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Article

Microwave Plasma Production of Metal Nanopowders

Joseph Lik Hang Chau *, Chih-Chao Yang and Hsi-Hsin Shih

Green Energy & Eco-Technology System Center, ITRI South Campus, Industrial Technology Research Institute, Tainan City 70955, Taiwan; E-Mails: WillyCYang@itri.org.tw (C.-C.Y.); Albert.HHShih@itri.org.tw (H.-H.S.)

* Author to whom correspondence should be addressed; E-Mail: jchau@itri.org.tw; Tel.: + 886-6-3847275; Fax: +886-6-3847288.

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Abstract: Metal and metal alloy nanopowders were prepared by using the microwave plasma synthesis method. The microwave plasma was operated in atmospheric pressure at a frequency of 2.45 GHz. The precursor decomposed thermally in the plasma reaction region and the products were then condensed in the heat exchanger, were separated from the gas by the powder filter, and then finally collected in the powder collector. The effect of various processing parameters such as plasma gas, carrier gas, cooling gas, precursor raw materials and feeding rate were studied in this work. Cu, Mo, W, Mo-Ni and Fe-Co nanopowders were successfully prepared by using the microwave plasma synthesis method. The processing conditions can be tuned to manipulate the particle size of the nanopowders.

Keywords: microwave plasma; nanopowders; synthesis parameters

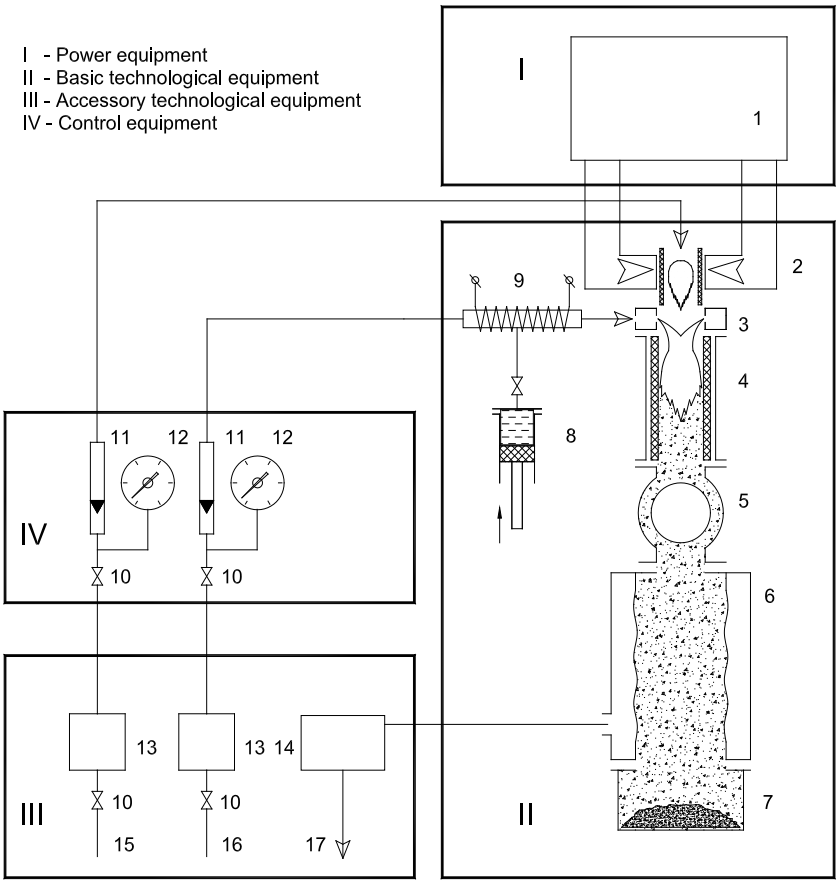
1. Introduction

Metal nanopowders have attracted great attention due to their distinctive properties and uses in optical, electronic, magnetic, and catalytic applications. It has been found that the electronic, optical, and catalytic properties deviate from the bulk metals when the size of the particle decreases to the 1–100 nm range [1–3]. In general, metal nanoparticles can be prepared by numerous methods such as solution-phase chemical reduction [4], UV photolysis [5], metal vapor deposition [6], thermal decomposition [7], sonochemical decomposition [8], electrochemical techniques [9], laser ablation,

sputtering, and ball milling/mechanical attrition [10–12]. Ball milling or mechanical attrition can be applied for metal nanopowder production. However, the process has some disadvantages such as the low production rate and product contamination. The induction plasma method can be employed for metallic nanopowders production, but the process suffers from high-energy consumption and low production efficiency. The microwave plasma synthesis method can be employed for the preparation of metal nanopowders [13]. The rapid evaporation, decomposition and pyrolysis of precursors result in nanopowders of high purity.

The microwave unit used in this study is designed for the production of ultrafine (usually below 100 nm) powders by means of condensation from high-temperature chemically reacting gas flow. Figure 1 shows the schematic drawing of the microwave plasma system. Products can be obtained from the chemical reactions that occur in the flow of oxygen or nitrogen due to the energy of microwave irradiation. Microwave plasma synthesis also shows good stability and can work at normal ambient pressure. The microwave plasma can be operated in atmospheric pressure at a frequency of 2.45 GHz, for which the free space wavelength is $\lambda = 12.24$ cm. This is in fact the frequency for most microwave plasma reactors. The maximum output power of the microwave generator is 5 KW. The synthesis was performed in a reaction tube made of quartz, passing a single mode cavity of a 2.45 GHz microwave system. The high energy microwaves generate plasma by dissociation, ionization, and recombination of gases which transfer the heat necessary for chemical reactions to occur. The thermal energy released during the recombination process can be used for the decomposition of chemical precursors. The complex plasma usually consists of electrons, ions, neutral atoms, molecules or particles and is maintained by collisions from various charged or activated chemical species [14]. In a typical microwave plasma reaction process, the chemical precursor is subjected to rapid heating followed by evaporation, thermal dissociation, and recondensation, which take place in thousandths of a second to produce ultrafine particle sizes. In the microwave plasma, the temperature can be controlled between 300 and 900 °C by selecting the suitable field strength, gas pressure, and gas species. The feeding rate of the precursor materials can be controlled mechanically by changing the size of the relative gears moving in the dosing device [15–17]. The precursor chemically reacts with the plasma species in the gas phase. The chemical reaction yields a highly over-saturated vapor, which yields an ultra-dispersed product upon condensation. The resulting product is then be cooled by the heat exchanger and transported into the collector filter where nanopowders can then be separated from the gas flow. Depending on the residence time in the plasma and other processing parameters, the mean particle size can be adjusted and controlled. The desired particle size can be obtained by manipulating the processing parameters.

Figure 1. Schematic drawing of the microwave plasma process: (1) microwave generator; (2) plasmatron; (3) input attachment for precursor; (4) reactor; (5) heat exchanger; (6) filter; (7) powder collector; (8) dosing device for precursor; (9) evaporator; (10) valves; (11) rotameters; (12) manometers; (13) system for gas purification; (14) scrubber; (15) inlet of plasma forming gas; (16) inlet of gas carrier and (17) outlet of gas.



2. Results and Discussions

2.1. Production of Cu Nanopowders

Nitrogen plasma forming gas (3000 L/h), nitrogen or hydrogen carrier gas (375 L/h for nitrogen or 1375 L/h for hydrogen), and nitrogen cooling gas (2000 L/h) were selected as the standard conditions (*i.e.*, gas and flow rate) for synthesizing Cu nanopowders. $CuCO_3$ powders were used as the precursor raw material. This material was selected because of its dry fine powder property that can easily be delivered into the plasma reaction zone by the dosing device. Most importantly, this material is not moisture sensitive or hygroscopic. The physical characteristics (e.g., solid state or liquid state) of the precursor raw material can become a dominant factor for the successful production of nanopowders by using the microwave plasma synthesis method. Nitrogen was used as the plasma forming gas and cooling gas in this reaction. Transmission electron microscopic (TEM) analysis showed that the Cu nanopowders had an irregular structure (Figure 2a,c). The average particle size observed was about 60 nm. All of the particles had sizes of below 150 nm. The relatively larger particle size observed was due to the higher feeding rate used in the synthesis, *i.e.*, 2.09 mL/min. From the XRD analysis

(Figure 2b,d), the calculated particle size was 77.5 nm, which appears to be a bit larger than the TEM data. From the X-ray diffractometry (XRD) results, a synthetic Cu_2O phase was also present in the sample that reacted in nitrogen (Figure 2d). This was attributed to the $CuCO_3$ raw material that could be completely reduced when only nitrogen gas was used in the reaction. The experiment showed that the Cu_2O diffraction peak could be significantly reduced when applying hydrogen carrier gas as the reducing agent. When introducing hydrogen as the carrier gas, the as-synthesized Cu_2O particles could be further reduced to Cu nanoparticles. From the XRD pattern, only very small amounts of Cu_2O (~5%) still existed in the sample after using hydrogen carrier gas. The synthetic Cu_2O phase could be completely eliminated by using CuCl powder as the precursor raw material as confirmed by the XRD study (Figure 3 b).

Figure 2. (**a**) Transmission electron micrograph of Cu nanopowders prepared using hydrogen carrier gas; (**b**) X-ray diffractometry (XRD) pattern of Cu nanopowders prepared using hydrogen carrier gas; (**c**) Transmission electron micrograph (TEM) of Cu nanopowders prepared using nitrogen carrier gas; (**d**) XRD pattern of Cu nanopowders prepared using nitrogen carrier gas.

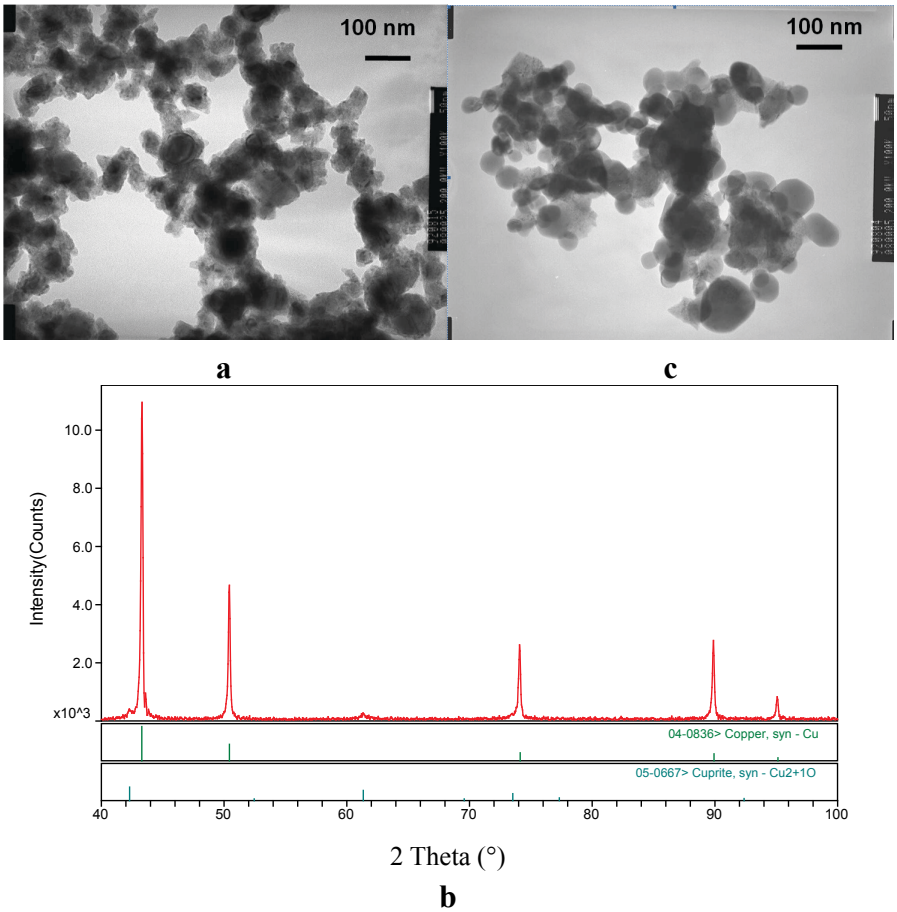


Figure 2. *Cont.*

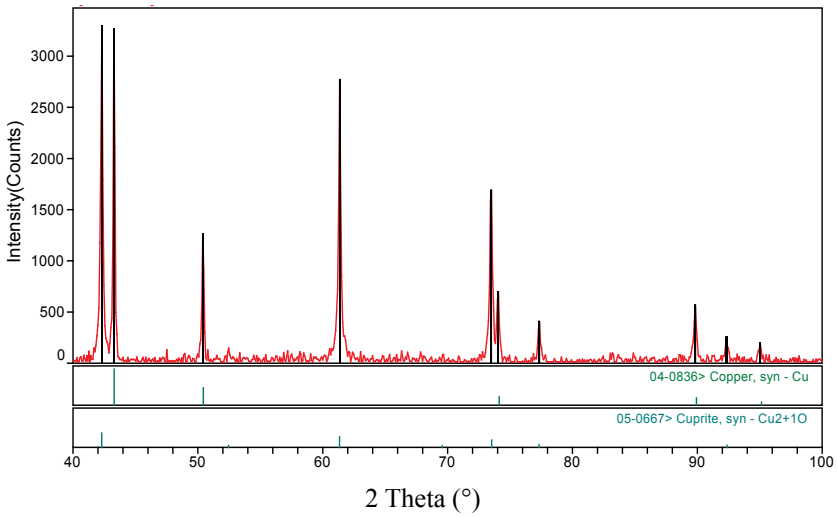


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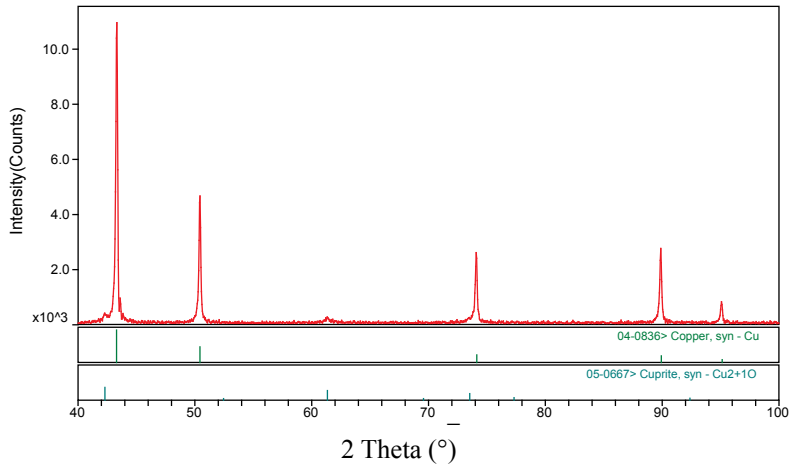
Figure 3. (**a**) XRD pattern of Cu nanopowders prepared using $CuCO_3$ precursor raw material; (**b**) XRD pattern of Cu nanopowders prepared using CuCl precursor raw material.



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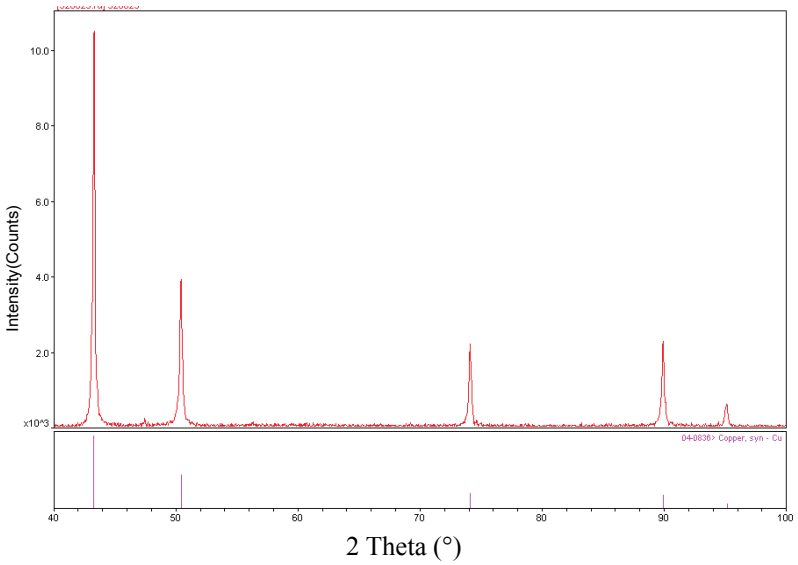
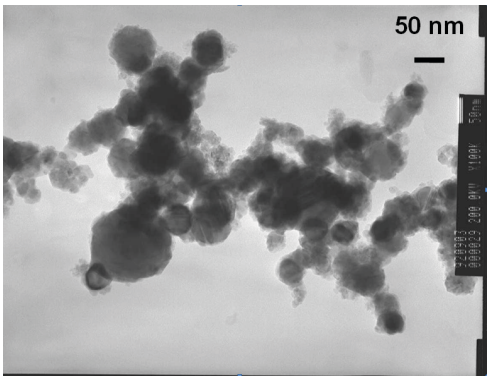


b

Nitrogen plasma forming gas (3000 L/h), hydrogen carrier gas (1375 L/h), and nitrogen cooling gas (2000 L/h) were selected as the operating condition for the large-scale production of Cu nanopowders. $CuCO_3$ powders were used as the precursor raw material. Speeding up the feeding rate of the precursor resulted in larger particles and a higher production rate. The feeding rate chosen in this study was 4.04 mL/min, which is the maximum rate of the powder dosing device. TEM analysis (Figure 4a) showed that the Cu nanopowders produced by the large-scale pilot production did not have a regular shape. The average particle size observed was about 65 nm. Cu particles with sizes larger than 150 nm were not observed. The larger particle size was due to the higher feeding rate used in the synthesis, *i.e.*, 4.04 mL/min. From the XRD results (Figure 4b), small amounts of synthetic Cu_2O phase were also present in the sample (~ 6%). After 4 h of reaction, about 30 g of Cu nanopowders could be collected in the collector bag.

Figure 4. (**a**) Transmission electron micrograph of copper nanopowders produced by large-scale pilot production; (**b**) X-ray diffraction pattern of copper nanopowders produced by large-scale pilot production.



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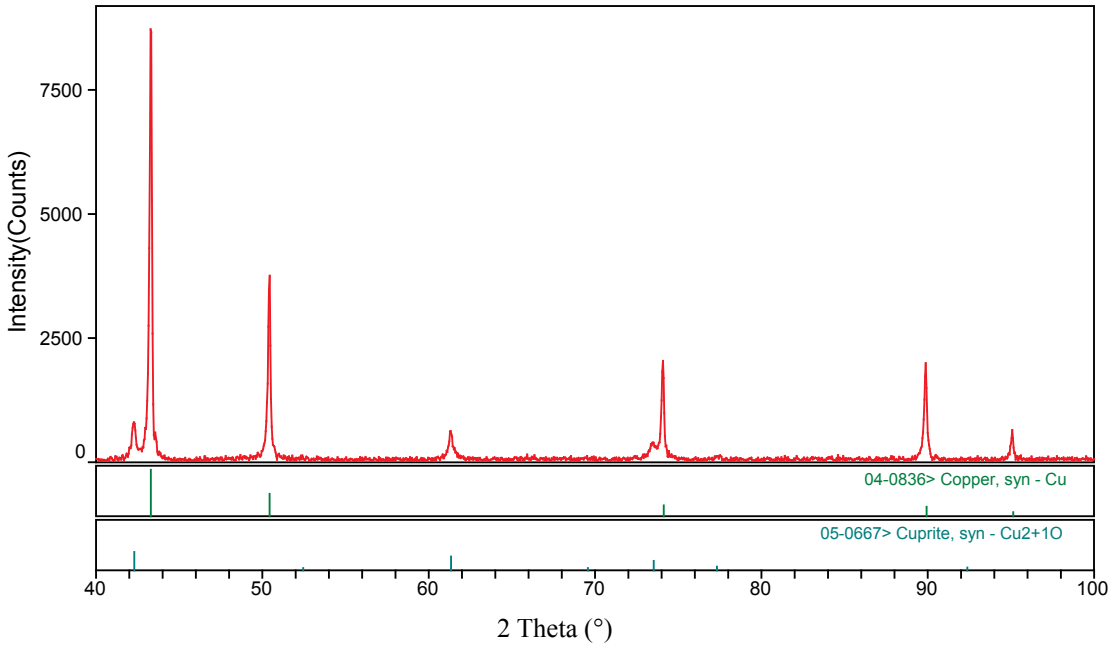

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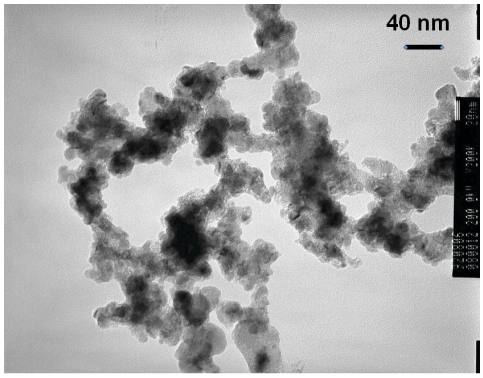
2.2. Production of Mo Nanopowders

Molybdenum nanopowders were successfully synthesized by using the microwave plasma system. $Mo(CO)_6$ was used as the precursor raw material. Nitrogen plasma forming gas (3000 L/h), nitrogen carrier gas (375 L/h), and nitrogen cooling gas (2000 L/h) were selected as the standard condition for synthesizing Mo nanopowders. The $Mo(CO)_6$ can be decomposed completely in the plasma reactor to form Mo particles. Mo monomers or clusters are first formed from the thermal decomposition of $Mo(CO)_6$ powder. These monomers and clusters can be further nucleated to form the Mo nuclei that can then be coagulated to become the Mo nanoparticles. The precursor material feeding rate is the same as synthesizing Cu nanopowders. Because of the fact that $Mo(CO)_6$ can be decomposed more easily than $CuCO_3$, much more nuclei can be formed initially so that the average particle size is significantly smaller than the Cu particles using the same feeding rate condition. Most of the particles have sizes below 50 nm. TEM analysis (Figure 5a) showed that the average particle size was about 20 nm. The particle size obtained from XRD analysis (Figure 5b) was about 42 nm, this value might also include the agglomerated nanosized particles. XRD patterns also showed that the synthesized powders had high crystallinity and confirmed the Mo crystal structure. This study shows that the microwave plasma synthesis can be a conventional method for obtaining Mo nanopowders with high purity.

Figure 5. (**a**) Transmission electron micrograph of Molybdenum nanopowders; (**b**) X-ray diffraction pattern of Molybdenum nanopowders.



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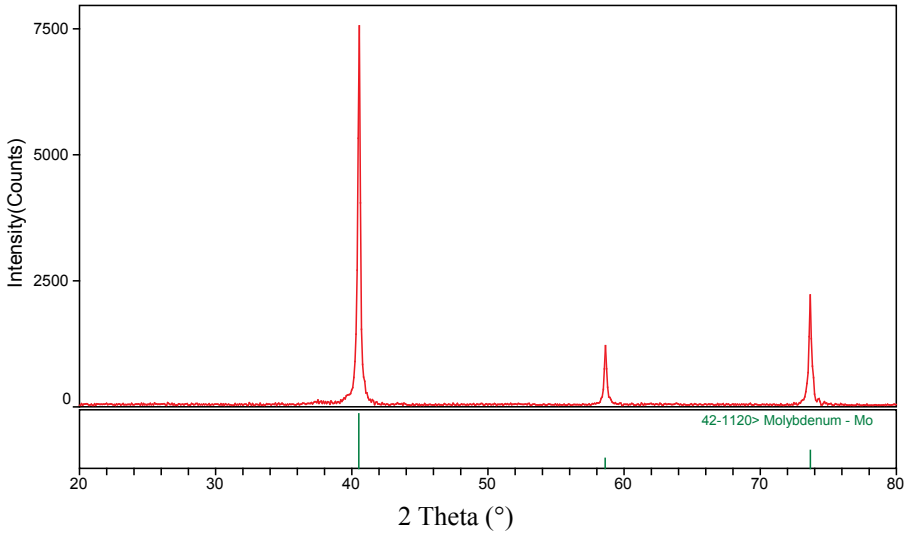

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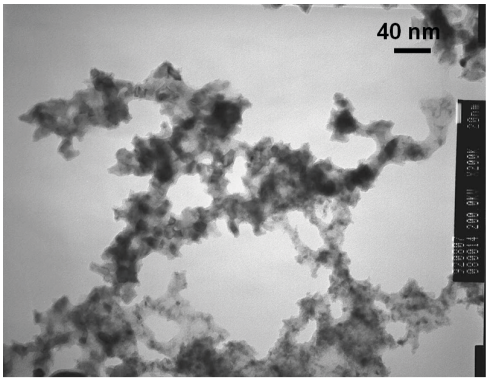
2.3. Production of W Nanopowders

Nitrogen plasma forming gas (3000 L/h), nitrogen carrier gas (375 L/h), and nitrogen cooling gas (2000 L/h) were selected as the standard condition for preparing tungsten nanopowders in this work. $W(CO)_6$ powders was used as the precursor raw material for synthesizing W nanopowders. The precursor feeding rate was 1.06 mL/min which is about half the speed of the Mo feeding rate. The raw material $W(CO)_6$, like $Mo(CO)_6$, can be decomposed easily and completely in the microwave plasma to form W nanoparticles. XRD analysis confirmed the tungsten crystal structure and showed that the product has a high crystallinity. The calculated particle size by using Scherrer's formula is about 30 nm. TEM results showed that all the particles had sizes below 50 nm (Figure 6). Reducing the precursor feeding rate meant decreasing the concentration of raw material in the plasma reaction region which led to a decrease of the nucleation and thus growth rate. The slower transfer rate of the precursor through the plasma reaction zone can increase the reaction time of atoms and molecules within the plasma region so that more products are formed. It should be noted that when using $Mo(CO)_6$ or $W(CO)_6$ as the precursor raw material in the microwave plasma synthesis, a bulk of powder was deposited onto the quartz tube of the reactor, which may be due to the high decomposition rate of the metal carbonyl compound.

Figure 6. (**a**) Transmission electron micrograph of Tungsten nanopowders; (**b**) X-ray diffraction pattern of Tungsten nanopowders.



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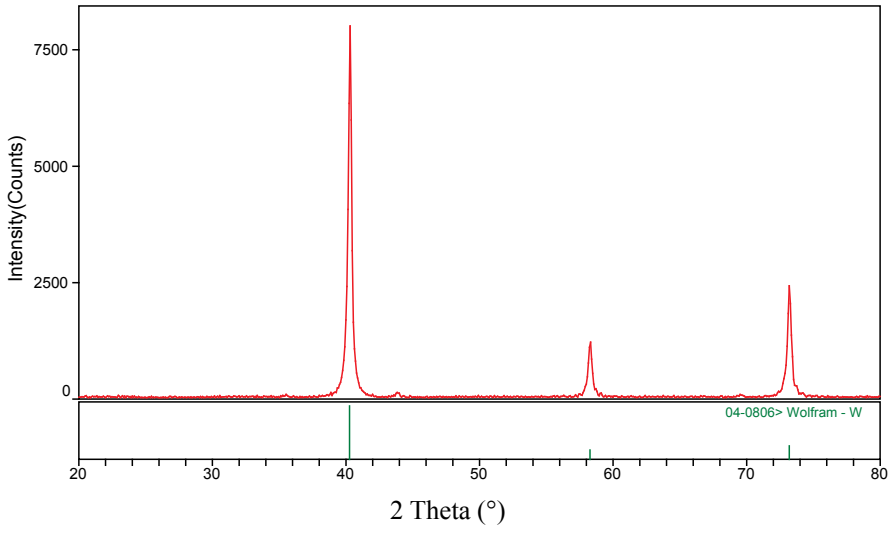

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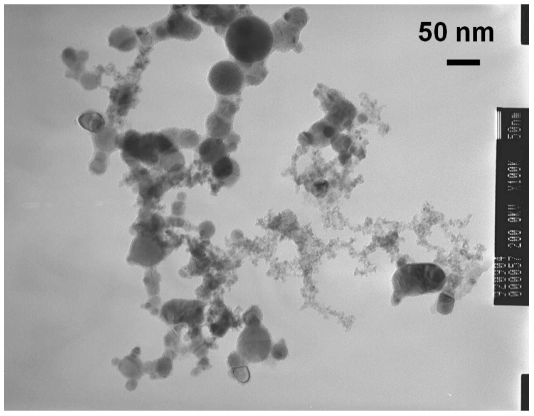
2.4. Production of Mo-Ni Nanopowders

Molybdenum-Nickel (Mo-Ni) bimetallic nanopowders were successfully synthesized using the microwave plasma system. $Mo(CO)_6$ and $NiCl_2$ powders were used as the precursor raw materials for preparing the Mo and Ni nanopowders, respectively. Nitrogen plasma forming gas (3000 L/h), hydrogen carrier gas (1375 L/h), and nitrogen cooling gas (2000 L/h) was selected as the standard operating condition for preparing Mo-Ni nanopowders. $Mo(CO)_6$ and $NiCl_2$ were initially mechanically mixed and put in the dosing device. The precursor materials decomposed simultaneously in the microwave plasma reaction zone to form Mo and Ni particles. TEM analysis (Figure 7a) showed that both small and large particles were present. XRD analysis (Figure 7b) showed that apart from the MoNi alloy phase, both Mo and Ni phases were present in the sample and the crystallinity was much lower than the respective pure metal.

Figure 7. (**a**) Transmission electron micrograph of Molybdenum-Nickel nanopowders; (**b**) X-ray diffraction pattern of Molybdenum-Nickel nanopowders.



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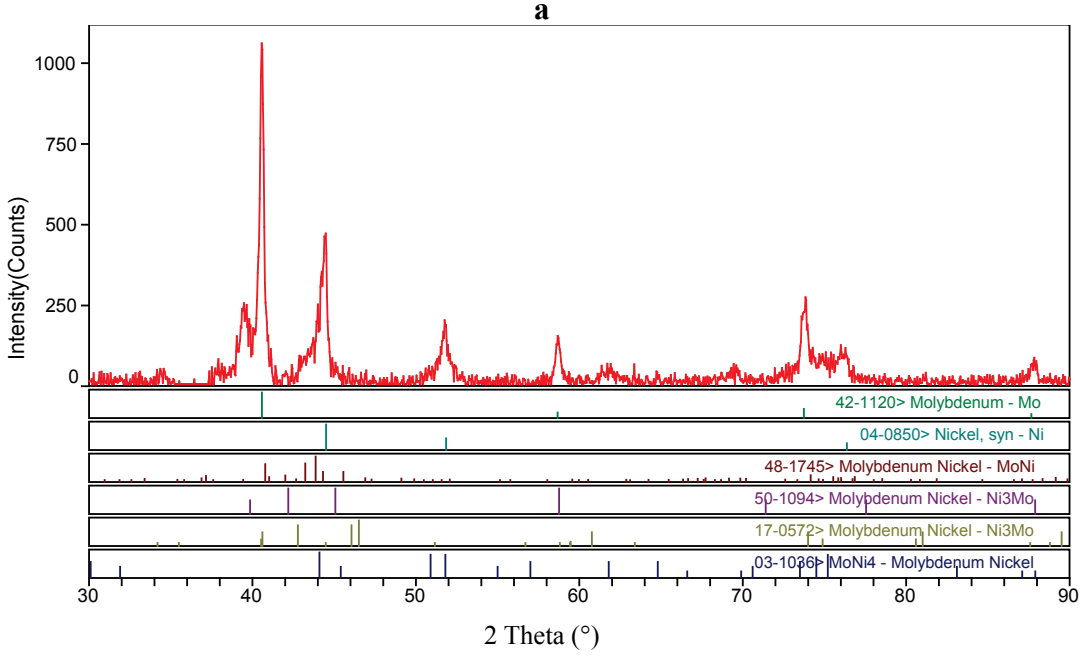

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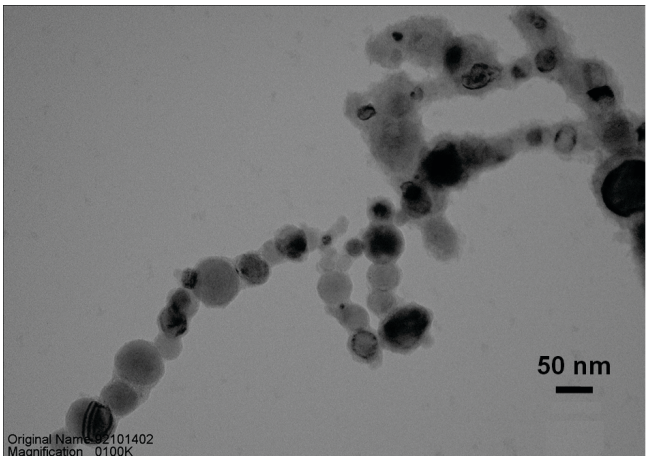
2.5. Production of Fe-Co Nanopowders

The iron-nickel alloy (Fe_xCo_{1-x}) has a high saturation magnetization and a high Curie temperature, which can be used as excellent soft magnetic material and also suitably for high temperature applications. In this study, nitrogen plasma forming gas (3000 L/h), hydrogen carrier gas (1375 L/h), and nitrogen cooling gas (2000 L/h) were selected as the processing condition for synthesizing iron-cobalt nanopowders. The hydrogen carrier gas also serves the role of a reducing agent in the synthesis process. Iron (III) chloride anhydrous powder and cobalt (II) chloride powder were used as the precursor materials and were pre-mixed uniformly with a mechanical method before putting them into the powder dosing device. Traditional paste mortar was used to finely grind the precursor powders in order to uniformly mix the two components. The particle size calculated from the XRD analysis for the sample using the feeding rate of 4.04 mL/min was about 45 nm. XRD characterization also demonstrated that a pure synthetic wairauite CoFe phase was obtained. No particles larger than 100 nm were present as confirmed by the TEM studies (Figure 8). This study showed that high purity and highly crystalline Fe-Co metal alloy nanopowders can be formed through the simultaneous thermal decomposition of $CoCl_2$ and $FeCl_3$ in N_2 atmosphere using H_2 as the carrier and reducing gas. It should also be noted that longer processing times should be avoided because of the hygroscopic property of the $NiCl_2$ precursor that can block the inlet of the solid phase dosing device. We believe that other metal alloys such as Fe-Ni and Fe-Mo could also be prepared using the same method. The Fe-Mo alloy particle is an efficient catalyst for the synthesis of carbon nanotubes with the CVD method [18].

Figure 8. (**a**) Transmission electron micrograph of Iron-Cobalt nanopowders; (**b**) X-ray diffraction pattern of Iron-Cobalt nanopowders.



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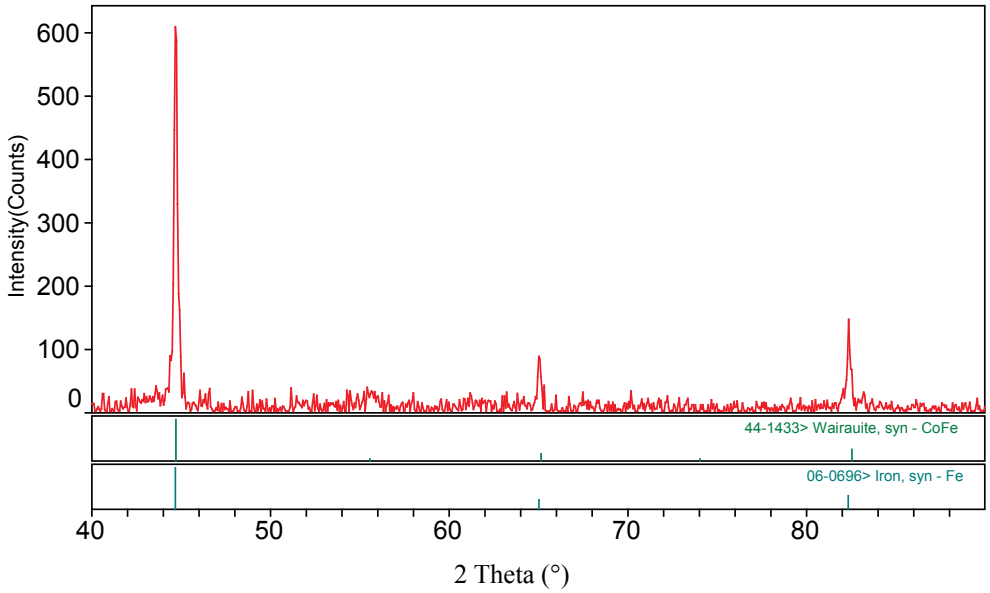

b

3. Experimental Section

During the microwave plasma synthesis of nanopowders, plasma gas, carrier gas, and cooling gas are first purified with a series of gas purifying systems. The precursor material (either liquid or powder) is put into the feed dosing device. The liquid precursor materials must first be heated, evaporated, and injected uniformly into the reaction quartz region by the movement of the carrier gas at a suitable flow rate. The powder precursor is then carried into the reaction quartz tube by the action of the motor fan together with the flow of carrier gas. The feeding rate of the precursor materials can be manipulated by controlling the up-moving rate of the piston in the feeding equipment (Figure 1(8)). The reaction temperature is directly related to the power of the microwave generator that can be controlled by adjusting the actual operating current. For example, during the preparation of metal oxides and nitrides, ionization and dissociation of the precursor species occur in the plasma, the dissociated species reacts to form nitride or oxide molecules. A nucleus can then be formed by the collision of these molecules, followed by the growth of the nuclei by further collisions. Much larger particles are formed by coagulation of the reactive species or molecules. Cooling gas will be used to quench the synthesized particle in order to inhibit further particle growth and minimize coagulation. The precursor is decomposed thermally in the plasma reaction region, and the products are then condensed in the heat exchanger, separated from the gas by the powder filter, and finally collected in the powder collector. Preparation of Cu, Mo, W, Mo-Ni and Fe-Co nanopowders using the microwave plasma synthesis method were studied, and the effect of various processing parameters (e.g., effect of plasma gas, carrier gas, cooling gas, precursor raw materials, and feeding rate) was investigated in this work.

The synthesized nanopowders were characterized by X-ray diffractometer (Philips 1700) equipped with a graphite crystal monochromator for phase analysis. The diffraction pattern was obtained by

scanning at a 2θ step-size of 0.04°. The particle size and morphology were studied by transmission electronic microscopy (JEM 2000EX).

4. Conclusions

This study shows that the microwave plasma synthesis can be a conventional method of obtaining nanopowders with high purity. Metal (Cu, Mo and W) and metal alloys (Mo-Ni and Fe-Co) were produced using the microwave plasma synthesis method. The processing conditions can be tuned to manipulate the structure and average particle size of the nanopowders. Experimental results suggest that the effect of feeding rate, plasma gas, carrier gas, and cooling gas is critical in controlling the particle size during the microwave plasma synthesis process. The as-synthesized pure nanopowders can be used directly and do not need further purification procedures. This technique can be used to prepare other metal alloy systems.

Author Contributions

J.L.H. Chau designed the experiments. J.L.H. Chau and C.C. Yang carried out the experiments. J.L.H. Chau, C.C. Yang and H.H. Shih prepared the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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