Journal of Alloys and Compounds 509 (2011) 5825–5828

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis of titanium nano-particles via chemical vapor condensation processing

A. Attar [a,*], M. Halali [a], M. Sobhani [b], R. Taheri Ghandehari [c]

[a] Sharif University of Technology, Tehran, Iran
[b] Materials and Energy Research Center, Karaj, Iran
[c] Azad University of Tehran, Tehran, Iran

ARTICLE INFO

Article history:
Received 13 October 2010
Received in revised form 22 February 2011
Accepted 23 February 2011
Available online 3 March 2011

Keywords:
Chemical vapor condensation (CVC)
Synthesis
Titanium
Nano-particles

ABSTRACT

In the present study, titanium nano-particles have been synthesized using chemical vapor condensation (CVC) process. Reaction of sodium and titanium tetrachloride vapors in the tube furnace resulted in the production of titanium nano-particles that were encapsulated in sodium chloride. Dried Argon gas was employed as a carrying agent. Titanium nano-particles were contained in an ethanol bath. Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) were employed for analysis and characterization of nano-particles. The size of primary particles was smaller than 100 nm and secondary particles were submicron agglomerations.

1. Introduction

Due to their core–shell structure and properties, Nano-capsules have raised interest among scientists and researchers. The non-metallic shell prohibits the agglomeration of metallic nano-powders to a large extent. In addition, the salt layer acts as a barrier against oxygen or other gases in the atmosphere which might otherwise react with the metal [1,2]. Chemical vapor condensation (CVC) is one of the major techniques used in the production of nano-powders. This method has the ability to provide high purity nano-particles with a uniform size distribution and minimum agglomeration [3]. Examples for successful applications of this process include production of carbon coated iron core–shell powders, magnetic fluid and ferromagnetic nano-particles [3–5].

Recently, novel techniques have been developed for the production of titanium powder. For instance, electronically mediated reaction (EMR) has been used for producing titanium powder by Park et al. In this process TiO_2 is reduced by a Ca–Ni alloy in a molten calcium chloride ($CaCl_2$) bath by applying a voltage between feed electrode and the reducing alloy [6]. In another research by Okabe et al. preform reduction process (PRP) based on the calciothermic reduction of titanium oxide has lead to production of titanium powder of about 99% mass purity [7]. Also preparations of metallic titanium powder have been developed with Armstrong and Hunter processes, utilizing the reduction of $TiCl_4$ vapor via the molten or vaporized sodium [8,9].

However, the synthesis of Ti nano-particles has not been studied extensively. Therefore, in this study synthesis of titanium nano-particle through reaction between sodium and $TiCl_4$ using chemical vapor condensation has been investigated.

2. Experimental procedure

The starting materials for this research were titanium tetrachloride (99.5%), sodium chunks (99.5%) and ethanol (99.9%); these were all obtained from Merck Co. Fig. 1 shows a schematic diagram of the experimental set up. Titanium tetrachloride was heated to 110 °C on a hot plate. At this temperature $TiCl_4$ has a vapor pressure of 0.47 atm.

Sodium chunks were placed in a ceramic boat and heated to the required temperature inside the quartz tube furnace. The temperature range was between 650 °C and 700 °C corresponding to vapor pressures of 0.07 atm and 0.14 atm respectively. High purity argon, acting as a carrier gas, was initially passed through silica gel columns and subsequently through a furnace tube at 300 °C containing copper chips. As a result, the carrier gas was dried and its oxygen content was reduced to 2 ppm. Argon with a volumetric flow rate of 0.3 l per min was injected into titanium tetrachloride liquid, carrying its vapor into the furnace that contained sodium chunks and sodium vapor.

Sodium vapor reacted with $TiCl_4$ vapor to produce titanium and sodium chloride Eq. (1). Fig. 2 is an XRD analysis of the products and clearly indicates the reaction products.

$$Na_{(g)} + TiCl_{4(g)} = 4NaCl + Ti \quad (1)$$

The reaction took place inside the quartz reaction tube. Since the bulk of the reaction was in gaseous phase, the titanium powder produced had very small particle sizes and was encapsulated in sodium chloride (Fig. 3). The products were carried into an ethanol bath. The product powders were subsequently dried in an oven at 60 °C for analysis.

A Joel 8030 diffractometer (Cu-Kα radiation) was used for XRD analysis. The crystallite size of the encapsulated powders was determined using Scherrer equa-

* Corresponding author. Present address: Department of Material Science & Engineering, Sharif University of Technology, Azadi St., Tehran, Iran.
Tel.: +98 5118911490; fax: +98 2616704817.
E-mail address: attar.amin@gmail.com (A. Attar).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.02.133

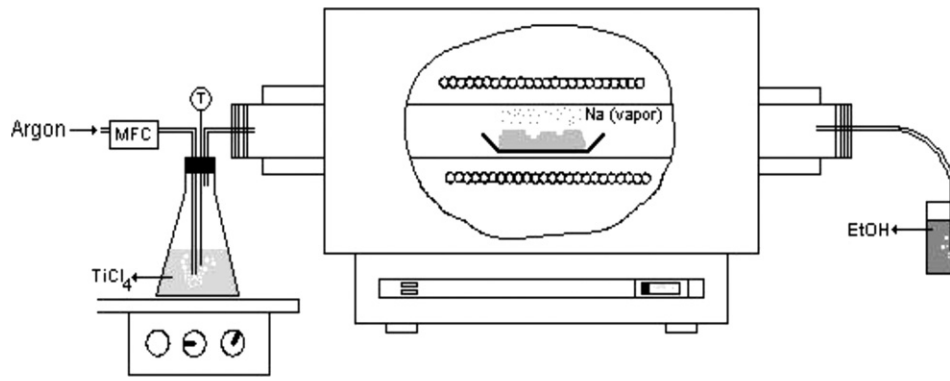

Fig. 1. The schematic diagram of the apparatus.

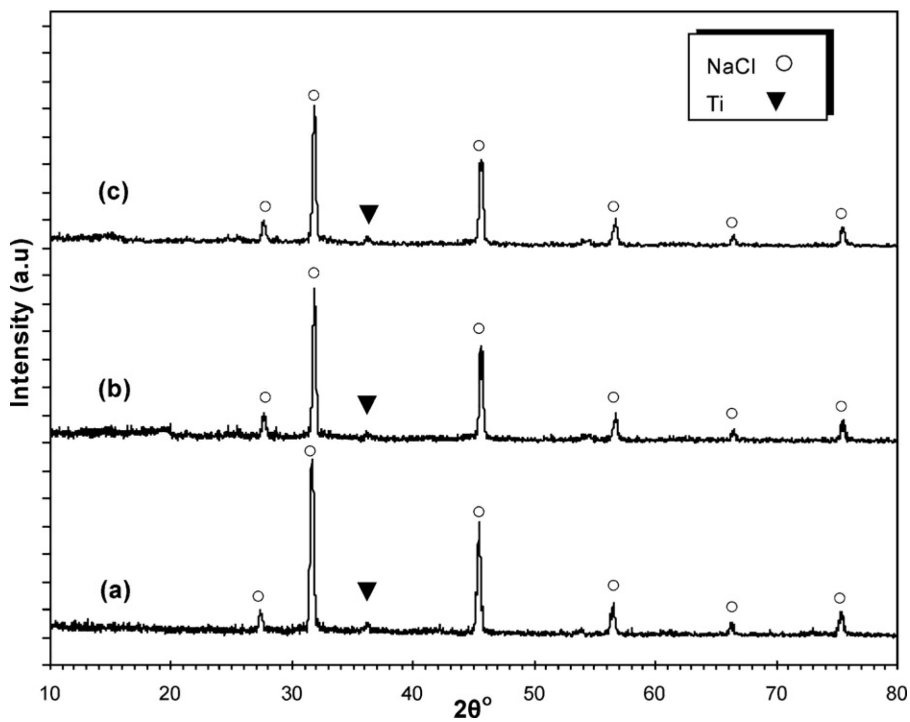

Fig. 2. XRD patterns of the (a), (b) and (c) samples which reacted respectively at 650, 675, 700 °C.

tion. A Cambridge S360 SEM was employed for microstructural observations. Prior to SEM analysis, the samples were dispersed inside ethanol in an ultrasonic bath. The suspension was subsequently spread on a copper plate to dry and was coated with gold. The size and morphology of the particles were determined using a Philips CM200 transmission electron microscope. For TEM analysis the suspension of powder in ethanol was allowed to settle on carbon coated copper grids.

3. Results and discussions

Fig. 2 shows XRD patterns for the three experimental conditions of this work. In all the three patterns, titanium and sodium chloride are major phases. This observation is in line with Eq. (1). It is interesting to notice that titanium peak(s) is not as strong as that of sodium chloride.

This observation is consistent with the stoichiometry of the reaction equation where there are four moles of sodium chloride for each mole of titanium. In addition, titanium particles are embedded in sodium chloride resulting in a shielding effect. Therefore NaCl peaks have been used in Scherrer equation Eq. (2) in order to specify the apparent crystallite size of encapsulated particles:

$$B(2\theta) = \frac{k\lambda}{L\cos\ \theta_o} \tag{2}$$

$B(2\theta)$ is the width of the diffraction line, k is a constant, λ is the wavelength, θ_o is the Bragg angle and L is the apparent crystallite size. In chemical vapor condensation synthesis of encapsulated Ti nano-particles, conditions are created where the vapor phase mixture of $TiCl_4$ and Na are thermodynamically unstable. Conditions will be provided if the degree of supersaturation be sufficient and the reaction/condensation kinetics permit [10]. The reduction mechanism of $TiCl_4$ by Na is initiated by direct reaction of $TiCl_4$ and Na, and then unreacted Na diffuses in to $TiCl_4$ and forms Ti core with a protective NaCl layer. Table 1 exhibits calculated particle sizes for the three experimental conditions of this study. It is observed that lowering the reaction temperature reduces particle size. Naturally, the calculated particle sizes refer to sodium chloride covering layer. As titanium particles are encapsulated inside the salt, their sizes should be smaller than 50 nm.

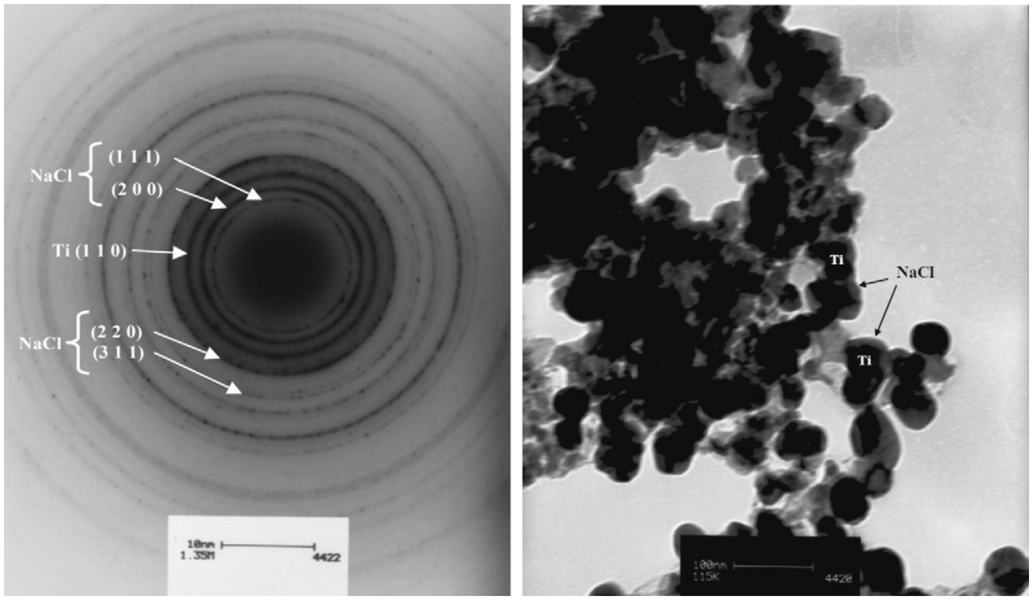

Fig. 3. TEM micrograph and electron diffraction pattern of sample (b).

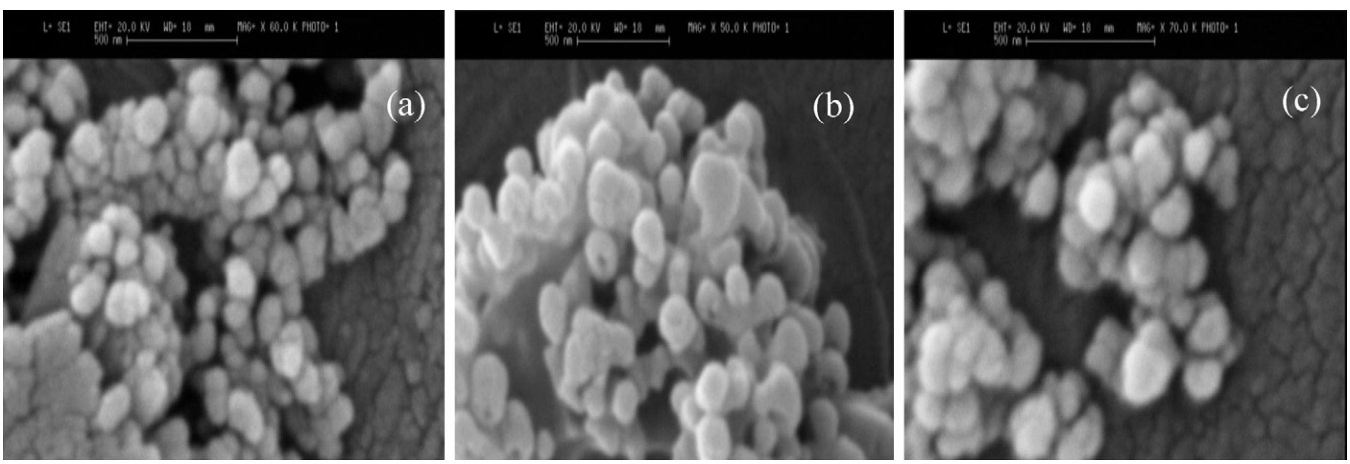

Fig. 4. SEM image of (a), (b) and (c) powders which were synthesized respectively at 650, 675 and 700 °C.

Table 1
Values of synthesized parameter.

Sample	Argon flow rate (cm^3/min)	$TiCl_4$ temperature (°C)	Tube furnace temperature (°C)	Crystallite size (nm)
(a)	300	110	650	14
(b)	300	110	675	19
(c)	300	110	700	25

Fig. 3 shows the TEM micrograph and electron diffraction pattern of sample (b) which is synthesized at 675 °C. Crystal habit planes were determined by the following equation:

$$L\lambda = rd \quad (3)$$

L is camera length, λ is the wave length of electron, r is ring radius (measured from electron diffraction pattern in Fig. 3) and d is habit planes distance. Formed rings of the electron diffraction pattern are related to the fine nano-particles of both Ti and NaCl. In the micrograph, darker areas refer to Ti and the gray ones implicate the salt cover. Titanium nano-particles are encapsulated in NaCl that prevents them from oxidation. This layer can be sublimated by heating the powder at about 800 °C in vacuum [11]. The sizes of the spherical encapsulated single particles are smaller than 100 nm.

SEM images of samples which were synthesized respectively at 650, 675 and 700 °C are shown in Fig. 4. It can be seen that several primary nano-particles have joined to form the secondary agglomerates with submicron size (about 500 nm). However, the Ti particles are separated from each other by salt.

4. Conclusion

Chemical vapor condensation has been applied for preparation of nano-sized titanium powder. Obtained particles were spherical and encapsulated by a NaCl layer. As reaction temperature increased, the size of Titanium nano-particles became larger. The size of single particles was about less than 100 nm that gathered together and formed agglomerated particles with submicron size.

References

[1] A.S. Edelstein, R.C. Cammarata, Nanomaterials: Synthesis, Properties and Application, Institute of Physics Publishing, Bristol/Philadelphia, 1996.
[2] J.C. Kim, S.J. Kim, Y.D. Kim, J.S. Kim, C.J. Choi, J. Alloys Compd. 483 (2009) 359–362.
[3] D.W. Lee, J.H. Yu, B.K. Kim, T.S. Jang, J. Alloys Compd. 449 (2008) 60–64.
[4] J.H. Yu, D.W. Lee, B.K. Kim, T. Jang, J. Magn. Magn. Mater. 304 (2006) e16–e18.
[5] D. Li, C.J. Choi, B.K. Kim, Z.D. Zhang, J. Magn. Magn. Mater. 277 (2004) 64–70.
[6] I. Park, T. Abiko, T.H. Okabe, J. Phys. Chem. Solids 66 (2005) 410–413.
[7] T.H. Okabe, T. Oda, Y. Mitsuda, J. Alloys Compd. 364 (2004) 156–163.
[8] M.A. Hunter, J. Am. Chem. Soc. 32 (1910) 330–336.
[9] D.R. Armstrong, S.S. Borys, R.P. Anderson, Method of making metals and other elements, U.S. Patent 5,779,761, 1998.
[10] M.T. Swihart, Curr. Opin. Colloid Interface Sci. 8 (2003) 127–133.
[11] D.Y. Maeng, C.K. Rhee, K.H. Kim, W.W. Kim, Mater. Sci. Eng. A 375–377 (2004) 609–614.