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Generation of NiTi Nanoparticles via High Voltage Spark Discharge in Inert Gas

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Abstract. Spark discharge method in inert gas, due to simplicity, no need for complex equipment and raw materials, ability to produce high-purity nanoparticles and mix metallic nanoparticles, is considered a susceptible method for the synthesis of nanoparticles with narrow size distribution. This method is capable to produce nanoparticles of electrical conductor materials and semiconductors. Also, with small changes in spark discharge system, this method can be capable to deposit thin layers of nanoparticles. Now, this method has been used for producing carbon, metal, alloy and metal oxide nanoparticles. Primary objective of this study was to construct a high voltage electrical discharge system. Next step was the synthesis of NiTi alloy nanoparticles in argon atmosphere, using the same Ni-50at%Ti alloy as electrodes. Characterization of NiTi nanoparticles by FESEM, EDX, DLS and HRTEM helps to determine the NiTi nanoparticles size distribution, morphology and composition. The results demonstrated primary nanoparticles ranging from 10 nm to 20 nm in size with a composition close to that of the electrodes.

INTRODUCTION

In recent decades, several studies have focused on nanoparticles (NPs) synthesis, properties and applications in various areas, all resulting from the unique properties which are due to their high specific surface area and quantum size effects [1]. There are many procedures to produce NPs but gas phase methods are increasingly applied too. Gas phase methods are more functional to produce pure NPs with narrow size distributions and crystalline structures [2]. Spark discharge system in gaseous atmosphere is an effective method to generate pure metallic, alloy and oxide NPs due to its simplicity, cost-effectiveness, and flexibility. In this method, ablation of electrodes creates small clouds of material which consequently form a high concentration of primary NPs with rapid cooling [3, 4].

Nickel-titanium (NiTi) NPs exhibit interesting properties like shape memory effect and superelasticity due to the reversible crystallographic structural changes from austenite (B2-cubic structure) to martensite (B19'-monoclinic structure) phase which is induced mechanically or thermally [5]. So, NiTi NPs could be used as nanoactuators in nano-electro-mechanical-systems [6] and thermo-responsive agents in nanofluids [7].

In this study, we investigate the ability of our spark discharge system to produce NiTi NPs and present the characterization results of our products.

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MATERIALS AND METHODS

Synthesis of NiTi NPs was performed by a novel design of spark discharge generator. As shown in Fig. 1, the spark discharge system that was built in our laboratory for the present project consists of a tubular chamber, as a reaction chamber, sealed by stainless steel flanges in which two opposing cylindrical electrodes are mounted at an adjustable distance with two micrometers. The reaction chamber is connected to gas purging and vacuum systems to purify the spark gap atmosphere. The electrodes are connected to a high voltage AC power supply and are parallel to a variable capacitor bank (max 22nF) which was kept constant at 20nF for the present study. The power supply periodically recharges the capacitors after the occurrence of discharge between the electrodes.

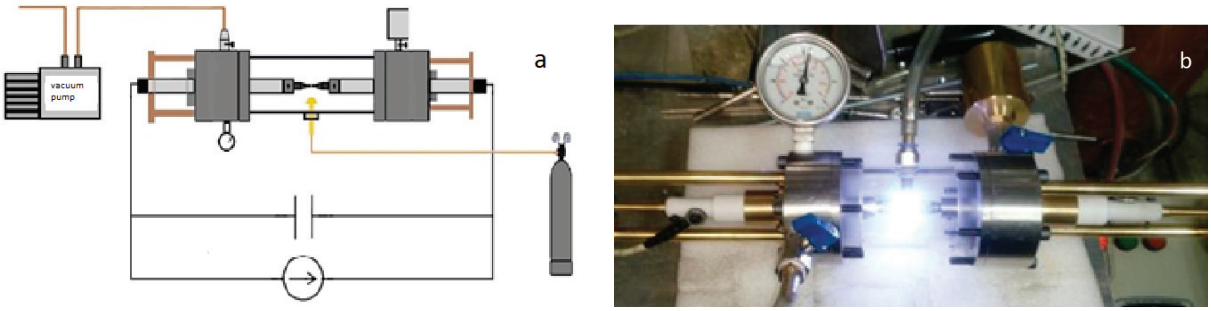

FIGURE 1. (a) Schematic of spark discharge system, (b) photograph of the reactor chamber.

We used a high voltage oscilloscope to measure the discharge voltage (V_d) and also record the V_d-time graphs as shown in Fig. 2. By considering the Fig. 2(a), discharge occurs at AC current with 3kV voltage and 150Hz repetition frequency. During spark generation, the spark gap becomes conducting due to gas ionization between the two electrodes, which leads to weakly damped fluctuations during each spark, as seen in Fig. 2(b).

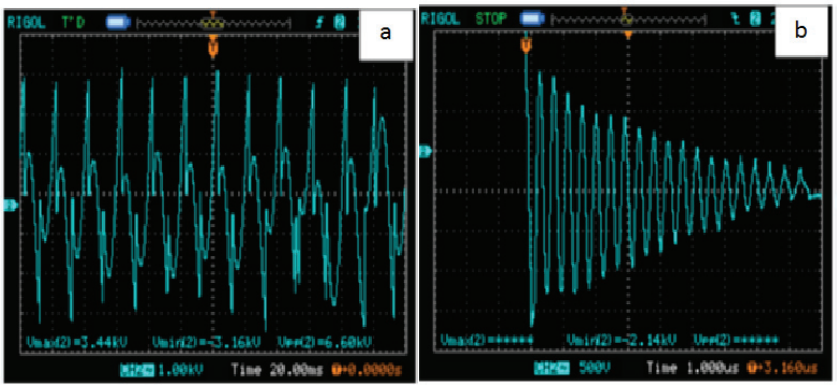

FIGURE 2. V_d-time graphs showing (a) spark frequency, and (b) voltage fluctuations of each discharge.

By Considering the equation $E = \frac{1}{2}CV_d^2$, the discharge energy only depends on the capacitance (C) and discharge voltage (V_d). So, in our measurements, the average energy of each spark discharge with 20nF capacitance and 3kV discharge voltage was about 400mJ.

In this study, we used 2mm diameter NiTi electrodes (50 at% Ni-Ti) at 2mm constant gap distance to produced NiTi NPs. A stream of 0.5 lpm Ar (99.999% purity) was directed toward the spark gap at a total pressure of about 3bar in the reaction chamber. By the high temperature of the sparks, materials were evaporated from the electrodes surface. Very small clouds of evaporated materials were rapidly cooled by radiation, expansion and mixing with the argon gas and led to produce primary NPs which were mostly deposited on the wall of the reaction chamber. The produced NiTi NPs were finally collected from the chamber and stored in n-Hexane without any exposure to air.

Field-emission scanning electron microscopy (FESEM), coupled with energy dispersive X-ray (EDX) analysis with TESCAN MIRA 3-XMU operated at 15kV were performed to study the size, morphology and composition of the produced NiTi NPs. Dynamic light scattering (DLS) analysis was performed with a DLS instrument (Zetasizer,

Malvern Instrument) on a dispersed sample of nanoparticles in n-Hexane at room temperature. The X-ray diffraction analyzes were performed on a PANalytic X'Pert Pro MPD with wavelength of 1.5406 °A CuKα1 to investigate the crystalline phase and structure of the produced NPs. High resolution transmission electron microscopy (HRTEM) studies were carried on a JEOL, JEM-2100F instrument at 80kV accelerating energy to study the size and morphology of NPs.

RESULTS AND DISCUSSION

The FESEM images of the NiTi NPs at two different magnifications and the EDX result are shown in Fig. 3. FESEM images indicate a narrow size distribution with an average size of 18nm for the primary particles. A few agglomerated particles can be observed in Fig. 3(a). The higher magnification in Fig. 3(b) indicates that the NPs are agglomerated due to their large surface energy which depends on the NPs production procedure. EDX analysis of NiTi NPs indicates that the average composition of NPs (Ni52 at%-Ti) is close to the composition of the electrodes material.

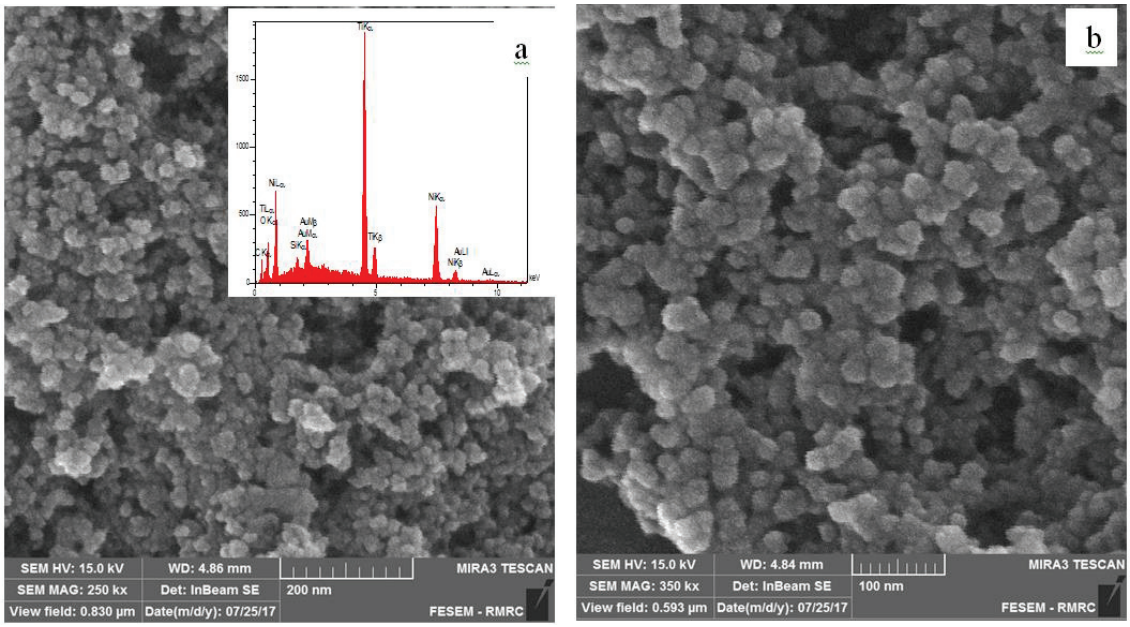

FIGURE 3. FESEM image of NPs at (a) 250 kx, and (b) 350 kx magnifications. The inset is the corresponding EDS spectrum of the produced nanoparticles.

Results of DLS measurement are shown in Fig. 4. As evident, average size of the produced NPs is about 18nm, in consistent with the FESEM results, but a low fraction of larger particles (<100nm) is also seen due to nature of the spark discharge method which has already reported in other studies [2, 3].

The XRD patterns of the NiTi bulk electrode material and the produced NiTi NPs are shown in Fig. 5, indicating the presence of cubic austenite (B2) phase in NiTi electrode and monoclinic martesite (B19'), TiO_2 and Ni phases in the produced NiTi NPs. But, no presence of cubic NiTi (B2) was observed. The calculated average grain size of the NiTi NPs by using Debye-Scherrer formula is about 15nm. As evident from the XRD data, the existence of TiO_2 phase in the NPs is probably due to the sample preparation procedure and exposure of NPs to air. It is predicted that TiO_2 formation at the surface of NPs leads to enrichment of Ni in their cores.

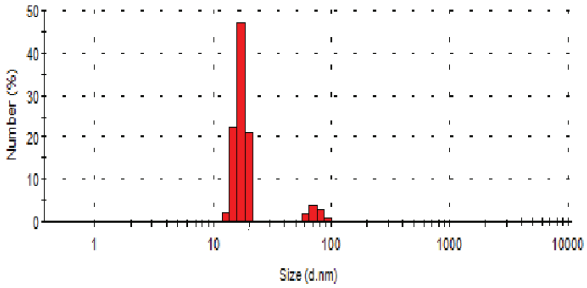

FIGURE 4. Particle size distribution of NiTi NPs.

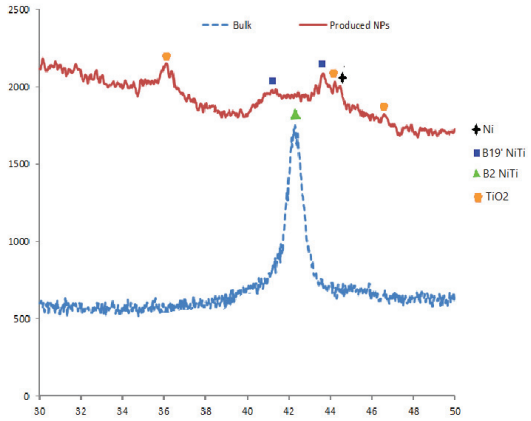

FIGURE 5. XRD patterns of NiTi electrode and the produced NiTi NPs.

Figure 6 is a representative result from HRTEM analysis of the produced NiTi NPs at two different magnifications. It shows the bimodal size distribution in the products and represents that smaller particles have average size of about 18nm which is in agreement with the DLS results. Agglomeration of NPs is frequently observed by electron microscopy. The wavy lines around the particles are because of the amorphous carbon layer which is formed by evaporation of n-Hexane in the sample preparation procedure. Some NPs indicate lighter parts in their surfaces around their dense cores, possibly due to surface oxidation in the sample preparation procedure and formation of TiO_2 at the surface of NPs which causes enrichment of Ni in the cores, supporting the XRD results [8].

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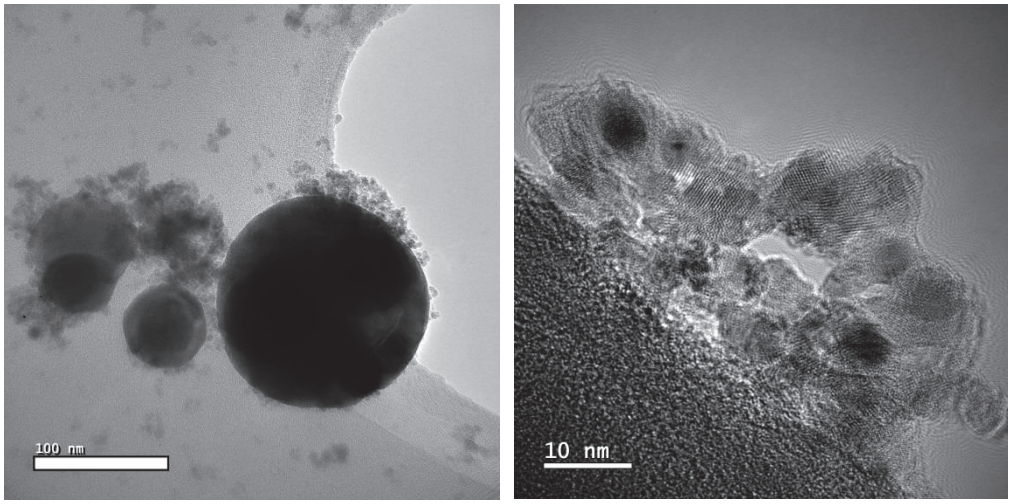

Figure 6. HRTEM micrographs of the NiTi NPs at two different magnifications.

CONCLUSION

In conclusion, an innovative approach was presented in this study to generate NiTi NPs by spark discharge method in the argon atmosphere and store of the products under n-Hexane. The generated NiTi NPs were characterized by different analysis. The results of FESEM, DLS and HRTEM analyses confirmed that the average size of the particles is about 18nm with a narrow size distribution and a low fraction of larger particles. Composition of the produced NiTi NPs estimated by EDX analysis was approximately Ni52at%-Ti which is close to the electrode composition by considering accuracy of the technique. The results of XRD analysis indicated that the generated NPs are composed of B19'-NiTi, TiO_2 and Ni phases and the crystallite size of B19'-NiTi phase in the produced NPs is about 15nm. HRTEM images show that some NPs have dense cores and lighter surfaces which, by comparing with

the XRD results, is related to the surface oxidation of the NPs due to the sample preparation procedure prior to characterization, resulting in the formation of TiO2 at the surface and Ni enrichment in the core of NPs.

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