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## EFFECT OF HOT PRESSING ON THE ELECTROCHEMICAL PROPERTIES OF Ti-Ni ALLOY

## WPLYW PRASOWANIA NA GORĄCO NA WŁAŚCIWOŚCI ELEKTROCHEMICZNE STOPU Ti-Ni

Ti<sub>2</sub>Ni alloy pellets were produced by mechanical alloying and hot pressing at 750°C for 0.5 h in vacuum. X-ray diffraction analysis showed that, after 8 h of milling, a starting mixture of elements mostly decomposed into an amorphous phase. Obtained powders and flakes have cleavage fracture morphology with huge number of dimples with different sizes. Hot pressing of materials caused formation of Ti<sub>2</sub>Ni main phase. Porosity of pellets strongly depended on size of agglomerates and pressure of pressing. Ti<sub>2</sub>Ni pellets were used as negative electrodes for Ni-MH<sub>x</sub> batteries. Maximum measured discharge capacity of studied materials was 220 mAh/g. Electrochemical properties resulted from size of agglomerates, degree of oxidation and pressure of pressing.

*Keywords:* mechanical alloying, hot pressing, SEM, XRD, electrochemical measurements

### 1. Introduction

Ti<sub>2</sub>Ni alloy is considered as material for Ni-MH<sub>x</sub> rechargeable batteries. Its theoretical electrochemical capacity equals 500 mAh/g. Unfortunately, due to poor cycle stability and formation of accumulation of irreversible metal hydride, Ti<sub>2</sub>Ni produced by arc melting had capacity at the level of 160 mAh/g [1].

Mechanical alloying (MA) is already succeeded method in synthesizing a wide range of alloys for energy storage [2-6]. The process consisting repeated fracturing, mixing and cold welding of fine blend of elemental particles, resulting in size reduction and chemical reactions [7]. This method provides formation of non-equilibrium nanocrystalline metal hydrides with good electrochemical properties such as: stable temperature-pressure cycle capacity during life-time of the system, high storage capacity and good corrosion stability [3,5].

MA was also used in the past to produce Ti<sub>2</sub>Ni-based materials in both amorphous and crystalline form. Due to this method of production initial absorption rate was improved due to reduction in particle size and creation of new clean surfaces [2,8].

Hot pressing of mechanically blended Ti-Ni element mixture were done in the past in order to obtain shape memory alloys with attractive properties such as: superelasticity, good corrosion resistance, low density and improved biocompatibility [9,10]. Nevertheless this method hasn't been used to produce Ti-Ni alloy for Ni-MH<sub>x</sub> batteries.

The use of such a combination of methods (mechanical alloying and hot pressing) of production can affect the density of pellets, thereby improving electrochemical properties. Moreover, combining two processes (heat treatment, pressing) can also be omitted one of the processes, reducing the production time.

In this work structure Ti<sub>2</sub>Ni structure, particle size and morphology and electrochemical discharge capacity were investigated. To best of our knowledge, there are no reports on combination mechanical alloying and hot pressing in order to improve electrochemical properties of Ti<sub>2</sub>Ni alloy.

### 2. Materials and experimental

Ti<sub>2</sub>Ni hydrogen storage alloy was prepared by mechanical alloying and hot pressing. During experiments following raw metallic powders were used: Ti and Ni. Purity of used powders was 99.9 wt%. Elemental powders were weighted and loaded into synthesis vials in a glove box – Labmaster 130. All handlings were carried out in argon atmosphere. A composition of starting materials mixture was corresponding to the stoichiometry of the “ideal” reaction.

MA process was performed using separately a SPEX 8000 Mixer Mill and a FRITSCH planetary mill Pulverisette 5. We used two types of mills in order to compare properties of resultant powders obtained from different types of mills. In both cases ball to powder ration was 5:1. MA process was carried out in argon atmosphere. Rotational speed of FRITSCH mill main disc equaled 200 rpm. Diameter of stainless steel

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balls was 12 mm. Every MA process lasted 8 h. All MA processes were stopped every hour to: dissipate heat, reduce excessive rise of temperature, crush bulk materials in vials, scrape powder adhered to balls and walls.

All obtained as-milled materials were hot pressed in vacuum to form 0.5 g pellets. Frequency induction sintering method of heating were used. A temperature of annealing was 750°C. Powders were pressed under pressure of 40 and 100 MPa. Because hot pressing was also annealing of materials, this process lasted 30 minutes to ensure formation of Ti<sub>2</sub>Ni phase.

X-ray diffraction (XRD) structural studies were made to follow structural changes during MA process and after hot pressing. All diffractograms were obtained by Panalytical Empyrean with Cu K $\alpha$ .

Microstructure and morphology of obtained powders were determined using a scanning electron microscopy (SEM) – Tescan digital microscopy imaging VEGA TS5135. In this publication included are images of powders at different magnifications in order to complete presentation of materials – both a size of the agglomerates and their morphology.

Optical microscopy (OM) Olympus GX 51 was used for quantitative porosity assessment of obtained pellets after hot pressing. Before analysis pellets were sanded and polished. Analysis of images was performed with ImageJ software program.

Pellets which were obtained after mechanical alloying and hot pressing were used as metal-hydride electrodes. They were sintered to conductive nickel handle, without any nickel nets which were used in our previous studies. Initial activation of samples was based on soaking of electrode in 6 M KOH for 24 h at room temperature with additional etching at 100°C for 1 hour in the same solution. Charge and discharge testing of electrodes was conducted in a three-compartment glass cell, using two electrodes: NiOOH/Ni(OH)<sub>2</sub> counter electrode, Hg/HgO/6 M KOH reference electrode. All electrochemical measurements were performed in 6 M KOH solution using Multi-channel Battery Interface ATLAS 0461. Examined electrodes were charged and discharged at 40 mAh/g. The cut-off potential vs. Hg/HgO/6 M KOH was -0.7 V. In order to compare cyclic stability of electrodes, capacity retaining rate at 18<sup>th</sup> cycle was used:

$$R_n = \frac{C_{18}}{C_{\max}} \times 100\% \quad (1)$$

where C<sub>18</sub> and C<sub>max</sub> are discharge capacities at the 18<sup>th</sup> cycle and maximum discharge capacity, respectively.

Materials obtained in SPEX mill and FRITISCH mill were labeled in this work as SPEX powder/material and FRITISCH powder/flakes/material respectively. Obtained sintered pellets were labeled as following: XY. X involves a type of used mill which was used for material production: S for SPEX and F for FRITISCH. Y refers to the pressure of materials pressing: 40 MPa or 100 MPa.

### 3. Results and discussion

Properties of materials obtained by MA and hot pressing have been studied by X-ray diffraction, microstructural

investigations as well as by electrochemical measurements. Fig. 1 shows XRD spectra of a mixture of Ti and Ni powders mechanically milled in FRITISCH ball mill for different time in argon atmosphere. Original clearly visible sharp diffraction peaks, correspond to Ti and Ni elements become broader, and their intensity decreased with milling time. Powder mixture milled for 8 hours was almost amorphous. Milling process

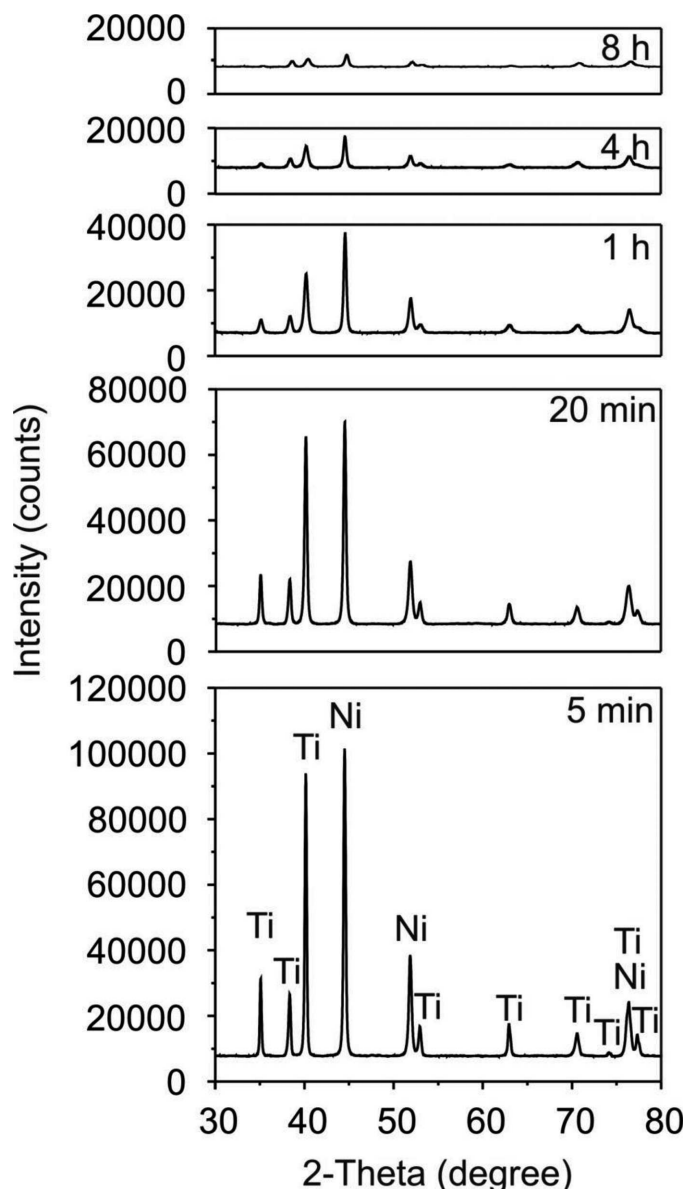


Fig. 1. XRD spectra of a mixture of Ti and Ni powders mechanically milled in FRITISCH ball mill for different time in argon atmosphere

was stopped after 8 hours to compare this results with previously published XRD spectra for amorphization of Ti-Ni mixture milled in SPEX ball mill [2]. Previously described amorphization process was very similar to that obtained using FRITISCH ball mill. FRITISCH material had two forms: flakes and powder. About 95 wt% of total FRITISCH material was contained in flakes. SPEX material was only in form of powder. Differences between forms of obtained materials are probably caused by different synthesis conditions: eg forces associated with the process, filling the reactor.

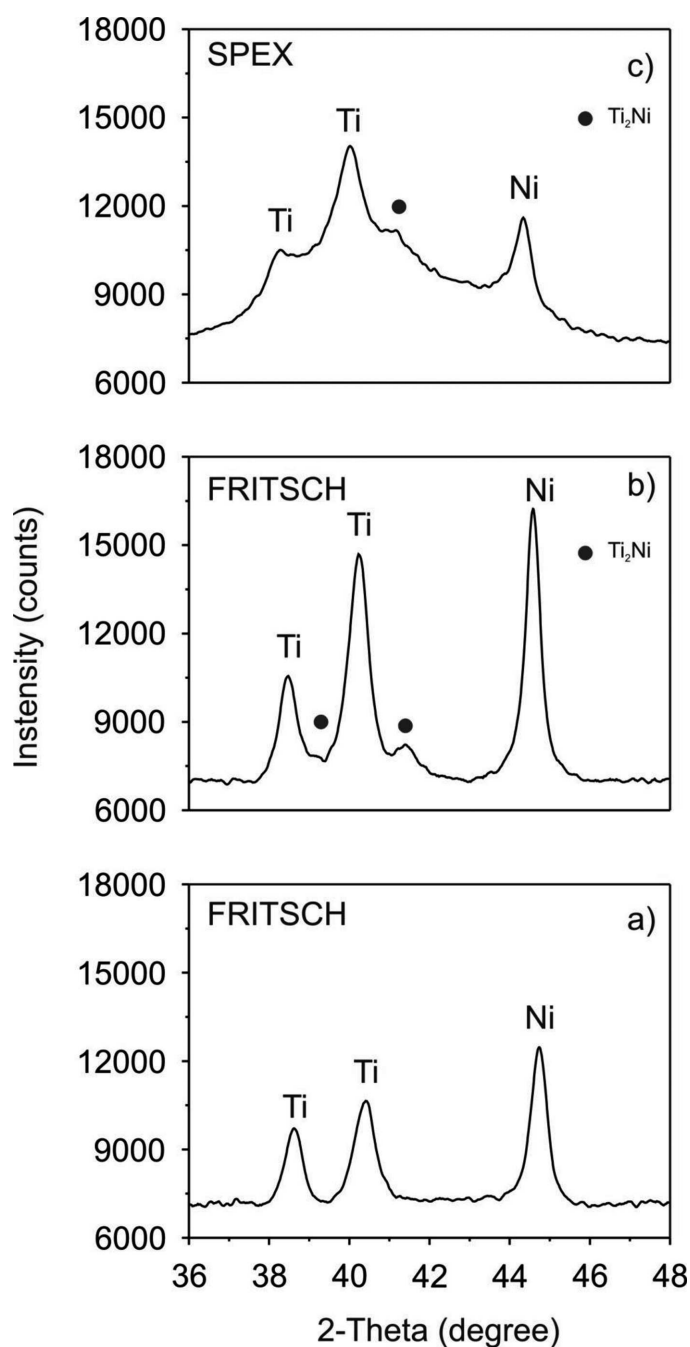


Fig. 2. XRD spectra of a mixture of Ti and Ni powders mechanically alloyed for 8h: flakes from FRITSCH ball Mill (a), powder from FRITSCH ball Mill (b) and powder from SPEX ball mill (c)

To compare effect of Ti-Ni material amorphization produced in used mills, XRD spectra of materials obtained after 8 hours of MA was placed in Fig. 2. Figure contains XRD spectra corresponded to SPEX powder and to both forms obtained from FRITSCH mill: flakes and powder. To facilitate an analysis of results, diffraction patterns contain only the most intense peaks. In all spectra, peaks assigned to residues of Ti and Ni crystallites are visible. SPEX powder is much more amorphous than FRITSCH powder, for which peaks are more

intense. For both powders peaks assigned to  $Ti_2Ni$  phase were observed. It means that as a result of MA process, in material appeared crystallites of desired  $Ti_2Ni$  phase. This situation wasn't noticed in the case of FRITSCH flakes, where only Ti and Ni peaks were visible. Accordingly to the fact, the flakes comprise about 95 wt% of total FRITSCH material can be considered that  $Ti_2Ni$  phase is almost not present in FRITSCH material.

Fig. 3 shows SEM pictures of powders and flakes obtained from MA process. Pictures with the lowest magnification present shape and size of crystal agglomerates. SPEX powder had size from a few up to two hundreds of micrometers. The upper limit of FRITSCH powder size was higher than for SPEX powder and equaled even more than five hundreds of micrometers. Some of FRITSCH powder agglomerates had sharp boundaries which wasn't observed for SPEX powder agglomerates. FRITSCH flakes had the biggest size. They had size of millimeters. Greater magnifications show morphology of obtained materials.

As soon as MA process was started, powder particles were subjected to compressive impact forces. A microstructure that forms during MA consists of layers of the starting materials mixture. A lamellar structure is increasingly refined during further mechanical alloying. A thickness of materials decreases with increase in mechanical alloying time resulting in amorphization of materials and alloy formation.

The SEM analysis of all three types of specimens cleavage fractured surface shows typical ductile appearance (Fig. 3). Obtained morphology was in agreement with the plastic deformation existing on the bonding surface during tensile fracture. On fractured surface which is rather rough, a huge number of dimples with different sizes, depths and shapes are visible. This kind of morphology was observed also for Ti-Al coatings fabricated by mechanical alloying [11]. Similar dimples are also obtained for samples which were tensile tested [12,13].

Both materials, obtained from SPEX and FRITSCH (mixture of flakes and powder) ball mills were hot pressed at  $750^\circ C$  at two pressures: 40 MPa and 100 MPa. Undesirable thin oxide layer was visible on the surface of all pellets. This layer was formed during the sintering process. In order to obtain better electrochemical properties, pellets were sanded. Fig. 4 shows XRD spectra of sanded pellets after pressing of both materials under 40 and 100 MPa. The most intense peaks on all patterns are related to  $Ti_2Ni$  fcc-type phase. Additionally to main phase, two minor phases are visible: TiNi and Ti. A part of titanium didn't react with Ni and didn't create  $Ti_2Ni$  alloy which could also resulted in formation of TiNi minor phase. Insets of all part of Fig. 4 present shifts between position of the most intense XRD peak of oxidized (not sanded) and not-oxidized pellets (sanded). The shift is more apparent for FRITSCH pellets than for SPEX pellets. The shift isn't visible only for S 100MPa pellet. Difference in the degree of oxidation is most likely caused by pressure of pressing and size of agglomerates which was much smaller for SPEX powder.

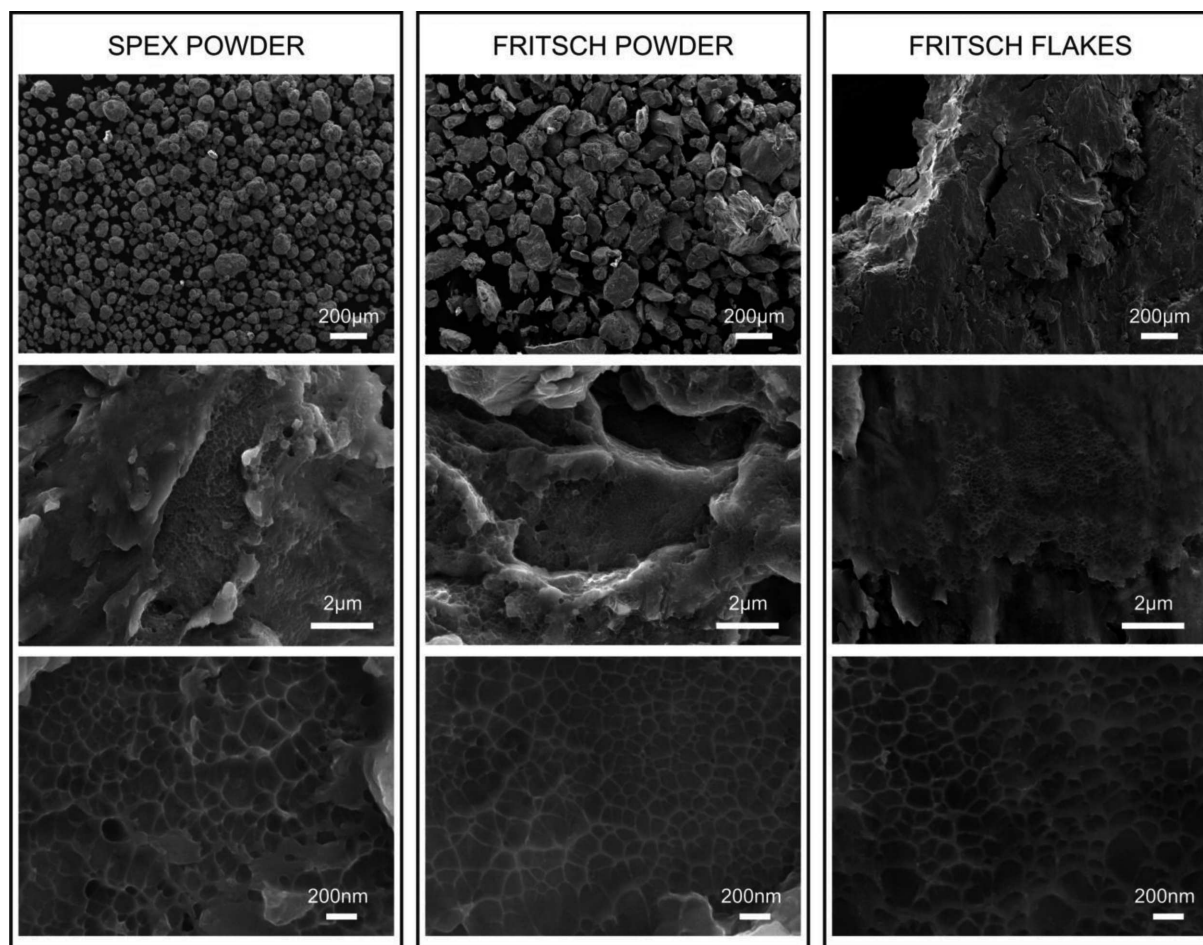


Fig. 3. SEM pictures of a mixture of Ti and Ni powders mechanically alloyed for 8h. Pictures taken at different magnifications

Fig 5. Shows OM pictures of pellets surface after sanding and polishing. All pellets were porous. Porosity depends heavily on type of material (size of agglomerates) and pressure of pressing. Higher pressure caused lower porosity. Porosity of pellets is summarized in Table 1. The highest porosity was obtained for F 40MPa pellet. It equals 26%. The same material pressed at 100 MPa had porosity of 7%. SPEX powder which particles were the smallest showed lower porosity. The best sinter was produced from SPEX powder after pressing under 100 MPa – porosity equals less than one percent. Porosity of pellets probably affects also mentioned above degree of oxidation. As a effect of sintering unfavorable grain growth was also observed.

TABLE 1

Porosity, maximum discharge capacity and capacity retaining rate at 18<sup>th</sup> cycle of mechanically alloyed and sintered Ti<sub>2</sub>Ni pellets

Sample	Porosity (%)	Maximum discharge capacity (mAh/g)	capacity retaining rate at 18 <sup>th</sup> cycle (%)
S 40MPa	5	182	33
S 100MPa	0.5	220	40
F 40MPa	26	130	7
F 100MPa	7	192	39

Table 1 and Fig. 6 reports discharge capacities of studied materials. Mechanically alloyed and hot pressed powders displayed the maximum discharge capacities at 2<sup>nd</sup> and 3<sup>rd</sup> cycle. Pellet with the worst electrochemical properties was F 40MPa. Maximum discharge capacity of this material was just 130 mAh/g. Additionally it had very weak capacity retaining rate, which equaled 7%. The highest discharge capacity was obtained by S 100MPa which equals 220mAh/g. This electrode is also characterized by the best capacity retaining rate at 18<sup>th</sup> cycle. However, it is only 40% which isn't satisfactory for Ni-MH<sub>x</sub> application. Electrochemical properties resulted directly from size of mechanically alloyed materials, degree of oxidation and pressure of pressing. The decrease in discharge capacity is caused by oxidation process and by disintegration of pellets material during hydrogenation of materials. Another possible reason for occurrence of this situation is formation of irreversible hydride phase.

S 100 MPa had higher discharge capacity than that the arc melted ones [1]. However capacity is lower than capacity obtained for cold pressed mechanically alloyed and annealed Ti<sub>2</sub>Ni powder [2]. Higher capacity of cold pressed annealed powders is caused by a few factors. Firstly in previous measurements nickel nets were used which acting as current collector. Secondly, to annealed material 10 wt% of Ni element was added. This addition increases electrical conductivity, catalyzes electrode reaction and the surface hydrogen dissociation. Finally, as we mentioned before, hot pressing affects

the growth of grains which is unfavorable for electrochemical properties.

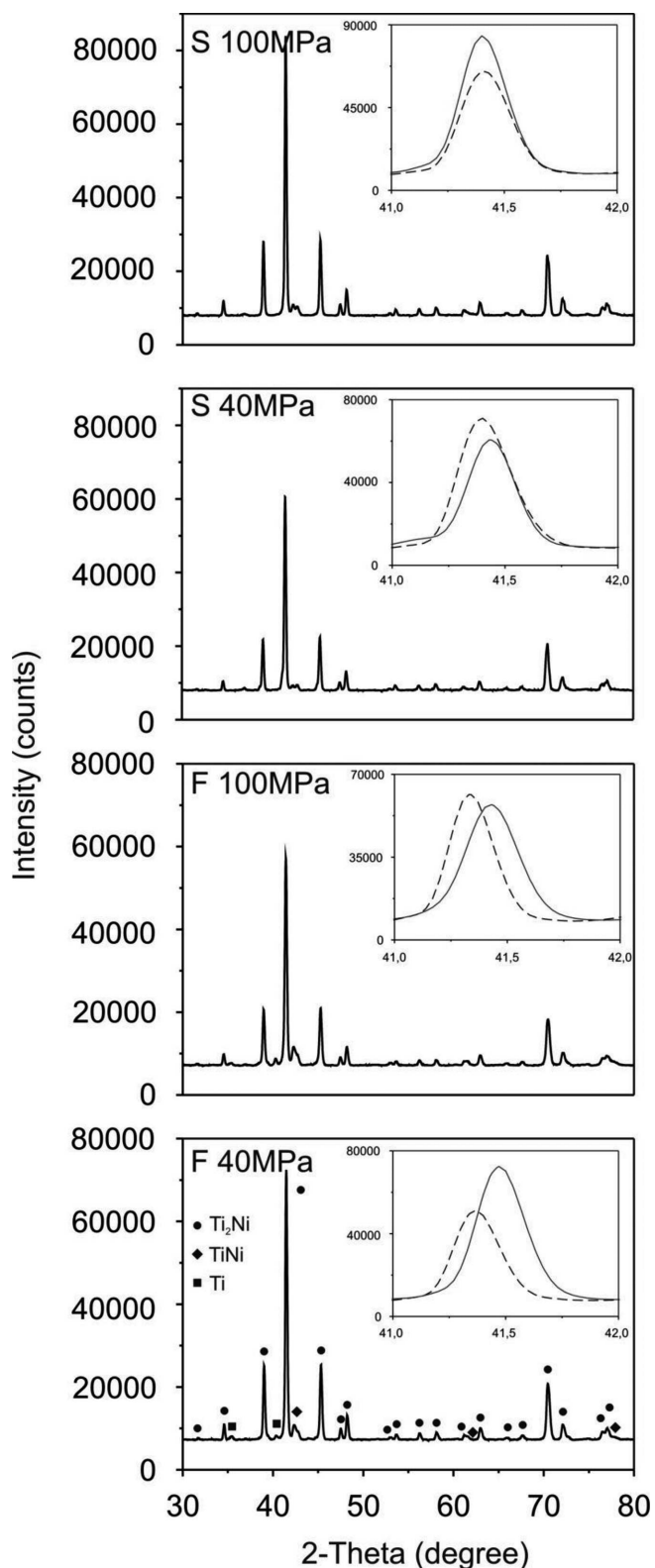


Fig. 4. XRD spectra of sintered  $Ti_2Ni$  alloys. Powders obtained from SPEX and FRITSCH ball mills were hot pressed under 40 and 100 MPa. Surface of pellets was sanded. Inset: XRD spectra of most intensive peak for sanded pellets (solid lines) and not sanded pellets (dashed lines)

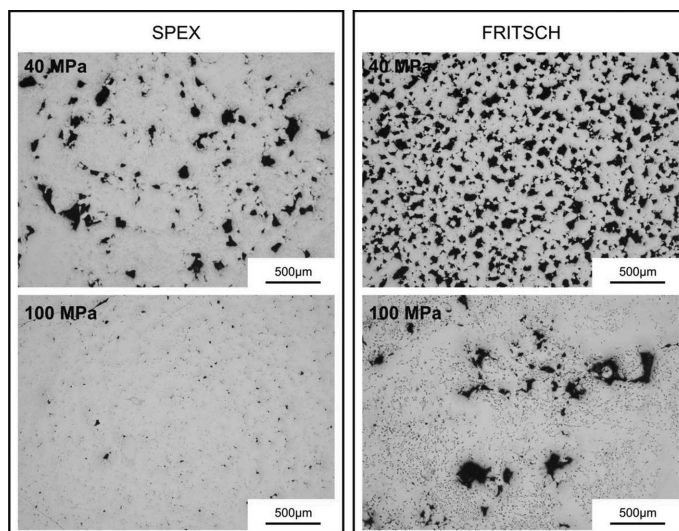


Fig. 5. Optical microscope micrographs of sintered  $Ti_2Ni$  alloys

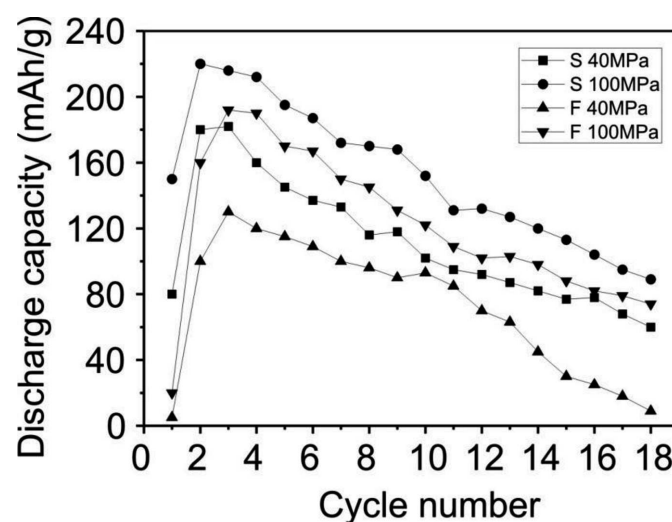


Fig. 6. Discharge capacity as a function of cycle number of electrodes prepared with  $Ti_2Ni$ . Solution 6 M KOH, temperature  $20^\circ C$ , charge conditions were  $40 \text{ mA g}^{-1}$ , the cut-off potential vs Hg/HgO/6 M KOH was  $-0.7 \text{ V}$

#### 4. Conclusions

$Ti_2Ni$  alloys for Ni-MH<sub>x</sub> battery was synthesized by mechanical alloying and hot pressing at  $750^\circ C$  for 0.5h. For MA process SPEX and FRITSCH ball mills were used. Ti-Ni materials were sintered in vacuum by frequency induction method under pressure of 40 and 100 MPa. Obtained pellets were measured to investigate structure, particle size and morphology and electrochemical discharge capacity.

We found out that 8 hours of milling of elemental mixture results in significant amorphization of materials. Powder form of powders promotes formation of  $Ti_2Ni$  phase during MA process. SPEX powder agglomerate size was much smaller than for FRITSCH powder and flakes. All of the materials had cleavage fracture morphology with visible dimples which indicates ductile fractures.

Sintered pellets had different porosities that resulted from size of agglomerates and pressure of pressing. S 100 MPa was

the material with the lowest obtained porosity – 0.5%. Also the same material exhibited the best electrochemical properties. Maximum discharge capacity for S 100 MPa equaled 220 mAh/g and stability of electrode was 40% after 18<sup>th</sup> cycle.

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