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The electronic and electrochemical properties of the TiFe-based alloys

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Abstract

Ti(Fe,M)-based alloys (M=Ni, Mo, Cr, Co) were mechanically alloyed (MA) under an argon atmosphere to synthesize nanostructured materials. XRD analysis showed that, after 25 h of milling, the starting mixture of the elements had decomposed into an amorphous phase. Following the annealing in high purity argon at 750 °C for 0.5 h, XRD confirmed the formation of CsCl-type structures with crystallite sizes of about 30 nm. These materials were used as negative electrodes for a Ni–MH_x battery. The alloying elements of the 3d transition metals, Ni, Mo, Cr and Co, were substituted for iron atoms, and the structural, electronic and electrochemical properties were studied. With increasing nickel content in TiFe_{1-x}Ni_x, the material showed an increase in discharge capacity which passed through a maximum for x=3/4. In the nanocrystalline TiNi_{0.6}Fe_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1} powder, a discharge capacity of up to 135 mA h g⁻¹ (at 40 mA g⁻¹ discharge current) was measured. For this composition the capacity degraded much more slowly with cycling in comparison to other studied compositions. The electronic structure was studied by the tight-binding version of the linear muffin-tin method in the atomic sphere approximation (TB-LMTO ASA). In the TiFe_{1-x}Ni_x alloys, increasing the content of the Ni impurities extended the valence bands and increased the density of states at the Fermi level. Similar effects were observed for the TiNi_{1/2}Fe_{1/8}Mo_{1/8}Cr_{1/8}Co_{1/8} system. Mechanical alloying proved to be a suitable procedure for obtaining TiFe-based alloy electrodes for Ni–MH_x batteries.

Keywords: Electrode materials; Transition metal alloys; Mechanical alloying; Electrochemical properties; Electronic band structure

1. Introduction

Mechanical alloying (MA) is a solid-state powder processing technique which involves repeated welding, fracturing and rewelding of powder particles in a highenergy ball mill [1,2]. MA has been proved to be a novel and promising method for alloy formation, especially in the preparation of nonequilibrium materials of various systems. The nonequilibrium alloy phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, amorphous alloys and nanostructures. This technique has already succeeded in synthesizing a wide range of alloy hydrides for energy storage or other energy related applications [3–10].

To be useful for storing hydrogen or energy the hydride (MH_x) should have the following characteristics: high reversible storage capacity, stable temperature–pressure cycling capacity during the lifetime of the system, suitable

hydrogen equilibrium pressure, good corrosion stability, small hysteresis in absorption–desorption (charge–discharge) kinetics and efficiency, good electrochemical catalyst for hydrogen atom generation and oxidation, long cycle life, low costs and availability of the intermetallics.

The nanostructured materials exhibit quite different properties from both crystalline and amorphous materials, due to a structure in which extremely fine grains are separated by what some investigators have characterized as 'glass-like' disordered grain boundaries [11]. Therefore, the hydrogenation behaviour of the amorphous structure is different than that of the crystalline material. Mechanical alloying has been recently used to make nanocrystalline Mg_2Ni -, TiFe-, ZrV₂- and LaNi₅-type alloys [3–10]. The nanostructured materials show substantially enhanced absorption and desorption kinetics, even at relatively low temperatures [4,9].

Among the four different types of hydrogen forming compounds, Ti-based alloys are among the most promising materials for hydrogen energy applications [4,12,13]. For example, titanium and iron form two stable compounds:

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TiFe₂and TiFe [14]. The first alloy does not absorb hydrogen. The second composition, which is one of the most frequently used hydrogen storage materials, forms two hydrides TiFeH (orthorhombic) and TiFeH₂ (monoclinic). On the other hand, the TiFe alloy, which crystallizes in the cubic CsCl-type structure, is lighter and cheaper than the LaNi₅-type alloys and can absorb up to 2 H/f.u. at room temperature. Nevertheless, the application of the TiFe material in batteries has been limited due to the poor absorption-desorption kinetics in addition to a complicated activation procedure. To improve the activation of this alloy, several approaches have been adopted. For example, the replacement of Fe by some amount of transition metal to form a secondary phase may improve the activation properties of TiFe [10,15,16], as well as ball milling of TiFe which is also effective for the improvement of the initial hydrogen absorption rate [17,18].

In our earlier work, the electrochemical properties of nanocrystalline TiFe_{1-x}Ni_xalloys synthesized by MA and annealing were studied [10]. It was found that the increasing the nickel content in TiFe_{1-x}Ni_x alloys leads initially to an increase in the discharge capacity, giving a maximum at x=3/4. In the nanocrystalline TiFe_{1/4}Ni_{3/4} powder, discharge capacity of up to 155 mA h g⁻¹ (at 40 mA g⁻¹ discharge current) was measured. As a continuation of our studies, in this paper the structural, electronic and electrochemical properties of nanocrystalline TiFe-based alloys were investigated, where the alloying elements of the 3d transition metals, Ni, Mo, Cr and Co, are substituted for Fe atoms.

2. Experimental and band calculations details

MA was performed under an argon atmosphere using a Spex 8000 D mixer mill with round bottom stainless steel vials. The purity of the starting metallic elements Ti, Fe, Ni, Mo, Cr and Co were 99, 99.5, 99.9, 99.8, 99+ and 99.8 wt.%, respectively. The composition of the starting powder mixture corresponded to the stoichiometry of the 'ideal' reactions. The elemental powders (Ti \leq 45 µm, Fe \leq 10 µm; Ni 3–7 µm; Mo <10 µm; Cr 45 µm and Co <2 µm) were mixed in the glove box (Labmaster 130) and poured into the vial. The mill was run up to 30 h for every

powder preparation. The as-milled powders were heat treated at 750 °C for 0.5 h under high purity argon to form regular CsCl-type phase. The MA process of the TiFebased mixtures was studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystallization behaviour of the mechanically alloyed materials was examined by differential scanning calorimetry (DSC 404, Netzsch). The change in the structure of powdered samples was observed using atomic force microscope (Nanoscope IIIa-Digital Instruments, USA) [10]. Typical crystallite sizes were estimated from the half-width of lines using the Scherrer equation.

The mechanically alloyed and annealed (nanocrystalline) materials with 10 wt.% addition of Ni powder, were subjected to electrochemical measurements as working electrodes after pressing (under 80 kN cm⁻²) to a 0.5-g pellet form between nickel nets acting as a current collector. The diameter of each electrode was 10.4 mm with a thickness of approximately 1.4 mm. Soaking of the electrodes in 6 M KOH solution for 24 h at room temperature with additional etching at 100 °C for 10 min in the same solution was sufficient for the initial activation. A detailed description of the electrochemical measurements was given in Ref. [8].

The band structures of the TiFe based alloys were calculated based on TB-LMTO method in the atomic sphere approximation (ASA) [19,20]. In this approximation, the crystal is divided into space-filling spheres, therefore with slightly overlapping spheres centered on each of the atomic sites. In the calculations reported here, the Wigner-Seitz (WS) sphere radii are such that the overlap is about 8.2–8.3%. The average WS radii (S_{av}) were scaled so that the total volumes of all spheres are equal to the equilibrium volumes of the unit cells with the lattice constants collected in Table 1. The input electronic configurations were taken as: core[Ar]+3d24s2 for the Ti atom, core[Ar]+3d64s2 for the Fe atom, core[Ar]+3d54s1 for the Ni atom, core[Ar]+3d54s1 for the Cr atom, core[Ar]+3d74s2 for the Co atom, and core[Kr]+3d54s1 for the Mo atom. The Perdew-Wang [21] potential with nonlocal corrections was used in the calculations and the spin-orbit interactions were taken into account in the form proposed by Min and Jang [22]. The combined correction terms [19] were included to compensate errors due to the ASA. The Brillouin zone k-point integrations were carried

Table 1

Structural parameters: experimental [10] (lattice constant *a*) and used in the calculations (Wigner–Seitz radii: S_A , atomic radii, where A=Ni, Fe, Mo, Cr or Co and S_{av} = average radii). *Q*, discharge capacity on 3rd cycle (current density of charging and discharging was 40 mA g⁻¹); $M_x \equiv Ni_{x/4}Mo_{x/4}Cr_{x/4}Co_{x/4}$ and $M'_x \equiv Fe_{x/4}Mo_{x/4}Cr_{x/4}Co_{x/4}$, where x = 0.5 and 0.4 for computational (S_{av} , S_{Ti} and S_A) and experimental (*a*, *Q*) values, respectively

x	x/4 - x/4 - x/4 - x/4	x/4 $x/4$						
	TiFe	$TiFe_{1-x}M_x$	$TiFe_{3/4}Ni_{1/4}$	TiFe _{1/2} Ni _{1/2}	$\mathrm{TiNi}_{1-x}\mathbf{M}'_{x}$	$TiNi_{3/4}Fe_{1/4}$	TiNi	
a (Å)	2.973	2.985	2.991	3.001	3.018	3.010	3.018	
S_{av} (Å)	1.4638	1.4697	1.4727	1.4776	1.4860	1.4820	1.4860	
S_{Ti} (Å)	1.5013	1.4432	1.5106	1.5156	1.4607	1.5202	1.5471	
$S_{\rm A}$ (Å)	1.4243	1.4954	1.4327	1.4375	1.5143	1.4418	1.4194	
$Q (mA h g^{-1})$) 0.7	6.3	55	125	135	155	67	



Fig. 1. Projections of the supercells (8 CsCl-type structures) used in the calculations for $TiFe_{1-x}Ni_x$ (x = 1/4, 1/2, 3/4), $TiFe_{1/2}Ni_{1/8}Mo_{1/8}Co_{1/8}Cr_{1/8}$ and $TiNi_{1/2}Fe_{1/8}Mo_{1/8}Co_{1/8}Cr_{1/8}$: lower layer (left panel) and upper layer (right panel). Black circles represent Ti atoms.

out using the tetrahedron method [23] on a grid of 256 and 1331 k-points in the irreducible part (1/48 and 1/8 for TiFe_{1-x}Ni_x and Ti-Fe-Ni systems doped by Mo-Cr-Co atoms, respectively) of the cubic Brillouin zone, which corresponds to 8000 k-points in throughout the Brillouin zone. The iterations were repeated until the energy eigenvalues of consecutive iteration steps were the same within an error of 0.01 mRy.

All considered alloys crystallize in the CsCl-type structure (B2 structure, Pm3m space group). In the case of TiNi and TiFe alloys only single unit cell (two atoms per cell) was used in the calculations. The situation is more complicated for doped systems and calculations were performed for slightly different stoichiometries: TiNi_{1/2} $Fe_{1/8}Mo_{1/8}Cr_{1/8}Co_{1/8}$ and $TiFe_{1/2}Ni_{1/8}Mo_{1/8}Cr_{1/8}Co_{1/8}$ $TiNi_{0.6}Fe_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1}$ experiment (for and TiFe_{0.6}Ni_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1} stoichiometries were used). A supercell is constructed, which consists of eight formula units (doubled lattice constant for x, y and z directions). Ti atoms were located in (0,0,0) type positions, and the rest of the atoms in the centers of cubes, in (1/2, 1/2, 1/2)type sites. We assumed a homogeneous distribution of impurities in our cell, as is presented in Fig. 1. We also assumed that the Ti sites do not accommodate the other types of atoms.

3. Results and discussion

The behaviour of the MA process was studied by XRD, microstructural investigations, AFM as well as by electrochemical measurements. Fig. 2 shows a series of XRD spectra of mechanically alloyed Ti–Fe and Ti–Ni powder mixtures (53.85 wt.% Ti+46.15 wt.% Fe; 44.93 wt.% Ti+55.07 wt.% Ni) subjected to milling for increasing lengths of time. The originally sharp diffraction lines of Ti and Fe or Ti and Ni gradually become broader (Fig. 2Aa and Ba) and their intensity decreases with milling time. The powder mixtures milled for more than 25 h have



Fig. 2. XRD spectra of a mixtures of Ti and Fe (Fig. 2A) and Ti and Ni (Fig. 2B) powders mechanically alloyed in an argon atmosphere: (a) initial state (elemental powders mixture); (b) after MA for 25 h and (c) heat-treated at 750 $^{\circ}$ C for 0.5 h.

transformed completely to the amorphous phase, without formation of another phase (Fig. 2Ab and Bb). During the MA process the crystalline size of the Ti decreases with the duration of MA and reaches a steady value of about 30 nm after 15 h of milling. This size seems to be favourable to the formation of an amorphous phase, which develops at the Ti-Fe or Ti-Ni interfaces. Formation of the nanocrystalline TiFe and TiNi alloys was achieved by annealing of the amorphous material in high purity argon atmosphere at 750 °C for 0.5 h (Fig. 2Ac and Bc). All diffraction peaks were assigned to those of CsCl-type structure with cell parameter a=2.973 Å and a=3.018 Å for TiFe and TiNi, respectively. When nickel is added to TiFe_{1-x}Ni_x the lattice constant *a* increases (Table 1).

Using TiFe and TiNi, the amorphization process was also studied by DSC. After MA the DSC curves stabilized exhibiting one exothermic effect at 692 and 460 °C for TiFe and TiNi, respectively. Taking into account the XRD results, one can assume that these effects are attributed to the crystallization of the amorphous phases formed during the MA process. The obtained results are in good agreement with earlier work [24]. The SEM technique was used to follow the changes in size and shape of the mechanically alloyed powder mixtures as a function of milling time. The microstructure that forms during MA consists of layers of the starting material. The lamellar structure is increasingly refined during further MA. The thickness of the material decreases with the increase in MA duration, leading to true alloy formation. The sample shows cleavage fracture morphology and inhomogeneous size distribution. The average crystallite size of the nanocrystalline TiFe-based powders, according to AFM studies, was of the order of 30 nm.

Table 1 reports the discharge capacities of the studied materials. The discharge capacity of electrodes prepared by application of MA and annealed TiFe alloy powder displayed very low capacity (0.7 mA h g^{-1}). Materials obtained when Ni was substituted for Fe in TiFe_{1-x}Ni_x led to a great improvement in activation behaviour of the electrodes. It was found that the increasing the nickel content in $TiFe_{1-r}Ni_r$ alloys led initially to an increase in discharge capacity, giving a maximum at x=3/4. In the annealed nanocrystalline TiFe $_{1/4}$ Ni $_{3/4}$ powder, a discharge capacity of up to 155 mA h g⁻¹ (at 40 mA g⁻¹ discharge current) was measured, which can be compared with the 161 mA h g⁻¹ reported earlier for mechanically alloyed TiFe_{0.4}Ni_{0.6} powder [18]. The electrodes mechanically alloyed and annealed from the elemental powders displayed the maximum capacities at the second or third cycle, but degraded slightly with cycling, This may be due to the easy formation of the oxide layer (TiO_2) during the cycling. It is worth noting that the discharge capacity of nanocrystalline TiNi_{0.6}Fe_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1} powder did not change much during cycling (Fig. 3). The alloying elements Mo, Cr and Co, substituted simultaneously for iron atoms in nanocrystalline TiNi3/4Fe1/4 master alloy



Fig. 3. Discharge capacities as a function of cycle number of electrode prepared with nanocrystalline TiFe (a), $\text{TiFe}_{1/4}\text{Ni}_{3/4}$ (b) and $\text{TiNi}_{0.6}\text{Fe}_{0.1}\text{Mo}_{0.1}\text{Cr}_{0.1}\text{Co}_{0.1}$ (c) (solution, 6 M KOH; temperature, 20 °C). The charge conditions were 40 mA g⁻¹. The cut-off potential versus Hg/HgO/6 M KOH was -0.7 V.



Fig. 4. Total and local DOS plots for the TiFe and TiNi systems.

		TiFe	TiFe _{3/4} Ni _{1/4}	$TiFe_{1/2}Ni_{1/2}$	$TiFe_{1/4}Ni_{3/4}$	TiNi
Total	DOS	0.354	1.325	2.249	2.468	2.806
(per f.u.)		(0.277)	(1.125)	(1.823)	(2.045)	(2.392)
	NOS	12.000	12.500	13.000	13.500	14.000
		(9.211)	(9.689)	(10.173)	(10.638)	(11.108)
Ti	DOS	0.193	0.554	1.092	1.360	1.673
		(0.158)	(0.485)	(0.940)	(1.214)	(1.524)
	NOS	3.800	3.762	3.721	3.684	3.783
		(2.473)	(2.457)	(2.446)	(2.429)	(2.466)
Fe	DOS	0.161	0.655	0.979	0.802	_
		(0.119)	(0.528)	(0.616)	(0.511)	_
	NOS	8.200	8.212	8.217	8.233	_
		(6.738)	(6.750)	(6.752)	(6.759)	
Ni	DOS	_	1.121	1.334	1.209	1.132
		_	(0.976)	(1.140)	(0.937)	(0.868)
	NOS	_	10.317	10.339	10.344	10.217
			(8.679)	(8.702)	(8.693)	(8.642)

Total and local densities of states at the Fermi level (DOS) [states/(eV atom)] and numbers of states (NOS) [electrons/atom] (d electron contributions in parenthesis)

prevented oxidation of these electrode materials. At the 2nd cycle a discharge capacity of 155 mA h g^{-1} was for the nanocrystalline obtained $TiNi_{0.6}Fe_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1}$ alloy. The behaviour of the

Table 2

discharge capacity in the $TiNi_{0.6}Fe_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1}$ mafrom terial was different that in the $TiFe_{0.6}Ni_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1}$ system (Table 1).

Application of titanium alloys as hydrogen storage



materials focused our attention also on the electronic structure of TiFe and its modification-mainly by Ni atoms but also by Mo, Cr and Co impurities. Earlier band structure calculations were performed by Liu and Ye [25] for TiFe and TiNi. Their stability was studied because of the shape memory effect observed in Ti-based materials belonging to so-called martensitic alloys. In spite of technical differences in the past [25] and present calculations the general outline of densities of states (DOS) is similar (see Fig. 4). In the case of TiFe the Fermi level $(E_{\rm F})$ is located in the deep valley of DOS and the value of DOS $(E = E_{\rm F})$ is low, 0.354 states/(eV f.u.). As was discussed in [25] starting from the TiFe alloy and going to the TiNi one the B2 structure becomes relatively less stable, the Fermi energy shifts towards higher peaks. The DOS ($E = E_{\rm E}$) reaches the value of 2.806 states/(eV f.u.). The width of the valence band is larger: 7.82 and 8.05 eV for TiFe and TiNi, respectively. The largest contribution to the DOS $(E_{\rm F})$ is provided by the d-type electrons. The values of DOS at $E = E_F$ for TiFe_{1-x}Ni_x (x=0, 1/4, 1/2, 3/4, 1) are collected in Table 2. The larger number of valence electrons provided by Ni atoms moves the Fermi level towards higher energies and DOS ($E = E_{\rm F}$) gradually increases with the increasing content of Ni atoms. The plots of DOS for TiFe_{1-x}Ni_x (x=1/4, 1/2, 3/4) are presented in Fig. 5. The bottom of valence band moves to lower energies and valence bands become wider. The center of gravity of the Ti d-electrons lying above $E_{\rm F}$ shifts towards lower energies close to the centers of gravity of d-electrons located on Fe and Ni atoms. Larger overlapping of bands leads to larger hybridization and charge transfer between atoms. The occupation number of electrons distributed between atoms are collected in Table 2. The strength of hybridization is visible in Fig. 5 on Ni projected DOS where sharp peak (mainly d electrons) for x=1/4 becomes broadened with increasing content of Ni atoms.

Figs. 6 and 7 present DOS plots for $TiFe_{1/2}M_{1/2}$ and $TiNi_{1/2}M'_{1/2}$, respectively (where $M_{1/2} \equiv$ $Ni_{1/8}Mo_{1/8}Cr_{1/8}Co_{1/8}$ and $M'_{1/2} \equiv Fe_{1/8}Mo_{1/8}Cr_{1/8}Co_{1/8}$). Decreasing the content of Fe atoms in the B2 type structure leads to higher values of DOS $(E_{\rm F})$ equal to 1.418 states/(eV f.u.) (see Table 3) for $TiFe_{1/2}M_{1/2}$. This value is higher than for TiFe but lower than for $TiFe_{1/2}Ni_{1/2}$. The width of valence band becomes narrower (7.86 eV) contrary to the $TiFe_{1-x}Ni_x$ series. The center of gravity of d electrons located on Ti atoms shifts towards higher energies. In the case of $TiNi_{1/2}M'_{1/2}$ alloy one can observe behaviour similar to that in the $TiFe_{1-x}Ni_x$ series: broadened (wider: 7.86 eV) valence band, center of gravity for Ti(3d) electrons shifted to lower energies and increased value of DOS ($E_{\rm E}$) equal to 1.892 states/(eV f.u.), but not as high as in $TiFe_{1/2}Ni_{1/2}$ (about 2.25, see Table 2). Local DOS of Ni atoms has a similar structure to Ni projected DOS for TiFe_{3/4}Ni_{1/4}: one dominating sharp peak located about 2.5 eV below the Fermi level.



Fig. 6. Total and local DOS plots for the $TiFe_{1/2}Ni_{1/8}Mo_{1/8}Co_{1/8}Cr_{1/8}$ system.

4. Conclusions

In conclusion, nanocrystalline TiFe_{1-x}Ni_x (x=0, 1/4, 3/4. 1), $TiFe_{0.6}Ni_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1}$ 1/2,and TiNi_{0.6}Fe_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1} alloys synthesized by MA and annealing were used as negative electrode materials for Ni-MH, batteries. XRD analysis showed that, after 25 h of milling, the starting mixture of the elements had decomposed into an amorphous phase. Following the annealing in high purity argon at 750 °C for 0.5 h, XRD confirmed the formation of the CsCl-type structures with a crystallite sizes of about 30 nm. The alloying elements of 3d transition metals, Ni, Mo, Cr and Co, were substituted for iron atoms, and the structural, electronic and electrochemical properties were studied. With increasing nickel content in $TiFe_{1-r}Ni_r$, the material showed an increase in discharge capacity which passed through a maximum for x = 3/4. In the nanocrystalline TiNi_{0.6}Fe_{0.1}Mo_{0.1}Cr_{0.1}Co_{0.1} powder, a discharge capacity of up to 155 mA h g^{-1} (at 40 mA g⁻¹ discharge current) was measured. For this composition the capacity degraded much more slowly with cycling in comparison to other studied compositions.

The electronic structure was studied by the tight-binding version of the linear muffin-tin method in the atomic sphere approximation (TB-LMTO ASA). In the $TiFe_{1-x}Ni_x$ alloys, an increasing content of Ni impurities



Fig. 7. Total and local DOS plots for the $TiNi_{1/2}Fe_{1/8}Mo_{1/8}Co_{1/8}Cr_{1/8}$ system.

broadened the valence band and increased the values of the densities of electronic states at the Fermi level about eight times.

Mechanical alloying is a suitable procedure for obtaining TiFe-based alloy electrodes for use in $Ni-MH_x$ batteries.

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References

- [1] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1.
- [2] J.S. Benjamin, Sci. Am. 40 (1976) 234.
- [3] A. Anani, A. Visintin, K. Petrov, S. Srinivasan, J.J. Reilly, J.R. Johnson, R.B. Schwarz, P.B. Desch, J. Power Sources 47 (1994) 261.
- [4] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, J. Alloys Comp. 253–254 (1997) 70.

Table 3

Total and local densities of states at the Fermi level (DOS) [states/(eV atom) and numbers of states (NOS) (electrons/atom)] (d electron contribution in parenthesis)

	$\mathrm{TiFe}_{1/2}\mathrm{M}_{1/2}$		$\mathrm{TiNi}_{1/2}\mathbf{M}_{1/2}'$	
	$\frac{M_{1/2}}{Mo_{1/8}} Ni_{1/8} Mo_{1/8} C$	r _{1/8} Co _{1/8} NOS	$M'_{1/2} \equiv Fe_{1/8}Mo_{1/8}Cn$ DOS	V _{1/8} Co _{1/8} NOS
Total (per f.u.)	1.418	11.875	1.892	12.625
	(1.211)	(9.120)	(1.538)	(9.815)
Ti	0.381	3.481	0.849	3.440
	(0.299)	(2.371)	(0.746)	(2.341)
Fe1(M) or Ni1(M')	0.933	8.700	1.107	10.786
	(0.825)	(6.915)	(0.925)	(8.817)
Fe2(M) or Ni2(M')	1.038	8.631	0.878	10.739
	(0.845)	(6.934)	(0.668)	(8.827)
Fe3(M) or Ni3(M')	0.871	8.702	1.182	10.799
	(0.754)	(6.911)	(1.018)	(8.823)
Fe4(M) or Ni4(M')	1.066	8.546	1.105	10.660
	(0.932)	(6.891)	(0.936)	(8.801)
Ni(M) or Fe(M')	0.693	10.602	1.296	8.535
	(0.530)	(8.781)	(0.921)	(6.894)
Мо	0.742	5.997	0.459	5.963
	(0.628)	(4.812)	(0.270)	(4.840)
Cr	2.252	6.391	0.985	6.385
	(2.176)	(4.901)	(0.676)	(4.934)
Co	0.702	9.581	1.332	9.584
	(0.608)	(7.853)	(0.915)	(7.855)

- [5] S. Orimo, K. Ikeda, H. Fujii, Y. Fujikawa, Y. Kitano, K. Yamamoto, Acta Mater. 45 (1997) 2271.
- [6] M. Jurczyk, W. Rajewski, G. Wojcik, W. Majchrzycki, J. Alloys Comp. 285 (1999) 250.
- [7] A. Szajek, M. Jurczyk, W. Rajewski, J. Alloys Comp. 302 (2000) 299.
- [8] W. Majchrzycki, M. Jurczyk, J. Power Sources 93 (2001) 77.
- [9] G. Liang, J. Huot, R. Schultz, J. Alloys Comp. 320 (2001) 133.
- [10] M. Jurczyk, E. Jankowska, M. Nowak, J. Jakubowicz, J. Alloys Comp. 336 (2002) 265.
- [11] H. Gleiter, Prog. Mater. Sci. 33 (1989) 223.
- [12] K.H.J. Buschow, P.C.P. Bouten, A.R. Miedema, Rep. Prog. Phys. 45 (1982) 937.
- [13] N. Comisso, G. Davolio, E. Soragni, G. Mengoli, J. Electroanal. Chem. 512 (2001) 92.
- [14] R.P. Elliott, Constitution of Binary Alloys, First Supplement, McGraw-Hill, New York, 1965.

- [15] B. Luan, N. Cui, H.K. Liu, H.J. Zhao, S.X. Dou, J. Power Sources 55 (1985) 197.
- [16] S.M. Lee, T.P. Perng, J. Alloys Comp. 291 (1999) 254.
- [17] H. Aoyagi, K. Aoki, T. Masumoto, J. Alloys Comp. 231 (1995) 804.
- [18] C.B. Jung, J.H. Kim, K.S. Lee, Nano-Struct. Mater. 8 (1997) 1093.
- [19] O.K. Andersen, Phys. Rev. B 12 (1975) 3060.
- [20] G. Krier, O. Jepsen, A. Burkhardt, O.K. Andersen, The TB-LMTO-ASA Program (source code, version 4.7), 1995.
- [21] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
- [22] B.I. Ming, Y.-R. Jang, J. Phys.: Condens. Matter 3 (1991) 5131.
- [23] P. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 223.
- [24] J. Eckert, L. Schultz, K. Urban, J. Non-Crystal. Solids 127 (1991) 90.
- [25] H.J. Liu, Y.Y. Ye, Solid State Commun. 106 (1998) 197.