ICOSAHEDRAL Ti-Zr-Ni THIN FILMS

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Icosahedral (i-phase) quasicrystals have many tetrahedral interstitial sites, which are structurally favourable for hydrogen absorption, making them good candidate as a hydrogen-storage material. It has been reported [1, 2] how Ti–Zr–Ni quasicrystals can absorb large amounts of hydrogen, equivalent to an M/H value of 1.7. Qiang et al. [3] reported that single-phase quasicrystals can be obtained by the casting method at the compositions of $Ti_{40}Zr_{40}Ni_{20}$ and $Ti_{33}Zr_{44}Ni_{18}Cu_5$, and a bulk glassy alloy is formed at the composition of $Ti_{12}Zr_{55}Ni_{13}Cu_{20}$. In our previous work we have demonstrated that it is possible to store up to 2 % of hydrogen to the nanocrystalline powder with the composition of $Ti_{40}Zr_{40}Ni_{20}$ prepared by melt-spinning followed by crushing the ribbons and subsequent hydrogenation [4].
In the present work we report the results of analytical electron microscopy study of $Ti_{40}Zr_{40}Ni_{20}$ based thin films, prepared by pulsed laser deposition at 157 nm.

Precursors for pulsed laser deposition were prepared by arc-melting of $Zr_{65,9}Ni_{34,1}$ alloy and Ti powder in such a ratio, that final material composition should be close to $Ti_{40}Zr_{40}Ni_{20}$. Sample was heated up to 1400°C by RF induction and melt was injected through the nozzle by 200 mbar of argon over-pressure on rotating copper wheel of 200 mm diameter. For pulsed laser deposition Fluorine laser (wavelength 157 nm) was used with energy of 20 mJ/pulse, repetition rate of 15 Hz and ablation time of 2 hours. Distance to the substrate was 0.5 cm and alumina, graphite and sapphire were used as a substrate. Nanoparticles, prepared with pulsed laser deposition were transferred to lacy-carbon copper grid. Analytical work was done on a Jeol 2010 F field-emission gun TEM equipped with a Link ISIS EDXS system (UTW Si(Li) detector) and Gatan PEELS.

In samples prepared by pulsed laser deposition (on sapphire substrates) nanosized particles, with a diameter up to 5 nm were observed (Fig. 1a). On HRTEM images we could not detect any particle with 5 or 3-fold symmetry, characteristic for quasi-crystals (Fig. 1b). To establish if this lack of i-phase is the consequence of chemical composition we performed quantitative EDXS analysis on numerous particles. The spread of the results (defined as relative standard deviation of measurements) was 9% in the case of Ti, 8% in the case of Zr and 25% in the case of Ni. Using standards for quantitative analysis and all precautions during spectra collection (absorption correction was neglected due to very small thickness of the particles) the relative standard deviation of the measurement should not exceed 5 %. We could state that the particles inside the sample prepared with pulsed laser deposition were chemically not homogeneous. In the continuation of our experiments we calculated the composition of the basic target alloy on the basis of Ni losses and we succeeded in the preparation of films much closer to the ideal composition for the processing of i-phase ($Ti_{40}Zr_{40}Ni_{20}$). In the present paper the results of high resolution analytical microscopy and EDXS analyses will be presented.

References:

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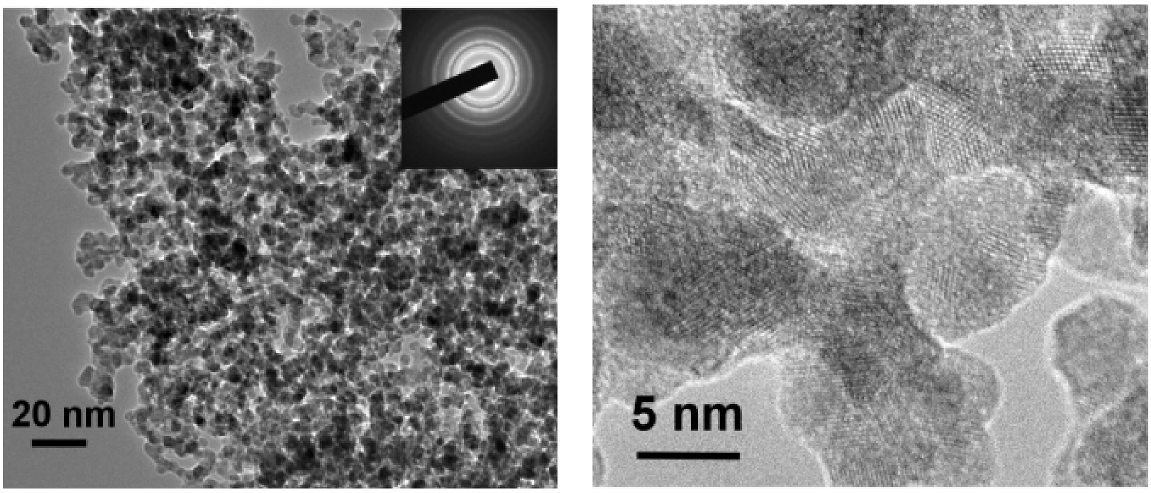

a. b.

Fig 1. a – TEM micrograph and SAED pattern (inset) of the sample prepared with pulsed laser deposition, b - HRTEM image of the particles