Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Letters 60 (2006) 766–770
materials letters
www.elsevier.com/locate/matlet

Efficient preparation for Ni nanopowders by anodic arc plasma

Zhiqiang Wei [a,b,*], Tiandong Xia [b], Lifeng Bai [c], Jun Wang [c], Zhiguo Wu [c], Pengxun Yan [c]

[a] School of Sciences, Lanzhou University of Technology, Lanzhou, 730050, PR China
[b] College of Materials Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, PR China
[c] Institute for Plasma and Metal Materials, Lanzhou University, Lanzhou 730000, PR China

Received 2 April 2005; accepted 3 October 2005
Available online 24 October 2005

Abstract

Sphere-shape nickel nanopowders were successfully prepared at high rate (up to 1.3 g/min) by anodic arc discharge plasma method. The morphology, crystalline structure, particle size and specific surface area of the samples were characterized via X-ray diffraction (XRD), transmission electron microscopy (TEM) and the corresponding selected area electron diffraction (SAED), and Brunauer–Emmett–Teller (BET) surface area analysis. The influences of the technology parameters on the yield rate and particle size of Ni nanopowders were studied, and the referential process parameters were obtained. The experimental results indicate that the crystal structure of the samples is FCC structure as same as that of the bulk materials. The specific surface area is 14.23 m^2/g, with the particle size distribution ranging from 20 to 70 nm, the average particle size about 47 nm obtained from TEM and confirmed from XRD and BET results. This technique is a convenient and effective method to prepare high quality nanopowders with uniform size, higher purity, narrow size distribution and spherical shape. The yield rate and particle size increase with the increase of the arc current or gas pressure when other factors are fixed.

Keywords: Anodic arc plasma; Ni nanopowders; Properties; Technology parameters

1. Introduction

Metal nanopowders exhibit unique physical and chemical properties that differ considerably from those of bulk solid state [1–4]. In recent years, metal nanopowders have been intensively investigated due to the technological importance, theoretical interest and various high performance applications, such as catalysts, ferrofluids, microwave devices, low temperature sinterable, high strength ceramics, high-dense magnetic recording materials, and lubricants [5–7]. Accordingly, the preparation and characterization for metal nanopowders has become an active field. Various techniques have been developed to prepare metal nanopowders, such as gas-phase chemical reaction [8], spray pyrolysis [9], water-heating reaction [10], laser ablation [11], flame processing [12], vapor deposition [13], microwave plasma synthesis [14], and sol-gel method [15]. However, these methods have some limitations. For example, gas-phase chemical reaction and water-heating reaction require a lower reaction temperature with the potential of low cost production, but fail in producing high quality nanopowders, and cannot suitable for mass-production. Sol-gel method can produce nanopowders at low cost, but this process-related contaminants are introduced during powder preparation. Microwave plasma synthesis technique can produce high quality nanopowders, but it is limited by the lack of scalable production technique for large quantities of non-agglomerated powders. Spray pyrolysis produces either large particle or aggregates nanopowders. Other processes such as laser ablation requires specialized high power laser equipment, vapor deposition requires ultra-high vacuum systems, resulting in added cost and complexity, thus severely limiting the potential of the producing metal nanopowders.

Arc discharge plasma method is a mature and advanced materials processing technique, which has been widely used to prepare metal nanopowders in the past [4,16]. In the process, a high temperature plasma jet is used to melt and vaporize the bulk metal, metal nanopowders formation from a supersaturated vapor in a narrow zone above the evaporation source by homogeneous nucleation followed by growth via condensation

* Corresponding author. School of Sciences, Lanzhou University of Technology, Lanzhou 730050, PR China. Fax: +86 931 2755806.
E-mail address: zqwei7411@163.com (Z.Q. Wei).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.10.008

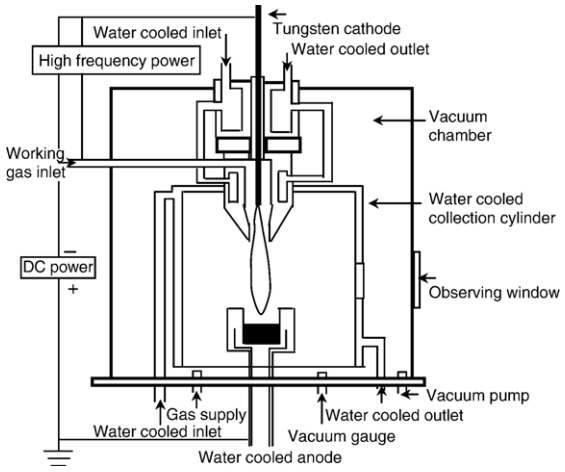

Fig. 1. Schematic diagram of the experimental installation.

and coagulation. This technique has many special characteristics, such as high enthalpy density, high temperature, high velocity, active environment and extremely high heating and cooling rates. These characteristics can be advantageously used in producing metal nanopowders. However, they require high power supply equipment, and commercial exploitation is limited by high synthesis cost, making them not suitable for mass production in the industry. Furthermore, the nanopowders properties cannot be improved by varying the technological parameters.

From a practical viewpoint, it is vital to develop a way to manufacture high quality nanopowders at high throughput with low cost. For this reason, an effective technique has been developed in our laboratory to prepare metal nanopowders. Some metals have been successfully prepared and there are sufficient evidence to state that this technique is a prospective production route insuring both controlled parameters and mass production. Some advantages are as follows: (1) our process is a convenient and inexpensive industrial process and operates in an inert atmosphere and no process-related contaminants are introduced during powder preparation; (2) the nanopowders prepared by this method have ultrafine particle size, higher purity, narrow size distribution and spherical shape; (3) most notably, the physical and chemical properties can be easily improved by varying the technological parameters (e.g. the type of inert gases, the ambient gas pressure, the arc current intensity, water-cooling condition and other factors) and it offers the possibility of obtaining nanopowders with desired properties; (4) major advantages include its cheap raw materials, ease of handling and suitability for mass production in the industry. In this work, we report on the high rate production of Ni nanopowders using anodic arc discharging plasma technique in an inert atmosphere. In addition, the samples were characterized via X-ray diffraction (XRD), transmission electron microscopy (TEM) and the corresponding selected area electron diffraction (SAED), Brunauer–Emmett–Teller (BET) surface area analysis. Moreover, the variation of yield rate and average particle size of the sample with arc current, type and pressure of the inert gases were investigated carefully and the optimal technology parameters were obtained.

2. Experimental

The schematic diagram of the experimental installation designed to obtain metal nanopowders is presented in Fig. 1. The apparatus mainly include the stainless steel vacuum chamber, the gas supply device, the DC power supply, the plasma generator with a high frequency initiator, the vacuum pump, the water-cooled collection cylinder, the water-cooled copper crucible with a diameter of 20 cm mounted in an electrically insulated manner and connected to the arc current

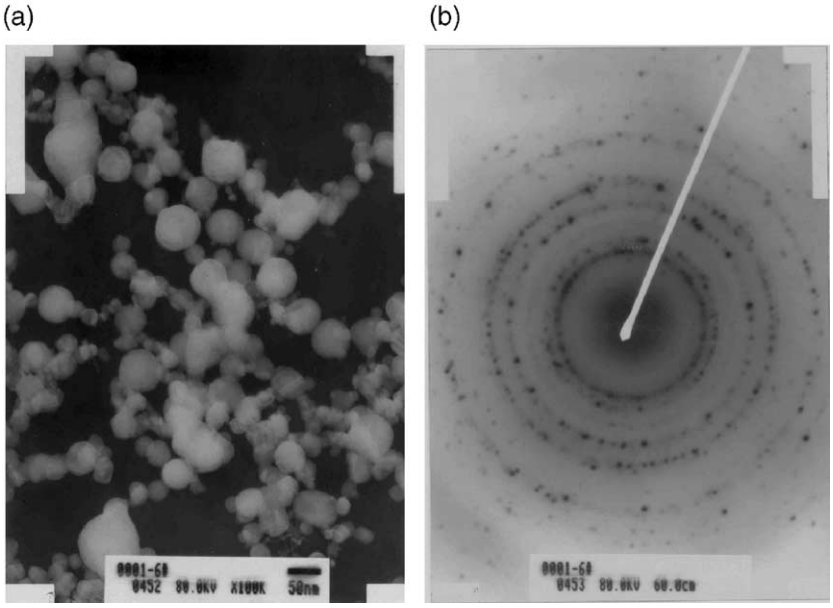

Fig. 2. (a) TEM micrograph and (b) the selected area electron diffraction pattern of Ni nanopowders.

supply as anode. The tungsten rod with 10-mm diameter is mounted in an insulated and axial sliding manner and is connected to a power supply as cathode. The temperature can be adjusted by appropriate positioning of the tungsten rod with respect to the crucible. The bulk raw material to evaporate is placed in the crucible.

In the process of preparation, the vacuum chamber was pumped to 10^{-3} Pa and was then backfilled with inert argon (purity 99.99%) to near 10^{3} Pa. The electric arc in the inert environment was automatically ignited between the tungsten electrode and the nozzle by the high frequency initiator. It was then maintained by the current source at the pre-established values of the voltage and current. Under argon pressure and electric discharge current heating, the ionized gases were driven through the nozzle outlet and from the plasma jet [17]. The bulk metal was heated and melted by the high temperature, and metal atoms were detached from the metal surface when the plasma jet heating energy exceeded the metal superficial energy, evaporating into free atom state. The above evaporation source was a region of supersaturated metal vapor, where the metal atoms diffused around and collided each other to decrease the nuclei-forming energy. When the metal vapor supersaturated, a new phase was nucleated homogeneously out of the aerosol systems [16]. The droplets were rapidly cooled and combined to form primary particles by an aggregation growth mechanism [18,19]. The free inert gas convection developed between the hot evaporation source and the cooled collection cylinder, which transported the particles out of this nucleation and growth region to the inner walls of the cylinder. The loose nanopowders could be obtained after a period of passivation and stabilization with working gas.

The structure and crystalline size of the powders were characterized by a Japan Rigaku D/max-2400 X-ray diffractometer using monochromatic high-intensity CuKα radiation ($\lambda = 1.54056$ Å), at a scanning speed of $2°–2\theta$ h min^{-1} from 30° to 100° (2θ). The average crystalline size of the powder was estimated from X-ray line broadening measurements according to Scherrer's formula. The particle size and morphology shape of the powders were examined by transmission electron microscopy (TEM) and the corresponding selected area electron diffraction (SAED) with a Japan JEOL JEM-1200EX microscope at an accelerating voltage of 80 kV. The specific surface area was measured by nitrogen sorption isotherms at 77 K. Data were conducted automatically on a micromeritics ASAP-2010 porosity analyzer (Micromerities Corp., USA). From the sorption data, the specific surface area of Ni nanopowders was evaluated by using the Brunauer–Emmett–Teller (BET) equation.

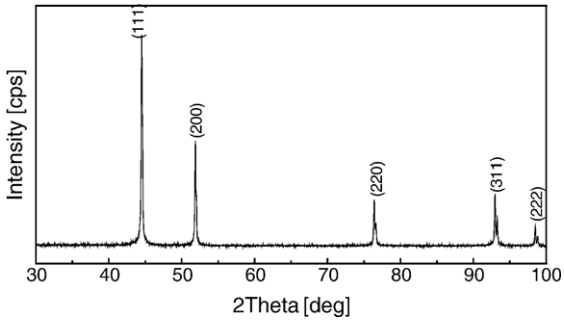

Fig. 4. XRD patterns of Ni nanopowders.

3. Results and discussions

3.1. TEM results

Fig. 2(a) shows a representative transmission electron microscopy (TEM) micrograph of Ni nanopowders. It can be seen from the graph that all of the particles have spherical shape, fairly uniform size and smooth surface. Few small particles aggregate into secondary particles because of their extremely small dimensions and high surface energy. The sphericity-chain shape is the result of magnetic force and surface tension collaboration between the ultra-fine particles. From the data obtained by TEM micrographs, the particle size histograms can be drawn and the mean size of the particles determined. Fig. 3 shows the particle size distribution of Ni nanopowders. It can be seen that the particle sizes range from 20 to 70 nm, the median diameter (taken as average particle diameter) is about 47 nm, being deduced from the images, which shows a relatively narrow size distribution.

Fig. 2(b) shows the corresponding selected area electron diffraction (SAED) pattern. It can be indexed to the reflection of face centered cubic (FCC) structure in crystallography, this result also investigated by means of X-ray diffraction. Tropism of the particles at random and small particles cause the widening of diffraction rings that are made up of many diffraction spots, which indicates that the nanopowders are polycrystalline structure. Electron diffraction reveals that each particle is composed of many small crystal nuclei, which is convincing proof that the particles grow in an aggregation model.

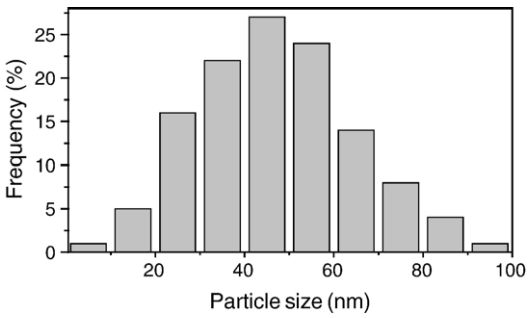

Fig. 3. Particle size distribution of Ni nanopowders.

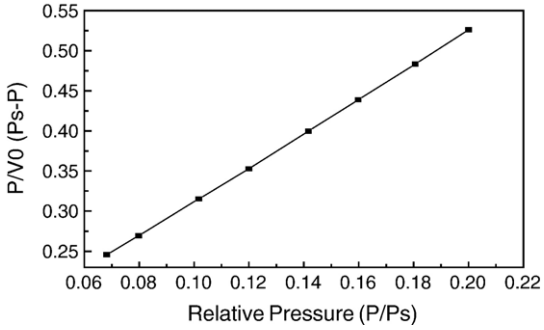

Fig. 5. BET plot of Ni nanopowders.

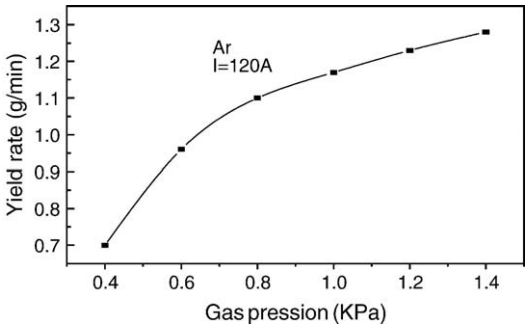

Fig. 6. Variation of yield rate of Ni nanopowders with the gas pressure.

3.2. XRD results

Fig. 4 shows the typical X-ray diffraction (XRD) pattern for the sample. Due to the small size effect and incomplete inner structure of the particle, the XRD diffraction peaks are low and wide. On the other hand, all the peaks with 2θ values of 44.52°, 51.88°, 76.40°, 92.96° and 98.48° corresponding to the (111), (200), (220), (311), and (222) planes of the bulk Ni, respectively, which can be assigned to Ni face centered cubic (FCC) phase. The XRD spectrum does not reveal any other phase except for the characteristic peaks of nickel. This result shows that the physical phases of the nickel nanopowders have higher purity prepared in this work.

From the full width at half maximum, the average crystalline size can be estimated with the (111) diffraction peak in the XRD spectra according to Scherrer's formula: $d = \frac{K\lambda}{B\cos\theta}$, where d is the crystallite size; $K=0.89$, which is the Scherrer constant related to the shape and index (hkl) of the crystals; λ is the wavelength of the X-ray (CuKα, 1.4954 Å); θ is the diffraction angle; and B is the corrected half-width of the diffraction peak (in radians) given by $B^2=B_m^2-B_s^2$, where B_m is the measured half-width and B_s is the half-width of a standard sample with a known crystal size greater than 100 nm, the effect of geometric (instrumental) broadening on the reflection peaks is calibrated. The average crystallite size is calculated to be around 42 nm, which is well consistent with the average particle diameter obtained from the TEM image of Fig. 2(a).

3.3. BET results

The surface area analysis was carried out on Ni nanopowders by BET method. Assuming the particles have solid, spherical shape with smooth surface and same size, the specific surface area can be related to the average equivalent particle size by the equation:

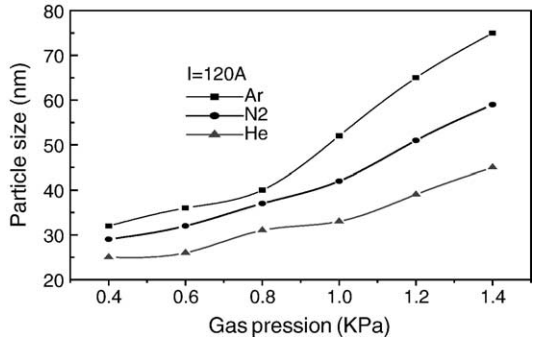

Fig. 7. Variation of average particle size of Ni nanopowders with the gas pressure.

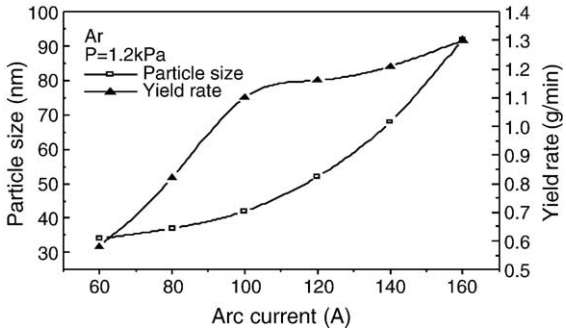

Fig. 8. Variation of yield rate and average particle size of Ni nanopowders with the arc current.

$D_{BET}=6000/(\rho S_w)$ (in nm), where D_{BET} is the average diameter of a spherical particle; S_w represents the measured surface area of the powder in m^2/g; and ρ is the theoretical density in g/cm^3. Fig. 5 shows the BET plot of Ni nanopowders. The specific surface area is 14.23 m^2/g, which is calculated with the multi-point BET-equation. The calculated average equivalent particle size is 46 nm. It is noticed that the particle size obtained from the BET and the TEM methods, which agree very well with the result given by X-ray line broadening. The results of TEM observations and BET methods further confirmed and verified the relevant results obtained by XRD as mentioned above.

3.4. Influence of technology parameters on nanopowders

The type and the pressure of inert gases are major factors for preparation of metal nanopowders. The yield rate and the particle size of Ni nanopowders were studied in argon, nitrogen and helium atmosphere in our experiment. Fig. 6 presents the influence of gas pressure on the yield rate of Ni nanopowders by anodic arc plasma with arc current of 120 A in argon atmosphere. It is noticed that the yield rate of the powders evidently increases with the increase of the gas pressure; the higher the gas pressure the higher nucleation and growth rates of the basic nuclei occur. Fig. 7 shows the influence of gas pressure of different inert gases on the particle size of Ni nanopowders with arc current of 120 A. These curves indicate that the particle size increases approximately linearly with the increase of the pressure for all gases. Under the same processing parameters, the particle size in argon atmosphere is largest, followed by that obtained in nitrogen atmosphere, then in helium atmosphere. The particle size obviously increases with the increase of the atomic weight for inert gases.

Fig. 8 shows the influence of the current on the yield rate and particle size of Ni nanopowders in argon atmosphere with the pressure of 1.2 kPa. As our previous experiment, the arc temperature increased when the arc current increased and much bulk metal was melted and detached from the metal surface and evaporated into atom soot; these are favorable for the formation of nanopowders. As a result, the yield

Table 1
Reference technology parameters of preparing metal nanopowders by anodic arc plasma

Gas pressure (kPa)	Atmosphere	Arc voltage (V)	Arc current (A)	Cooled conditions	Yield rate (g/min)	Particle size (nm)
0.4∼1.4	He, N_2, Ar	20∼30	60∼160	Water	0.5∼1.3	20∼100

rate and particle size of the powders increases with the increase of arc current when other factors are fixed.

In our experiments, some metal nanopowders have been prepared and abundant evidence showed that various technology parameters (such as the type of inert gases, the pressure of ambient gas, the arc current intensity, water-cooling condition and other factors) have much influence on the powder properties (particle size, morphology and other characteristics) and that the properties can be easily improved by varying the technological parameters. The effects of the technology parameters on nanopowders properties were investigated and the referential technology parameters were obtained and summarized in Table 1.

4. Conclusions

(1) Ni nanopowders were successfully prepared at a high rate (up to 1.3 g/min) by anodic arc discharge plasma technique in inert atmosphere. The nanopowders prepared by this method achieved uniform size, higher purity, narrow size distribution and spherical shape; this technique is a prospective production route insuring both controlled parameters and mass production.

(2) The crystalline structure of the samples is FCC structure as same as that of the bulk materials, the specific surface area is 14.23 m^2/g, with the particle size distribution ranging from 20 to 70 nm, and an average particle size about 47 nm obtained from the TEM and confirmed by XRD and BET results.

(3) The yield rate and particle size of Ni nanopowders were affected by many technological parameters (e.g. the type of inert gases, the ambient gas pressure, the arc current intensity, water-cooling condition and other factors). The technology parameters for preparing metal nanopowders were investigated and the optimal conditions were obtained.

Acknowledgements

We appreciate the financial support of the Natural Science Foundation of Gansu province, PR China (No. 3ZS042-B25-017).

References

[1] H. Gleiter, Nanocrystalline materials, Prog. Mater. Sci. 33 (4) (1990) 223.
[2] Y.J. Chen, M.S. Cao, Q. Tian, A novel preparation and surface decorated approach for a-Fe nanopowders by chemical vapor–liquid reaction at low temperature, Mater. Lett. 58 (2004) 1481.
[3] W.W. Zhang, Q.Q. Cao, Structural, morphological, and magnetic study of nanocrystalline cobalt–nickel–copper particles, J. Colloid Interface Sci. 257 (2003) 237.
[4] Z.L. Cui, L.F. Dong, C.C. Hao, Microstructure and magnetic property of nano-Fe particles prepared by hydrogen arc plasma, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. A 286 (2000) 205.
[5] H. Gleiter, Materials with ultrafine microstructures: retrospectives and perspectives, Nanostruct. Mater. 1 (1992) 1.
[6] B.J. Chen, X.W. Sun, C.X. Xu, Growth and characterization of zinc oxide nano/micro-fibers by thermal chemical reactions and vapor transport deposition in air, Physica. E 21 (2004) 103.
[7] D.H. Chen, D.R. Chen, Hydrothermal synthesis and characterization of octahedral nickel ferrite particles, Powder Technol. 133 (2003) 247.
[8] M.S. Cao, Q.G. Deng, Synthesis of nitride–iron nano meter powder by thermal chemical vapor-phase reaction method, J. Inorg. Chem. 12 (1) (1996) 88.
[9] J. Karthikeyan, C.C. Berndt, J. Tikkanen, Plasma spray synthesis of nanomaterial powders and deposits, Mater. Sci. Eng. A238 (1997) 275.
[10] H.G. Zheng, J.H. Lang, J.H. Zeng, Preparation of nickel nanopowders in ethanol–water system (EWS), Mater. Res. Bull. 36 (2001) 947.
[11] G.F. Gaertner, P.F. Miquel, Particle generation by laser ablation from solid targets in gas flows, Nanostruct. Mater. 4 (3) (1993) 559.
[12] J.L. Katz, P.F. Miquel, Synthesis and applications of oxides and mixed oxides produced by a flame process, Nanostruct. Mater. 4 (5) (1994) 551.
[13] B. Gunther, A. Kumpmann, Ultrafine oxide powders prepared by inert gas evaporation, Nanostruct. Mater. 1 (1) (1992) 27.
[14] D. Vollath, K.E. Sickafus, Synthesis of nanosized ceramic oxide powders by microwave plasma reactions, Nanostruct. Mater. 1 (5) (1992) 427.
[15] D.H. Chen, X.R. He, Synthesis of nickel ferrite nanopowders by sol-gel method, Mater. Res. Bull. 36 (2001) 1369.
[16] B. Ioan, Nanoparticle production by plasma, Mater. Sci. Eng. B 68 (1999) 5.
[17] J. Andre, W. Kwan, Arc-discharge ion sources for heavy ion fusion, Nucl. Instrum. Methods Phys. Res. A 464 (2001) 569.
[18] C. Kaito, Coalescence growth mechanism of smoke particles, Jpn. J. Appl. Phys. 24 (1985) 261.
[19] J.H. Scott, S.A. Majetich, Morphology, structure, and growth of nanopowders produced in a carbon arc, Phys. Rev. B52 (1995) 12564.