Nanoparticles prepared from NiTi orthodontic wire

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Abstract

Nanoparticles were synthesized from NiTi orthodontic wire with the synthetic aerosol process Ultrasonic Spray Pyrolysis and characterized with SEM and TEM microscopes, with EDX analysis and zeta potential measurements. The shape memory effect of these particles has been surmised through the analysis of the obtained results and available literature. Investigation showed that on the particles the titanium volume had been oxidized, entrapping the nickel content inside the particle cores. Even though Ti oxides have inhibited the shape memory effect of the material somewhat, it probably does not eliminate this property. First tests have also been investigated using these nanoparticles in the electrospinning process for textile fabrication.

Keywords: nickel titanium, nanoparticles, shape memory effect

Introduction

Nickel titanium alloys exhibit shape memory effect and superelasticity properties in addition to good corrosion resistance and biocompatibility. This makes them used widely in biomedical applications such as stents, guide wires, orthodontic wires, orthopedic devices, filters and surgical devices. Fabricating nickel titanium alloys has some difficulties, as the properties of the material are very sensitive to the starting chemistry and subsequent processing [1]. The reversible solid state martensitic transformation gives this material its unconventional properties. At higher temperatures the material obtains the cubic crystal structure austenite, while at lower temperatures it is in its monoclinic crystal structure martensite. When the material is in its martensite phase it can be deformed up to 6-8% while rearranging the atomic planes without breaking the atomic bonds, also known as twinning [2]. Upon heating the material it then takes the structure and form of the austenitic phase. Cooling the material in this state then transforms it into the martensitic phase (Figure 1). It has been speculated whether these material traits would carry over onto the nanosized particles, as a lot of materials have different properties as nanoparticles compared to their bulk counterpart [3]. Shape memory alloy nanoparticles could open up new possibilities for this type of material, especially when used with nanoparticles of different shapes. Rods, thin films, or spherical particles coupled with a shape memory effect could produce some interesting results, based on their application. There are several ways of producing nickel titanium nanoparticles from laser ablation [4, 5], ultrasonic electrolysis [6], electro explosion of NiTi wire by spark plasma sintering [7], gas flash evaporation [8] and others.

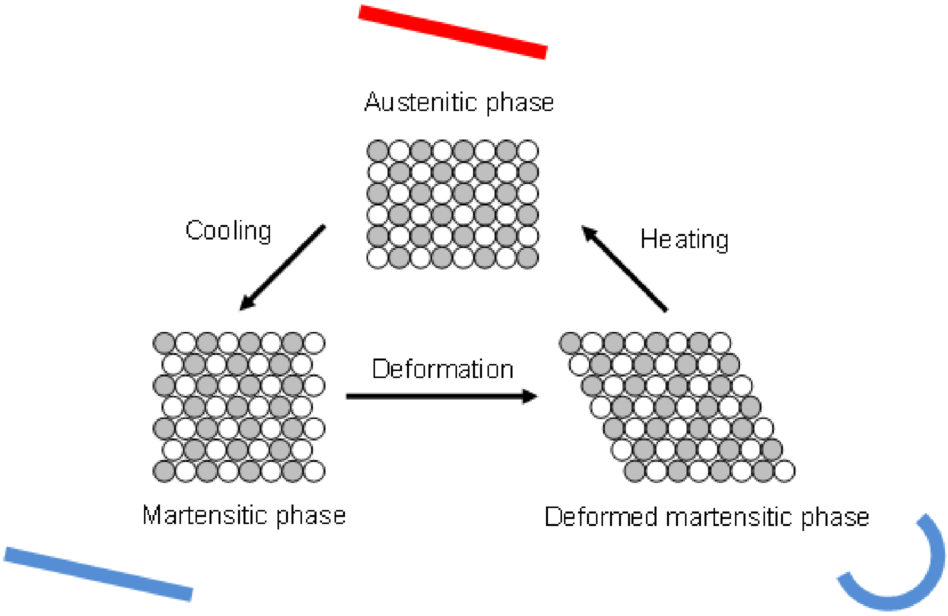

Figure 1: Schematic of phase transformation in a shape memory alloy

In our experimental work, NiTi nanoparticles were synthesized with Ultrasonic Spray Pyrolysis (USP), a simple synthetic aerosol technique [9]. This method uses a solution of the desired material as a precursor for nanoparticle production. The precursor is subjected to ultrasound to produce aerosol droplets, carried into a furnace by an inert gas, where nanoparticles are produced from the droplets with the addition of a reaction gas [9–11]. The size of the particles depends on the concentration of precursor used, the reactor temperature, and the droplet sizes. The process can produce nanoparticles of a lot of different materials and can be modified to produce core-shell structures, porous structures, etc.

Materials and methods

A precursor solution for the USP process was prepared from orthodontic wires with a composition of 51,46% Ti and 48,54% Ni, dissolved in 12 ml of aqua regia (HNO_3 + 3 HCl) and diluted in water. This solution was used in a USP device at the IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany [9–12]. The wires were dissolved into chlorides of Ni and Ti, and hydrogen gas was introduced in the USP for chloride reduction. The particles were collected in wash bottles containing ethanol to prevent oxidation. For the experiments, the following parameters were used [12]:

- Precursor concentrations: 0,5 and 0,25 g/l of dissolved NiTi wire (small concentrations are required to produce nanoparticles with sizes around 100 nm)
- Ultrasound frequency: 2,5 MHz
- Furnace temperature: 900°C
- Gas flow: N_2, at 1 l/min (aerosol carrier) and H_2, at 1,5 l/min (reduction of chlorides)

SEM images were acquired at 20 kV accelerating voltage, TEM and EDX analyzes were used for characterization of the particles, with 200 kV accelerating voltage, with line analyzes and elemental mapping. We also conducted Zeta potential measurements of the particles.

Results

A TEM image of the obtained particles is shown in Figure 2. The structure of the particles can be seen from microscopy images, with darker areas representing nickel, while the lighter areas of the particle are composed mainly of titanium dioxide. EDX analysis confirms this composition in Figures 3 and 4.

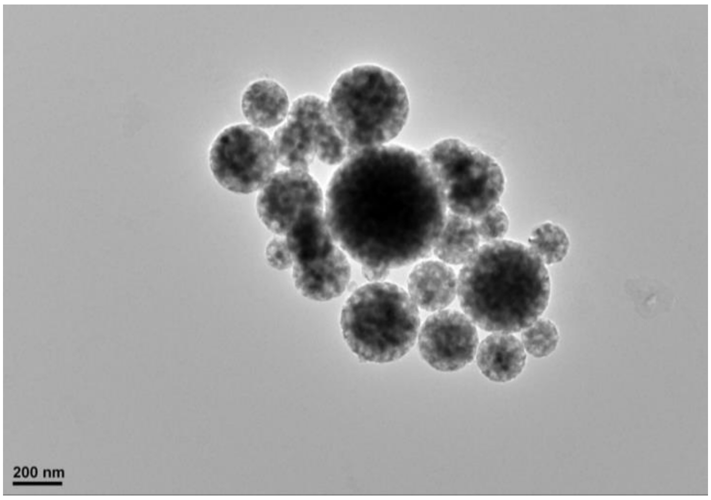

Figure 2: TEM image of nanoparticles obtained with USP

The images show less nickel content than originally anticipated from the synthesis precursor, while there is more nickel in the larger particles than the smaller ones. The particle sizes range from 60 to 600 nm, while the particles larger than around 160-180 nm show more nickel content. The lighter parts of the nanoparticle in the images represent titanium dioxide. The darker areas represent nickel in the particles, as TEM imagery shows denser materials in a darker hue (Figures 2 and 3).

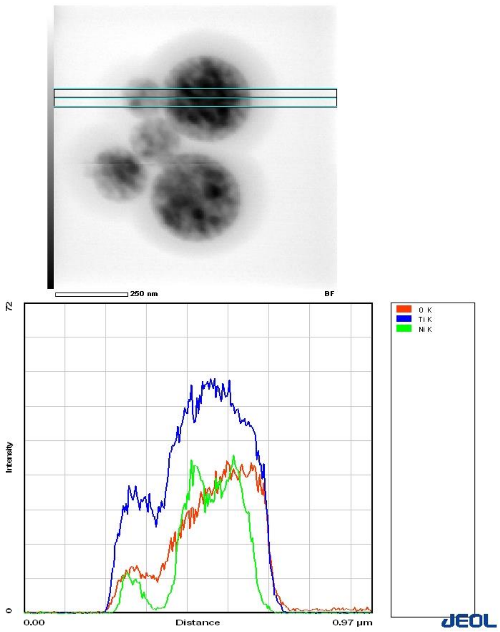

Figure 3: Line profile clearly showing a titanium oxide layer around the nickel content in the particle

Particles below 160-180 nm contain individual kernels or small areas of Ni inside the particles. Particles larger than 160-180 nm are more enriched in nickel; however, the individual kernels are enclosed in clusters, most likely in elemental form. It is assumed that Ni has not oxidized due to the high reactivity of Ti and TiO_2 formation energy compared to Ni. In these larger particles, the Ni and TiO_2 ratio is relatively equal, compared to the smaller particles where TiO_2 is more abundant.

This suggests that the initial precursor concentration of Ni and Ti in solution used with USP was not equal to the concentrations of each individual aerosol droplet. The varying concentrations of Ni and Ti in the droplets have thus formed a distribution of smaller and larger particles with different compositions. The presence of oxygen in the obtained nanoparticles inhibits shape memory and superelasticity properties, as titanium migrates from the lattice to form oxides. In bulk form the formation of titanium oxides presents good anti-corrosive and biocompatibility properties. while in nanoparticles there are not as many titanium atoms available and atoms removed from the lattice hinder the shape memory effect.

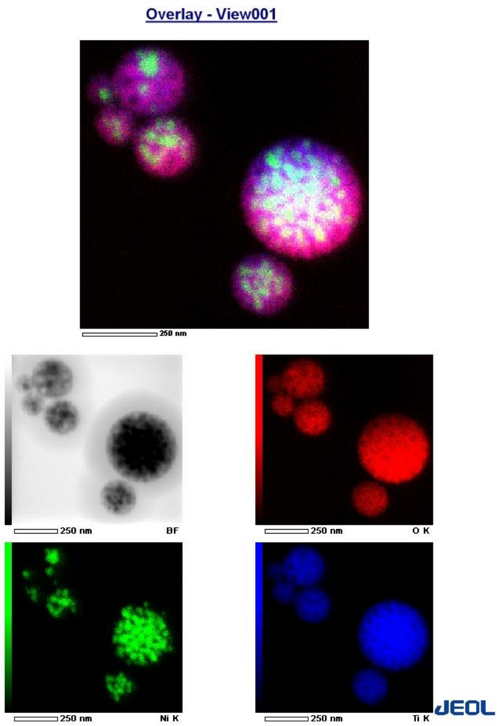

Figure 4: EDX mapping of several particles displaying nickel content inside the cores of particles with an outer layer of titanium oxide

A possible option for removing the oxygen content is changing the precursor solution with other solutions, or changing the collection of particles, to prevent oxidation after particle formation. Chemical etching [13] and argon ion sputtering [14] could remove the present oxide. A DSC investigation of similar particles done by Fu and Shearwood [15] has revealed that oxidized NiTi particles do exhibit shape memory effect, as phase transformation has been observed with particles made with electro-explosion of NiTi wire comprised of 50% Ti and 50% Ni. Their nanopowder also had an outer oxide layer present, mostly in the form of TiO_2.

After Ar ion beam sputtering, some oxygen content has been removed, however the TiNi nano-powder still showed phase transformation with DSC analysis, within nearly the same transformation temperature range comparable to bulk TiNi alloy (10–100 °C) [15].

Zeta potential

Zeta potential measurements were carried out on a Malvern Zetasizer Nano ZS in order to determine the long-term stability of the obtained particles. A lower potential (positive or negative) means the medium molecules can be displaced more easily and the particles aggregated. With low potential, the result is an increase in agglomeration of the particles due to Van der Walls interactions, and with a high potential, fewer agglomerations can be expected [16]. The measurements were carried out with a standard measurement protocol in a pH level range from 2 to 12 in increments of 2. The refractive index of the particles used was 2.325 (Ni to TiO_2 ratio was estimated at 50:50, the refraction indexes of Ni and TiO2 are 1.98 and 2.5, respectively) [17], [18]. The zeta potential could not be measured at pH 12, which could be a result of unknown solution properties (such as temperature dependent refractive index) or because of insufficient particle concentration in the solution.

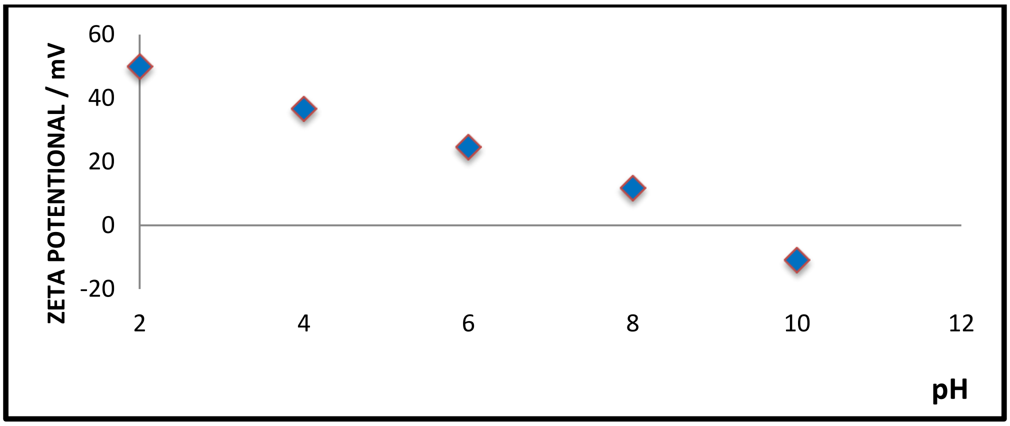

Figure 5: Zeta potential measurements at different pH levels

The measurements in Figure 5 show relatively low zeta potential values, suggesting agglomeration of the particles taking place. An approximate threshold for the stability of the particles is around ±30 mV. The measurements have shown the average zeta potential to be in the range from +50 mV at pH 2 down to +11.9 mV at pH 8 and reaching -10.9 at pH 10. The degree of stability of the measured particles over time is therefore not very favorable. This gives us a few suggestions for longer suspension stability over time; a different collection medium could be used, the pH values should be kept at a desirable level or the ionic strength of the medium could be altered.

Electrospinning

Electrospinning was conducted of the obtained NiTi particles. The purpose of these experiments was to establish the feasibility of creating novel shapes of the shape memory alloys, normally not obtainable through conventional nitinol production processes, especially as NiTi presents relatively a lot of difficulties when being processed, melted, shaped or machined. This could produce movement in textiles, and make them dynamic and flexible in ways not seen before. Using this process further, and if the particles can be spun onto fibers in sufficient concentrations, shapes such as hollow wires could, potentially, be produced [12]. These particles are, of course, required to have shape memory alloy properties in order for them to be usable in this manner.

Conclusion

The nanoparticles made from shape memory alloy nickel titanium wires had high oxygen content and formed TiO_2. Nickel was formed in individual kernels inside the particles, with a lower content in particles of sizes below 160-180 nm. Particles above this size had a relatively equal ratio of Ni and TiO_2. Formation of titanium dioxide is a feature that is not favorable for the shape memory effect in particles of these sizes (from 60 to 600 nm in diameter). Further work needs to be done on removing the oxygen content via synthesis modifications and final particle processing. Zeta potential measurements have revealed that the particle collection medium (alcohol was used) alone is not suitable for long-term stability of the particles and modifications need to be made for longer stability over time. The obtained nanoparticles were also used in a textile fabrication process known as electrospinning, the results of which are not contained in this work.

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