Powder Technology 246 (2013) 413–418

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Studies on a supersonic thermal plasma expansion process for synthesis of titanium nitride nanoparticles

B. Bora [a,1], N. Aomoa [a], M. Kakati [a,*], H. Bhuyan [b]

[a] Thermal Plasma Processed Materials Laboratory, Centre of Plasma Physics-Institute for Plasma Research, Sonapur 782 402, India
[b] Department of Physics, Pontificia Universidad Catolica de Chile, Santiago, Chile

ARTICLE INFO

Article history:
Received 17 May 2012
Received in revised form 13 February 2013
Accepted 25 May 2013
Available online 1 June 2013

Keywords:
Titanium nitride nanoparticle
Plasma processing
Plasma torch
Optical emission spectroscopy

ABSTRACT

The paper reports studies on supersonic thermal plasma expansion process for rapid, controlled synthesis of titanium nitride nanoparticles with enhanced particle characteristics, by injecting $TiCl_4$ and NH_3 at two different reaction zones, namely hot zone and colder tail zone of a thermal plasma jet assisted chemical reactor. Two different chamber pressures of 30 mbar and 10 mbar were maintained to investigate the effect of pressure on the characteristics of the product particles. The nanoparticles synthesized by injecting reactants to the colder tail zone at 10 mbar chamber pressure show sub-10 nanometer average sizes with cubic shapes. On the other hand, particles synthesized by injecting the reactants to the hot zone shows better crystal structure and bigger size. The optical spectrums obtained from the injection zone indicate the presence of both atomic and ionic species in the plasma which are the growth precursors for the synthesis of titanium nitride particles. Plasma temperature at the injection zone was estimated from the plasma emission spectra by Atomic Boltzmann Plot method.

1. Introduction

Titanium nitride (TiN) has been studied extensively both in bulk and nanocrystalline form because of its many attractive features, such as extreme hardness, good electrical conductivity, chemical inertness and very high melting temperature [1]. Micron sized particles of titanium nitride showed low sintering ability, and this is why its uses were mostly confined in the form of thin coatings [2]. However, more recent studies using nanometer sized TiN particles show enhanced sinterability even without using additives and catalysts [2,3]. Nanoparticles of titanium nitride have been used also as an additive in titanium containing alloys to enhance the mechanical/electrical properties of the resulting nano-composites [4,5]. TiN nanopowder with large surface area combined with its characteristic good conductivity should be ideal for use in super-capacitors [6]. It was recently demonstrated that they can also act as a catalyst support material for proton exchange membrane fuel cells (PEMFC) showing better performance than conventional platinized carbon electro-catalysts [7,8].

As a processing medium for high temperature nanomaterials, thermal plasmas have established a visible edge in terms of their typically high production rate and excellent crystallinity of the product materials [9–18]. Thermal plasma assisted techniques are usually very fast, most often a single step process and continuous in contrast to batch processes. Ease of producing plasma in controlled environment has made the high pressure, high temperature thermal plasma as one of the best processing medium for production of nanostructured nitrides or carbides in bulk quantities [17,18].

However, the thermal plasma assisted techniques often produce broad particle size distribution and serious inter-particle agglomeration. We have demonstrated in the recent past that these typical problems associated with conventional plasma techniques can be avoided in a supersonic plasma jet based reactor configuration, which can produce narrow size dispersion because of uniform temperature profile of the expanded plasma jet, and less agglomeration due to the directed supersonic velocity of the particles embedded in the plasma [13–15]. The plasma jet was accelerated to supersonic velocity in the first place by connecting the discharge zone (plasma torch) to the particle nucleation region (sample collection chamber) through a converging nozzle and maintaining an appropriate pressure difference across the same. We have also demonstrated that a non equilibrium electron population could have charged up the nano-particles all negatively after nucleation in this system, thereby curbing unwanted coagulation among particles and ensuring better particle size distribution [14]. We had reported synthesis of free-flowing, blue-black stoichiometric TiN particles by this reactor configuration by injecting NH_3 and $TiCl_4$ to the relatively hotter zone of the plasma just after the anode (termed as hot zone afterwards) of a non-transferred dc thermal plasma torch [13]. These studies led to the realization that decrease in temperature at the injection zone may help the average crystallite/particle size to reduce further. On the other hand, numerical studies on supersonic thermal plasma

* Corresponding author. Tel.: +91 94350 36180; fax: +91 361 2632079.
E-mail address: mayurkak@gmail.com (M. Kakati).
[1] Present Address: Comisión Chilena de Energía Nuclear (CCHEN), Casila 188-D, Santiago, Chile.

0032-5910/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.powtec.2013.05.038

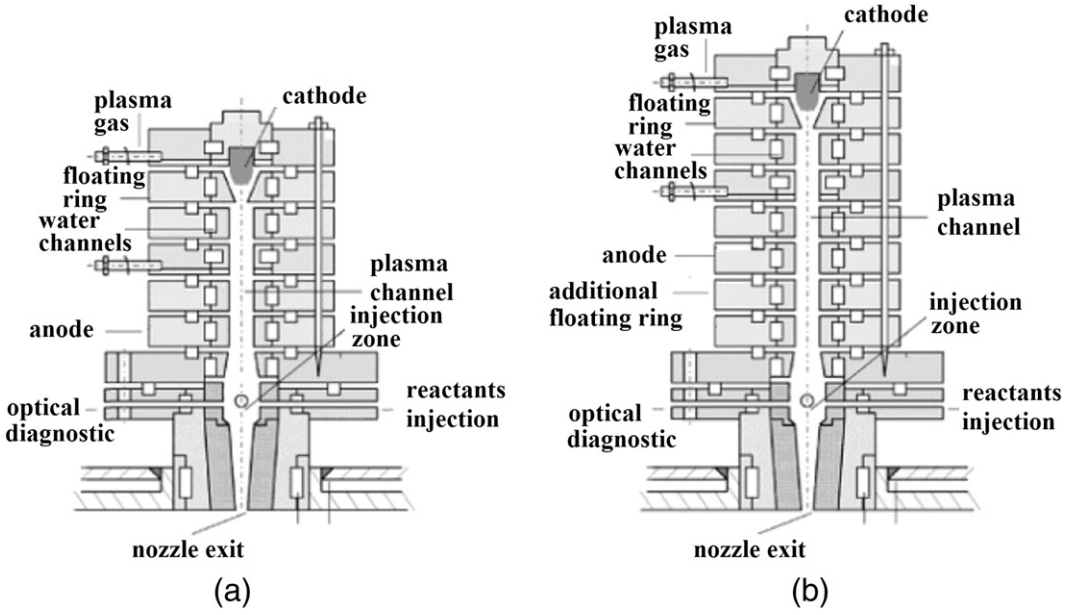

Fig. 1. Reactor configurations for injection of reactants (a) at the hot zone just after the anode and (b) at the colder tail zone of the plasma flame, where the torch has two additional floating rings after the anode.

expansion process indicated improvement of average particle sizes with reduction in sample collection chamber pressure [16]. This present communication reports some further studies towards this direction, where reactants were injected at the colder tail zone (termed as colder tail zone afterward) of the plasma jet in order to produce particles with enhanced control over particle size characteristics. Moreover, the influence of sample collection chamber pressure was also explored over two distinct pressure values. The synthesized particles were characterized by the standard techniques like XRD, SEM-EDX, TEM, HRTEM and UV visible spectroscopy. Optical emission spectroscopy (OES) was carried out to investigate the plasma chemistry during the synthesis of the TiN nanoparticles and measure plasma temperature at the reactant injection position.

2. Material and method

A dc cascaded plasma torch consisting of a conical thoriated tungsten cathode and a ring shaped copper anode separated by stack of insulated, interspaced copper rings is used as the plasma source. It is connected to a sample collecting vacuum chamber through a converging nozzle across which a high pressure difference is maintained, and the plasma jet accelerates to supersonic speed. Details of the basic experimental system are found elsewhere [13,14]. In this present experiment two different configurations of the plasma torch reactor are used for injecting the reactants to the hot zone and the colder tail zone of the plasma jet as shown in Fig. 1. The anode is directly connected to an injection section followed by a converging nozzle for injecting the reactant at the hot zone of the plasma jet (hot zone configuration) as shown in Fig. 1(a). On the other hand, two additional rings are inserted between the anode and the injection section to inject the reactants at the colder tail zone of the plasma jet (colder tail zone configuration) as shown in Fig. 1(b). The nozzle exhausts into a low pressure sample collection chamber with a movable substrate holder to collect the particles for further analysis. During this experiment the substrate was kept at a distance of 12 cm from the nozzle exit.

A unique feature of the experimental reactor configuration is that the plasma discharge zone remains effectively isolated from the particle nucleation/growth zone (sample collection chamber) through the supersonic nozzle, which allows reduction of pressure in the later down to few mbar levels. It is in contrast to the conventional thermal

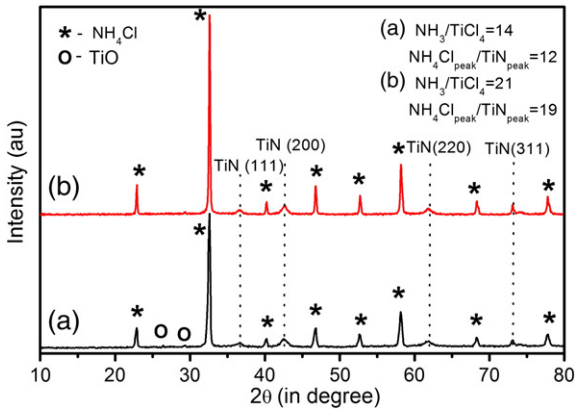

Fig. 2. XRD patterns of the as synthesized titanium nitride particles (13.2 kW, 30 mbar sample collection chamber pressure) by injecting the reactants at the colder tail zone for (a) $NH_3/TiCl_4$ molar ratio of 14 and (b) molar ratio of 21, showing presence of TiN (JCPDS-ICDD 00-038-1420), NH_4Cl (JCPDS-ICDD 00-007-0007) and TiO (JCPDS-ICDD 00-023-1078).

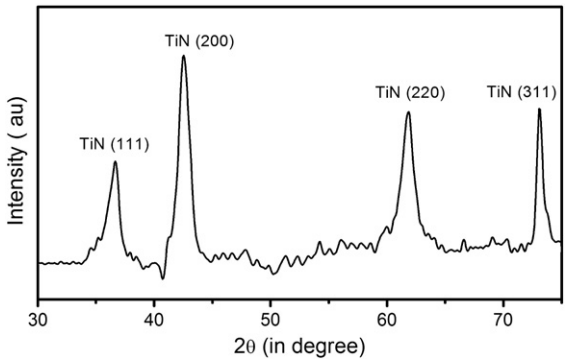

Fig. 3. XRD pattern of the TiN nanoparticles for colder tail zone configuration (13.2 kW, 30 mbar chamber pressure, and $NH_3/TiCl_4$ molar ratio of 14) after post annealing.