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SYNTHESIS OF NiTi/Ni-TiO₂ COMPOSITE NANOPARTICLES VIA ULTRASONIC SPRAY PYROLYSIS

SINTEZA KOMPOZITNIH NANODELCEV NiTi/Ni-TiO₂ Z ULTRAZVOČNO RAZPRŠILNO PIROLIZO

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In this paper we present the production of NiTi/Ni-TiO₂ composite nanoparticles via the synthesis method called ultrasonic spray pyrolysis (USP). The precursor solution for the synthesis of spherical NiTi particles was prepared from an orthodontic wire with a chemical composition of Ni (amount fraction $x = 51.46\%$) and Ti ($x = 48.54\%$). TEM microscopy, in combination with EDX analyses, was used for a detailed characterization of the obtained NiTi nanoparticles. The results showed the nanoparticle sizes ranging from 60 nm to 600 nm, depending on the parameters of the production procedure. This showed the versatility of the new USP synthesis procedure, proving its usefulness for different materials and applications.

Keywords: ultrasonic spray pyrolysis, NiTi/Ni-TiO₂ composite nanoparticles, characterization, TEM microscopy

V tem prispevku je predstavljena izdelava NiTi/Ni-TiO₂ kompozitnih nanodelcev po metodi ultrazvočne razpršilne pirolize (USP). Sferični nanodelci NiTi so bili izdelani iz ortodontske žice s kemijsko sestavo Ni (množinski delež $x = 51,46\%$) in Ti ($x = 48,54\%$). Za karakterizacijo nanodelcev je bila uporabljena TEM-mikroskopija v kombinaciji z EDX-analizo. Rezultati meritev so pokazali velikostno porazdelitev narejenih nanodelcev v razponu od 60 nm do 600 nm v odvisnosti od parametrov izdelave. To potrjuje vsestranskost novega izdelovalnega postopka USP in njegovo uporabnost za različne materiale in aplikacije.

Ključne besede: ultrazvočna razpršilna piroliza, kompozitni nanodelci NiTi/Ni-TiO₂, karakterizacija, TEM-mikroskopija

1 INTRODUCTION

During the recent swarm of nanosized materials in the last decade, nanosized particles of nickel titanium, a shape-memory alloy in the macroscopic world, have not been overlooked. The potential of the nanoparticles of NiTi lies in their biocompatibility, magnetic and photocatalytic properties.¹ As such, they have a potential for applications in the anode of solid-oxide fuel cells or in the conductive electrolytic layer of proton-exchange-membrane fuel cells. Replacing platinum with nickel titanium nanoparticles in automotive catalytic converters would also significantly reduce their costs. They also have a potential in coatings, plastics, nanowires, nanofibers and textiles or as a temperature-control system.²

The most widely used method for producing nickel titanium nanoparticles is laser ablation of the alloy in a liquid. Laser ablation has some advantages as a production method, such as a disperse distribution of the colloids in the solvent, no use of toxic chemical precursors, chemically pure nanoparticles and its applicability for different materials.³ The produced NiTi nanoparticles form a titanium oxide layer on the surface, creating a core-shell structure of the nanoparticles. The thickness of the layer varies, depending on the organic liquids used for the suspension.⁴ Other production methods of NiTi

nanoparticles include ultrasonic electrolysis, mechanically assisted synthesis (nickel and titanium powders in a planetary ball mill),⁵ electro-explosion of a NiTi wire with spark-plasma sintering,⁶ gas-flash evaporation,⁷ thin-film deposition in combination with nanosphere lithography,⁸ electric-discharge plasma in liquid⁹ and biosynthesis/bioreduction.¹⁰

For the purposes of positioning the teeth to a desired location in orthodontics, NiTi wires have been proved to be very useful. This alloy's shape-memory effect and superelasticity provide a good combination of care for the patient and a reasonable treatment duration.¹¹ Even though nickel is considered toxic, the nickel titanium alloy is biocompatible due to the high reactivity of titanium in oxygenated environments. As such, a titanium dioxide layer is formed on the surface of a shape-memory alloy, providing a good corrosion resistance and preventing nickel from migrating outwards from the alloy, causing biocompatibility of the alloy. To further improve the handling of such orthodontic tools, a project involving nickel titanium nanoparticles for orthodontics was proposed. A replacement for the bulk nickel titanium wire with a textile or polymer fiber coated with NiTi nanoparticles via electrospinning and then removing the fiber could produce a hollow wire for orthodontic purposes. This wire could potentially have the same

shape-memory and superelasticity properties, while possibly reducing the material needed for the wire production. After producing such a hollow NiTi wire, its properties would have to be compared with the original NiTi orthodontic wire already in use.

In our research of the nanoparticle production, we had some successes with the production of gold nanoparticles with the ultrasonic-spray-pyrolysis method (USP).¹² This is a simple, low-cost process, available to produce nanoparticles from different materials. The concept of USP is to produce aerosol droplets of a solution with a dissolved material, desired for the nanoparticles. These micro-sized droplets of the precursor solution are generated by the ultrasound. The frequency of the ultrasound and the surface tension of the solution determine the size of the droplets. The droplets are a few micrometers in diameter and are produced as the ultrasound reaches the surface of the liquid, generating cavitation (a formation, growth and implosive collapse of the bubbles in a liquid).^{13,14} The generated droplets are then carried by a carrier gas into the furnace, where the reactions for the nanoparticle formation occur. The gas can be a mixture of a carrier gas and a reaction gas or, in some cases, a single gas acting as the carrier and reaction gas at the same time. When the droplets reach the furnace, the heightened temperature starts to evaporate the solvent and the droplets shrink in size. The dissolved material required for the nanoparticles starts to diffuse into the core of the droplet. The solvent evaporates completely and the dried porous particle then reacts with the reduction gas. The reacted particle is then sintered into the solid final particle, which is then carried away by the carrier gas into the collection bottles.¹⁵ This is the principle of the one-particle-per-droplet mechanism.

The final size of the particle is thus mainly dependent on the size of the droplets, the precursor concentration and the reactor temperature. The droplet size is controlled with the ultrasound frequency, as higher frequencies produce smaller droplets. Higher precursor concentrations cause a higher concentration in a droplet and a bigger final particle size.¹² The temperature must be high enough for the reactions to occur. However, very high

temperatures evaporate the solvent faster, leaving less time for the diffusion of the material. When this occurs, the result is the creation of porous particles and particles with irregular shapes. In some cases the material reaction occurs on the surface of the droplets, creating shell structures. In the case of creating ideally spherical particles, an ideal temperature must be found, low enough to allow the time for diffusion, while still high enough for the required reactions to occur. This could be done experimentally or theoretically, where a lot of diffusion and reaction data would have to be acquired. A two-step USP process can also be employed, capable of creating core-shell structures with two different materials.¹³

In this work we present the results of our first experimental work in the field of NiTi/Ni-TiO₂ composite-nanoparticle production via USP. With this research we want to simplify the field of nanotechnology, allowing a transfer of this production to the industrial level.

2 MATERIALS AND METHODS

For the synthesis of NiTi/Ni-TiO₂ composite nanoparticles, we used an orthodontic wire composed of amount fraction of Ni $x = 51.46\%$ and $x = 48.54\%$ of Ti. To prepare the precursor for USP, the wire was dissolved in aqua regia (12 mL or 24 mL of HNO₃ + 3HCl) and the resulting solution was topped off to the required volume with water (a total volume of 500 mL).

The resulting solution was then used for generating aerosol droplets with a USP device assembled at the IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany. The device contains an ultrasonic atomizer with an ultrasound generator and a reservoir for the precursor, a thermostat for keeping the precursor solution at a constant temperature, a quartz tube and furnace for the reaction of precursor droplets, some tubing leading the aerosol into and out of the furnace, and collection bottles with alcohol and water for the nanoparticle collection (**Figure 1**). The ultrasonic atomizer (Gapsol 9001, RBI/France) was producing aerosol droplets with one transducer at the selected frequency of 2.5 MHz.

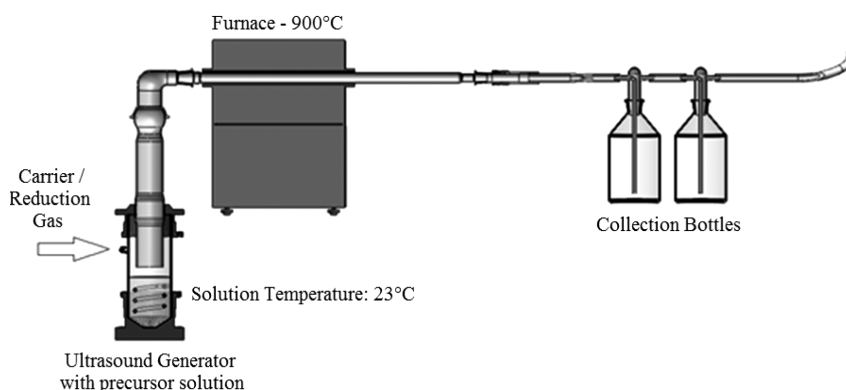


Figure 1: Schematic presentation of the USP device

Slika 1: Shematska predstavitev USP-naprave

The experiment of the USP procedure was run in several steps. First, nitrogen was flushed into the system at a rate of 1 L/min to remove air from the tubes. When the furnace reached the selected temperature, hydrogen was added to the flow of nitrogen, at a rate of 1.5 L/min. After a while, a steady flow of nitrogen and hydrogen was established. At this time, the ultrasonic generator was turned on, creating aerosol droplets from the precursor solution. The droplets were then carried via gas into the furnace, where the reactions occurred, and the final particles were then carried out of the furnace and collected in the collection bottles. The retention time of the droplets/particles in the quartz tube of 1 m length and 20 mm diameter was about 30 s. The temperature of the precursor solution was kept at 23 °C and the furnace temperature at 900 °C. The system parameters (the solution temperature, furnace temperature, steady volume of the solution in the ultrasonic atomizer, etc.) were being monitored for the duration of the experiment. The collection bottles in the first experiments contained water and, in later experiments, alcohol for the prevention of agglomeration and titanium oxide formation. The experiment parameters are provided in **Table 1**.

Table 1: Technological parameters of the performed experiments

Tabela 1: Tehnološki parametri opravljenih eksperimentov

Expe- riment	Concen- tration (g/L)	Tempe- rature (°C)	Gas flow N ₂ (L/min)	Gas flow H ₂ (L/min)	Time (h)	Collec- tion
1	0.5	900	1	1.5	5.5	Water
2	0.25	900	1	1.5	5.5	Water
3	0.5	900	1	1.5	5.0	Ethanol
4	0.25	900	1	1.5	5.0	Ethanol

A transmission electron microscope (TEM) with an EDX analysis was used for the characterization of the obtained nanoparticles and analysis of their morphology.

3 RESULTS

The NiTi/Ni-TiO₂ composite orthodontic wire was dissolved in aqua regia (HNO₃ + 3HCl) and diluted with water. The oxidizing properties of chloride ions and chlorine etch away nickel and titanium from the lattice, creating nickel chlorides NiCl₂ and titanium chlorides TiCl₄. The addition of hydrogen gas inside the furnace then reduces the chlorides and creates particles with nickel and titanium. The resulting sizes of the produced nanoparticles are dependent on the precursor concentration and ultrasound frequency used for the creation of aerosol droplets, as reported previously.¹² The obtained solution was left overnight for particle sedimentation. The excess fluid was removed and the resulting samples were characterized with TEM and EDX analysis. The analysis showed nearly ideally spherical nanoparticles with different sizes (**Figure 2**), according to the concentration and the ultrasound frequency. The obtained nanoparticles consisted of titanium, nickel and oxygen (**Fig-**

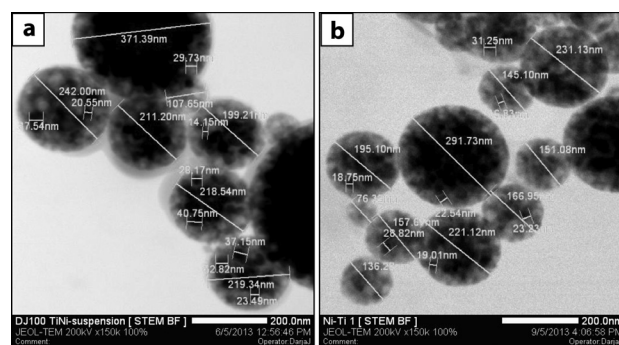


Figure 2: Sizes of NiTi/Ni-TiO₂ composite nanoparticles depending on the precursor concentration: a) 0.5 g/L NiTi, experiment numbers 1 and 3, b) 0.25 g/L NiTi, experiment numbers 2 and 4

Slika 2: Velikosti kompozitnih nanodelcev NiTi/Ni-TiO₂ pri različnih koncentracijah prekursorja: a) 0,5 g/L NiTi, številki poskusov 1 in 3, b) 0,25 g/L NiTi, številki poskusov 2 in 4

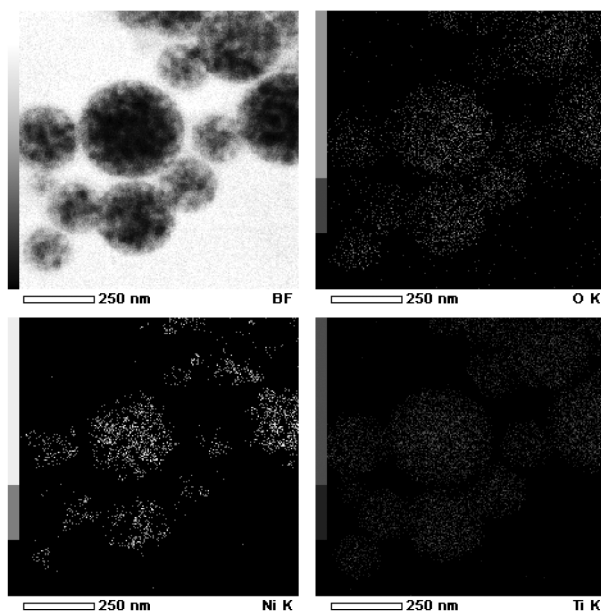
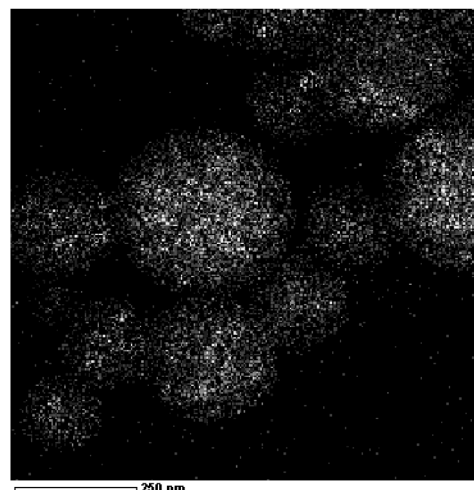


Figure 3: Element mapping of NiTi/Ni-TiO₂ composite nanoparticles (No. 1)

Slika 3: Porazdelitev elementov pri kompozitnih nanodelcih NiTi/Ni-TiO₂ (št. 1)

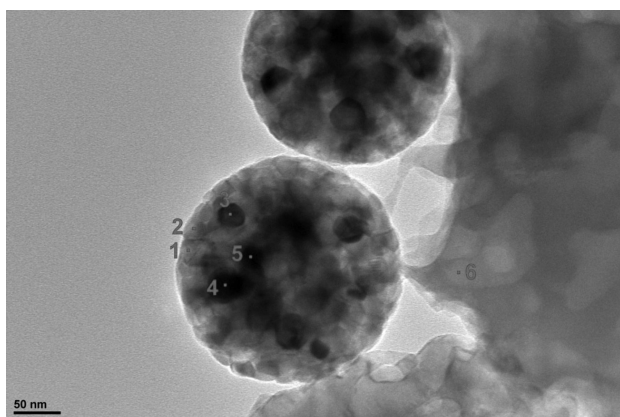


Figure 4: Points for the EDX analysis on the NiTi/Ni-TiO₂ composite nanoparticles' surface (No. 1)

Slika 4: Mesta na površini kompozitnih nanodelcev NiTi/Ni-TiO₂ (št. 1), kjer je bila izvršena EDX-analiza

ure 3). The ratio between nickel and titanium was lower than expected; with the orthodontic wire used for the experiments it was about 1 : 1, while with the nanoparticles the values for the nickel amount were much lower (**Figure 4** and **Table 2**).

Table 2: Chemical composition of the points on the NiTi nanoparticles' surface form **Figure 4**

Tabela 2: Kemijska sestava točk na površini nanodelcev NiTi s **sluke 4**

Point	$x(\text{Ni})/\%$	$x(\text{Ti})/\%$	$x(\text{O})/\%$
1	/	44.29	54.05
2	/	41.72	56.60
3	31.22	28.21	39.36
4	40.78	20.65	38.02
5	21.78	26.88	50.70

4 DISCUSSION

The production steps for the synthesis of nanoparticles from an orthodontic NiTi wire and their usage with the process of electrospinning are shown in **Figure 5**. With electrospinning the particles are spun onto fibers like building blocks, producing a thin shell with the properties of the nanoparticle material. The fibers could

then be removed, for example, with chemical etching, producing new, otherwise hard-to-obtain shapes.

The high reactivity of titanium with oxygen is a problem for pure nickel titanium nanoparticle formation. The results suggest that the nanoparticles are formed from titanium oxide with smaller amounts of nickel. Even though the reaction takes place in a hydrogen/nitrogen atmosphere, a high amount of oxygen also comes from the water of the precursor, as the reaction runs at a high temperature. Some effort was made to reduce the amount of titanium oxide formation with the use of alcohol in the collection bottles. A smaller amount of oxygen in alcohol allowed this reduction to occur to a certain degree, while the total elimination of the titanium oxide formation from the particles was not achieved. To obtain such particles, a different solution would be required for the dissolution of the NiTi wire. Organic compounds and alcohol were used previously; however, the results of such experiments were unsatisfactory. The use of such solutions as the precursor resulted in destroyed particles or no particles being collected in the collection bottles, or alcohol complexes being formed. The use of organic compounds would also increase the cost and complexity of the process, while not producing the desired product.

The analysis of the particles also showed that the larger particles contain more nickel than the smaller ones. This can also be seen from the TEM figures (**Figure 2**), where the darker, blackened areas represent nickel in the particles, whereas the lighter, grayer areas represent titanium dioxide. The different shades in the figure are the result of different densities shown by the TEM imagery; nickel is darker because it has about twice the density of titanium dioxide (the nickel density is 8.9 g/cm³ versus titanium dioxide with 4.23 g/cm³). Smaller particles, up to about 180 nm, are grayer, which suggests there is a smaller amount of nickel, and this is supported by the EDX analysis. In **Figure 3**, less nickel is seen in smaller particles. As such, the bigger particles (more than 180 nm) have a core of nickel and a coating of titanium dioxide. A further analysis is required for determining whether the core of the bigger particles is purely nickel or the desired nickel titanium alloy.

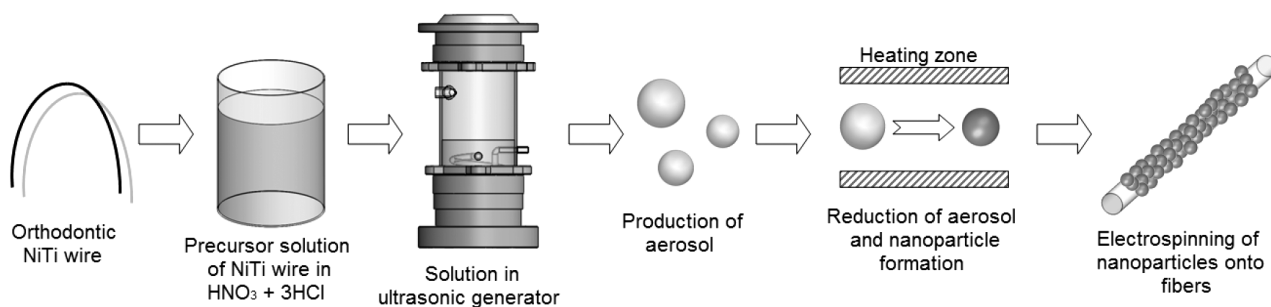


Figure 5: Production steps for the synthesis of nanoparticles from an orthodontic NiTi wire and their usage in electrospinning

Slika 5: Koraki pri sintezi nanodelcev iz ortodonske NiTi-žice in njihova uporaba pri elektropredanju

It is very difficult to obtain pure nickel titanium particles with USP due to the high reactivity of titanium with oxygen. Even though pure nickel titanium particles could be obtained, they would have to be stored in a virtually oxygen-free environment to prevent a titanium oxide formation on the surface of pure particles. As a source for nickel titanium used in these experiments, the orthodontic NiTi wire already has an outside layer of titanium dioxide. In order to use this wire as a precursor the layer would have to be removed. This would complicate the process of creating the precursor to more than just dissolving the wire in aqua regia. At this point, using different sources for nickel and titanium, such as nickel and titanium powders, would probably be more reasonable. Further research into the available precursor solutions for NiTi nanoparticles and collection media has to be performed.

Even though the resulted particles were not pure NiTi, but rather Ni-TiO₂, such particles do have some promising properties.^{1,16,17} They have a photocatalytic function and can be used as a nickel titania nanocomposite coating, providing a good corrosion resistance and also a heightened hardness. The nickel containing TiO₂ nanoparticles is also promising as the material for high-temperature fuel-cell electrodes, as well as the catalyst for hydrogen cleavage in hydrogenation processes. Nickel titania particles were synthesized with a number of processes, such as adsorption of Ni to TiO₂, sol-gel methods, gas condensation and photodeposition of nickel nanoparticles on titanium dioxide.^{1,16–19} However, with this experiment, the USP process was proven to be a versatile process, capable of creating nanoparticles of various materials.

5 CONCLUSION

Particles of Ni-TiO₂ were synthesized with USP, using a dissolved orthodontic NiTi wire as the precursor. The particles were formed at 900 °C, with nitrogen as the carrier gas and hydrogen as the reduction gas and were collected in water or alcohol. The TEM and EDX analysis showed that spherical particles with different compositions were created. The particles larger than 180 nm were composed of nickel with an outside layer of titanium dioxide, while the smaller particles were mainly composed of titanium dioxide. Further research and analysis of the particles obtained are needed for a better understanding of the particle formation with the experiment parameters used. With the current selection of the precursors, reaction gas and collection medium, it is difficult to obtain pure NiTi particles, which are desired. For this reason, an investigation of different precursor solutions, gases and collection media should be conducted.

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