Plasma synthesis of metal nanopowders

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DOI: 10.1533/9780857098900.1.69

Abstract: This chapter begins by discussing the benefits and applications of metal nanopowders. This is followed by an introduction of plasma technology and a review of various types of plasma methods used in the synthesis of metal nanopowders. The chapter includes a description of the formation of metal nanopowders by a nucleation and growth mechanism from the vapour phase. Finally, it discusses the relationship between metal nanopowder characteristics (e.g. average size and size distribution) and plasma processing parameters.

Key words: arc discharge, metal nanopowders, nucleation and growth, plasma torch, spark discharge.

4.1 Introduction

Conventional powder metallurgy technology is based on the powders with average sizes between a few and hundreds of micrometres. However, there is a rapidly expanding technology known as nanotechnology that is based on materials with a size scale in the nanometres. These nanoscaled materials are produced in many forms (e.g. thin film, powder or bulk) by various processing methods. In the case of powder form, nanopowders are commonly defined as powders with averages sizes below 100 nm. They have attracted enormous attention because of the flexibility of their use as either the final products or as the precursors in the formation of bulk nanostructured materials. One of the most commonly used methods of producing metal nanopowders is known as plasma synthesis. This is a physical method that converts metals from bulk or powdered forms into nanopowders via evaporation and condensation processes. This chapter gives a review of the production of nanopowders using plasma processing technologies, as well as the potential benefits and applications of metal nanopowders.

4.2 Potential benefits and applications of metal nanopowders

Nanopowders exhibit unique and improved optical, thermal, chemical, electrical and physical properties (El-Sayed, 2001; Feldheim, 2002) compared to corresponding bulk materials. These unique properties allow nanopowders to
have (i) enhanced chemical reaction, (ii) faster sintering kinetics, (iii) higher electrical resistivity, (iv) superparagnetism (Huber, 2005), (v) microwave absorption (Rittner and Abraham, 1998) and (vi) localized surface plasmon resonances (Harra et al., 2012). They are ideal candidates for catalysts, sintering aids, microwave absorption (Rittner, 2002), magnetic recording media, magnetic fluids, magnetic ink (Liu et al., 2002), rocket propellants (Wood and Scott, 2002; Galfetti et al., 2006), conducting ink/paste (Kim et al., 2007), permeable reactive barriers for soil decontamination (Nurmi et al., 2005), biomarkers (Tartaj et al., 2003) and biosensors applications (Harra et al., 2012). Latest advancement in heat transfer fluids, is the development of nanofluids, which are engineered colloidal mixtures of the base fluids and nano-sized metallic particles (1–100 nm). These nanofluids exhibit increased thermal conductivity and improved heat transfer rate, thereby making them very efficient coolant media (Godson et al., 2010; Chopkar et al., 2006).

4.2.1 What is plasma?

Plasma consists of an equal number of positive and negative charged particles (Dendy, 1990), which are produced from either complete or partial ionization of gas atoms or molecules. It is an electrically neutral but conductive medium and it responds to a magnetic field. Therefore, plasma is considered to be the fourth state of matter because it has properties unlike other states of matter, such as solid, liquid and gas. Plasma can be classified into thermal or non-thermal plasma depending on relative temperatures between the electrons, ions and neutral particles. When a thermal equilibrium is reached between the electrons and heavy particles and the temperatures of electrons and heavy particles are kept the same, this is known as thermal (‘hot’) plasma. A non-thermal (‘cold’) plasma occurs when the electron temperature is much hotter than those of ions and neutral particles (e.g. usually at room temperature). In both thermal and non-thermal plasma, the electron temperature can reach several thousand degrees celsius. Hence, conventional material manufacturing processes such as cutting, welding and coating applications have used the intense heat source provided by thermal plasma. The advent of nanotechnology has opened up another use of thermal plasma in the processing of metal nanopowders. This review is focussed on the synthesis of metal nanopowders using a plasma source generated from electrical arc discharge, spark discharge and radio frequency discharge processes.

4.3 Electrical arc discharge synthesis of metal nanopowders

There have been many research activities into the use of electrical arc discharge to produce metal nanopowders. An electrical arc discharge is an
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4.3.1 Transferred arc plasma in gaseous atmosphere

For the transfer arc plasma, the anode electrode material is made from metal (e.g. Al, Cu, Fe, Co, Ni etc.) and is consumed in the synthesis of metallic nanopowders. The anode material is placed inside a crucible made from either graphite or copper. A copper crucible requires water cooling to avoid excessive heating. The cathode electrode is made from tungsten and is a non-consumable electrode. A gas (e.g. Ar, N₂, He, H₂) is introduced into the process chamber (Fig. 4.1) and the plasma is maintained between electrodes in a small spacing less than 5 mm. Water cooling of the chamber wall is essential to avoid excessive heat transfer via conduction, convection and radiation from the high temperature thermal plasma (Tanaka and Watanabe, 2008).

The plasma heats up the anode material to above its boiling point. This leads to the evaporation of the anode material and subsequent cooling of metal vapour by collision with the background gas species. This reduces the diffusion rate and develops a supersaturated vapour, where the metal atoms diffuse around and collide with each other to form clusters of nuclei. Homogenous nucleation from the supersaturated vapour results in the formation of a nucleation zone and more nuclei are formed, some of which are rapidly cooled and combine to form primary particles by Brownian coagulation and an agglomeration growth mechanism (Lunden and Flagan,
1995; Weber and Friendlander, 1997), thereby developing the growth zone. Figure 4.2 illustrates the evolution of nanopowders from the electric arc discharge process.

Figure 4.3(a) shows typical spherical copper nanopowders produced using the electric arc discharge method operated at an applied current of 10 A, an electrode gap spacing of 5 mm and 10 slpm (standard l min$^{-1}$) of nitrogen gas at atmospheric pressure. The primary particle size is below 100 nm, as shown in the log-normal cumulative size distribution plot (Fig. 4.3(b)).

The size of nanopowders increases with increasing applied current but decreases with increasing electrode gap spacing (Forster et al., 2012). The increasing current enhances the energy input of the arc to the system and raises the temperature of the anode metal target. This leads to higher vapour pressures and higher vapour concentrations, which in turn results in the growth in the primary particle size, as well as agglomerate size. However, an increase in the electrode gap spacing generates a greater length of the plasma, accompanied by a linear rise of the arc voltage and increasing energy input to the system. The expansion of the plasma causes the ‘surface’ of plasma to enlarge and radiation heat losses. Therefore, only part of additional energy input is available for heating the molten metal. Furthermore, a large plasma volume dilutes the metal vapour and reduces the metal vapour concentrations, which in turn causes a shrinking mean particle size and less agglomeration of the nanopowder. The size of nanopowder is also influenced by the gas flow rate and gas composition. The larger gas flows enhance quenching of vapour, reduce particle concentration and therefore slow down growth and agglomeration kinetics, leading to smaller primary particle sizes. The change of gas from Ar to N$_2$ increases both the temperature and voltage of the arc.

4.2 Schematic diagram of the evolution of metal nanopowders from the vapour phase.
plasma, increasing the input energy to the system and enhances the melting and evaporation processes (Savas and Ceyhun, 2011). This results in large particle sizes similar to the particle growth caused by increasing the arc.
current. Active hydrogen atoms generated in the arc plasma can also enhance the evaporation rate (Lee et al., 2010). This is due to the hydrogen atoms dissolving in the molten metal and forming bubbles. The recombination of atoms releases exothermic heat and raises the temperature of melt. Furthermore, the release of bubbles as they reach the surface enhances the evaporation area, leading to a higher evaporation rate. Consequently, this results in coarse particles size owing to increasing growth and agglomeration. Transferred arc plasma in gaseous atmosphere has been used to produce nanopowders from a range of metallic systems, as summarized in Table 4.1. The nanopowders are usually collected as dry powders using filters.

### 4.3.2 Transferred arc plasma in liquid medium

The replacement of the gaseous atmosphere with a liquid medium has led to the creation of a submerged arc discharge method for the production of nanopowders. This is done by submerging the transferred arc plasma in a liquid medium (e.g. water, ethylene glycol or cryogenic liquid) to enhance the quenching of metal vapour owing to a higher heat transfer coefficient compared with a gaseous atmosphere. In addition, this method enables the production of a colloidal solution, containing nanopowders dispersed in a liquid medium, in a single step operation. Figure 4.4 shows various types of metal nanopowders produced by submerged arc discharge in cryogenic liquid (Chang and Ren, 2004) using currents of up to 60 A. The primary particles are spherical and have a median size below 100 nm. The primary particle size increases with increasing current owing to enhanced input energy of plasma to the system, which encourages growth and agglomeration.

Ashkarran (2011) has reviewed the production of various metallic (e.g. Ag, Au) nanopowders using submerged electrical arc discharge in water. However, water decomposition (electrolysis) can occur during the production of gold nanopowders by arc discharge in water. Consequently, gaseous hydrogen and oxygen are formed in the water as small bubbles partly dissolved in

<table>
<thead>
<tr>
<th>System</th>
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<tbody>
<tr>
<td>Cu</td>
<td>Forster (2012); Wei et al. (2006); Kassaee et al. (2010)</td>
</tr>
<tr>
<td>Al-Mn</td>
<td>Lee et al. (2010)</td>
</tr>
<tr>
<td>Ag</td>
<td>Chen et al. (2007)</td>
</tr>
<tr>
<td>Co-Cr</td>
<td>Ma et al. (2005)</td>
</tr>
<tr>
<td>FeCoNiAl</td>
<td>Geng et al. (2005)</td>
</tr>
<tr>
<td>Fe, Fe-TiN</td>
<td>Sakka et al. (2002)</td>
</tr>
<tr>
<td>Ni-Cu</td>
<td>Song et al. (2010)</td>
</tr>
<tr>
<td>Co</td>
<td>Meng el al. (2012)</td>
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the water. The gold nanopowders are negatively charged by electrons from the cathode during the arc discharge process, which in turn saturate with atomic oxygen and create hydrogen bonds with water particles in a water
environment. As a result, negatively charged 15–35 nm gold nanopowder micelles are formed in the water medium (Lung et al., 2007) owing to hydrogen bonding between the water molecule and the gold nanopowder. Hence a stable suspension is achieved without any stabilizers and surfactants.
because the negatively charged gold nanoparticles are surrounded by water molecules. Ethylene glycol is another liquid medium that can interact chemically with the aluminium nanopowders formed by the submerged arc process. The ethylene glycol protects the particles’ surface against oxidation and self-ignition on exposure to air, as well as serving as a solvent, coating and/or stabilizing agent where the particles are capped by the ethylene glycol molecules, thereby giving monodispersed spherical Al nanopowders with a relatively small size of 26.6 nm (Kassaee and Buazar, 2009).

So far only noble metal nanopowders can be produced using submerged arc discharge in water. However, the use of inert cryogenic liquid can offer the production of a wide range of metal nanopowders.

### 4.3.3 Spark discharge method

Electrical arc discharge in both gaseous and liquid media yields metal nanopowders with a polydispersed size distribution. A spark discharge method has been developed to produce nanopowders with a narrow size distribution (Vons et al., 2010; Tabrizi et al., 2009). In this method, a high voltage power supply is used to charge a capacitor bank which is connected in parallel to a spark gap between two metal electrodes of the material required to be converted into nanopowders, as shown in Fig. 4.5. Several kilovolts are required to cause an electrical breakdown of the gas between electrodes, over a very short time (<10 ms) interval (i.e. spark discharge), owing to the rapid release of the store energy in the capacitor bank. This results in very high temperatures typically of the order of 20 000K, which is sufficient to evaporate a small amount of the metal electrodes with subsequent condensation of the vapour into metal nanopowders by the surrounding cooling gas. These powders have mean primary particle sizes below 10 nm and are carried away by the inert gas and collected by filters. Several hundreds of discharges per
second \( (f_s) \) can be generated depending on the current used to charge the capacitance bank according to:

\[
f_s = \frac{I}{CV_b}
\]

where \( I \) is the applied current (mA), \( C \) is the capacitance (nF) and \( V_b \) is the breakdown voltage (kV) of gas. If we assume \( V_b = 4 \text{ kV} \), \( I = 10 \text{ m} \) and \( C = 10 \text{ nF} \), then an \( f_s \) of 250 Hz can be obtained.

The mean primary particle size remains constant as the gas flow rate increased from 5–10 slpm. This is attributed to the fact that particle formation is essentially completed in the high concentration laminar flow region between the electrodes, where dilution is dominated by diffusion and is thus flow independent. Hence the particle diameter that develops in this region is close to the primary particle diameter. However, at very low flow rates below 5 slpm, there is more time for newly formed particles to coagulate in the low-concentration turbulent dilution region outside the electrode gap, resulting in the coarsening of primary particles (Tabrizi et al., 2009a). An increase of the electrode gap from 0.5–3 mm leads to a reduction in evaporation rate due to the increasing volume of the plasma. The mean diameter of primary particle increases with increasing electrode spacing owing to a higher vapour loading (Lehtinen and Zachariah, 2002). The increase in capacitance results in an increase in the spark energy and leads to higher vapour loading in the particle growth region. Consequently, the mean diameter and particle concentration increase with the capacitance. Finally, the spark frequency increases linearly with the nanopowder production rate. However the size distribution widens with increasing repetition frequency as a result of coagulation. At a higher frequency, more coagulation takes places at high concentration before dilution is completed, leading to coarsening of particles. Table 4.2 lists a range of metal nanopowders that have been produced by the spark discharge method.

The transferred arc plasma method offers an ideal research tool for the production of nanopowders from a range of metal and alloy systems using relatively low cost equipment. However, transferred arc plasma methods based on a single pair of electrodes are limited to a small production yield.

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<th>System</th>
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<tr>
<td>Pd</td>
<td>Vons et al. (2010)</td>
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<tr>
<td>Au</td>
<td>Tabrizi et al. (2009a)</td>
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<tr>
<td>Cr-Co, Au-Pd, Ag-Pd</td>
<td>Tabrizi et al. (2009b)</td>
</tr>
<tr>
<td>Ag-Cu, Pt-Au, W-Cu</td>
<td>Tabrizi et al. (2010)</td>
</tr>
<tr>
<td>Al, Cu</td>
<td>Bau et al. (2010)</td>
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at a rate of a few milligrams to a few grams per hour depending on the type of material and processing conditions. A recent report using a multiple-electrode configuration in an arc discharge process has dramatically increased the production yield to 329 g h\(^{-1}\) (Meng et al., 2012) for the production of cobalt nanopowders. Hence, further development is needed to scale up this method for industrial scale production of nanopowders.

4.3.4 Non-transferred arc plasma in a gaseous atmosphere

In the non-transferred arc method, the anode converts into a nozzle and the plasma can extend beyond one of the electrodes in the form of a plasma jet by gas at a relatively high flow rate. As a result, the electrodes do not participate in the process but have the sole function of plasma generation. Figure 4.6 shows a schematic diagram of a non-transferred arc plasma torch set up for metal nanopowder production. Non-transferred arc plasma torch technology has been developed since the 1970s for deposition of ceramic and hardmetal coatings, chemical waste destruction (Selwyn et al., 1999) and spheriodisation (Kumara et al., 2006) of metal and ceramic powders.

The electrodes used in a non-transferred arc torch are generally water cooled. Non-transferred arc torches are available commercially with levels of power between 1 kW and 6 MW (Heberlein, 1992). The heating efficiency ranges between 50% and 90% and increases with an increase in gaseous flow, which is much higher than in the transferred arc plasma process. This leads to an increase in both equipment and maintenance costs. Gases, liquid reactants or solid feedstock are injected into the plasma to produce gaseous species by either a chemical reaction or an evaporation process. These vaporized species react with either the plasma gas or a quenching gas in the condensation region outside the plasma jet. A high cooling rate of quenching
gas or a fast expansion of the plasma jet encourages homogeneous nucleation. This is followed by coagulation and agglomerate growth processes, producing nanopowders (Fauchais et al., 1997).

A 7–9 kW dc plasma torch is insufficient to cause complete evaporation of a micrometre-sized silver powdered feedstock delivered at a rate in excess of 2 g min\(^{-1}\). This leads to the formation of sub-micrometre silver powders with sizes exceeding 100 nm (Lee et al., 2007). However, the introduction of H\(_2\) gas of up to 0.9 l min\(^{-1}\) (lpm) into 15 lpm of Ar plasma gas can reduce the primary particle size of Ag nanopowders to below 100 nm. H\(_2\) gas enhances the heat transfer owing to high thermal conductivity and H\(_2\) plasma gives a higher reactivity than molecules in the gas state (Matsumoto and Kobayashi, 1987; Akatauka et al., 1988). Therefore, the raw silver powder feedstock can be evaporated completely when H\(_2\) gas is mixed into Ar plasma gas. In addition to Ag nanopowders, FeAl nanopowders processed by a dc plasma torch have been reported. 30–70 nm sized FeAl nanopowders are formed after passing the micrometre-sized FeAl powders at a rate of 14 g min\(^{-1}\) into a 15.3 kW dc plasma torch using an Ar/N\(_2\) mixture of 221:31 lpm ratio, respectively (Suresh et al., 2008).

However, problems of clogging and cooling of the plasma jet occur when the solid particles are inserted into the plasma jet at the nozzle exit. A central injection is developed to improve the particle feeding into the plasma jet by using a multiple-cathodes configuration system (Marques et al., 2009), as shown in Fig. 4.7. The cathodes require three power supplies and the anode is either a graphite or water-cooled copper ring. Hence, it is important for efficient insertion of powder feedstock and sufficient heating by the plasma jet to enable complete evaporation of the powder feedstock during the synthesis of nanopowders. At the moment, there is a very limited published work on the effects of the processing conditions of a dc plasma torch on the evolution of metal nanopowders. However, an industrial company such as Intrinsiq Nanomaterials Limited (Intrinsiq Nanomaterials Limited.

![4.7 Schematic diagram of a multiple-cathode configuration plasma torch with central powder injection.](image-url)
http://www.intrinsiqmaterials.com/Materials.html.) has made use of a twin dc plasma torch technology, known as ‘TESIMA’ to generate a wide range of metal nanopowders (e.g. Al, Ag, Cu, Ni, W, stainless steel, Co, Ti, Mo) at production rates of kilograms per hour, depending on material and processing conditions.

Metal nanopowders have been produced using radio frequency (RF) plasma torches. These torches are inductively coupled discharges, generated by suitable coils connected to RF power supplies ranging from 30–600 kW operating at working frequencies between 200 kHz and 40 MHz. Figure 4.8 shows a schematic diagram of an RF plasma torch apparatus comprising induction coils, confinement tube, gas distributor (e.g. torch head) and injection probe. The induction coils provide the electromagnetic field to couple the energy to the plasma. The confinement tube is to confine the plasma and is made from an air-cooled quartz (Power <10 kW), a water-cooled quartz (Power <30 kW) or a water-cooled ceramic (30<600 kW). The gas distributor introduces different gas streams into the discharge chamber: sheath gas to protect the walls and a central plasma-forming gas. A water-cooled central injection probe is positioned through the torch head and allows the introduction of gaseous reactants or powders into the central part of the discharge region. This enables either chemical reaction or evaporation of the feedstock to form gaseous species, which are condensed into nanopowders by a quenching gas. The plasma gas does not come into contact with electrodes, thus eliminating possible sources of contamination and allowing the operation of such plasma torches with a wide range of gases including inert, reducing, oxidizing and other corrosive atmospheres. Tekna Plasma Systems Inc. is an equipment
manufacturer in Canada, which supplies turn-key RF plasma torch facilities for the production of nanopowders (Boulos, 2004).

The amount of 40 μm sized copper powder feedstock evaporated is found to increase with increasing feed rates from 0.33–3.5 g min⁻¹ in a 40 kW RF plasma torch using Ar central gas and Ar+H₂ sheathing gas. Consequently, the average size of plasma processed copper nanopowder increases from 50–280 nm with increasing evaporation rate. This is because of a higher supersaturation of vapour, which leads to greater homogeneous nucleation and heterogeneous condensation, giving coarser nanopowders (Kobayashi et al., 2008). The residence time of copper powder feedstock in the high-temperature region increases with increasing plasma reactor chamber pressures from 39–67 kPa. This leads to an increase in powder evaporation and an increasing amount of copper vapour. A high degree of supersaturation is produced and heterogeneous condensation occurs increasing the size from 139–250 nm at 39 kPa and 67 kPa, respectively. The amount of evaporated copper powder feedstock also increases with increasing H₂ flow rate. This is because of the increase in heat transfer by the introduction of more H₂ gas into the plasma.

Zhang (Zhang et al., 2012) has produced tungsten nanopowders by reacting 20–150 μm sized ammonium paratungstate powder feedstock in a hydrogen plasma provided by a 30 kW RF plasma torch. The reduction of ammonium paratungstate by hydrogen is found to be dependent on the rate of powder feedstock. Only metallic alpha-tungsten nanopowders are produced at a relatively small feed rate of 19 g min⁻¹. As the feed rate increases to 26 g min⁻¹ or higher, additional non-equilibrium beta-tungsten and tungsten oxide phases are found to coexist with the alpha-tungsten phase. The reductive process of ammonium paratungstate to metallic tungsten is an endothermic process and when excess ammonium paratungstate is injected into the plasma flame, it has difficulty in absorbing enough energy and reacting completely. This leads to the formation of tungsten oxide. Finally, the average size of tungsten nanopowder can be reduced from 30–20 nm by increasing chamber cooling. This improves the quenching of vapour species, inhibiting the growth and agglomeration process. A similar approach has been used to produce 60–100 nm sized nickel nanopowders by hydrogen reduction of nickel hydroxide or carbonate using hydrogen plasma provided by an RF plasma torch (Bai et al., 2009).

4.4 Conclusions

The thermal plasma technologies offer a flexible and scalable platform for the production of nanopowders from a range of metal and alloy systems, without the need for post-purification or waste handling needed by other chemical synthesis routes. They can produce metal nanopowders that have primary
particle sizes below 100 nm with either monodispersed or polydispersed particle size distribution. The as-produced nanopowders can be collected as dry powders or suspensions in liquid media. The technologies can also be applied to other nanomaterials including oxides, carbides, nitrides and composites.

4.5 References


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