Scientific paper

Synthesis of Chromium-Nickel Nanoparticles Prepared by a Microemulsion Method and Mechanical Milling

Irena Ban,[1,2,*] Janja Stergar,[1] Miha Drofenik,[1,3] Gregor Ferk[1] and Darko Makovec[3]

[1] *University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia*

[2] *Center of Excellence NAMASTE, Jamova 39, SI-1000 Ljubljana, Slovenia*

[3] *Jožef Stefan Institute, Department for Materials Synthesis, Jamova 39, SI-1000 Ljubljana, Slovenia*

** Corresponding author: E-mail: irena.ban@um.si*
Tel: +386 2 2294 417; Fax: +386 2 2527 774

Received: 21-03-2013

Abstract

A chemical and a physical method have been applied for the preparation of chromium-nickel alloy nanoparticles. These particles were designed to be used for controlled magnetic hyperthermia applications. Microemulsions with Ni^{2+} and Cr^{3+} and/or $NaBH_4$ as precursors were prepared using the isooctane/CTAB, n-butanol/H_2O system. The samples of Cr_xNi_{1-x} nanoparticles with the desired composition were obtained after the reduction of their salts with $NaBH_4$ and afterwards heat treated in a TGA in a N_2 atmosphere at various temperatures. The Cr_xNi_{1-x} materials were also prepared by mechanical milling. Utilizing a ball-to-powder mass ratio of 20 : 1 and selecting the proper alloy compositions we were able to obtain nanocrystalline Cr_xNi_{1-x} particles. Thermal demagnetization in the vicinity of the Curie temperature of the nanoparticles was studied using a modified TGA-SDTA method. The alloy's phase composition, size and morphology were determined with XRD measurements and TEM analyses.

Keywords: Mechanical alloying, magnetic nanoparticles, magnetic hyperthermia, Curie point.

1. Introduction

Nanoparticles usually show novel magnetic, optical, electronic and chemical properties that are significantly different from those of bulk materials because of their extremely small sizes and large specific surface areas. They have various potential applications in catalysis, mechanical, optical and electronic devices, superconductors, dyes, pigments and in medicine, with magnetic resonance imaging (MRI) contrast enhancement, cell separations and magnetic hyperthermia.[1]

Magnetic hyperthermia, a technique using magnetic particles and based on a proposal of Gilchrist in 1957, continues to be an active area of research. It has been found that the viability of cancer cells is reduced and their sensitivity to chemotherapy and radiation is increased when malignant human or animal cells are heated to temperatures between 41 and 46 °C.[2] Magnetic fluid hyperthermia involves the applications of magnetic nanoparticles as mediators into the tumor tissue and heating them with an alternating magnetic field (AMF). The generated heat can be controlled using nanoparticles with a variable Curie temperature.[3] When exposed to an alternating magnetic field, superparamagnetic particles can generate heat by relaxation losses.[4]

Many techniques have been used to synthesize nanoparticles, such as ion-beam sputtering, sol-gel methods, co-precipitation, microwave irradiation and microemulsion syntheses.[5,6] Water-in-oil (w/o) microemulsions, also known as reverse micelles, are convenient and effective techniques for the size-specific synthesis of metal and alloy nanoparticles. They consist of an oil phase containing spherical agglomerates of surfactant and co–surfactant molecules surrounding an aqueous core, i.e., reverse micelles, which effectively constrain the growth process of precipitates, formed during chemical reactions, thus limiting the size of the particles.[4-7] In the present paper, we first report about the synthesis of Ni-Cr alloy nanoparti-

les using a microemulsion system: CTAB, n-butanol/isooctane/water and their structural and magnetic properties. With the simultaneous reduction of Cr^{3+} and Ni^{2+} ions using sodium borohydride ($NaBH_4$) at room temperature, the formation of CrNi alloy particles was performed. Subsequently, a different process called a high energy ball milling of blended Ni and Cr elemental powders was carried out in a nitrogen atmosphere to obtain a nanostructured NiCr alloy with the appropriate Curie temperature. The size, structure, properties and composition of the resultant nanoparticles were characterized using TEM, XRD, TGA and calorimetric measurements.

2. Material and Methods

2. 1. Synthesis of Nanoparticles

2. 1. 1. Microemulsions

The nanoparticles were prepared using water-in-oil microemulsions consisting of cetyltrimethylammonium bromide (CTAB), a surfactant, n-butanol as co-surfactant and isooctane as the oil phase. The chromium (III) nitrate nonahydrate, nickel (II) chloride hexahydrate and sodium borohydride ($NaBH_4$) were precursors of the aqueous phase. The titration method[8] was applied to determine the region of the microemulsion's stability, Fig.1.

Two types of microemulsions were prepared: i) by solubilizing aqueous Ni^{2+} (aq) (0.4 M) and Cr^{3+} (aq) (0.1M) ions and ii) by adding sodium borohydride $NaBH_4$ (0.8 M) into a mixture of CTAB, n-butanol and isooctane. After completely mixing equal volumes of both microemulsions for two hours under a nitrogen atmosphere, the solution turned black. The reduction reactions were vigorous, with the production of gas. After the evolution of gas (H_2), the mixtures were centrifuged to separate the black nanoparticles. The precipitates were first washed with methanol several times. The resulting powders containing the aggregates of $Cr_{0.1}Ni_{0.9}$ and $Cr_{0.2}Ni_{0.8}$ were black. At the end the "as prepared" alloy $Cr_{0.2}Ni_{0.8}$ and $Cr_{0.1}Ni_{0.9}$ powder were heat treated with a TGA-SDTA at 200, 300, 400 and 600 °C.

2. 1. 2. Ball Milling

A series of Cr_xNi_{1-x} alloys were prepared to find the specific compositions with a Curie temperature around 42 °C. Blends of elemental metal powders of Cr (particle size < 74 μm) and Ni (particle size < 150 μm) were ball milled in a SPEX 8000M mill at 1425 rpm, using hardened steel vials and a ball-to-powder weight ratio of 20 : 1. The vials were loaded and sealed under a nitrogen atmosphere.

In order to obtain a highly homogenous composition over the resulting bulk alloy the ball milling was continued for up to 20 h, as a continuation of the milling revealed no significant change in the x-ray diffraction pattern of the final powder blends.

2. 2. Methods of Characterization

All the Cr_xNi_{1-x} particles were characterized in terms of their morphology and magnetic properties. The d_{hkl} values and the crystallite size d_x (Scherrer equation) were determined using XRD measurements (AXS–Bruker/ D5005 diffractometer with CuKα radiation, λ = 1.54178 Å).

The structural characterization was performed using electron microscopy, i.e., a JEOL 2010F. The transmission electron microscope was used to determine the particle's morphology and the particle size.

TGA-SDTA 851^e thermoanalyzer from Mettler Toledo System, was used for the heat treatment of the particles in a N_2 atmosphere and for the Curie temperature (T_c) determination of samples prepared with both synthesis methods. Here, a small permanent magnet was fixed on the upper side of the balance.

For the experimental determination of the magnetic power losses, a measurement system was built, as shown elsewhere.[9] A conventionally built system generated an alternating magnetic field with a nominal field strength from 9.2 kA/m to 16.2 kA/m, at a frequency of 100 kHz and was equipped with a calorimeter to measure the magnetic heating effects. The heat effect of the magnetic nanoparticles in the AMF was determined with an immediate measurement of the temperature in the calorimeter. The measurements were preformed until the steady-state temperature was achieved.

3. Results and Discussion

3. 1. Microemulsions

The stability range of the microemulsions was first determined as a function of the concentration of the solutes in the aqueous phase by the titration method (Fig. 1).

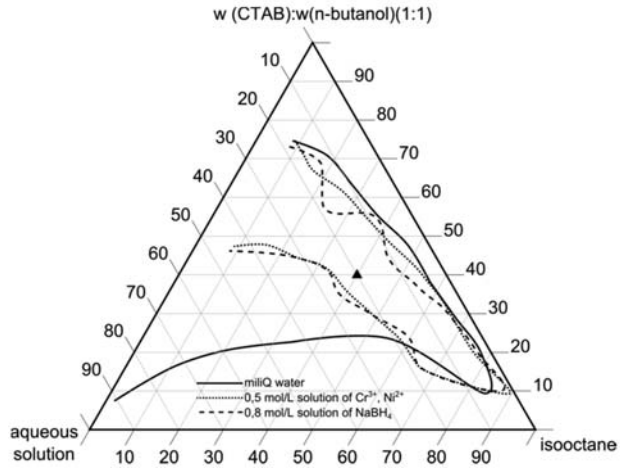

Fig. 1. Phase diagram constructed on the basis of the titration method (miliQ water, 0.5 mol/L aqueous solution of Cr^{3+} and Ni^{2+} and 0.8 mol/L aqueous solution of $NaBH_4$).

In this method an aqueous solution of Cr^{3+} and Ni^{2+} and/or aqueous solution of $NaBH_4$ is titrated into a mixture of oil phase (isooctane) and surfactant (CTAB)/cosurfactant (n-butanol). Two types of microemulsions were prepared (see the Experimental section).

After the stability region of the microemulsion system water/CTAB, n-butanol/isooctane phase was determined; the Cr-Ni nanoparticles within the microemulsion region (▲) with compositions $Cr_{20}Ni_{80}$ and $Cr_{10}Ni_{90}$ were synthesized. Fig. 2 shows a typical XRD spectrum of as-prepared $Cr_{20}Ni_{80}$ and its products heated at 200, 300, 400 and 600 °C in a nitrogen atmosphere (TGA). The XRD patterns display three characteristic broad peaks at 2θ = 44.57 °, 51.94 ° and 76.51 °. The "as-prepared" nanoparticles were amorphous, while after heating the crystallite size and/or crystallinity increased with the temperature. The peak at 2 Θ = *37* ° belongs to the NiO which is formed during synthesis, although the inert atmosphere (N_2) was used.

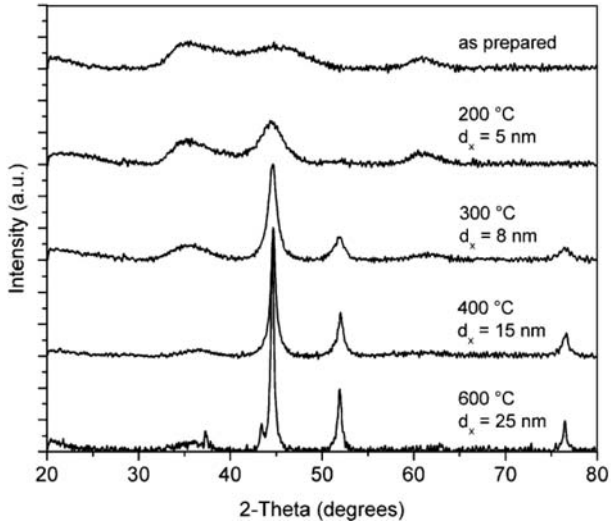

Fig. 2. Typical X-ray powder-diffraction patterns of synthesized chromium-nickel ($Cr_{20}Ni_{80}$) alloy, as prepared and at different temperatures.

The EDS analysis confirmed that the compositions of the Cr-Ni nanoparticles were coincident with the molar ratios $[Cr^{3+}] : [Ni^{2+}] = 20 : 80$ used for the synthesis.

A transmission electron micrograph of the $Cr_{20}Ni_{80}$ nanoparticles synthesized using the microemulsion method and heat treated at 400 °C, is shown in Fig. 3. This micrograph indicates that the nanoparticle size distribution is relatively broad with an average particle size of 5-10 nm, comparable to that estimated from the x-ray diffraction broadening and the Scherrer equation. The particles are partially agglomerated and at some locations also larger grains in the shape of platelets, can be observed. However, the amount of these particles was estimated to be relatively small.

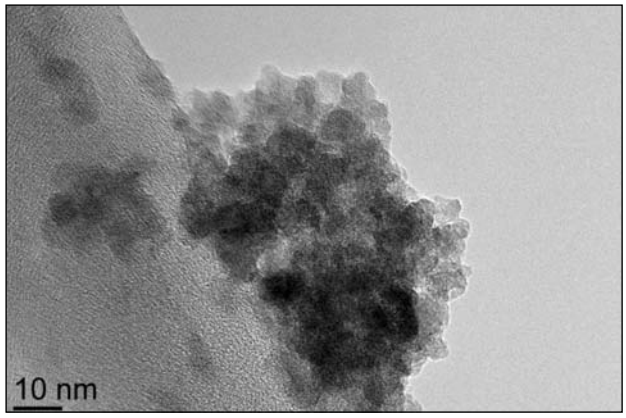

Fig. 3. TEM micrograph of nanoparticles synthesized using microemulsion method and heat treated at 400 °C.

We also measured the T_c for the samples synthesized using the microemulsion method and heated to 400 °C in a N_2 atmosphere. Unfortunately, the results did not fulfill our expectations. The measured T_c temperature (320 °C) was close to that of pure nickel, indicating that a compositional heterogeneity exists in the form of Ni-rich areas, most probably in the form of a "core-shell" structure. This is due to the different standard oxidation potentials of elements.[10]

3. 2. Ball Milling

These XRD results reveal the straightforward formation of Cr_xNi_{1-x} alloys throughout the milling process, Fig. 4. A progressive shift of the Bragg peaks to higher diffraction angles in both cases *(111)* and *(200)* is observed as the Ni (at %) content increases. The lattice constant and the interplanar distances d_{111} (Å) enlarge with the Cr (at %) content, see Tab 1.

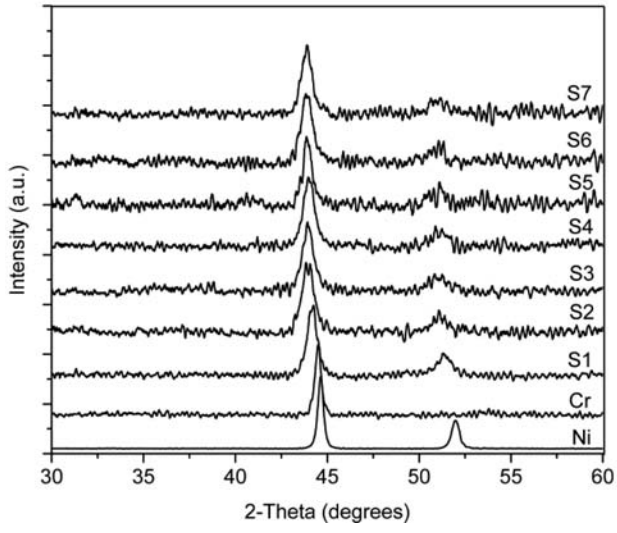

Fig. 4. XRD patterns of the binary powder blends of the various Cr_xNi_{1-x} samples obtained after 20 h of ball milling under a N_2 atmosphere in hardened steel vials and physical mixture of Cr and Ni (first line).

From the x-ray line broadening and the use of the Scherrer equation, the mean crystallite size for each composition was estimated, see Table 1. The size and strain broadening were separated using Williamson-Hall plot. The average strain for the prepared samples was $\varepsilon \approx 0.14$ %.

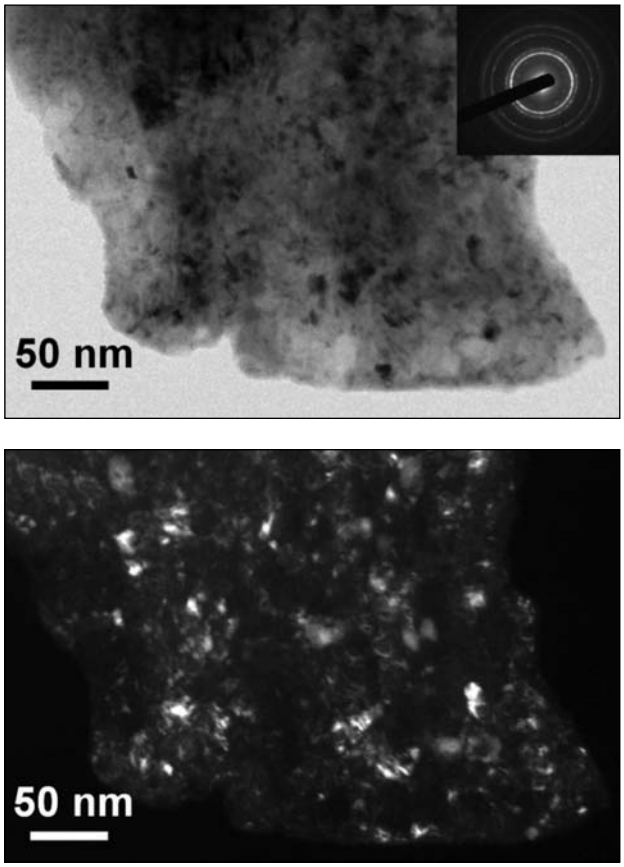

Fig. 5. BF (a) and DF (b) TEM image of the sample $Cr_{29}Ni_{71}$ (inset of Figure 5 (a): the corresponding diffraction pattern).

A transmission electron micrograph of the $Cr_{29}Ni_{71}$ nanoparticles synthesized using ball milling method is shown in Fig.5. which shows bright-field (BF) and dark-field (DF) TEM images of the sample $Cr_{29}Ni_{71}$. The sample consists of micrometer-sized particles, which comprises of nanocrystallites. The nanocrystallites with size ranging from approximately 5 nm up to 30 nm are clearly visible in the DF image formed by part of the brightest diffraction ring. The diffraction pattern corresponds to the cubic structure of the alloy.

The Curie temperatures (T_c) for the physically synthesized particles with various compositions were measured and are shown in Table 1. The results reveal that the Curie temperatures of the Cr_xNi_{1-x} alloy particles can be adjusted by varying the Cr/Ni molar ratio, i.e., the T_c of the Cr_xNi_{1-x} magnetic particles increase with an increase of the Ni content and approach to that of pure nickel at 357 °C.

Table 1. Composition, Curie temperature T_c, average crystallite size from X-ray diffraction d_x and d_{111} spacing of Cr-Ni materials.

Sample	*w* (at %)	T_c (°C)	d_x (nm)	d_{111} (Å)
S1	$Cr_{10}Ni_{90}$	340	12	2.054
S2	$Cr_{15}Ni_{85}$	262	12	2.059
S3	$Cr_{20}Ni_{80}$	138	12	2.059
S4	$Cr_{26}Ni_{74}$	69	14	2.057
S5	$Cr_{27}Ni_{73}$	52	18	2.062
S6	$Cr_{28}Ni_{72}$	44	14	2.064
S7	$Cr_{29}Ni_{71}$	43	14	2.061

The Curie point of the magnetic particles was followed using the so-called thermomagnetic curve (TM), as an apparent change in weight caused by a decrease in the magnetization of the particles due to the thermal demagnetization.

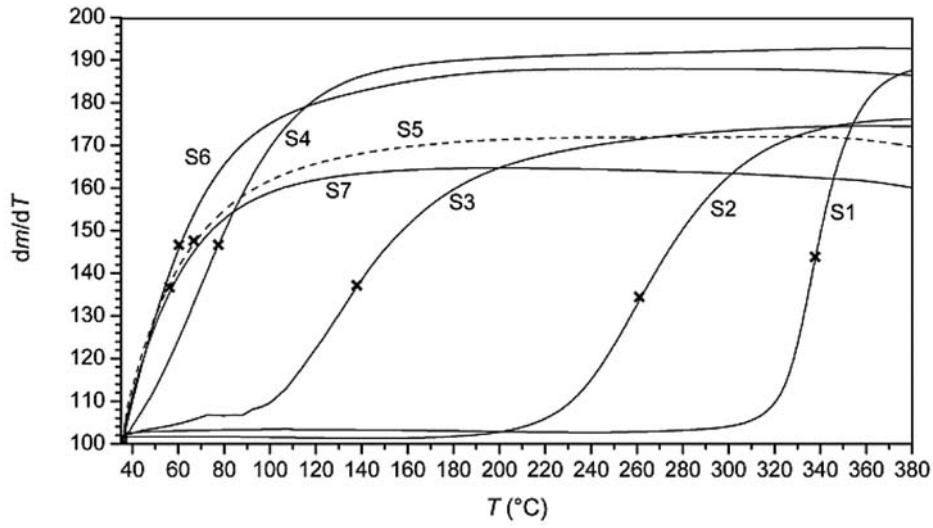

Fig. 6. Thermomagnetic curves of Cr_xNi_{1-x} samples (10 K/min, 25-400 °C, N_2).

The temperatures belonging to the 50 % of broad-peak heights of the demagnetization curves were referred to as the Curie temperature of the samples. The slightly asymmetric shapes of the TM curves indicate the heterogeneities in the alloy composition. This is to be expected, because the powder particles undergo severe mechanical deformation and compositional fluctuations during mechanical alloying.[4]

For particles in the superparamagnetic state, heating effects can be generally achieved in an AMF (alternating magnetic field) due to the Néel-type relaxation losses or energy dissipation during the particle rotation in a liquid (Brown losses). The heating effects of the solid powdered samples **$Cr_{28}Ni_{72}$** with a Curie temperature of **44 °C**, which is in a medically appropriate range, were carried out, i.e., a calorimetric measurement of the magnetic powder losses. The mediator nanoparticles for hyperthermia must efficiently absorb the AMF energy below the T_c. Also, the magnetic measurements of the solid powdered sample were performed in a conventionally built system that generates an alternating magnetic field with a nominal field strength of 9.2–16.2 kA/m and a maximum frequency of 100 kHz. The temperature rise of the calorimeter loaded with the powdered sample at different magnetic fields is shown in Fig. 7:

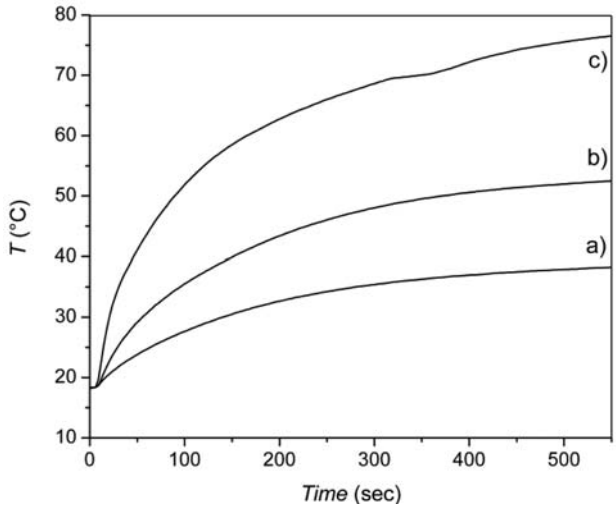

Fig. 7. Time dependence of the self-heating temperature on the magnetic field at 100 kHz and the different intensities of magnetic field for $Cr_{28}Ni_{72}$, H: a) 9.20 kA/m, b) 12.52 kA/m, c) 16.18 kA/m.

In these experiments, the self-heating temperature achieved exceeds the nominal Curie point of 45 °C. This is the result of heterogeneity in the particle's composition, visualized in terms of a relatively broad T_c maximum and a relatively broad particle size distribution, both of which contribute to an increase in the final stationary temperature over that predicted by the nominal Curie point.

4. Conclusions

Chromium-nickel alloy particles with the desired composition and Curie point were synthesized using microemulsions and mechanical alloying. The XRD patterns indicate that both methods yield a solid solution; however, the planned Curie point (43 °C) was only exhibited by samples prepared by mechanical alloying ($Cr_{29}Ni_{71}$).

The T_c of samples synthesized by microemulsion method ($Cr_{20}Ni_{80}$) was high (320 °C), indicating compositional heterogeneity and probably core-shell structure.

In summary, the mechanical milling yielded particles with the target Curie point; however, it introduces a heterogeneity to the particle size distribution and the composition, which increases the Curie temperature of the nanoparticles, as noted when the samples were applied in a self-regulating, magnetic fluid, hyperthermia experiment.

To overcome the problems regarding the biocompatibility of the metallic ions released from alloys to the tissue, the particles should be coated with bio-compatible layer (silica, gold, …)

Also the size distribution of nanoparticles would be narrower and consequently, the results of calorimetric measurements would probably not exceed the therapeutic Curie point of 45 °C. The second possibility is application of another method like sol-gel, for the synthesis of nanoparticles, which also has some advantages like high chemical homogeneity, low processing temperature and the possibility of controlling the size and morphology of the particles.

5. Acknowledgements

This work was supported in part by the Ministry of Higher Education, Science and Technology of the Republic of Slovenia within the National Research Program. The TEM analyses were carried out by Dr. Sašo Gyergyek, Jožef Stefan Institute. The authors also thank Dr. Miloš Beković, Faculty of Electrical Engineering and Computer Science, University of Maribor, for the calorimetric measurements.

6. References

1. Y. Akin, I. M. Obaidat, B. Issa, Y. Haik, *Cryst. Res. Technol.* **2009**, *44*, 386–390.
2. M. Bettge, J. Chatterjee, Y. Haik, *Biomag. Res. Tech.* **2004**, *2*, 1–6.
3. I. Ban, J. Stergar, M. Drofenik, G. Ferk, D. Makovec, *J. Magn. Magn. Mater.* **2011**, *323*, 2254–2258.
4. R. E. Rosensweig, *J. Magn. Magn. Mater.* **2002**, *252*, 370–374.
5. C. Wang, D. Chen, T. Huang, *Colloids Surf.* **2001**, *189*, 145–154.

6. D. Makovec, A. Košak, M. Drofenik, *Nanotechnology* **2004**, *15*, 1–7.
7. B. Cushing, V. Golub, C. O´Connor, *J. Phys. Chem. Solids.* **2004**, *65*, 825-829.
8. H. R. Rabie, D. Helou, M. E. Weber, J. H. Vera, *J. Colloid Interface Sci.* **1997**, *189*, 208–215.
9. M. Beković, A. Hamler, *IEEE Trans. Magn.* **2010**, *46*, 552–555.
10. T. Yamauchi, Y. Tsukahara, T. Sakata, H. Mori, T. Yanagida, T. Kawai, Y. Wada, *Nanoscale* **2010**, *2*, 515–523.

Povzetek

Za pripravo nanodelcev zlitine Cr_xNi_{1-x} smo uporabili kemijsko in fizikalno metodo. Delci so namenjeni uporabi v biomedicini, zlasti na področju kontrolirane magnetne hipertermije. Najprej smo pripravili mikroemulzije z Ni^{2+}, Cr^{3+} in/ali $NaBH_4$ prekurzorji v sistemu izooktan/CTAB, n-butanol/H_2O. Vzorce Cr_xNi_{1-x} nanodelcev z željeno sestavo smo dobili po redukciji njihovih soli z $NaBH_4$ in naknadnem segrevanju v TGA v atmosferi N_2 pri različnih temperaturah. Nanodelce Cr_xNi_{1-x} smo sintetizirali tudi s pomočjo mehanskega mletja zmesi kromovih in nikljevih prahov. Mleli smo v visokoenergijskem krogličnem mlinu SPEX 8000M. Z uporabo primernega masnega razmerja med mlevnimi kroglicami in prahom 20:1 in izbiro primerne sestave smo dobili nanodelce zlitine $Cr_xNi_{1-x.}$ Curiejevo temperaturo nanodelcev smo določili z uporabo modificirane TGA-SDTA metode. Sestavo nanozlitine, velikost in morfologijo delcev smo določili s pomočjo meritev XRD in TEM analize.