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Nanodelci pripravljeni iz NiTi ortodontske žice

Nanoparticles prepared from NiTi orthodontic wire

Povzetek

Nanodelci so bili sintetizirani iz NiTi ortodontske žice z aerosol tehniko, imenovano ultrazvočna razpršilna piroliza, ter okarakterizirani s TEM mikroskopijo, z EDS analizo in z meritvami zeta potenciala. Na podlagi pridobljenih rezultatov in dostopne literature se je oblikovala domneva, da imajo ti nanodelci oblikovni spomin. Preiskava je pokazala, da je titan oksidiral, medtem ko je nikelj ostal ujet v središču delcev. Čeprav nastali Ti oksidi ovirajo spominski efekt pri tovrstnih materialih, pa se ta lastnost verjetno ne izniči popolnoma. Narejeni nanodelci so bili nato uporabljeni v procesu elektropredenja za izdelavo tekstila.

Ključne besede: nikelj titan, nanodelci, efekt oblikovnega spomina

Abstract

Nanoparticles were synthesized from NiTi orthodontic wire with the aerosol process Ultrasonic Spray Pyrolysis and characterized with TEM microscope equipped with EDX analysis and by zeta potential measurements. The shape memory effect of these nanoparticles has been surmised through the analysis of the obtained results and available literature. Investigation showed that on the nanoparticles the titanium volume had been oxidized, entrapping the nickel content inside the nanoparticle 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

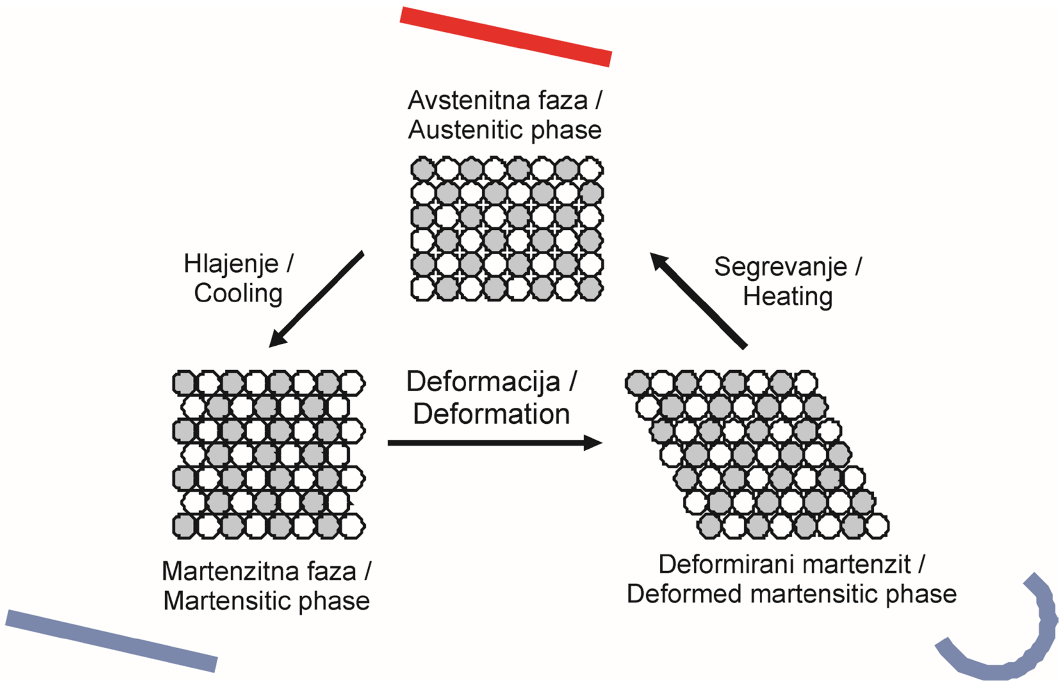
1 Uvod

Zlitine niklja in titana poleg dobre korozijske odpornosti in biokompatibilnosti izkazujejo še oblikovni spomin in superelastične lastnosti. Zaradi teh dveh funkcionalnih lastnosti so pogosto uporabljene v biomedicinskih pripomočkih, kot so žilni vsadki, vodilne žice, ortodontske žice, ortopedske naprave, filtri in kirurške naprave. Izdelava nikelj titanovih zlitin je težavna zaradi velike občutljivosti na začetno kemijsko sestavo in kasnejšo

1 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, orthopaedic devices, filters and surgical devices. Fabricating nickel titanium alloys has some difficulties, as the properties of the material are very sensitive to the starting obdelavo [1]. Prav reverzibilna martenzitetna transformacija v trdnem stanju je tista, ki daje tem materialom nekonvencionalne lastnosti. Pri višjih temperaturah imajo ti materiali kubično kristalno strukturo avstenita, pri nižjih temperaturah pa imajo monoklinsko kristalno strukturo martenzita. V martenzitni fazi se lahko takšni materiali deformirajo vse do 6-8 %, in to s prerazporeditvijo atomskih ravnin brez pretrganja atomskih vezi, kar je poznano kot dvojčenje [2]. S segrevanjem prehajajo v fazo avstenit oziroma s hlajenjem spet nazaj v martenzit (slika 1). V teh okvirih je bilo postavljenih veliko vprašanj, povezanih z dejstvom, ali takšni materiali svoje lastnosti obdržijo tudi na nanodelcih, saj imajo le-ti v splošnem popolnoma drugačne lastnosti [3]. Nanodelce z oblikovnim spominom bi zato lahko uvrstili med atraktivne materiale,

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



Slika 1. Shematski prikaz faznih premen pri zlitini z oblikovnim spominom

Figure 1. Schematic presentation of phase transformation in a shape memory alloy

saj bi lahko odprli številne možnosti za nove uporabe, še posebej ob kombinaciji z nanodelci različnih oblik kot npr.: palice, tanke plasti ali sferičnimi delci. Poznani so številni načini proizvodnje nikelj titanovih nanodelcev, in to s pomočjo laser ablacije [4, 5], ultra zvočne elektrolize [6], elektro-eksplozije žice NiTi s SPS (spark plasma sintering) [7], FE (flash evaporation) plina [8] in drugi.

V našem eksperimentalnem delu smo za izdelavo NiTi nanodelcev uporabili metodo, imenovano ultrazvočna razpršilna piroliza (Ultrasonic Spray Pyrolysis – USP), ki je sorazmerno preprosta metoda za sintezo nanodelcev iz aerosola [9]. Pri tej metodi uporabljamo za sintezo nanodelcev raztopino z raztopljenim želenim materialom. Na gladino te raztopine usmerimo ultrazvok, ki ustvarja kapljice aerosola. Te kapljice nato prenesemo v reaktorsko peč z inertnim plinom, kjer se z dodatkom reakcijskega plina iz vsake kapljice ustvari nanodelec [9-11]. Velikost nanodelcev je odvisna od koncentracije materiala v raztopini, temperature reaktorske peči in velikosti kapljic. Ta proces lahko uporabimo za izdelavo nanodelcev iz različnih materialov, z različnimi oblikami (oblike jedro-lupina, porozne strukture, itd.), sicer pa ga lahko uvrstimo med procese, ki omogočajo raznolikost, kar pomeni, da so ovire pri izdelavi odvisne predvsem od tipa želenega materiala nanodelcev. Za zlitine NiTi je poznano, da so zahtevne, in sicer že pri običajnih metodah izdelave.

2 Materiali in metode

Izhodna raztopina za USP sintezo je bila pripravljena iz ortodontskih žic s sestavo 51,46 m.% Ti in 48,54 m.% Ni, ki so bile raztopljene v 12 ml zlatotopke (HNO_3 + 3 HCl) ter razredčene z vodo. Ta raztopina je bila uporabljena v napravi za USP na

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 nanoparticles 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.

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 nanoparticles 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.

2 Materials and Methods

A precursor solution for the USP process was prepared from orthodontic wires with a composition of 51,46 wt.% Ti and 48,54 wt.% Ni, dissolved in 12 ml of aqua solution (HNO3 + 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

IME Inštitutu za procesno metalurgijo in recikliranje kovin, RWTH Aachen v Nemčiji [9-12]. NiTi material se je raztopil v kloride Ni in Ti, pri čemer je bil vodikov plin v procesu USP uvajan za redukcijo kloridov. Končne nanodelce smo zbirali v steklenicah z etanolom, s čimer smo preprečili oksidacijo nanodelcev. Za sintezo so bili izbrani naslednji parametri [12]:

- koncentracija v raztopini: 0,5 in 0,25 g/l raztopljene NiTi žice (za izdelavo nanodelcev okrog 100 nm so potrebne majhne koncentracije),
- frekvenca ultrazvoka: 2,5 MHz,
- temperatura peči: 900°C,
- pretok plina: N_2 z 1 l/min (nosilec aerosol) in H_2 z 1,5 l/min (redukcija kloridov).

Karakterizacija sintetiziranih nanodelcev je bila opravljena s TEM mikroskopijo in z EDS analizo s pospeševalno napetostjo 200 Kv. Opravljene so bile meritve zeta potenciala.

3 Rezultati

TEM posnetek sintetiziranih nanodelcev je prikazan na sliki 2. Iz posnetka je razvidna struktura nanodelcev, kjer temnejši deli predstavljajo območja, bogata na niklju, medtem ko so svetlejša območja bogata s titanovim dioksidom. EDS analiza – prikazana na slikah 3 in 4 potrjuje opis takšne sestave.

Na sliki 3 je prikazan delež niklja manjši, kot je sicer njegova vsebnost v izhodni raztopini (t.i. prekurzor), pri čemer pa je vsebnost niklja višja v večjih delcih v primerjavi z manjšimi. Analiza velikosti nanodelcev pokaže, da so le-te v razponu od 60 do 600 nm, vendar je moč zaznati večjo količino niklja v večjih nanodelcih (160-180 nm). Svetlejši deli nanodelcev prikazujejo titanov dioksid, medtem ko temnejše površine prikazujejo nikelj - na

reduction. The nanoparticles were collected in wash bottles containing ethanol to prevent their 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: N2, at 1 l/min (aerosol carrier) and H2, at 1,5 l/min (reduction of chlorides)

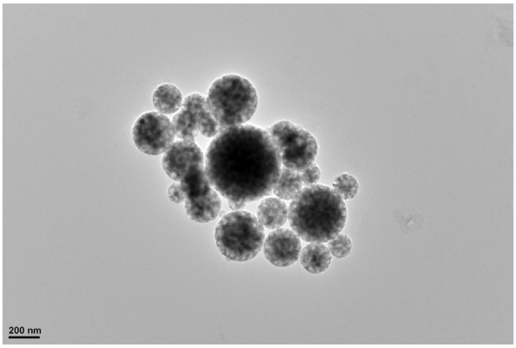
TEM and EDX analyses were used for characterization of the nanoparticles, with 200 kV accelerating voltage, with line analyses and elemental mapping. We also conducted Zeta potential measurements of the nanoparticles.

3 Results

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

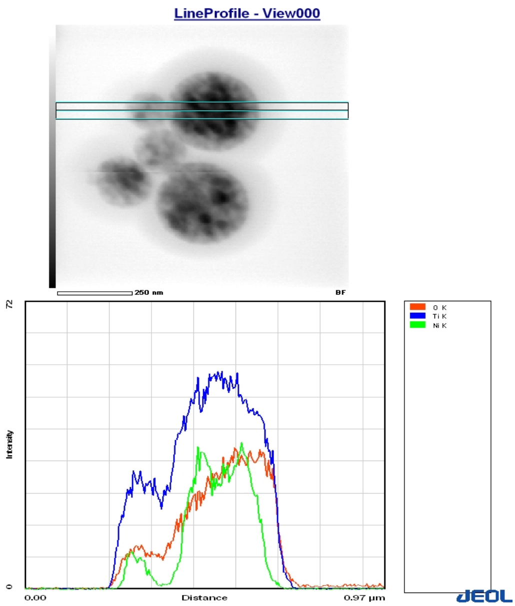
The images show a lower nickel content than originally anticipated from the synthesis precursor, while there is more nickel in the larger nanoparticles than the smaller ones. The particle sizes range from 60 to 600 nm, while the nanoparticles larger than around 160-180 nm show more nickel content. The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

Nanoparticles below 160-180 nm contain individual kernels or small areas of



Slika 2. TEM slika nanodelcev, sintetiziranih z USP

Figure 2. TEM image of NiTi nanoparticles obtained with USP

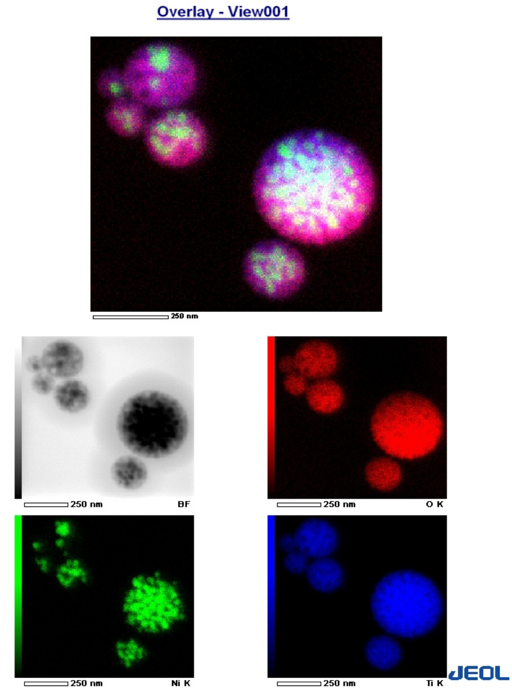


Slika 3. Linijski profili, ki kažejo plast titanovega oksida okoli področij bogatih z nikljem v nanodelcu

Figure 3. Line profile clearly showing a titanium oxide layer around the nickel content in the nanoparticle

TEM sliki temnejši odtenki predstavljajo mesta elementov z večjo gostoto (titanov

Ni inside. Nanoparticles 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 TiO2 formation energy compared to Ni. In these larger nanoparticles, the Ni and TiO2 ratio is relatively equal, compared to the smaller nanoparticles where TiO_2 is more abundant.



Slika 4. EDS porazdelitvena analiza za elemente v nanodelcih: nikelj se nahaja po volumnu ter je obdan s plastjo titanovega oksida

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

This suggests that the initial precursor concentration of Ni and Ti in solution used dioksid ima gostoto 4.23 g/cm^3, medtem ko ima nikelj gostoto 8.9 g/cm^3).

Nanodelci z velikostjo pod 160-180 nm vsebujejo Ni ali v obliki posameznih jeder ali pa se le-ta nahaja v manjših območjih, ki so razpršena po celotnem volumnu. Pri večjih nanodelcih (2r> 160-180 nm) so nikljeva jedra medsebojno združena. Nikelj se v teh jedrih nahaja v elementarni obliki in ga je primerjalno več kot pri manjših nanodelcih. EDS analize še kažejo, da Ni ni oksidiral, kar je skladno s strokovno literaturo, kjer je znano, da ima Ti višjo reaktivnost in tvorbeno entalpijo za oksid TiO_2 v primerjavi z Ni. Nadaljnja primerjava kaže, da je v večjih nanodelcih vsebnost Ni in TiO_2 približno ekvivalenta, med tem ko je pri manjših nanodelcih TiO_2 več kot Ni.

Rezultati preiskav nakazujejo, da koncentracija Ni in Ti v izhodni raztopini, ki je bila uporabljena za USP, ni enaka koncentraciji Ni in Ti v posameznih aerosol kapljicah. Zaradi navedenega je verjetno prišlo do nastanka večjih in manjših nanodelcev, ki imajo različno kemijsko sestavo. Prisotnost kisika v nanodelcih (v obliki TiO_2) preprečuje oblikovni spomin in super-elastične lastnosti, saj se titan nahaja v oksidu in ne v kristalni strukturi NiTi. Če primerjamo to s klasičnimi materiali, kjer je prisotnost titanovih oksidov dobrodošla, saj le-ti pripomorejo k boljši korozijski odpornosti in biokompatibilnosti, pa je pri nanodelcih to nezaželeno, saj zaradi manjšega števila Ti atomov le-ti nimajo izrazitega efekta oblikovnega spomina.

Za nadaljnje delo je tako prednostna naloga odstraniti kisik iz procesa. Eno izmed možnosti predstavlja zamenjava začetne raztopine s takšnimi, ki imajo zelo nizko vsebnost kisika ali z uporabo organskih raztopin brez kisika. Raziskati je potrebno tudi zbiranje nanodelcev s preprečevanjem oksidacije po nastanku nanodelcev. Možnosti za odstranitev oksida po sintezi

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 nanoparticles 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.

A possible option for removing the oxygen content is changing the precursor solution with other solutions, or changing the collection of nanoparticles, to prevent oxidation after nanoparticle formation. Chemical etching [13] and argon ion sputtering [14] could remove the present oxide. A DSC investigation of similar nanoparticles done by Fu and Shearwood [15] has revealed that oxidized NiTi nanoparticles do exhibit shape memory effect, as phase transformation has been observed with nanoparticles made with electro-explosion of NiTi wire comprised of 50 at.% Ti and 50 at.% 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 NiTi nanopowder still showed phase transformation with DSC analysis, within nearly the same transformation temperature range comparable to bulk NiTi alloy (10-100 °C) [15].

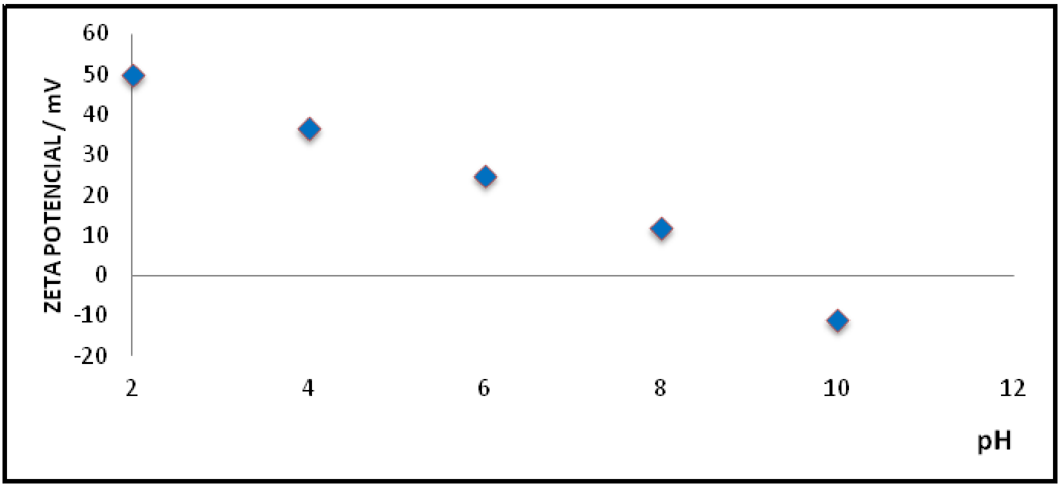
nanodelcev predstavljata kemijsko jedkanje [13] ali obstreljevanje z ioni argona [14]. DSC raziskava podobnih nanodelcev, ki sta jo opravila Fu in Shearwood [15] je pokazala, da oksidirani delci NiTi izkazujejo oblikovni spomin, saj je bila opažena sprememba faze v delcih, narejenih s pomočjo elektro-eksplozije NiTi žice s 50 at.% sestavo Ti in 50 at.% Ni. Pri teh nanodelcih je bila sicer prisotna zunanja oksidna plast, večinoma v obliki TiO_2. Po obstreljevanju s curkom ionov Ar, ki so odstranili vsebnost kisika, je preostali NiTi nano-prašek z DSC analizo še vedno izkazoval fazne spremembe, ki so bile s pomočjo temperaturnih razlik primerljive z osnovno zlitino NiTi (10-150°C) [15].

4 Zeta potencial

Meritve zeta potenciala so bile opravljene na Malvern Zetasizer Nano ZS z namenom ugotoviti dolgoročno obstojnost sintetiziranih nanodelcev. Nižji potencial (pozitiven ali negativen) v splošnem nakazuje, da se

4 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 nanoparticles. A lower potential (positive or negative) means the medium molecules can be displaced more easily and the nanoparticles aggregated. With low potential, the result is an increase in agglomeration of the nanoparticles 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 nanoparticles used was 2.325 (Ni to TiO2 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.



Slika 5. Meritve zeta potenciala pri različnih pH vrednostih

Figure 5. Zeta potential measurements at different pH levels

molekule srednje velikosti lažje premikajo, kar vodi k njihovi aglomeraciji. Tako lahko pri nanodelcih z nižjim potencialom pričakujemo višjo stopnjo aglomeracije zaradi van der Waalsovih interakcij [16], pri višjem potencialu pa se zmanjšuje možnost aglomeracije nanodelcev. Meritve so bile opravljene na podlagi standardnega meritvenega protokola v pH območju od 2 do 12 s korakom 2. Lomni količnik uporabljenih nanodelcev je bil 2.325 (razmerje Ni/TiO_2 je bilo ocenjeno na 50:50, lomni količnik Ni in TiO_2 pa je bil 1.98 in 2.5) [17], [18]. Zeta potencial se ni mogel izmeriti pri pH 12, kar je lahko posledica neznanih lastnosti raztopine (kot npr. vpliv temperature na lomni količnik) ali prenizka koncentracija nanodelcev v raztopini.

Meritve na sliki 5 prikazujejo sorazmerno nizke vrednosti zeta potenciala, kar nakazuje na prisotnost aglomeracije nanodelcev. Predpostavljena mejna vrednost napetosti za stabilnost nanodelcev je približno mV. Meritve so pokazale, da je povprečen zeta potencial v območju od mV pri pH 2 do mV pri pH 8 vse do mV pri pH 10. Na podlagi meritev lahko sklepamo, da je stabilnost nanodelcev skozi čas sorazmerno nizka. Na podlagi tega lahko podamo nekaj predlogov, ki bi podaljšali stabilnost nanodelcev: drug zbiralni medij, ohranjanje optimalne pH vrednosti ali pa povečanje ionskega deleža v mediju.

5 Elektropredenje

Elektropredenje je bilo uspešno izvedeno s pomočjo sintetiziranih NiTi nanodelcev. Namen teh poskusov je bil ugotoviti izvedljivost izdelave novih oblik zlitin z oblikovnim spominom, ki jih ni mogoče izdelati z običajnimi proizvodnimi metodami, zlasti zaradi velike težavnosti izdelave, obdelave in oblikovanja teh

The measurements in Figure 5 show relatively low zeta potential values, suggesting agglomeration of the nanoparticles taking place. An approximate threshold for the stability of the nanoparticles 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 nanoparticles over time is therefore not very favourable. 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.

5 Electrospinning

Electrospinning (Fig.6) was successfully conducted of the obtained NiTi nanoparticles. 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 nanoparticles can be spun onto fibres in sufficient concentrations, shapes such as hollow wires could, potentially, be produced [12]. These nanoparticles are, of course, required to have shape memory alloy properties in order for them to be usable in this manner.

vrst zlitin. Takšen material bi lahko koristil tekstilni industriji, saj bi lahko tekstil naredil dinamičen ter fleksibilen, kot še nikoli doslej. S tem procesom, če bi nanodelci lahko bili spleteni v vlakna v zadostnih koncentracijah, bi lahko bile proizvedene številne oblike, kot so na primer votle žice [12]. Seveda pa bi takšni nanodelci morali imeti oblikovni spomin, da bi lahko bili uporabni za takšen namen.

6 Zaključek

Nanodelci, narejeni iz NiTi zlitine z oblikovnim spominom, imajo visoko vsebnost kisika, saj nastane TiO_2. Nikelj se nahaja v posameznih jedrih, pri čemer ga je pri nanodelcih z velikostjo pod 160-180 nm manj kot pri večjih. Večji nanodelci imajo skoraj enako razmerje Ni in TiO_2. Nastanek titanovega dioksida za oblikovni spomin nanodelcev (med 60 in 600 nm) ni ugoden. Nadaljnje delo bo vezano na potrebno odstranitev kisika iz nanodelcev ali z modifikacijo sinteze ali z ustreznim zaključnim procesiranjem nanodelcev. Meritve zeta potenciala so pokazale, da alkohol kot medij za zbiranje nanodelcev ni primeren za dolgoročno stabilnost nanodelcev, zato se morajo uvesti takšne tehnološke spremembe, ki bode zagotovile večjo stabilnost nanodelcev na daljši rok. Sintetizirani nanodelci so bili uspešno uporabljeni v procesu izdelave tekstila, t.i. imenovanem elektropredenje, vendar pa rezultati niso prikazani.

6 Conclusion

The nanoparticles made from shape memory alloy nickel titanium wires had high oxygen content and formed TiO2. Nickel was formed in individual kernels inside the nanoparticles, with a lower content in nanoparticles of sizes below 160-180 nm. Nanoparticles above this size had a relatively equal ratio of Ni and TiO2. Formation of titanium dioxide is a feature that is not favourable for the shape memory effect in nanoparticles 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 nanoparticle processing. Zeta potential measurements have revealed that the nanoparticle collection medium (alcohol was used) alone is not suitable for long-term stability of the nanoparticles and modifications need to be made for longer stability over time. The obtained nanoparticles were also used successful in a textile fabrication process known as electrospinning, the results of which are not contained in this work.

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