Journal of Alloys and Compounds 678 (2016) 403–409

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis of high purity tungsten nanoparticles from tungsten heavy alloy scrap by selective precipitation and reduction route

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form
19 March 2016
Accepted 31 March 2016
Available online 2 April 2016

Keywords:
Tungsten nanoparticles
Recycling of scrap
FTIR
TEM

ABSTRACT

In this paper we report synthesis of tungsten nanoparticles of high purity >99.7 wt% from heavy alloy scrap using a novel chemical route of selective precipitation and reduction. The effect of Poly(-vinylpyrrolidone) polymer on controlling the particle size is established through FTIR spectra and corroborated with TEM images, wherein the average size decreased form 210 to 45 nm with increasing PVP content from zero to 2 g under different experimental conditions. This process is economical as raw material is a scrap and the efficiency of the reaction is >95%.

1. Introduction

Tungsten (W) is used extensively for high temperature applications owing to its high melting point of 3410 °C. However the same leads to many difficulties in processing the material through conventional metallurgical processes; hence powder metallurgical (PM) routes are applied to obtain near net shaped products of W. Even through PM routes consolidation of micron-sized W particles require very high temperatures of the order of 2500 °C with prolonged heating cycles of 12 h or more. This has lead to the development of activated sintering methodologies such as addition of transition metals or use of W nanoparticles (NPs). Use of transition metals such as Fe, Co, Ni, Cu, in combination with W leads to better densification at lower temperatures but significantly reduces the density of the material [1]. In order to obtain high density at lower temperature the only option available is to use W NPs. Hence W NPs emerge as front runners for critical applications where both high temperature and high density are required.

Due to the above mentioned advantages W NPs have been identified as suitable materials for numerous applications in strategic sectors like aerospace for various engine components and jet vanes, in defence for kinetic energy projectiles and nose cones and in electronic industry such as contact plugs, heat sinks and bit lines [2,3]. These potential applications of W NPs in wide spread areas has lead to a thrust in the fields of synthesis, characterization and property evaluation of W NPs over the past decade. Two different approaches have been adopted to produce W NPs namely top-down and bottom-up routes. In the top down approach mechanical milling has been extensively used for production of nanocrystalline W particles [4–6]. This approach has gained considerable interest in various industries due to its low cost and high volume manufacturing capability. However, the biggest problem with this approach is lack of proper control on the particle size, shape and distribution. Other setbacks include the introduction of imperfections into the surface structure, crystallographic damage of the processed material and addition of unwanted impurities [7–9]. Such imperfections lead to additional challenges in the design and fabrication of devices. To address these issues plethora of methodologies have been developed through bottom-up approach, which include chemical reduction [10–12], pulsed laser route [13], sonoelectrochemical synthesis [14], molten salt route [15], microwave plasma route [16], laser ablation route [17], chemical vapor synthesis [3], self-propagating high-temperature synthesis [18] thermal decomposition [19] and combustion synthesis [20]. Though various bottom-up approaches have been reported thus far, none of them address the reusability of W scrap as a source for producing W NPs. They all employ metal salts or complexes in various forms, which leads to high cost of production.

In the present scenario recycling of W scrap has become important as it addresses the dwindling resources of ores,

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http://dx.doi.org/10.1016/j.jallcom.2016.03.303
0925-8388/

environmental issues and economical factors. A staggering ~30% of present world W demand is met through recycling of scrap. Different methodologies adopted for recycling of W scrap includes hydrometallurgy, oxidation-reduction route and electrolytic process [21–25]. None of the above mentioned routes describe the synthesis of W NPs from scrap; therefore in this paper we report a simple and cost effective approach to synthesize high purity W NPs from W heavy alloy scrap.

2. Experimental

Tungsten scrap generated in house at Defense Metallurgical Research Laboratory with a nominal composition of Ni- 7.9 wt%, Co- 2.1 wt%, Fe- 1.9 wt% and W ~88% was taken in the form of turnings as starting material. The chemical composition of the scrap was obtained by analyzing the turnings using inductively coupled plasma optical emission spectrometer (ICPOES). In order to prepare a stock solution of tungsten scrap containing 20 g/L, approximately 2 g of W scrap was weighed on an analytical balance and transferred to a 250 mL teflon beaker. A tri-acid mixture of 6 mL HCl + 2 mL HNO_3 + 1 mL HF were pipetted out using a calibrated pipette and poured into the teflon beaker along the ridge. The beaker was kept in a fume hood for 10 min during which the turnings of W scrap completely dissolved. Poly(vinylpyrrolidone) (PVP) polymer of different concentrations were taken and dissolved in 100 mL of de-ionised water. Three different experiments were carried out to study the effect of PVP on controlling the particle size of the W NPs as shown in Table 1. To the polymeric solution the dissolved W scrap solution was added and stirred thoroughly using a magnetic stirrer, pH of the solution at this stage is 2.6–2.8. To the above mixture 20 mL of HCl was added in a drop wise manner under constant stirring to maintain a pH value 1–2. A clear pale yellow color solution turns into a turbid yellow solution at this stage. This solution was heated to 100 °C in a water bath for 2 h before collecting the precipitate through centrifugation. After collecting the precipitate, it was washed twice with dilute HCl to remove any impurities of iron, nickel and cobalt. The powder was dried in a vacuum desiccator before carrying out the hydrogen reduction. To carry out hydrogen reduction the sample was transferred into a ceramic boat and placed in a tubular furnace, the furnace was programmed to reach 750 °C ± 10 °C at a heating rate of 10 °C/min and allowed to hold at the designated temperature for 2 h. Throughout the furnace cycle until complete cooling down to room temperature, hydrogen gas was passed through the furnace at a rate of 0.5 L/min. The product was collected and weighed before carrying out further characterizations.

A Bruker TENSOR 27 model Fourier transform infrared (FTIR) spectrometer was used to record the transmission spectra of the tungstic acid precipitate and the final product obtained from various experiments. These spectra were further analyzed to ascertain the role of PVP on effective binding to the NPs. Thermal behavior of tungstic acid powder samples were analyzed using a TA instruments Q100 differential scanning calorimeter (DSC) in the temperature region of 50–500 °C. A Philips-PW3020 X-ray diffractometer (XRD) consisting an X-ray source of Cu Kα with 0.15405 nm wavelength was used to obtain the diffraction patterns of the samples at various stages of processing. Size, morphology and structure of the tungstic acid precipitates and the final reduced samples were obtained using an FEI QUANTA environmental scanning electron microscope (ESEM) and FEI TECNAI G2 transmission electron microscope (TEM). To obtain TEM images and selected area electron diffraction (SAED) patterns, re-dispersed NPs solution was drop coated onto a 3 mm carbon coated copper grid and analyzed in bright field mode. A combination of analytical techniques including JY- ULTIMA inductively coupled plasma optical emission spectrometer (ICP-OES), LECO TC-600 oxygen and nitrogen determinator, LECO CS-444 carbon and sulfur analyzer and LECO RH-404 hydrogen analyzer were used to obtain the chemical composition of the resultant product. To carry out analysis in ICP-OES, 0.5 g of the powder was dissolved in a CEM microwave accelerated reaction system (MARS) using mixture of 8 mL HNO_3 + 1 mL HF and made up to 50 mL in a volumetric flask using double distilled water. Analysis of this solution was carried out to check for various impurities present in the solution. For analysis of C, S, H, O & N, ~0.2 g of the powder was taken to determine the level of impurities present in the sample.

Table 1
Experimental conditions adopted for the synthesis of tungsten nanoparticles along with average particle size obtained from TEM and efficiency of the reaction.

Experiment	Scrap taken (g/L)	HCl (mL)	HNO_3 (mL)	HF (mL)	PVP (g/L)	Particle size (nm)	Efficiency (%)
(a)	20	6	2	1	nil	210 ± 28	96.2
(b)	20	6	2	1	10	75 ± 14	95.4
(c)	20	6	2	1	20	45 ± 9	95.1

3. Results and discussion

In order to dissolve the W scrap turnings using tri-acidic mixture, heating of the sample is avoided as this reaction is highly exothermic reaction. Therefore the whole reaction was carried out in a fume hood to avoid acid fumes. Fig. 1 shows the schematic

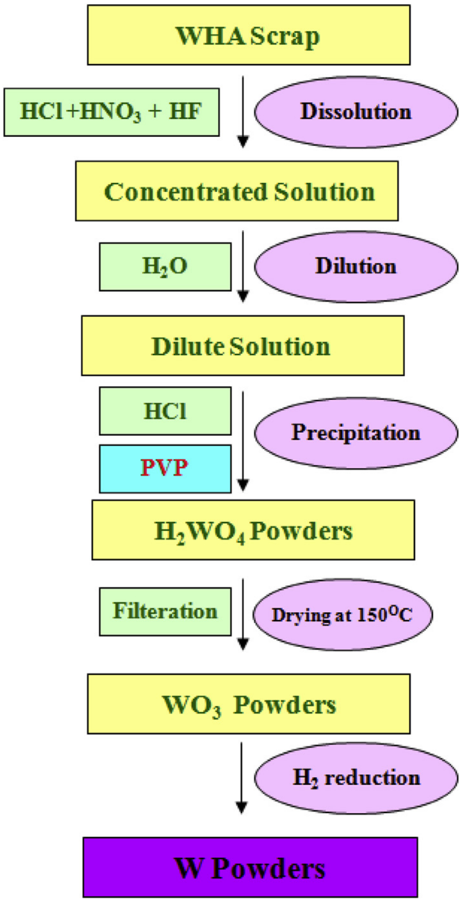

Fig. 1. Schematic diagram of the various stages involved in synthesis of tungsten nanoparticles from tungsten heavy alloy scrap.