Materials Science & Engineering B 229 (2018) 6–12

Contents lists available at ScienceDirect

Materials Science & Engineering B

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

Preparation of high purity nano-silicon powders by direct current arc plasma evaporation method

Zhen Li*, Junjie Huang, Zhenzhong Zhang, Fangxia Zhao, Yang Wu

College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China

ARTICLE INFO

Keywords:
Nano-silicon powders
Direct current arc plasma evaporation
Average particle diameter
Yield
Evaporation mechanism

ABSTRACT

Direct current arc plasma evaporation method was used in this paper for the industrial preparation of high purity and highly-dispersed nano-silicon powders and the development its high-tech nano products. The influence of cathode current, filling pressure, pressure ratio of Hydrogen to Argon (P_{H2}/P_{Ar}) on the particle size and the yield of nano-silicon powders was studied by orthogonal design method in experiment. The evaporation mechanism was also discussed in this paper. The results showed that high purity of 99.93 wt% was achieved with near spherical shape and cubic crystal structure. The average particle size of nano-silicon powders produced in the process in this paper ranged from 35 nm to 63 nm with the yield of 9.2 g h^{-1}–175.2 g h^{-1}. The mechanism of silicon powders evaporation was discussed in the paper, which led to the findings of high yield attributed to the co-existence of molecular evaporation and boiling evaporation coexist.

1. Introduction

As a new functional powder materials with its unique quantum size effect and physical and chemical properties [1], nano-silicon powders were widely used in the field of ceramic industry [2], refractory materials fabrication [3], lithium silicon batteries [4–7], biological product [8] and other fields. For example, when nano-silicon powders were added into the lithium ion battery anode material, with their theoretical capacity as high as 4200 mAh g^{-1}, they can greatly enhance the electrochemical performance of lithium-ion battery and drastically ease the volume expansion effect of ordinary silicon powders [9]. A variety of methods were developed for the preparation of nano-silicon powders such as ball milling [10], chemical etching [11,12], silane decomposition [13], plasma enhanced chemical vapor deposition[14] and so on. These methods can be used to prepare nano-silicon powders with different particle sizes but encountered many challenges such as low purity, low yield, uneven particle size distribution and difficult reunion. Together with their high production cost, these methods cannot be used for large-scale factory production. Whereas the Direct Current (DC) arc plasma evaporation method is an effective method to overcome these challenges. The method has been successfully adopted in the fabrication of Fe [15], Cu [16], Co [17] and Ag [18]. However, the preparation of nano-silicon powders by this method was rarely reported. This paper chose the self-developed three-electrode nano-powders continuous production line. The influence of cathode current, filling pressure and the pressure ratio of hydrogen to argon (P_{H2}/P_{Ar}) on the particle size and the yield of nano-silicon powders were studied by orthogonal design method in experiment. The evaporation mechanism was also discussed in this paper. This experiment had laid a theoretical and experimental foundation for the industrial preparation of high purity and high dispersion nano-silicon particle and the development of its high tech nano products.

2. Experimental

2.1. Materials

The raw materials of this study are a silicon block with a high purity of 99.99 wt%, and the aerated gas are hydrogen and argon with purity greater than 99.99 wt%. Many thanks to Anyang Huatuo Metallurgical for providing silicon block, and Nanjing Sanle for supplying gas.

2.2. Characterization

The crystalline phases of the as-prepared samples were analyzed with X-ray diffraction (XRD) by an X' Pert PRO diffractometer system with Cu Kα radiation (k = 0.154056 nm) in the range of 2θ = 10–80°. The composition of the particles was analyzed by X-ray fluorescence analysis (XRF). The determination of oxygen content in nano-silicon powders was studied by using oxygen-nitrogen analyzer. Selected-area electron diffraction (SAED) was used to observe the polycrystalline structure. Transmission electron microscopy (TEM) samples were

* Corresponding author.
E-mail address: 648822963@njtech.edu.cn (Z. Li).

https://doi.org/10.1016/j.mseb.2017.12.013
Received 15 July 2017; Received in revised form 28 November 2017; Accepted 13 December 2017

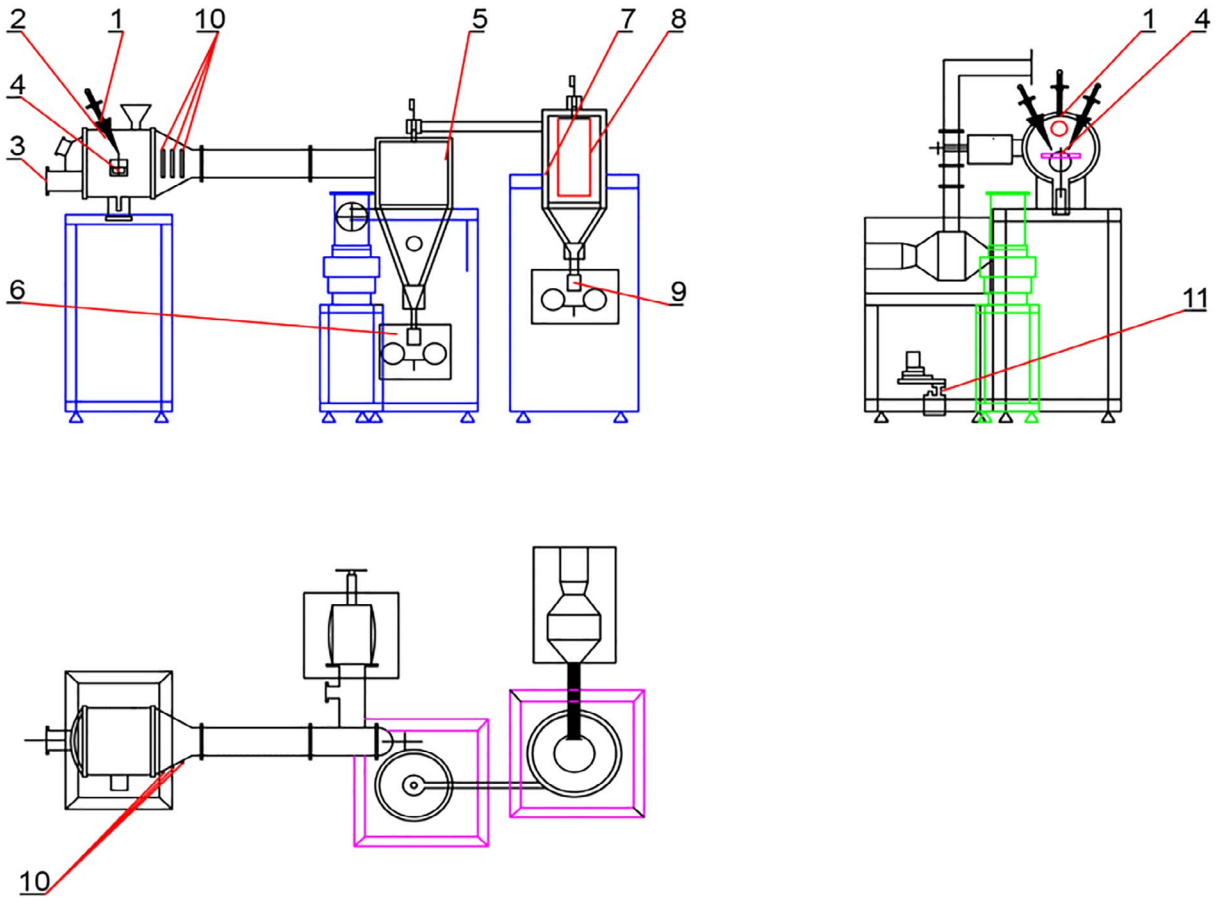

Fig. 1. Schematic diagram of three-electrode DC arc plasma evaporation device for continuous preparing nano-silicon powders: 1-Arc gun; 2-Preparation chamber; 3-Glove box; 4-Water-cooling crucible; 5-Cyclone grade chamber; 6-Vacuum packing box; 7-Collection chamber; 8-Sieve; 9-Vacuum packing box; 10-Gas inlet; 11-Pump.

prepared by dropping one drop of dilute suspension on copper coated carbon TEM grid and the solvent was then dried.

2.3. Improvement of power equipment

Fig. 1 shows the schematic diagram of three-electrode DC arc plasma evaporation device for continuous preparing nano-silicon powders. It can be seen from the figure that the device mainly consists of the arc gun, powder room, grading room, powder room and vacuum glove room. The equipment has the following improvements compared with the traditional: (1) From single gun to three guns, which not only prepare three different metal composite powders but also increase the productivity. (2) Non-reactive coating to the inner wall of the water-cooled graphite crucible, it can improve the utilization of raw materials and preventing the reaction of molten silicon and graphite. (3) Increase the use of low pressure grading chamber that can effectively classify the powders particle size and improve the quality of powders.

2.4. Preparation of nano-silicon powders

A large number of experiments show that the main factors affecting the preparation of ultrafine powders by plasma evaporation are cathode current intensity, filling pressure and the pressure ratio of hydrogen to argon (P_{H2}/P_{Ar}). Hence the average particle diameter and the productivity rate through L_9 (3^3) orthogonal experiments were investigated in this paper. Before the experiment, it is required to purify the entire system and place the silicon block into the double crucible in powder chamber. The preparation chamber was evacuated to 5×10^{-3} Pa and filled with a certain ratio of hydrogen to argon. Under certain working parameters, change the distance between the electrode plates, the voltaic arc was ignited and then the silicon block was melted to vapors. When silicon atoms get enough kinetic energy from the silicon liquid surface and evaporate out into the powder room with circulating inert gas by the Roots blower. It collides with inert gas and results in the rapid loss of energy. As a result, it cools down and nucleated followed by the growth of powders. After one two-cyclone classification, nano-silicon powders were finally deposited in the powder room. To be cooled after the equipment into the argon to atmospheric pressure, then collecting and sealing after passivation for some time. Table 1 shows technical parameters data of L_9 (3^3) orthogonal experiments. According to the characters of the melting point of silicon, the current intensity is set to 250 A, 350 A and 450 A; the filling pressure is set to 0.02 MPa, 0.04 MPa and 0.06 MPa and the P_{H2}/P_{Ar} is set to 1/9, 3/7, 1/1.

2.5. Statistical analysis of particle size distribution of nano-silicon powders

The software of Simple PCI (US, Compix Company) was applied to calculate the average particle diameter with multiple images of the TEM. Statistics require that each sample requires 5 pictures above the TEM chart, and there are more than 100 valid particles on each chart.

Table 1
Technical parameters data of L_9 (3^3) orthogonal experiments.

No.	1	2	3	4	5	6	7	8	9
P_{H2}/P_{Ar}	1/9	1/9	1/1	3/7	3/7	1/9	3/7	1/1	1/1
Cathode current (A)	350	250	250	250	350	450	450	350	450
Filling pressure (MPa)	0.02	0.04	0.02	0.06	0.04	0.06	0.02	0.06	0.04