FILM ABLATION OF IRON-NICKEL PIXEL TARGET

Thesis
Submitted to
The School of Engineering of the
UNIVERSITY OF DAYTON

in Partial Fulfillment of the Requirements for
The Degree
Master of Science in Materials Engineering
by
Xiaoxu Niu
UNIVERSITY OF DAYTON
Dayton, Ohio
August, 2010
THROUGH THIN FILM ABLATION OF IRON-NICKEL PIXEL TARGET

APPROVED BY:

P. Terrence Murray, Ph.D.
Committee Chairman
Professor,
Materials Engineering

Daniel Eylon, Ph.D.
Committee Member
Professor and Director,
Materials Engineering

Andrew Sarangan, Ph.D.
Committee Member
Associate Professor,
Electro-Optics

Malcolm W. Daniels, Ph.D.
Associate Dean
School of Engineering

Tony E. Saliba, Ph.D.
Dean, School of Engineering
ABSTRACT

THROUGH THIN FILM ABLATION OF IRON-NICKEL PIXEL TARGET

Name: Niu, Xiaoxu
University of Dayton
Advisor: Dr. P. T. Murray

A novel multi-element nanoparticle synthesis technique, noted pixel target ablation (PTA) is reported here. In the experiments described here, Iron-Nickel pixel targets were prepared on a transparent disc by sputtering and by photolithography. By irradiating the target materials from the backside, the laser energy breaks the target materials into metal atoms, which then forms nanoparticles by recombination in the gas phase. The nanoparticles were subsequently captured by a substrate. The degree of interaction between the two metals species and the plume dynamics of this method were examined. The average composition and size distribution of synthesized nanoparticles were studied using X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) respectively. The results show that this process has congruent transformation of target materials weight ratio to particle composition, and controllable particle size distribution with no agglomeration. Additionally, the structure of the particles was determined by the use of X-ray diffraction (XRD). Samples were prepared by ablation in vacuum and in the presence of a background gas. A mixture of single-metallic and alloyed nanoparticles were collected. The implications of these observations for multi-element nanoparticle synthesis are discussed.
ACKNOWLEDGEMENTS

I am deeply grateful to Dr. Paul T. Murray, for giving me the opportunity and providing the project with every resource possible. Dr. Murray is a great teacher from quantum mechanics down to English grammar. I will forever remember the lessons from him: think critically; ask the simple questions; and squeeze out the most information from your data. Trying something new is always exciting, I never could have been this excited without all of the wonderful tutorials from Dr. Andrew Sarangan. Beside lots of hands on experience, one important lesson I learned from him is that, its very easy to say how something will work, but until you actually start doing it, you never know. Last, but certainly not the least, many thanks are due to Dr. Eunsung Shin, Neal Pierce, Dr. Tyson Back and Jia Jia Wei, who have been tremendously supportive throughout this project and offered many helpful advices.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>viii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I    INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>Motivation</td>
<td>1</td>
</tr>
<tr>
<td>Review of Studied Area</td>
<td>4</td>
</tr>
<tr>
<td>The Impregnation Method</td>
<td>4</td>
</tr>
<tr>
<td>The Colloidal Method</td>
<td>6</td>
</tr>
<tr>
<td>The Microemulsion Method</td>
<td>8</td>
</tr>
<tr>
<td>Pulsed Laser Deposition</td>
<td>9</td>
</tr>
<tr>
<td>II   EXPERIMENTAL</td>
<td>11</td>
</tr>
<tr>
<td>Target Preparation</td>
<td>11</td>
</tr>
<tr>
<td>Through Thin Film Ablation</td>
<td>15</td>
</tr>
<tr>
<td>III  RESULTS AND DISCUSSION</td>
<td>18</td>
</tr>
<tr>
<td>Subject</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Plume Dynamics</td>
<td>18</td>
</tr>
<tr>
<td>Plume Photography</td>
<td>18</td>
</tr>
<tr>
<td>Optical Emission Spectroscopy</td>
<td>20</td>
</tr>
<tr>
<td>Time of Flight Analysis</td>
<td>23</td>
</tr>
<tr>
<td>Nanoparticle Characterization</td>
<td>26</td>
</tr>
<tr>
<td>Transmission Electron Microscope</td>
<td>26</td>
</tr>
<tr>
<td>X-Ray Photoelectron Spectroscopy</td>
<td>27</td>
</tr>
<tr>
<td>X-Ray Diffraction</td>
<td>30</td>
</tr>
</tbody>
</table>

### IV CONCLUSION AND FUTURE WORKS 32

#### Conclusion 32

#### Future Works 33

### APPENDICES

#### A IRON-NICKEL PHASE DIAGRAM 34

#### B LASER ENERGY CALCULATION ON TARGET VAPORIZATION 35

### BIBLIOGRAPHY 43
LIST OF FIGURES

1  STEM images of nanoparticles synthesized by the impregnation method . . 5
2  TEM images and corresponding size distribution histograms of nanoparti-
   cles synthesized by the colloidal method . . . . . . . . . . . . . . . . . . 7
3  TEM images of nanoparticles synthesized by the microemulsion method . . 9
4  SEM images of nanoparticles synthesized by pulsed laser deposition . . . 10
5  Schematic procedure of target preparation process by photolithography. . 12
6  Optical microscope images of pixel targets with different composition. . . 13
7  A sketch of the through thin film ablation (TTFA) system. . . . . . . . . . 16
8  Photographs of the ablation plume along with intensity analysis. . . . . . 19
9  Optical emission spectrum recorded from PTA of pixel targets. . . . . . . 21
10 Speed distribution of nanoparticles for different Ar pressures. . . . . . . 23
11 Speed distribution of nanoparticles for different targets. . . . . . . . . . 25
12 TEM micrographs and size distributions of nanoparticles. . . . . . . . . . 26
13 Wide-scan, core level XPS spectra. . . . . . . . . . . . . . . . . . . . . 28
14 Narrow-scan, core level XPS spectra. . . . . . . . . . . . . . . . . . . . 29
15 X-ray diffraction patterns. . . . . . . . . . . . . . . . . . . . . . . . . . . 31
16 Iron-nickel phase diagram. . . . . . . . . . . . . . . . . . . . . . . . . . . 34
17 Energy consumption of pixel target evaporation process. . . . . . . . . . 36
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOE</td>
<td>Buffered Oxide Etch</td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>PMMA</td>
<td>Para-methoxymethamphetamine</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier Tube</td>
</tr>
<tr>
<td>PTA</td>
<td>Pixel Target Ablation</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of Flight</td>
</tr>
<tr>
<td>TTFA</td>
<td>Through Thin Film Ablation</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

This chapter covers a brief introduction of multi-element nanoparticle synthesis, including:
(1) the most commonly used preparation methods; (2) the major problems those techniques
are facing, such as, particle agglomeration and precise compositional control; (3) how this
report tackles those problems; as well as, (4) a review on related literature.

Motivation

Nanoparticles, sized between 1 and 100 nanometers, are defined as small objects that
behave as a whole unit in terms of their properties. Nanoparticles show novel magnetic,
electronic, optical and chemical properties, which are different than those of bulk materials
due to their extreme small sizes and large specific surface areas [1–4]. Among the various
types of nanoparticles, bi-metallic and multi-metallic catalysts have attracted much attention
with regard to improving the selectivity and stability of metallic active sites [5–10]. Among the various
types of nanoparticles, bi-metallic and multi-metallic catalysts have attracted much attention
with regard to improving the selectivity and stability of metallic active sites [5–10]. Applications include the areas of carbon nanotube growth; fuel cells; solar cells; advanced
sensors; medicine; ultrafast data communication; and optical data storage [11–17]. However, the catalytic performances of the supported nanoparticles strongly depends on the
preparation method. Consequently, different methods have been developed to favor metal-
metal interactions, as well as synthesis of uniformly sized nanoparticles dispersed over
substrates. Examples include, the impregnation method [18–20], the colloidal method [21–23], the microemulsion method [24–27] and pulsed laser deposition [1, 28–32]. However, in spite of substantial efforts expended on developing these techniques, most of the techniques have proved to be difficult for preparing well dispersed nanoparticles that are uniformly sized at the same time.

Pixel target ablation (PTA) ameliorates most of these problems, and potentially represents a highly versatile and powerful approach to the preparation of well dispersed and uniformly sized nanoparticles for catalytic applications [33]. PTA is a novel technique, in which pixel target materials are ejected from a transparent disc as a result of pulsed laser irradiation from the backside. Rapid energy deposition results in heating and ionization of target material and leads to the formation of a high temperature plume. The origin of PTA denoted through thin film ablation (TTFA) is already being exploited in a number of technological applications, such as chemical sensing, carbon nanotube growth and nano-composite DNA thin film preparation [34]. Pixel target ablation (PTA) goes a step further than TTFA, by incorporating TTFA and photolithography. With the advantage of TTFA on particle size distribution and the flexibility of photolithography on compositional control, PTA has the potential of forming high quality multi-element nanoparticles through a simple and straightforward process.

PTA is suitable for the synthesis of catalytic, multi-element nanoparticles for a number of reasons. First, virtually any element mixture in any composition can be transformed into nanoparticles with a narrow size distribution. Consequently, PTA avoids the use of dangerous or expensive liquid or gaseous precursor chemicals. Second, nanoparticles prepared
by PTA can directly be collected on virtually any supports, thereby eliminating the need to handle potentially toxic nanopowders. Since nanoparticles originate from a high temperature plasma gas, interactions of multiple metals and background gas are made possible. Finally, the sizes and compositions of the nanoparticles generated by PTA can be adjusted to generate materials for specific catalytic and other applications.

Although metal alloys are the preferred form of targets for the ease of compositional control in laser ablation synthesis of multi-metallic nanoparticles [5], the limited availability of alloys restricts the compositions of nanoparticles that can be readily created. PTA, on the other hand, is a versatile and straight-forward technique. The method developed involves the preparation of multi-metallic pixel target thin film on a transparent disc first by lithography and followed by through thin film ablation. The possible creation of multi-metallic nanoparticles requires: (1) evaporation of the target thin film, which is accomplished by rapidly heating of the target; and (2) collision of the hot plasma gas mixture. In the PTA process, the former was achieved by the use of high power and short pulse-length laser, and the latter was accomplished by operating the PTA under a certain pressure inert gas atmosphere. Reactive ambient gas can also be used depending on applications. Metal combinations and compositions can be varied through photolithography to achieve the desired nanoparticle when the above conditions are present.
Review of Studied Area

The Impregnation Method

The impregnation method is a simple and straightforward chemical preparation technique that is widely used [18–20]. It includes an impregnation step, followed by a reduction step. During the impregnation step, metal precursors are mixed with high-surface-area carbon black in aqueous solution to form a homogeneous mixture. As a catalyst support, carbon black plays a major role in terms of penetrating and wetting the precursors, as well as, limit nanoparticle growth. The chemical reduction step can be carried out by liquid phase, such as ferric acid, or gas phase, like a flowing hydrogen stream, reduction under elevated temperature. Many studies have indicated that synthetic conditions, such as the nature of the metal precursors used, the reduction method and the heating temperature are crucial in the impregnation process [19, 20]. Tomoyuki et al. [18] prepared some PtRu catalysts on a carbon support by an impregnation-reductive pyrolysis method at various temperatures, with $Pt(NH_3)_2$ and $Ru(NO_3)_3$ as precursors. Their results showed that there is a slight compositional variation between individual nanoparticles, depending on the particle size. STEM images of the synthesized nanoparticles are shown in Figure 1.
Because the metal composition is pre-controlled, this route is advantageous for preparing stoichiometric and homogeneous nanoparticles with a narrow size distribution through an easy preparation process. However, the chemistry behind the synthesis of single-source precursors is complicated and use many organic compounds, which may lead to catalyst poisoning and limit its application. Another major drawback of the impregnation method is the difficulty in controlling nanoparticle size and distribution due to the nature of nanosized particle agglomeration in solvent.
The Colloidal Method

The colloidal method is another extensively explored technique for multi-element nanoparticle synthesis [21–23]. It usually includes the following steps: (1) preparation of precursor containing colloids; (2) deposition of the colloids onto a support, such as high-surface-area carbon, in a different media with different thermal treatment; and (3) chemical reduction of the mixture. Reductive agent, stabilizer and shell-removing approaches are usually required in this method. Yunjie Huang et al. recently reported a route using \((WO_3)_n\times H_2O\) as colloidal source to prepare Pd/C catalyst for formic acid oxidation. Their TEM images showed that the Pd/C nanoparticles have an average size of 3.3 nm and a narrow size distribution (shown in Figure 2) [22].

This metal colloids technique can prepare catalysts with much higher specific surface area compared with that of the impregnation method. By this method, nanoparticles with well-defined, completely alloyed particles and a very narrow particle size distribution (< 3nm) were obtained, and showed comparable activity with that of state-of-the-art commercially available catalyst [21, 23] However, the particle growth and agglomeration control in this method seem to be problematic. In addition, due to the complexity of the preparation steps and the relatively high cost, it is still not favorable in practical applications [2].
Figure 2. TEM images and corresponding size distribution histograms of (a) Pd/C-A and (b) Pd/C-B catalysts [22].
The Microemulsion Method

Microemulsion is a fairly new technique for synthesizing multi-element nanoparticles that has developed in recent years [24–27]. In this method, the first step is nanoparticle formation through a water-in-oil microemulsion reaction, followed by a reduction step. The microemulsion serves as a nano-scaled reactor in which the chemical reaction takes place. The microemulsion is a nano-scaled aqueous liquid droplet containing a metal precursor. The droplets are engulfed by surfactant molecules and uniformly dispersed in an immiscibly continuous organic phase. The reduction step can be carried out either by adding a reducing agent into the microemulsion system [24], or by mixing it with another reducing agent-containing microemulsion system [25]. As a result, the reduction reaction is confined to the inside of the nano-scaled micromulsion. The sizes of formed metal particles can be easily controlled by the microemulsion size [26, 27]. The surfactant molecules can function as protective agents to prevent nanoparticles from agglomeration, but the removal of surfactant molecules needs to be carried out. P. Holec et al. prepared magnesium ferrite nanoparticles via microemulsion method mediated hydrolytic decomposition of mixed alkoxide solutions for the first time. TEM revealed the particles size of about 39 nm (shown in Figure 3) [25].

The main advantage of the microemulsion method is its ease in controlling metallic composition and particle size within a narrow distribution by varying the synthetic conditions. However, like the colloid method, the microemulsion method also uses costly surfactant molecules and requires a substantial number of separation and washing steps, which may be not suitable for large-scale production.
Figure 3. TEM images of the MgFe$_2$O$_4$ sample heated at 800°C [25].

**Pulsed Laser Deposition**

Pulsed laser deposition is an extremely simple technique. It consists of a target and a substrate housed in a vacuum chamber. A high-power laser is used as an external energy source to vaporize materials and to deposit thin films. A set of optical components is used to focus and raster the laser beam over the target surface [1, 28–32]. J. Lin et al. synthesized FeCo nanoparticles via ablating a high-purity FeCo target in distilled water using pulsed laser. SEM and STEM results are shown in Figure 4 [29].

In term of the advantages of this process, first, the decoupling of the vacuum hardware and the evaporation power source makes this technique so flexible that it is easily adaptable to different operational modes. Second, particle deposition can be carried out in a reactive environment containing any kind of gas with or without plasma excitation. Finally, similar to the PTA process, virtually any metal or mixtures in any composition and
form, e.g. sheet, film, powder, can be transformed into nanoparticles [28]. However, due to the unavoidable phenomenon of splashing, agglomeration is a big drawback and has been frequently discussed when dealing with nanoparticles. Despite numerous proposed solutions for splashing, such as mechanical particle filter [30], plume manipulation [31], target surface improvement [32] and so on, a narrow particle distribution is still very hard to achieve using this technique.

Figure 4. (a) SEM and (b) STEM images of FeCo nanoparticles in colloid synthesized by 7 min irradiation [29].
CHAPTER II

EXPERIMENTAL

The photolithography target preparation process and TTFA experimental method are reported in this chapter.

Target Preparation

Photolithography was conducted on a mask aligner. A scheme of the process is shown in Figure 5. Briefly, a 40 nanometer thin layer of iron (Fe) was sputtered onto a 5 cm diameter disc of UV-transparent fused silica. Followed by spin coating a thin layer of Paramethoxymethamphetamine (PMMA) resists. A designed pixel pattern, with a periodicity of 100 micrometers was then transferred into the resist layer by 365 nm UV-light. An exposure time of 35 seconds and soft contact between mask and sample surface were carried out. After dissolving the exposed resist, the whole target was soaked in 50:1 buffered oxide etch (BOE) to etch away metal thin films on exposed areas. The remaining resist was then dissolved in acetone to get Fe pixel metal array with 90 micrometers in side length. For the second metal sputtering, a layer of PMMA resists was spin coated onto the same target again. Alignment was carried out with an inverse mask design to expose the areas without Fe pixels. Exposed resist was dissolved, followed by 40 nanometers nickel (Ni) thin film sputtering. Finally, Ni thin film pixels landed above the remaining resists were
lifted off due to sidewall solvent attack in acetone. A Fe-Ni bi-metal pixel thin film target was made citeosswald,alexander.

Figure 5. Schematic procedure of target preparation process by photolithography.
Figure 6. Optical microscope images of (a) Fe100 target; (b) Fe50-Ni50 target; and (c) Ni100 target. The pixels are 40 nanometers high and had a periodicity of 100 micrometers.
With a high degree of spatial resolution, approximately 1 million isolated pixels were produced on a 5 cm disc. During the PTA process, taking into consideration the $1 \text{ cm}^2$ laser beam spot, about 10,000 pixels were ablated for each laser shot. Three targets with compositions of Fe100, Fe50-Ni50 and Ni100 were made for the examination of compositional control. The images obtained by optical microscope are shown in Figure 6. It is important to note that, in Figure 6b, Fe pixels are slightly smaller than Ni pixels. This is caused by sidewall undercut of the etching process in step 4 of target preparation (shown in Figure 5). Therefore, the actual measured composition on the Fe50-Ni50 target is close to Fe45-Ni55. This undercut inaccuracy can be easily avoided by dual lift-off lithography according to our recent results, detailed procedural will be discussed with further characterization results in future works.
Through Thin Film Ablation

In Figure 7, the PTA system is shown. The setup consists of a rotatable target holder that supports the pixel target (5 cm diameter and 0.5 cm thickness fused silica disc with 40 nm bi-metal pixel thin film coating). The target under laser illumination was rotated to a fresh area after each laser strike. A pulsed laser beam (Lambda Physik Complex 200 Excimer Laser, λ=248 nm, 600 mJ/pulse, 10 ns pulse duration) was focused to a spot of about 1 cm diameter, off axis on the surface of the target backside, arriving at an angle of about 45 degrees. Nanoparticles created in the ablation plume were then collected on a single crystal silicon wafer and a standard transmission electron microscope (TEM) grid located 2 inches from the target position as shown in Figure 7. A notch filter with a photomultiplier tube located at one inch from the target is used to detect light at selected wavelengths. An oscilloscope analyzes the PMT output. The time dependence of the detected signal gives the TOF of the excited species at the imaged region. Consequently, it is possible to readily characterize the synthesized nanoparticles as well as monitor the particle formation process. In the current setup, the distance between the target and collection site could be adjusted. This assembly was placed inside a vacuum chamber to control the ambient gas conditions during PTA (Ar in the present experiments).
The composition of the nanoparticles formed are, in principle, related to the bi-metal target pixel ratio. The nanoparticle size is primarily determined by the laser power density (i.e. fluence, energy of the photons and pulse duration), target thin film thickness, atomic mass, the density of the ambient gas, as well as the target-substrate distance. Other parameters, such as the pixel size, thin film density, light absorbance, heat capacity, boiling point and vapor pressure of the target also influence the properties of the nanoparticles [1]. The PTA system reported here enables the systematic exploration of all these variables within a single experiment, and allows for the rapid determination of conditions under which the synthesis of nanoparticles suitable for specific applications can be accomplished.
A picture of Fe50-Ni50 PTA plume is also shown in Figure 7. It is important to note that in PTA, due to the nature of thin film target ablation, only a small and in principle known amount of material is ablated, therefore producing almost no large particles by eliminating splashing and also added the benefit of minimizing particle agglomeration. This is another advantage of PTA compared to other preparation methods.
CHAPTER III

RESULTS AND DISCUSSION

In this chapter, the primary mechanism of PTA, background gas effects, as well as the interaction and formation of nanoparticles are described by the characterization of plume dynamics, using optical emission spectroscopy (OES) and photomultiplier tube (PMT) data. Bi-metal nanoparticles synthesized were characterized by X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD) and transmission electron microscopy (TEM).

Plume Dynamics

Plume Photography

Figure 8 shows photographs of the ablation plume along with intensity analysis. The plume photographs clearly show the highly directional nature of PTA and the effects of background pressure. In vacuum, (Figure 8a, 8c and 8e) photographs record the relative weak fluorescence and short plasma expansion (about 0.6 inches in distance). Whereas in five torr Ar, the plasma expands to 1.3 inches in distance for each target (Figure 8b, 8d and 8f) due to raised background gas density.
Figure 8. Photographs of the ablation plume along with intensity analysis for PTA of Fe100 pixel target in (a) vacuum, (b) 5 torr Ar; Fe50-Ni50 pixel target in (c) vacuum, (d) 5 torr Ar; and Ni100 pixel target in (e) vacuum, (f) 5 torr Ar.
Photography adds another dimension to ablation diagnostics by providing two-dimensional snapshots of the three-dimensional plume propagation. A direct comparison of plume intensity between PTA in vacuum and in five torr Ar for each experiment is clearly shown in Figure 8. Raising the background pressure resulted in an increase in fluorescence from all species due to collisions and a slowing of the plume relative to the propagation in vacuum, which led to an increased interaction between two or more target materials. In summary, the background gas density is critical for multi-element nanoparticle formation, but can be readily controlled in PTA.

**Optical Emission Spectroscopy**

Plume dynamics were characterized by optical emission spectroscopy since the laser density required for pixel target ablation usually results in a bright plume extending several centimeters from the target (as shown in Figure 8). The plume was viewed from above and optically imaged at the surface of the target. The optical emission spectra were acquired from experiments with Fe100, Fe50-Ni50 and Ni100 target. In Figure 9, shown as points are the spectra acquired. The spectral intensities increase continuously with increasing wavelength. Shown by the solid curves in the spectra are the best fit to the data using the Plank’s blackbody formula.
Figure 9. Optical emission spectrum recorded from PTA of Fe100 pixel target in (a) vacuum, (b) 5 torr Ar; Fe50-Ni50 pixel target in (c) vacuum, (d) 5 torr Ar; and Ni100 pixel target in (e) vacuum, (f) 5 torr Ar.
Planck’s law states that:

\[ I(\nu, T)d\nu = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu \]  

(1)

In Equation 1, \( I(\nu, T)d\nu \) is the amount of energy per unit surface area per unit time per unit solid angle emitted in the frequency range between \( \nu \) and \( \nu + d\nu \) by a black body at temperature \( T \); \( h \) is the Planck constant; \( c \) is the speed of light in a vacuum; \( k \) is the Boltzmann constant; \( \nu \) is frequency of electromagnetic radiation; and \( T \) is the temperature in Kelvin. Curve fitting to the spectra was carried out for the purpose of determining the extent to which the continuous spectrum can be described as blackbody radiation and therefore process temperature can be estimated. As shown in Figure 9, overall the fits are good and indicate the temperature of the plume to be 2481 K, 2711 K and 2720 K for Fe100, Fe50-Ni50 and Ni100 targets in vacuum respectively. In five torr Ar, they are 2567 K, 2761 K and 2795 K respectively.

The derived temperatures for all experiments are well above the melting point of bulk Fe (1808 K) and Ni (1726 K), and close to the boiling point of bulk Fe (3134 K) and Ni (3005 K), suggesting that the iron and nickel species are mostly in molten droplet form with some possible gas phase at the starting point of ablating plume. It also indicates that a hot environment was provided for particle collision and recombination (the Fe-Ni phase diagram is shown in Appendix A). Thus, addition of a well mixed particle source to the PTA chamber has all the ingredients for multi-element nanoparticle formation. It is also interesting to reflect that, with photolithography made pixel targets, there are almost no limitations to the combination or composition of the particle source.
Time of Flight Analysis

In order to further explore the formation of multi-element nanoparticles, particle kinetic energy distributions were also examined using a photomultiplier tube (PMT). In Figure 10 and Figure 11, the first peak represents the scattered laser light being detected by the PMT, and the second peak indicates the TOF of the fastest species for each experiment. As shown in Figure 10, the speed of the fast species varies for different background gas conditions, while keeping all other variables constant. They are 2116 m/s, 668 m/s and 552 m/s in vacuum, two torr Ar and five torr Ar respectively. In addition to the fastest species, a population of slower species with the speed of around 242 m/s, corresponding peaks centering at 105 us, were shown in all cases.

Figure 10. Photo multiplier tube (PMT) measured speed distribution of nanoparticles formed by TTFA of Fe50-Ni50 pixel target (a) in 5 torr Ar; (b) in 2 torr Ar; and (c) in vacuum.
Due to the relatively small mass of atomic species, e.g., Fe, Fe$_2$, it is safe to conclude that the fast particle peaks correspondent to those gas phase species, and the slow particle peaks represent heavier and bigger molten droplets. Figure 10 is in excellent agreement with the previously mentioned hypothesis that a higher background gas density results in slowing down of the nanoparticles and increasing collision. It is important to note that, although increased collision is favorable in multi-element particle synthesis, more background gas atoms in system could also lead to less final particle collection.

Figure 11 shows the speed distribution of ablated species for different targets with different pixel compositions while keeping Ar pressure at five torr constant. A clear difference in speed distributions is shown for Fe100 target and Ni100 target (Figure 11a and 11c). A doublet is also shown for the Fe50-Ni50 target ablation (Figure 11b), indicating two populations of nanoparticles, with the speed of 181 m/s and 130 m/s respectively, were generated.
Figure 11. Photo multiplier tube (PMT) measured speed distribution of nanoparticles formed by TTFA of (a) Fe100 pixel target; (b) Fe50-Ni50 pixel target; and (c) Ni100 pixel target.

Since the only variable in Figure 11 is the target material composition, the doublet shown is most likely a result of the kinetic energy difference between iron and nickel single metal particles. As previously mentioned, the physical properties of the target materials (atomic mass, thin film density, light absorbance, heat capacity and so on), played an important role in determining the particle kinetic energy and consequently, effects multi-element interaction, partial interaction between the two metals would be expected. However, given the flexibility of the target preparation process, such as pixel size and thickness control for each element, and the fine tune ability of PTA parameters like target-substrate distance, background gas density, and so on, a greater speed match can be and need to be achieved in future works.
Nanoparticle Characterization

Transmission Electron Microscope

Figure 12. TEM micrographs and size distributions of nanoparticles formed by TTFA of Fe50-Ni50 pixel target (a) in vacuum and (b) in 5 torr Ar.

In Figure 12, TEM pictures of Fe50-Ni50 nanoparticles collected on carbon film are shown as a function of Ar gas pressure, together with their corresponding size distributions. For particles made in vacuum, there was a large amount of small particles well dispersed on
carbon film with a narrow size distribution. Mean particle diameters were about 4 nm in
diameter, some big particles sizing 30 to 50 nm were also collected. In the case of five torr
Ar background gas, less nanoparticles, with 10 nm average size and a slightly broader size
distribution were collected, which apparently is a result of increased collisions by greater
Ar density.

It is interesting to note that, in vacuum, well dispersed nanoparticles with virtually no
agglomeration were formed. In the case of five torr Ar, a small amount of agglomeration
was found locally, however, the overall dispersion is still better than other techniques dis-
cussed in the review section and lowering the Ar pressure may help to reduce it even more.
This is a tremendous advantage of PTA over other multi-element techniques. By reduc-
ing the amount of material ablated, the phenomenon of splashing was largely eliminated.
However, not only is the amount of material ablated smaller, it is actually a known amount
since the pixel thickness and size, as well as laser spot size on the target are known, which
makes a number of quantitative experiments for different material combinations possible
and could lead to more exciting explorations.

**X-Ray Photoelectron Spectroscopy**

The composition of nanoparticles were measured by XPS and compared with the target
atom ratio. The collected XPS spectra were analyzed using CasaXPS software. Figure 13
shows the wide-scan XPS spectra of Fe50-Ni50 specimen made in five torr Ar. For ele-
mental composition analysis, the peak areas of the Fe 2p and Ni 2p core level spectra were
measured and the overall composition of Fe and Ni was 41:59. This is consistent with the
approximate target atom ratio of 45:55.
Figure 13. Wide-scan, core level XPS spectra of Fe50-Ni50 nanoparticles made in 5 torr Ar.

A good congruent transformation of Fe-Ni pixel atom ratio to particle composition has been achieved. This is in excellent agreement with our previously mentioned hypothesis that, designed multi-element ratio can be transferred into multi-element nanoparticle composition by direct laser ablation.

For further analysis of the chemical structure of the investigated samples, three areas of the XPS spectrum have been examined by using XPS narrow scan: the Ni 2p region near 853 eV (Figure 14a), the Fe 2p region near 710 eV (Figure 14b) and the C 1s region near...
285 eV (Figure 14c). Most of the metal particles are shown as oxide form as predicted due to the high activity of nanoparticles. Specifically, the main peak from Fe 2p, centered at 712 eV, agrees with the Fe$^{3+}$ 2p$_{3/2}$ spectra from $\alpha$-Fe$_2$O$_3$, and the strong satellite peak of Ni 2p indicating Ni$^{2+}$ state [35]. When scanning the C 1s XPS region, major difference for the specimen carbon and the typical environment carbon binding energy are noted. The binding energy peak of C 1s appears as a doublet. They are centered at 285 eV and 289 eV respectively, which are both greater than the typical binding energy of 284 eV for environment carbon.

Figure 14. Narrow-scan, core level XPS spectra of Fe50-Ni50 nanoparticles made in 5 torr Ar.

It was predicted that the synthesized particles would be in oxide form in air, due to their large surface area resulted high activity. However, the formation of Fe-Ni domains in the particle lattice has not yet been demonstrated, and, therefore x-ray diffraction was also car-
ried out to acquire structural evidence for the formation of Fe-Ni sites. For the narrow scan of C 1s region, according to the handbook of x-ray photoelectron spectroscopy [35], the detected carbon could be attributed to MeCH$_2$NH$_2$ and MeCOOH respectively. The formation of those two compounds can be understood by the fact that para-methoxymethamphetamine (PMMA) was used as photo resists during target preparation process, and methanol was used to clean target organic residual. The fact that photo resist residual was also ablated from the target might have a significant impact on metal particle interaction in plume, as well as kinetic energy distribution. A better organic cleaning process will be adapted for future PTA works.

**X-Ray Diffraction**

The x-ray diffraction patterns for Fe50-Ni50 nanoparticles made in five torr Ar is shown in Figure 15. Lines characteristic of $\alpha$-Fe (bcc) at 2$\theta$ values of 44.67 and 65.02 (PDF card 00-006-0696), as well as that of $\gamma$-Ni (fcc) at 44.37 and 76.08 (PDF card 00-001-1258) both show up as expected. In the mean time, the alloyed form of Fe50-Ni50 peak centered at 43.70 and 50.96 (PDF card 01-071-6116) also appeared in the diffraction patterns, confirming the coexistence of single metal form and alloyed form nanoparticles [36].
XRD provides evidence for the formation of Fe-Ni alloy nanoparticles. In the meantime, single metal nanoparticles were also collected. As mentioned in above sections, partial interaction caused by speed differences and organic residual ablation could be two possible reasons for why this mixture of nanoparticle forms. Detailed kinetic energy distribution study on ablation plume and a better target cleaning process would aid the improvement of particle uniformity in future works. For applications where a mixture of different forms of particles are desirable, PTA of pixel target is a flexible, as well as repeatable technique; providing many possibilities as a bottom-up approach.
CHAPTER IV
CONCLUSION AND FUTURE WORKS

Conclusion

In summary, PTA has shown to be a versatile technique for the creation of bi-metallic nanoparticles that are narrow in size distribution and controllable in composition with no agglomeration. The good congruent transformation of target materials weight ratio to particle composition makes more complex multi-element nanoparticle synthesis possible. PTA, in which TTFA in conjunction with photolithography, has also shown to be valuable for the further exploration and clarification of basic laser ablation mechanism, therefore, benefiting the further discovery and optimization of nanoparticle catalysts.
Future Works

Future works will mainly focus on the relationship between particle kinetic energy distribution and controllable parameters in order to further increase the interaction between two or more target materials and improve particle uniformity. If majority of the particles are alloyed form, a peak shift would occur in XPS [37]. According to the results in this report, thinner pixels, longer substrate-target distance, and reduce background gas pressure (e.g. 100 mtorr), might produce better and more alloyed particles, and consequently will result in a better confirmation. In addition, heated substrate, different target pattern designs, and interactive background gas could definitely lead to more interesting results. The use of mass spectrometer analysis, could reveal more detailed information on ablated species, mass distribution, kinetic energy distribution and charge distribution. Detailed compositional controllability will also be examined in future works.
Figure 16. Equilibrium Fe-Ni phase diagram shows which phases are to be expected at equilibrium for different combinations of nickel content and temperature [38].
APPENDIX B

LASER ENERGY CALCULATION ON TARGET VAPORIZATION

Calculation of how much energy is needed to totally vaporize the target material within the laser footprint was carried out to compare the laser energy density used in PTA experiments [39–41].

Target pixels are 90 micrometers in side length, which means 90% of the laser spot area are filled with thin film pixels with 40 nanometers in thickness \( (h) \). The energy needed to totally vaporize the target material \( (\Delta E) \) from room temperature \( (T_r = 293 \, K) \) is the sum of the energy needed (1) to rise the temperature to the melting point \( (\Delta E_{r1}) \), (2) to melt pixels from solid phase to liquid phase \( (\Delta E_m) \), (3) to rise the temperature to the boiling point \( (\Delta E_{r2}) \), and (4) to vaporize pixel materials from liquid phase to gas phase \( (\Delta E_v) \), as shown in Equation 2 and Figure 17 [42, 43]:

\[
\Delta E = \Delta E_{r1} + \Delta E_m + \Delta E_{r2} + \Delta E_v
\]  

(2)
Figure 17. Energy consumption of pixel target evaporation process.

And:

\[ \Delta E_{r1} = M \cdot C_p^s \cdot (T_m - T_r) \]  
\[ \Delta E_m = M \cdot \frac{\Delta H_{fus}}{m} \]  
\[ \Delta E_{r2} = M \cdot C_p^l \cdot (T_b - T_m) \]  
\[ \Delta E_v = M \cdot \frac{\Delta H_{vap}}{m} \]
Where \( M \) is the mass of pixels within laser spot area, \( C_p^s \) and \( C_p^l \) are the heat capacity in solid phase and liquid phase respectively under atmosphere, \( \Delta H_{fus} \) is the heat of fussion, \( \Delta H_{vap} \) is the heat of vaporization, \( T_r \), \( T_m \) and \( T_b \) are the room temperature, the melting point and the boiling point respectively in kelvins.

For iron element [44], atomic mass (\( m_{Fe} \)) is 56 g/mol; density at 293 K (\( d \)) is 7.87 g/cm\(^3\); specific heat capacity \( C_{Fe}^s = 0.45 \) J/g · K, \( C_{Fe}^l = 0.80 \) J/g · K [45]; heat of fusion (\( \Delta H_{fus,Fe} \)) is 13.80 KJ/mol; heat of vaporization (\( \Delta H_{vap,Fe} \)) is 349.6 KJ/mol; melting point is 1808.2 K and boiling point is 3023 K. For Fe100 target, there are 10,000 pixels within 1 cm\(^2\) laser spot area (a), so the mass of iron pixels (\( M_{Fe} \)) is:

\[
M_{Fe} = a \times 90\% \times h \times d
\]
\[
= 1 \text{cm}^2 \times 90\% \times (40 \times 10^{-7}) \text{cm} \times 7.87 \text{g/cm}^3
\]
\[
= 2.83 \times 10^{-5} \text{g}
\]
From Equation 3, 4, 5 and 6:

\[
\Delta E_{r1,Fe100} = M_{Fe} \cdot C_{p,Fe}^s \cdot (T_m - T_r)
\]
\[
= 2.83 \times 10^{-5} g \times 0.45 J/g \cdot K \times (1808.2 - 293) K
\]
\[
= 0.02 J
\]

\[
\Delta E_{m,Fe100} = M_{Fe} \cdot \frac{\Delta H_{fus,Fe}}{m_{Fe}}
\]
\[
= 2.83 \times 10^{-5} g \times \frac{13.80 \times 10^3 J/mol}{56 g/mol}
\]
\[
= 0.007 J
\]

\[
\Delta E_{r2,Fe100} = M_{Fe} \cdot C_{p,Fe}^l \cdot (T_b - T_m)
\]
\[
= 2.83 \times 10^{-5} g \times 0.80 J/g \cdot K \times (3023 - 1808.2) K
\]
\[
= 0.027 J
\]

\[
\Delta E_{v,Fe100} = M_{Fe} \cdot \frac{\Delta H_{vap,Fe}}{m_{Fe}}
\]
\[
= 2.83 \times 10^{-5} g \times \frac{349.6 \times 10^3 J/mol}{56 g/mol}
\]
\[
= 0.176 J
\]

Therefore, from Equation 2:

\[
\Delta E_{Fe100} = \Delta E_{r1,Fe100} + \Delta E_{m,Fe100} + \Delta E_{r2,Fe100} + \Delta E_{v,Fe100}
\]
\[
= (0.02 + 0.007 + 0.027 + 0.176) J
\]
\[
= 0.23 J
\]
For nickel element [44], atomic mass \( m_{Ni} \) is 59 \( g/mol \); density at 293 K \( (d) \) is 8.91 \( g/cm^3 \); specific heat capacity \( C_{Ni}^s = 0.73 \ J/g \cdot K \), \( C_{Ni}^l = 0.80 \ J/g \cdot K \) [45]; heat of fusion \( (\Delta H\text{fus}_Ni) \) is 17.48 \( KJ/mol \); heat of vaporization \( (\Delta H\text{vap}_Ni) \) is 377.5 \( KJ/mol \); melting point is 1728 \( K \) and boiling point is 3263 \( K \). For Ni100 target, there are also 10,000 pixels within 1 \( cm^2 \) laser spot area, so the mass of nickel pixels \( (M_{Ni}) \) is:

\[
M_{Ni} = a \times 90\% \cdot h \cdot d \\
= 1 \text{cm}^2 \times 90\% \times (40 \times 10^{-7}) \text{cm} \times 8.91 \text{g/cm}^3 \\
= 3.21 \times 10^{-5} \text{g}
\]
From Equation 3, 4, 5 and 6:

$$\Delta E_{r1\cdot Ni100} = M_{Ni} \cdot C_{p,Ni}^s \cdot (T_m - T_r)$$
$$= 3.21 \times 10^{-5} \times 0.44 \times K \times (1728 - 293)K$$
$$= 0.02 J$$

$$\Delta E_{m\cdot Ni100} = M_{Ni} \cdot \frac{\Delta H_{fus,Ni}}{m_{Ni}}$$
$$= 3.21 \times 10^{-5} \times \frac{17.48 \times 10^3 \text{J/mol}}{59 \text{g/mol}}$$
$$= 0.009 J$$

$$\Delta E_{r2\cdot Ni100} = M_{Ni} \cdot C_{p,Ni}^l \cdot (T_b - T_m)$$
$$= 3.21 \times 10^{-5} \times 0.73 \times K \times (3263 - 1728)K$$
$$= 0.036 J$$

$$\Delta E_{v\cdot Ni100} = M_{Ni} \cdot \frac{\Delta H_{vap,Ni}}{m_{Ni}}$$
$$= 3.21 \times 10^{-5} \times \frac{377.5 \times 10^3 \text{J/mol}}{59 \text{g/mol}}$$
$$= 0.20 J$$

Therefore, from Equation 2:

$$\Delta E_{Ni100} = \Delta E_{r1\cdot Ni100} + \Delta E_{m\cdot Ni100} + \Delta E_{r2\cdot Ni100} + \Delta E_{v\cdot Ni100}$$
$$= (0.02 + 0.009 + 0.036 + 0.20) J$$
$$= 0.27 J$$
On Fe50-Ni50 target, the iron-nickel pixel area ratio is 45:55, therefore the mass of iron and nickel pixels are:

\[ M_{Fe} = a \times 45\% \cdot h \cdot d \]
\[ = 1cm^2 \times 45\% \times (40 \times 10^{-7})cm \times 7.87g/cm^3 \]
\[ = 1.29 \times 10^{-5}g \]

\[ M_{Ni} = a \times 55\% \cdot h \cdot d \]
\[ = 1cm^2 \times 55\% \times (40 \times 10^{-7})cm \times 8.91g/cm^3 \]
\[ = 1.75 \times 10^{-5}g \]

Follow the same calculation procedural shown above (Equation 2, 3 and 4), the amount of laser energy needed for Fe50-Ni50 target is:

\[ \Delta E_{Fe50-Ni50} = \Delta E_{Fe45} + \Delta E_{Ni55} \]
\[ = 0.10J + 0.15J \]
\[ = 0.25J \]

Therefore, at least 0.25 J/pulse of laser energy is needed to evaporate the iron pixels within laser spot area on Fe50-Ni50 target.
Given that the transmittance of the fused silica support (A) is 56% in 248 nm wavelength (measured by photodiode), and the energy lost in four mirrors, one lens and one window is about 40%, which means 60% of the laser output reached to the target support. The laser energy output for different targets ($E_{out\cdot Fe100}$, $E_{out\cdot Fe50-Ni50}$ and $E_{out\cdot Ni100}$) needed are calculated:

\[
E_{out\cdot Fe100} = \frac{0.23J}{56\% \cdot 60\%} = 0.68J
\]
\[
E_{out\cdot Fe50-Ni50} = \frac{0.25J}{56\% \cdot 60\%} = 0.74J
\]
\[
E_{out\cdot Ni100} = \frac{0.27J}{56\% \cdot 60\%} = 0.80J
\]

So, theoretically speaking, the laser energy used in this report (600 mJ/pulse) might not high enough to totally evaporate the target materials within one laser spot area, this could result in liquid droplets been ablated instead of individual atoms, which may further lead to the formation of relatively bigger particles, and agreed with the results in this report. Increased laser energy or reduced pixel target thickness will be carried out in future works.


