Structure and magnetic properties of titanium nickelide nanoparticles synthesized by pulsed laser ablation method

A K Drozdova[1], V N Cherepanov[1], V A Svetlichny[1], L I Kveglis[2], M N Volochaev[3] and D A Velikanov[3]

[1] National Research Tomsk State University, 634050, Tomsk, Russia
[2] Siberian Federal University, 660041, Krasnoyarsk, Russia
[3] Institute of Physics n. a. L. V. Kirensky FRC KSC Siberian Branch of the Russian Academy of Sciences, 660036, Krasnoyarsk, Russia

E-mail: anna_drozdova709@mail.ru

Abstract. We have successfully synthesized magnetic titanium nickelide nanoparticles with equiatomic composition by pulsed laser ablation method. Using transmission electron microscopy and microanalysis was revealed that particles represent the homogeneous conglomerates containing identical amount of Ni and Ti atoms. The magnetization value of nanoparticles was estimated.

1. Introduction
Recently multipurpose materials, including alloys with the shape memory effect (SME) and a superelasticity (SE) applied in medicine. The leader among materials with SME is Ni-Ti-based alloy [1]. The combination of well biocompatibility and magnetic properties of material [2] can expand considerably the application area Ni-Ti alloys in medicine. For example, this alloy can be used for creation of magnetic nanoparticles. Furthermore, magnetic nanoparticles are actively applied in medical and biological researches by unique optical, electric and magnetic properties [3]. The particles operated by a magnetic field are used both for address delivery of medicaments and for stress rupture of cages-targets. For this reason structure and magnetic properties characterization of Ni-Ti nanoparticles is perspective.

2. Experiments
Ni-Ti nanoparticles was synthesized from a $Ni_{51}Ti_{49}$ bulk monocrystal by pulsed laser ablation method in water as colloidal solution with further drying up on air at ~50 °C using technique [4]. Structure of Ni-Ti nanoparticles was investigated by transmission electron microscopy (TEM) on HT-7700 (Hitachi, Japan) equipped with energy-dispersive spectrometer XFlash60/6T (Bruker, Germany) at 110 kV accelerating voltage. Magnetic properties were investigated by vibrating magnetometer with Puzey electromagnet [5].

3. Results and discussion
Figure 1 shows that synthesized particles can be divided into two types: spherical with 50–100 nm diameter and flake-like with 5–20 nm size.

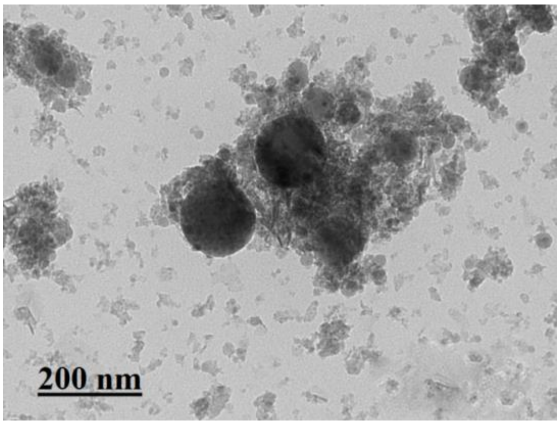


Figure 1. TEM image of Ni-Ti nanoparticles.

Element mapping (figure 2) was carried out for the purpose of chemical element identification and the analysis of their distribution in Ni-Ti nanoparticles. The results of element mapping indicate that the nanoparticles contain Ni, Ti, and also oxygen which are formed on their surface at oxidation. Ni and Ti are distributed in nanoparticles evenly, and their ratio is close to structure of the initial exemplar.

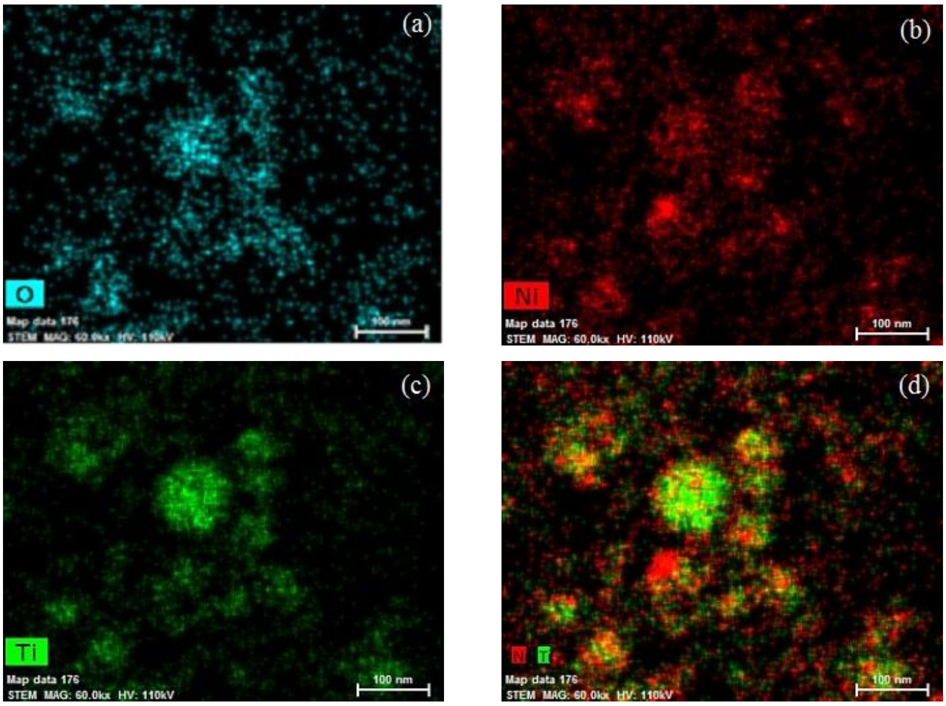
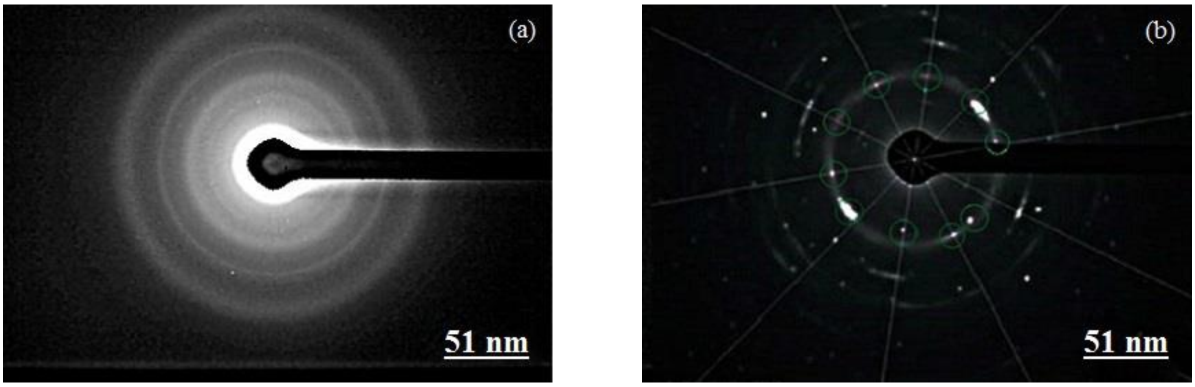


Figure 2. Element mapping received from Ni-Ti nanoparticles: **(a)** – in X-rays of oxygen K_{α}; **(b)** – in X-rays of nickel K_{α}; **(c)** – in X-rays of titanium K_{α}; **(d)** – the combined image in X-rays of titanium and nickel.

Figure 3 represents diffraction patterns from the titanium nickelide nanoparticles synthesized by pulsed laser ablation method (figure 3(a)) and from Ni-Ti particle wich appeared at the junction of three grains in the bulk $Ni_{51}Ti_{49}$ sample subjected to plastic deformation [2]. Also in [2], we found magnetic lenticular crystals of Ni_4Ti_3 phase which appeared after a plastic strain. Interpretation of diffraction patterns showed that lenticular crystals contain icosahedral phases (Frank-Kasper structures). Figure 3(c) shows the combined diffraction pattern (figures 2(a) + 2(b)) which indicates the complete coincidence of diffraction patterns represented on figures 2(a), 2(b). It allows to assume that icosahedral clusters with Frank-Kasper structure present in Ni-Ti nanoparticles synthesized by pulsed laser ablation method.



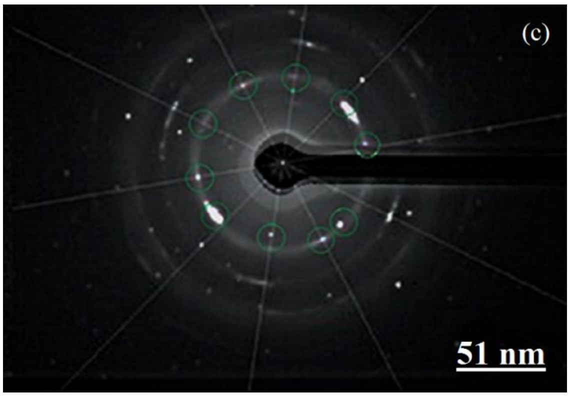


Figure 3. The comparison of diffraction pictures: **(a)** – from the titanium nickelide nanoparticles, received by method of pulse laser ablation; **(b)** – from plastically deformed $Ni_{51}Ti_{49}$ alloy exemplar; **(c)** – the combined diffraction pattern of electrons (figures 2(a) +2(b)).

Icosahedral clusters appear due to the atom displacements under the influence of temperature and pressure gradients that lead to ferromagnetic properties appearance in material. Ferromagnetism in Ni-Ti system disappears when the titanium content is higher than 10 % (at.) according to the phase diagram [6]. However, in our experiments the ferromagnetic phase appears in samples of equiatomic structure both after a plastic deformation and after a laser ablation because the condition of material considerably is removed from equilibrium in fields of tension and temperatures.

Figure 4 shows M-H curves of Ni-Ti nanoparticles (figure 4(a)) at temperatures T = 296 K (1) and 77 K (2) and also the temperature dependence of the magnetic moments at 3 kOe (figure 4(b)).

Magnetic measurements indicated that particles behave as superparamagnetic [7]. Furthermore, superparamagnetism was demonstrated in bulk samples contained the lenticular crystals [8]. The calculation by scattered waves (SW) method [8] showed that not-deformed $Ni_{10}Ti_6$ cluster with Frank-Kasper structure (FK-16) has a small magnetic moment (the average magnetic moment per atom is ~$0.3\mu_B$) and deformed (elongated by 8 % along the selected axis) $Ni_{10}Ti_6$ cluster has the average magnetic moment per atom is ~$1.2\mu_B$ while magnetization of clear nickel is only $0.6\mu_B$. Although, the average magnetic moment of $Ni_{51}Ti_{49}$ alloy samples is equal to zero due to chaotic distribution of clusters in alloy. Increase the magnetization of Ni-Ti alloy is caused by emergence of a resultant magnetic moment due to external influence (mechanical or temperature). Cooperative deformation of clusters with Frank-Kasper structure results in regularity of magnetic moment in system of these clusters [9]. Experimental and theoretical studies carried out this work have shown that the method of pulsed laser ablation allows obtaining the titanium nickelide nanoparticles that have magnetic properties which can be used for production of promising materials to be applied to new nanotechnologies.

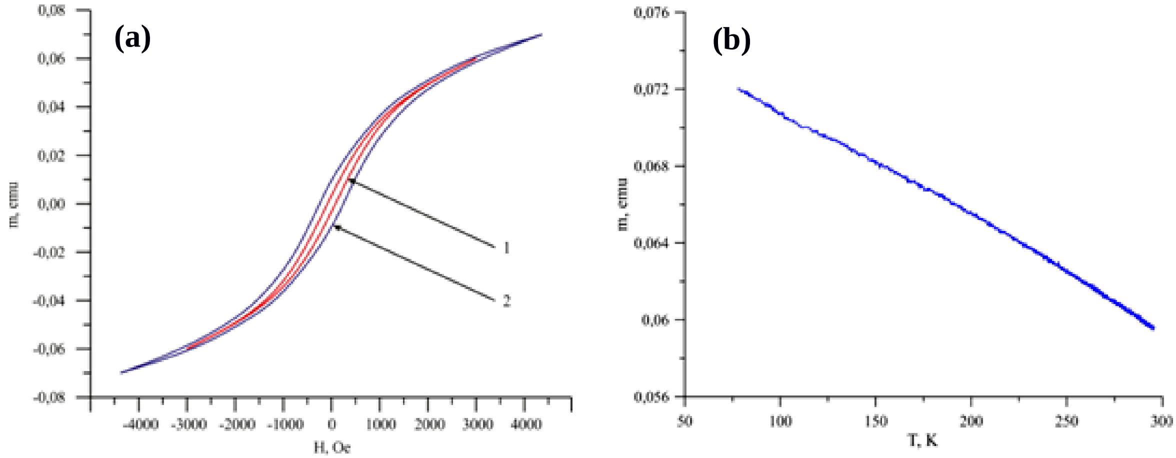


Figure 4. M-H curves for Ni-Ti nanoparticles **(a)**: 1 – T = 296 K; 2 – T = 77 K; temperature dependence of magnetic moments **(b)**.

4. Conclusions

In summary, we have firstly demonstrated synthesis of magnetic titanium nickelide nanoparticles with equiatomic composition by pulsed laser ablation method. TEM measurements have shown that synthesized Ni-Ti particles with equiatomic composition have a spherical form with 50–100 nm diameter. Magnetic measurements indicated that particles behave as superparamagnetic.

References

[1] Gunter V E, Yasenchuk Y F, Klopotov A A and Khodorenko V N 2000 *Tech. Phys. Lett.* **26** (1) 71–6
[2] Dzhess A V, Noskov F M, Kveglis L I et. al. 2016 *Fund. problems of mat. science* **13** (1) 96–104
[3] Giannaccini M, Giannini M, Calatayud M P et. al. 2014 *Intern. J. Mol.Sci*. **15** 1590–605
[4] Svetlichny V A, Shabalin A V and Lapin I N 2016 *Russian Phys. J.* **59** (12) 30–4
[5] Edelman I S, Patrin G S, Velikanov D A, et. al. 2008 *JETP Lett.* **87** (5) 310–3
[6] Lyakishev N P 2001 *Phase diagrams of double metal systems: Reference book* **3** 655–7
[7] Heard K M 1984 *Physics-Uspekhi* **142** (2) 331–55
[8] Noskov F M, Nyavro A V, Cherepanov et. al. 2017 *Vestnik SibSAU* **18** (1) *in press*
[9] Khomskii D I, Kugel K I, Sboychakov A O and Streltsov S V 2016 *JETP* **122** (3) 484–98