

MORPHOLOGY OF Ni-Ti CORE-SHELL NANOPARTICLES

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Abstract

Gas aggregation sources based on physical vapour deposition are nowadays commonly used for the preparation of metallic nanoparticles or composite nanostructures containing metals, oxides, nitrides, polymers, etc. The most common configuration of the device for the preparation of core-shell Ni-Ti nanoparticles consists of the primary aggregating source producing the Ni core followed by a second chamber with a Ti target overcoating the core by a shell. The size distribution of core nanoparticles and the thickness and homogeneity of the shell depend on the geometry of the deposition chambers, pressures of working gas, and the power (current, voltage) on both magnetrons. Unfortunately, the power on the Ti magnetron could significantly modify not only the parameters of the coated layer but also the size of the Ni core. The influence of the Ti magnetron current on the final size and homogeneity of complex core-shell particles was studied by high-resolution transmission electron microscopy, scanning (transmission) electron microscopy, and energy-dispersive X-ray spectroscopy. A threshold current value leading to significant morphological changes of nanoparticles was identified.

Keywords: NiTi nanoparticles, magnetron sputtering, core shell, TEM

1. INTRODUCTION

Due to their exceptional properties and diverse applications, nanoparticles have emerged as transformative materials in various scientific and technological fields [1]. Their unique optical, magnetic, and chemical properties, and ability to interact with biological systems at the molecular level make them ideal for uses ranging from electronics and catalysis to medicine and environmental remediation. The versatility and effectiveness of nanoparticles are paving the way for innovations in drug delivery, imaging, sensors, and energy storage, underscoring their pivotal role in advancing modern technology [2, 3].

NiTi core-shell nanoparticles hold significant promise for specialized applications due to their distinct structural and functional properties. These nanoparticles combine a nickel core, known for its ferromagnetic properties [4], with a titanium shell that provides biocompatibility and corrosion resistance [5]. This combination makes NiTi core-shell nanoparticles good candidates for applications in biomedical devices, where the magnetic core can be used for targeted drug delivery or magnetic resonance imaging (MRI), while the biocompatible shell ensures safe interaction with biological tissues [5]. Other potential uses of these nanoparticles are in self-propagating exothermic reactions for material joining instead of multilayer reactive thin films [6].

The production of NiTi core-shell nanoparticles can be effectively achieved using magnetron sputtering by using two planar magnetrons [7]. Magnetron sputtering allows precise control over the deposition parameters; by adjusting the sputtering conditions, such as the geometry of the deposition chambers, pressures of working

gas, and the power (current, voltage) on both magnetrons, it is possible to finely tune the properties of the resulting nanoparticles, including the thickness and uniformity of the core and shell layers.

Achieving the desired ratio of core to shell, which is desirable for using the nanoparticles in joining [8], or the optimal core structure, which affects the magnetic properties of the nanoparticles [9, 10], requires careful tuning of the sputtering parameters. Direct observation and characterization using advanced techniques like transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) are essential to ensure the quality and consistency of the produced nanoparticles.

In this work, NiTi core-shell nanoparticles were produced by magnetron sputtering. The effect of varying magnetron currents on particle morphology was studied by high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy.

2. MATERIAL AND METHODS

Ni@Ti core-shell nanoparticles were prepared using magnetron sputtering with two planar magnetrons. The sputtering system consisted of a primary gas aggregation cluster source (GAS) for creating Ni nanoparticles (NPs) and a secondary chamber for coating them with a Ti film. The primary GAS included a water-cooled aggregation chamber with a diameter of 100 mm and a DC planar magnetron with an 81 mm diameter fitted with a 1.5 mm thick Ni target. This chamber was operated at a pressure of 48 Pa. The secondary chamber featured another DC magnetron, also 81 mm in diameter, but with a 4 mm thick Ti target. Both magnetrons ran under constant current. The exact deposition conditions are listed in **Table 1**. Argon, with 99.996% purity, was used as the working gas. Further details about the experimental setup are available in the work by Hanus et al. [19].

Table 1 Conditions during preparation of specimen by DC magnetron sputtering – current (I), voltage (U) and power (P) on two magnetrons

Ti			Ni		
I (mA)	U (V)	P (W)	I (mA)	U (V)	P (W)
250	188	46	200	270	54
500	203	100	200	269	54
750	212	160	200	269	54

The nanoparticles were deposited onto a glass substrate. The samples for the TEM analysis were prepared by depositing the nanoparticles, suspended in methanol, onto a Cu grid with a lacey carbon support film. A Jeol 2200FS transmission electron microscope was employed in both TEM and STEM modes, equipped with bright field (BF) and high-angle annular dark field (HAADF) detectors and energy dispersive spectroscopy. Moreover, high-resolution TEM images were captured.

3. RESULTS

The produced nanoparticles were characterized by STEM, as shown in **Figure 1**. Most nanoparticles exhibit a core-shell structure with a mostly hexagonal core shape. The diameter of particles increases with increasing the Ti magnetron current. Particularly for the diameter of the core, a mean diameter of 12 nm is observed for the current 250 mA. A considerable increase in the core diameter can be seen for the particles produced with Ti magnetron currents above 500 mA. The mean diameter of the Ni cores or currents 500 mA and 750 mA was 20 nm. The particle sizes range between 12 nm to 25 nm for a current of 750 mA. The size distribution of the particles is less uniform, with a more significant presence of both large and small particles. In contrast, for a current of 500 mA, the size distribution is more uniform. The thickness of the shell varies from 1 nm to 6 nm for all particles produced with different values of Ti magnetron current. Particles with low shell thickness keep the hexagonal shape of the core, while the higher shell thickness results in the round shape of the particles.

The increase in the core size results in a change in the Ni/Ti ratio. Assuming a constant mean shell thickness of 2 nm and an increase in the mean diameter of the core from 12 nm to 25 nm, the volumetric ratio of Ni to Ti changes approximately from 1:1 to 3:1. Correspondingly, the atomic ratio shifts from 2:1 to 9:2. These changes differ from the desirable ratios required for the formation of stoichiometric NiTi or NiTi₂ phases [11].

The high-angle annular dark field shows a sharp boundary between the shell and core (Figure 1d-f) enhanced by the mass-thickness contrast. The higher brightness of the core compared to the shell indicates elements with higher atomic numbers in the core.

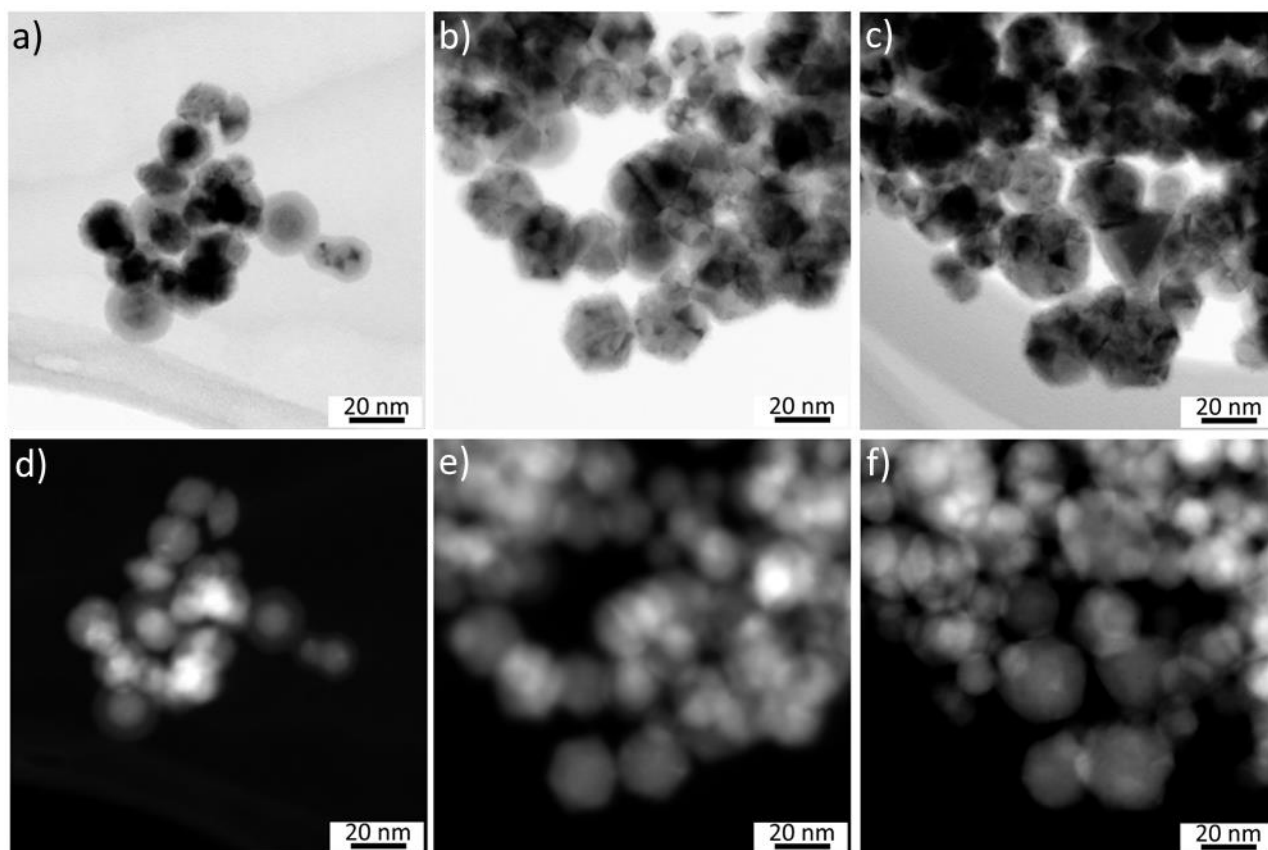


Figure 1 Ni@Ti core shell nanoparticles, a-c) STEM BF, d-f) STEM HAADF. Current on Ti magnetron: a,d) 250 mA, b,e) 500 mA, c,f) 750 mA

HRTEM images were captured (**Figure 2**) to examine the core and shell structure. The Fast Fourier Transform (FFT) images of the particles produced at all used Ti magnetron currents revealed a powder diffractogram consistent with the simulated face-centered cubic (fcc) Ni structure found in JEMS. The fcc structure of the Ni core is mentioned for its significantly higher unsaturated magnetization compared to the hexagonal close-packed (hcp) structures known in the literature [9]. The smaller particles (**Figure 2a**) keep a single crystalline structure of the core, while inside the larger particles (**Figure 2b,c**), fragmentation into areas with several different orientations can be observed. No signs of periodicity were observed inside the shell of the particles. No additional spots were observed in FFT images. These observations indicate the amorphous structure of the shell, except for diffraction spots with distances corresponding to fcc Ni.

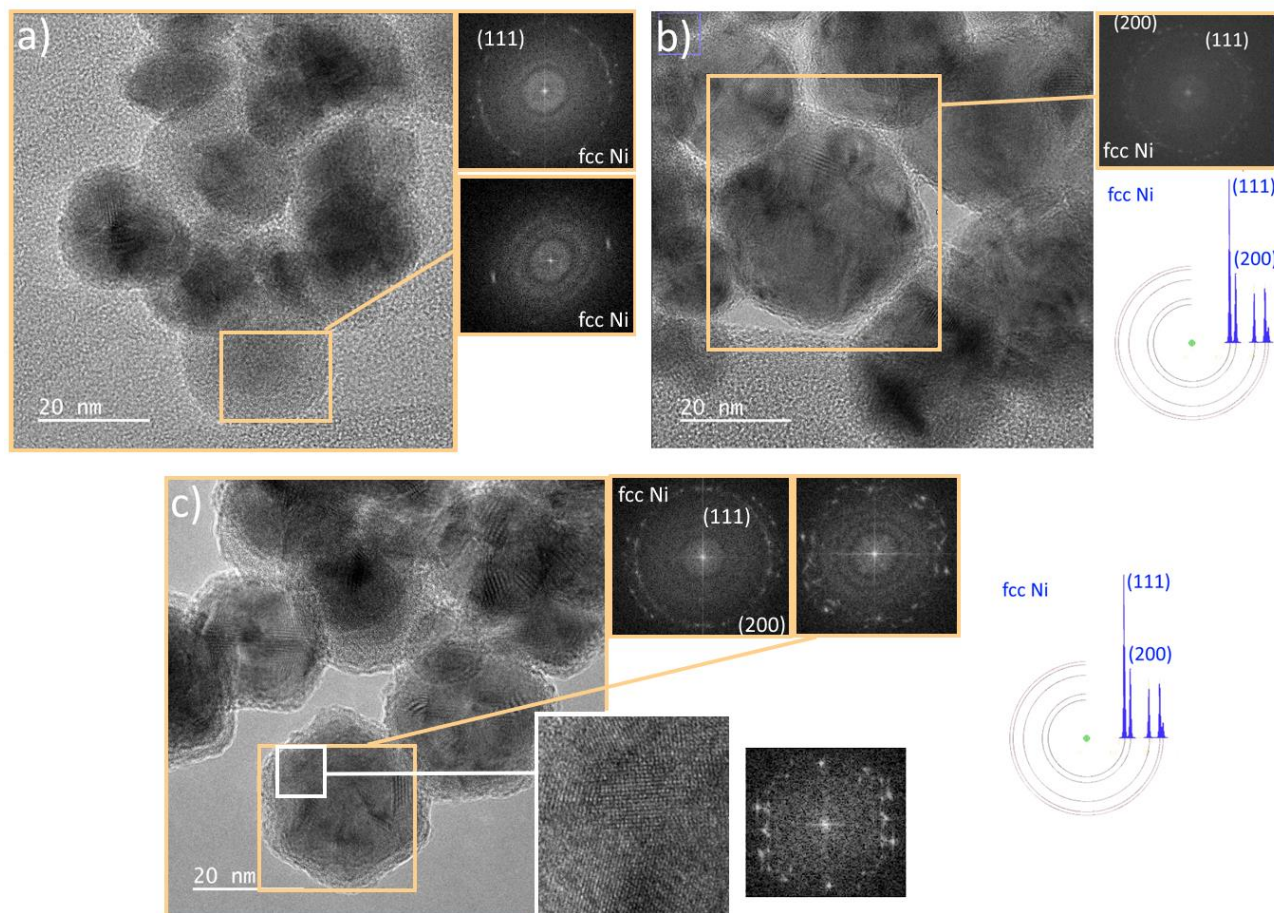


Figure 2 HRTEM images of the nanoparticles produced with different Ti magnetron currents and FFT images of the chosen areas: a) 250 mA, b) 750 mA, c) 500 mA. The corresponding FFT images are taken from the areas denoted by an orange rectangle. The diffraction patterns are compared to JEMS simulated image of the powder diffractogram of fcc Ni

The chemical composition of the core and the shell was further confirmed by EDS. The maps (**Figure 3**) confirm the presence of Ni in the core and Ti and O in the shell. High intensity of both Ti and O signals is visible in particles with visibly thicker shells in the BF images (**Figure 1**). The presence of both Ti and O is also evident in some of the thinner shells. However, some particles with purely oxide shells can be found. No significant effect of the Ti magnetron current on the thickness of the shell was observed. The thickness varies from 1 nm to 6 nm, with only cores with diameters under 15 nm exhibiting shell thickness above 2 nm.

The strong effect of variation of Ti magnetron current on the core of the nanoparticles and a negligible impact on the shell thickness was observed. The thickness of the shell is, in theory, influenced both by the magnetron current and the pressure in the deposition chamber. The higher the pressure, the slower the Ni cores travel through the chamber. At that time, a thicker shell is deposited. However, the higher pressure may also cause the formation of larger Ni nanoparticles in the process. In the used deposition setup, the pressure in the first deposition chamber was kept constant at 48 Pa [7]. The higher gas conductivity of the nozzle in the second chamber, as compared to the nozzle of the primary GAS, ensured that the pressure in the second chamber was about $\frac{1}{4}$ compared to the GAS. However, it seems that the change of the Ti magnetron current influences the exact pressure in the second chamber. For a threshold Ti magnetron current of 500 mA, significant change in the size of the Ni cores occurs.

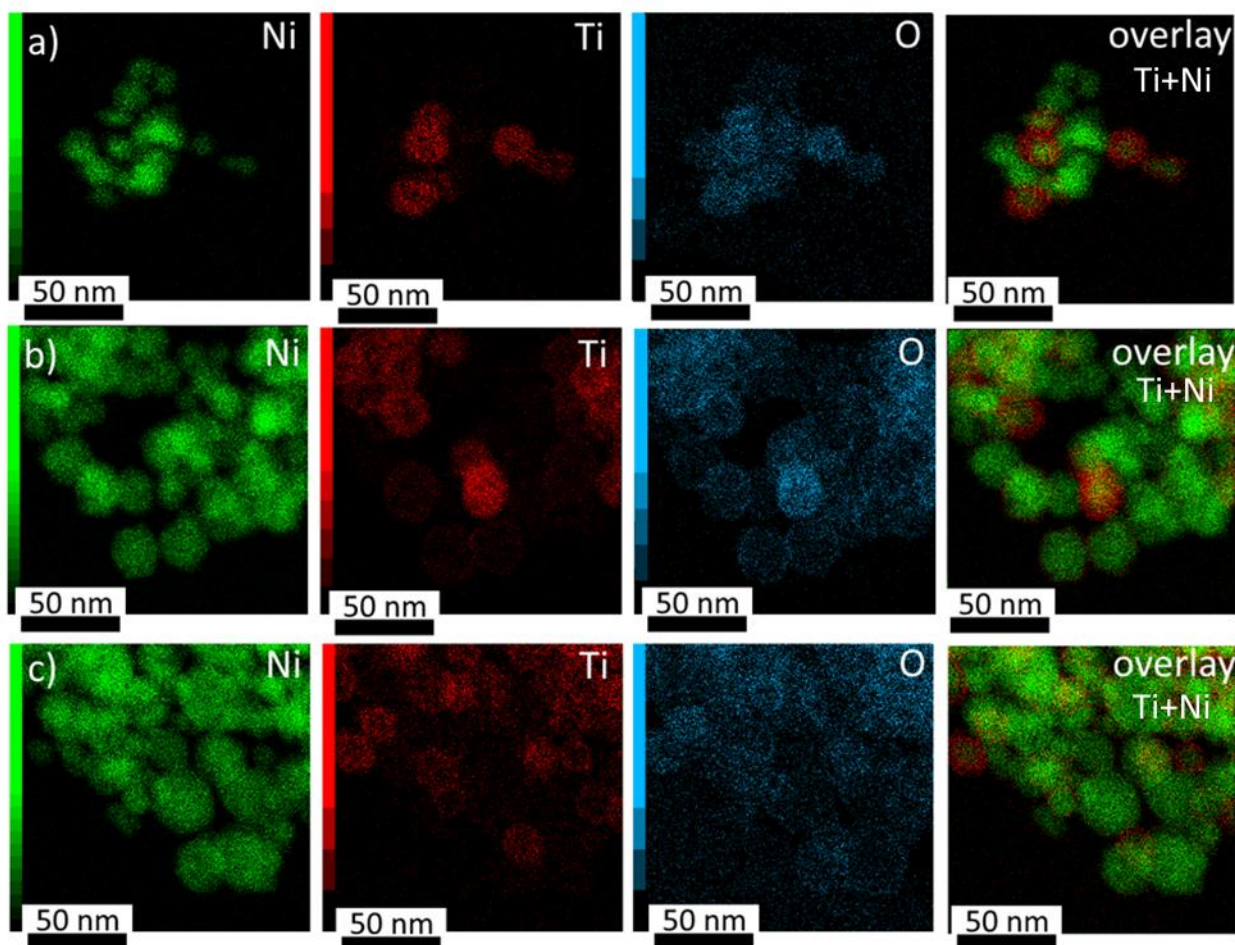


Figure 3 EDS maps of the observed cluster on nanoparticles, a) 250 mA, b) 500 mA, c) 750 mA current on Ti magnetron

4. CONCLUSION

In this study, Ni@Ti core-shell nanoparticles were produced using magnetron sputtering, and the impact of varying the Ti magnetron current on their morphology was investigated. The nanoparticles featured a polycrystalline fcc Ni core and an amorphous TiO shell. Increasing the Ti magnetron current above 500 mA led to a rapid increase in core diameters (mean diameter increased from 12 to 25 nm). Varied shell thicknesses (1 to 6 nm) were observed for all used Ti magnetron currents. These results highlight the importance of all sputtering parameters to control nanoparticle size and morphology, which is crucial for their applications.

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REFERENCES

- [1] KHAN, I., SAEED, K., KHAN, I. Nanoparticles: Properties, applications and toxicities. *Arabian Journal of Chemistry*. 2019, vol. 12, no. 7, pp. 908-931. ISSN 1878-5352. DOI: <https://doi.org/10.1016/j.arabjc.2017.05.011>.
- [2] ALTAMMAR, K.A. A review on nanoparticles: characteristics, synthesis, applications, and challenges. *Front Microbiology*. 2023, vol. 14, article 1155622. DOI: 10.3389/fmicb.2023.1155622. PMID: 37180257; PMCID: PMC10168541.

- [3] DREADEN, E.C., ALKILANY, A.M., HUANG, X., MURPHY, C.J., EL-SAYED, M.A. The golden age: gold nanoparticles for biomedicine. *Chemical Society Reviews*. 2012, vol. 41, pp. 2740-2779.
- [4] JAJI, N., LEE, H.L., HUSSIN, M.H., AKIL, H.M., ZAKARIA, M.R., OTHMAN, M.B.H. Advanced nickel nanoparticles technology: From synthesis to applications. *Nanotechnology Reviews*. 2020, vol. 9, no. 1, pp. 1456-1480. DOI: <https://doi.org/10.1515/ntrev-2020-0109>.
- [5] KURAPOV, Y.A., LITVIN, S.E., BELYAVINA, N.N. et al. Synthesis of pure (ligandless) titanium nanoparticles by EB-PVD method. *Journal of Nanoparticle Research*. 2021, vol. 23, article 20. DOI: <https://doi.org/10.1007/s11051-020-05110-3>.
- [6] SEN, S., LAKE, M., KROPPEM, N., FARBER, P., WILDEN, J., SCHAAF, P. Self-propagating exothermic reaction analysis in Ti/Al reactive films using experiments and computational fluid dynamics simulation. *Applied Surface Science*. 2017, vol. 396, pp. 1490-1498. ISSN 0169-4332. DOI: <https://doi.org/10.1016/j.apsusc.2016.11.197>.
- [7] HANUŠ, J., et al. *Journal of Physics D: Applied Physics*. 2017, vol. 50, article 475307.
- [8] MA, Y., LI, H., YANG, L., HU, A. Microstructures and Reaction Properties of Ti/Ni, Ti/Al and Ni/Al Multilayer Films. *Journal of Nano Research*. 2018, vol. 54, pp. 22-34. DOI: [10.4028/www.scientific.net/JNanoR.54.22](https://doi.org/10.4028/www.scientific.net/JNanoR.54.22).
- [9] GONG, J., WANG, L.L., LIU, Y., YANG, J.H., ZONG, Z.G. Structural and magnetic properties of hcp and fcc Ni nanoparticles. *Journal of Alloys and Compounds*. 2008, vol. 457, nos. 1-2, pp. 6-9. ISSN 0925-8388. DOI: <https://doi.org/10.1016/j.jallcom.2007.02.124>.
- [10] LIN, L., LI, S., HESSEL, V., STAROSTIN, S.A., LAVRIJSEN, R., ZHANG, W. Synthesis of Ni nanoparticles with controllable magnetic properties by atmospheric pressure microplasma assisted process. *Inorganic Materials: Synthesis and Processing*. 2017. DOI: <https://doi.org/10.1002/aic.16054>.
- [11] ADAMS, D.P., RODRIGUEZ, M.A., McDONALD, J.P., BAI, M.M., JONES, E. Jr., BREWER, L., MOORE, J.J. Reactive Ni/Ti nanolaminates. *Journal of Applied Physics*. 2009, vol. 106, article 093505.