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Structural- and hydriding-properties of the $Zr(V_{0.25}Ni_{0.75})_{\alpha}$ ($1 \leq \alpha \leq 4$) alloy system

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Abstract

Previous investigations on the $Zr(V_xNi_{1-x})_2$ alloy system showed that $Zr(V_{0.25}Ni_{0.75})_2$ has a very high reversible capacity (≈365 mA h g^{-1}, discharge current $i_{dis}=100$ mA g^{-1}). This alloy does not crystallize in a perfect single phase, a second phase (Zr_7Ni_{10}) was observed. In order to understand the influence of the second phase and to optimize the alloy composition for high capacity, the influence of the stoichiometry was investigated. A series of alloys $Zr(V_{0.25}Ni_{0.75})_{\alpha}$ ($1 \leq \alpha \leq 4$) were prepared by r.f. levitation melting. The main phase in all the tested alloys was the cubic C15-Laves phase. A second phase was observed in the samples with $\alpha \leq 2.5$, whereas the alloys with $\alpha > 2.5$ are single phase. The lattice parameter shows a significant step in the range of $2 \leq \alpha \leq 2.5$. The electrochemically measured capacity is highest for $\alpha = 2$ ($C = 1.0$ H/M, 394 mA h g^{-1}, $i_{dis}=5$ mA g^{-1}). The alloy system $Zr(V_{0.25}Ni_{0.75})_{\alpha}$ ($1 \leq \alpha \leq 4$) is very adaptable to changes in the stoichiometry. However, the distribution of A and B elements on the A and B sites is crucial for high capacity. A part of the vanadium atoms move from B sites to A sites in the overstoichiometric systems $Zr(V_{0.25}Ni_{0.75})_{\alpha}(2 < \alpha)$. The overstoichiometric (AB_3) alloy $ZrV_{1.5}Ni_{1.5}$ crystallizes in the cubic C15-Laves phase and shows a very high capacity of 800 mA h g^{-1} ($i_{dis}=2$ mA g^{-1}). However, only 400 mA h g^{-1} can be discharged at a 20 mA g^{-1} discharge current.

Keywords: Metal hydrides; Electrode; Laves phase; AB_2

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1. Introduction

In a detailed study [1] of the system $Zr(V_xNi_{1-x})_2$ ($0 \leq x \leq 0.4$) it was found, that the alloy $Zr(V_{0.25}Ni_{0.75})_2$ reaches the highest electrochemical discharge capacity (345 mA h g^{-1}, discharge current $i_{dis}=100$ mA g^{-1}) and shows the best discharge kinetics. Different pretreatments (HF solution, hot KOH) have been shown to be very effective in improving the discharge kinetics of $Zr(V_{0.25}Ni_{0.75})_2$ and increased the discharge capacity to 364 mA h g^{-1}, $i_{dis}=12$ mA g^{-1}) [2]. The $Zr(V_xNi_{1-x})_2$ alloys all form the cubic C15 Laves phase, however, there was always a second phase observed [3]. Sawa and Wakao [4] studied overstoichiometric alloys of the composition $Zr(V_{0.33}Ni_{0.67})_{2+\alpha}$ in the range of $0 \leq \alpha \leq 1$. They observed a slight increase of the discharge capacity in the range $0 \leq \alpha \leq 0.4$, however, the calculation of the number of interstitial sites as well as the experimental data showed a decrease of the hydrogen capacity with increasing $\alpha \geq 0.4$. Measured discharge capacities for $Zr(V_{0.33}Ni_{0.67})_{2+\alpha}$ were 297 mA h g^{-1} for $\alpha = 0$ and 311 mA h g^{-1} for $\alpha = 0.4$, respectively. $Zr(V_{0.33}Ni_{0.67})_{2.4}$ (C15 Laves phase) has a lattice constant of 7.048 Å and $\Delta H^0 = 24.89$ $kJ \cdot mol_H^{-1}$ and $\Delta S^0 = -69.39$ $J \cdot K^{-1} \cdot mol_H^{-1}$, while for $Zr(V_{0.33}Ni_{0.67})_2$ a lattice constant of 7.102 Å and $\Delta H^0 = 29.24$ $kJ \cdot mol_H^{-1}$ and $\Delta S^0 = -72.09$ $J \cdot K^{-1} \cdot mol_H^{-1}$ was observed.

This paper reports the results of a study of the properties of the $Zr(V_{0.25}Ni_{0.75})_{\alpha}$ ($1 \leq \alpha \leq 4$) alloy system as active electrode materials.

2. Experimental

The $Zr(V_{0.25}Ni_{0.75})_{\alpha}$ ($1 \leq \alpha \leq 4$) alloy samples (6 g, ≈1 cm^3) were prepared by r.f. levitation melting of the appropriate amounts of the elements, i.e. Zirconium from Goodfellow GB, 99.8% Zr, Vanadium from Koch-Light GB, 99.7% V, and Nickel from Johnson Matthey GB, 99.99% Ni. The elements were cut and cleaned from oxides with a file. The metals were then washed in acetone and subsequently introduced into the vacuum (10^{-7} mbar) of the r.f. levitation oven. The metals were initially heated up to 1480 °C. The power was reduced and the samples were held at 1350 °C for 5 min. Thereafter the power was switched off and the samples were quenched in contact with the water cooled copper crucible to room temperature

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within seconds. The samples were mechanically broken in pieces and immediately introduced into a stainless steel reactor. Subsequently the latter was evacuated (10^{-2} mbar) and then floated with hydrogen gas at room temperature (20 °C) and 40 bar. The samples were left for about 1 h for complete hydriding and then dehydrided under vacuum (10^{-2} mbar). The hydriding–dehydriding procedure was repeated 3 times before the samples were completely dehydrided in vacuum (10^{-2} mbar) at approximately 100 °C.

X-ray diffraction was performed with copper radiation (CuKα λ=1.5406 Å). Channel width was set to 2Θ=0.05° and the angular resolution was found to be 2Θ=0.2° (FWHM). The count time was set to 8 s per channel resulting in a maximum count rate of approximately 5000 counts for the main peak in the spectrum (1.5% error in the count rate).

For the electrochemical measurements approximately 25 mg of the alloy powder was mixed with copper powder (Merck p.a. <63 μm) under the open atmosphere in the weight ratio of 1:3 and cold pressed (500 MPa) to a pellet (d=7 mm). The pellets were fixed with a cylindrical Teflon-clip on a nickel holder. The electrodes were charged and discharged electrochemically in a 6M KOH electrolyte in a cell open to the atmosphere. A nickel plate was used as counter electrode and potentials were referred to a mercury/mercury oxide electrode. The discharge cut-off potential was −0.6 V with respect to the Hg/HgO/OH$^-$ reference electrode. The electrodes were tested in a half-cell experiment with constant charge (2.5 mA, i.e. 100 mA g^{-1}) and discharge (2.5 mA, i.e. 100 mA g^{-1}) current. Upon reaching 30 activation cycles the discharge capacity was measured as a function of the discharge current.

3. Results and discussion

All alloys $Zr(V_{0.25}Ni_{0.75})_\alpha$ ($1 \leq \alpha \leq 4$) crystallize mainly in the cubic C15 Laves phase structure. Fig. 1 shows the lattice constant calculated for the cubic C15 phase as a function of α. The lattice parameter of the alloys with $1 \leq \alpha \leq 2$ is almost constant (a=7.45 Å) indicating that these alloy samples have a common main phase and the excess A-element, i.e. zirconium, precipitates out of the main C15-phase. The numerous extra lines (Fig. 2) in the diffraction spectra's for the samples with $\alpha \leq 2.25$ are attributed to different Zr–V and Zr–Ni phases. Single phase (C15) alloys were obtained in the range of $2.5 \leq \alpha \leq 3.5$ for the $Zr(V_{0.25}Ni_{0.75})_\alpha$ system. Since the C15 phase is an AB_2 phase, a part of the B-elements, i.e. vanadium and nickel, in the overstoichiometric alloys have to occupy A-sites. This leads to a pronounced decrease in the lattice constant. The lattice parameter of the alloys with $\alpha > 3.5$ is approximately constant (a=6.92 Å) and a few extra lines show up in the X-ray diffraction spectrum. We assume that the vanadium atoms occupy A-sites in the alloys with $\alpha > 2$. Therefore, the missing vanadium on B-sites should be replaced. The alloy $Zr(V_{0.5}Ni_{0.5})_3$ crystallizes in a perfect C15 Laves phase, i.e. an alloy of the AB_2−type $(ZrV_{0.33})(V_{0.58}Ni_{0.75})_2$ is formed.

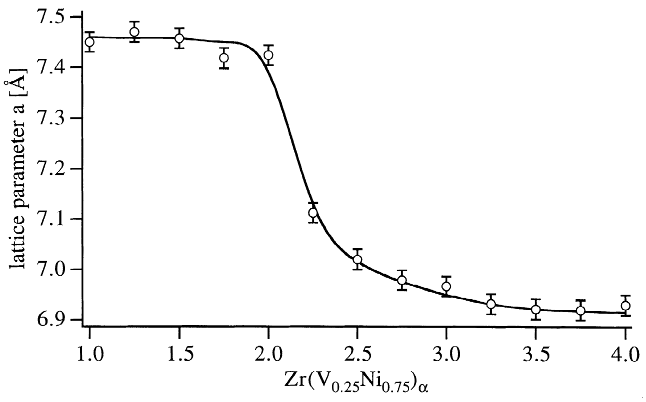

Fig. 1. Lattice parameter for the cubic C15 Laves phase as a function of the stoichiometry α in the $Zr(V_{0.25}Ni_{0.75})_\alpha$ alloy system.

The maximum electrochemically measured reversible capacity as a function of α is shown in Fig. 3. The highest reversible capacity of the system $Zr(V_{0.25}Ni_{0.75})_\alpha$ was found for $Zr(V_{0.25}Ni_{0.75})_2$ (H/M=1.0, C=394 mA h g^{-1}).

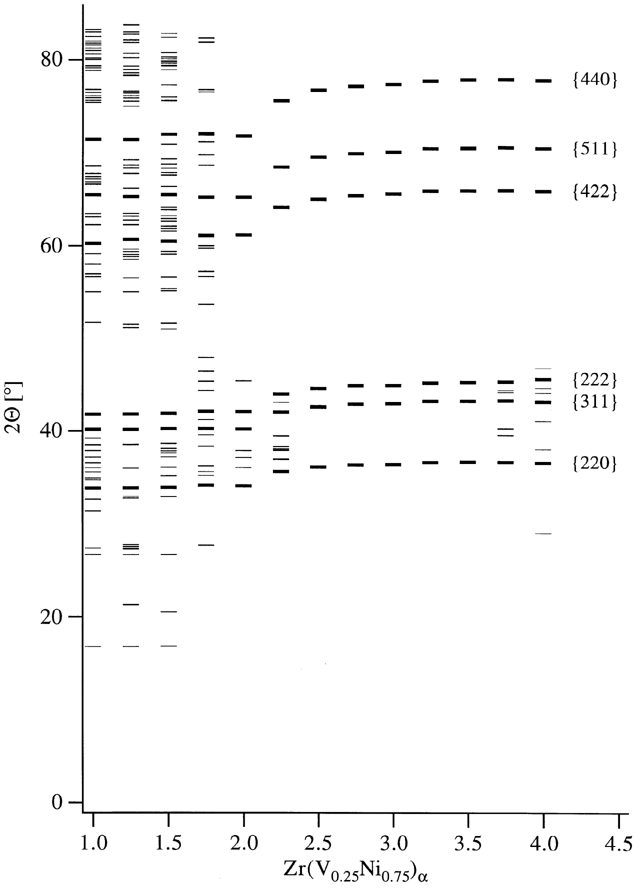

Fig. 2. Detected X-Ray diffraction lines (Intensity>5% of maximum Intensity) for the $Zr(V_{0.25}Ni_{0.75})_\alpha$ alloy system. The lines which belong to the C15 Laves phase are printed bold and the Miller index {hkl} is given.

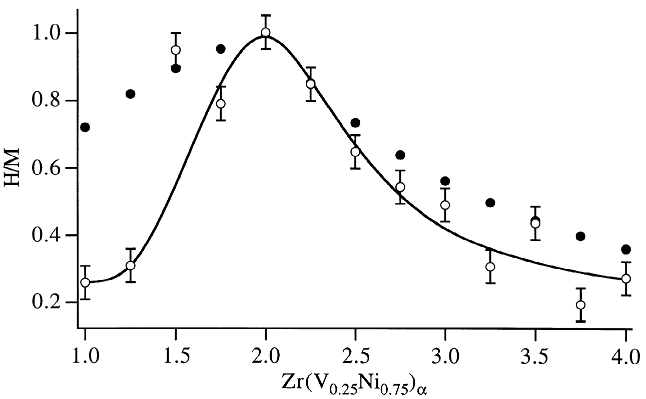

Fig. 3. Calculated hydrogen to metal ratio [H/M] from the electrochemically measured discharge capacity (○) of the $Zr(V_{0.25}Ni_{0.75})_{\alpha}$ alloy electrodes as a function of the stoichiometry α. Discharge capacity measured with a discharge current of 5 mA g^{-1}. The filled markers (●) represent the theoretically calculated capacities [5].

The measured capacities match the theoretically calculated capacities quite well for $\alpha>2$. The discrepancy between the measured and the calculated capacities in the range of $1\leq\alpha<2$ is due to the bad kinetics of those alloys. The alloy $Zr(V_{0.5}Ni_{0.5})_3$ shows an extremely large discharge capacity of 800 mA h g^{-1} (H/M=2) at low discharge current (i_{dis}=2 mA g^{-1}). At higher discharge current the capacity drops to approximately 400 mA h g^{-1} (i_{dis}=20 mA g^{-1}).

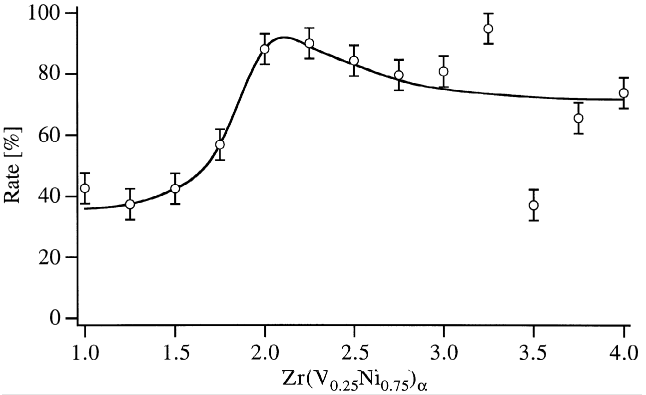

Fig. 4. Electrochemical measured rate capability, i.e. ratio of the discharge capacity measured with a discharge current of 50 mA g^{-1} to the discharge capacity measured with a discharge current of 5 mA g^{-1}, of the $Zr(V_{0.25}Ni_{0.75})_{\alpha}$ alloy electrodes as a function of the stoichiometry α.

The high rate dischargeability, i.e. the ratio of the discharge capacity measured with a discharge current of 5 mA g^{-1} to the capacity measured with a discharge current of 50 mA g^{-1}, is shown in Fig. 4. The high rate dischargeability for the overstoichiometric alloy electrodes ($\alpha>2$) is between 75% and 90%. However, it drops down to 40% for the alloys with $\alpha<2$. This can be attributed to the excess of zirconium which leads to a lower equilibrium pressure and a lower electrocatalytic activity of the alloy surface.

4. Conclusion

The main phase in all the tested alloys was the cubic C15-Laves phase. A second phase was observed in the samples with $\alpha\leq2.5$, whereas the alloys with $\alpha>2.5$ are single phase. The lattice parameter shows a significant step in the range of $2\leq\alpha\leq2.5$. The electrochemically measured capacity is highest for $\alpha=2$ (C=0.94 H/M, 394 mA h g^{-1}).

The overstoichiometric (AB_3) alloy $Zr(V_{0.5}Ni_{0.5})_3$ crystallizes in the cubic C15-Laves phase and shows a very high capacity of 800 mA h g^{-1} at low discharge current (i_{dis}=2 mA g^{-1}). However, only 400 mA h g^{-1} can be discharged at a 20 mA g^{-1} discharge current.

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