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Hydrogen absorption in vanadium- and niobium-based topologically close-packed structures

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Abstract

Hydrogen absorption properties of Franck–Kasper phases formed in V–Ni and Nb–Ni systems have been investigated systematically. The A15 V–Ni phase absorbs up to 0.85 H/M under a pressure of 84 bar, the σ V–Ni phase absorbs 0.46 H/M under 75 bar and μ Nb–Ni absorbs 0.10 H/M under 50 bar. The pressure–composition curves were measured for those alloys at 25°C. Substitution of V by Nb and Ti in σ V–Ni phase does not lead to significant changes in hydrogenation properties of this phase.

Keywords: Franck–Kasper phases; Hydrides; A15 phase; σ phase; μ phase

1. Introduction

Several intermetallic compounds are studied for their ability to store large amounts of hydrogen by forming intermetallic hydrides. The absorption/desorption reaction is reversible in a large domain of temperature and pressure and therefore those materials find numerous applications in low pressure static hydrogen storage, hydrogen gettering or purification etc. The application which has the largest industrial development can be found in nickel-metal hydride (Ni-MH) batteries, which supply cellular phones and laptop computers in replacement of toxic and less-capacitive nickel–cadmium ones. The compounds best studied for those applications belong to limited structural types: $CaCu_5$ type (exemplified by $LaNi_5$), CsCl type (exemplified by TiFe), C14 or C15 Laves phases (exemplified by $ZrMn_2$) or vanadium-based bcc solid solutions. However, other classes of intermetallic compounds offer potential interest as regards to hydrogen storage. Topologically (or tetrahedrally) close-packed structures, also known as Franck–Kasper phases, have never been studied regarding their hydrogenation properties with the exception of the extensively studied Laves phases. A15 (cubic, Cr_3Si type), σ (tetragonal, CrFe type) or μ (rhombohedral, W_6Fe_7 type) Franck–Kasper phases (i) can be formed with elements presenting strong affinity for hydrogen like V or Nb; (ii) present solely tetrahedral interstices which are those generally occupied in intermetallic hydrides; (iii) exist in wide ranges of stoichiometry in binary and ternary systems, which should allow to modify the thermodynamic properties of the hydrides by varying the intermetallic compound compositions.

This work presents, to our knowledge, the first report of hydrogen absorption by binary σ and μ phases and by A15 V_3Ni phase. Different attempts to modify the hydrogen storage properties by introduction of a third element will be presented.

2. Experimental

The intermetallic compounds were synthesized by induction melting or arc melting (ternary V–Ni–Ti and Nb-containing compounds). The as-cast ingots were subsequently homogenized and equilibrated by a convenient annealing treatment (wrapped in tantalum foil in sealed silica tubes under secondary vacuum or argon atmosphere). The degree of homogeneity, crystal structure, lattice parameters and ratio of each phase present in the samples were characterized by optical metallography, electron probe micro-analysis (EPMA) and Rietveld analysis of powder X-ray diffraction patterns (software Fullprof [1]). The results of the characterization are shown in Table 1. The hydrogenation measurements (capacity and pressure–composition (P–C) characteristics) were conducted in a conventional Sievert's apparatus [2] at room temperature. The capacities are expressed in hydrogen atoms per metal

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atom of the nominal composition of the alloy (H/M). Before measurements of *P–C* isotherms, the alloys are pumped under primary vacuum (10^{-2} mbar). Measurements at high pressure (>25 bar) were corrected taking into account the non-ideality of the gas according to Hemmes et al. [3].

3. Results

3.1. Binary compounds

The V-richest σ phase could be obtained at the nominal composition $V_{75}Ni_{25}$ together with small amount (7 wt.%) of the A15 phase. The Rietveld refinement, including atomic positions, confirms the model proposed by Kasper and Waterstrat [4] (CrFe type, $P4_2/mnm$, *tP30*). The A15 so-called V_3Ni phase could be obtained as a major phase in an alloy of nominal composition $V_{78}Ni_{22}$ annealed at 850°C. The composition of the phase measured by EPMA is $V_{77.5(6)}Ni_{22.5(6)}$ and the presence of V(Ni) bcc solid solution and σ secondary phases are explained by incomplete peritectoid formation reaction quite expected if one considers the high difference between the liquidus temperature (1600°C) and the temperature of formation of the A15 phase by peritectoid reaction (900°C) [5]. Again, the crystal structure as proposed by Waterstrat and Dickens [6] is confirmed (Cr_3Si type, $Pm\bar{3}n$, *cP8*). All the results obtained concerning phase existence and compositions are in perfect agreement with the binary V–Ni phase diagram as reported by Smith et al. [5].

The σ phase could be hydrogenized at room temperature under a pressure of 75 bar, pressure at which the quantity of absorbed hydrogen reached 0.46 H/M. After desorption at 200°C under vacuum, the *P–C* curve was measured at 25°C and is drawn in Fig. 1.

Hydrogenation of the A15 V–Ni phase presents particular features in comparison with intermetallic hydrides as can be observed in Fig. 2. Hydrogenation occurs, at rather high pressure in the first cycle (most of the capacity is absorbed between 10 and 60 bar) but the desorption is hardly observed even at pressure down to 3×10^{-2} bar. The capacity absorbed under 84 bar is high: 0.85 H/M. Desorption is obtained by pumping the sample under primary vacuum at 80°C. Subsequent absorption allows to recover the capacity absorbed at the first cycle but at very low pressure (most of the capacity absorbed below 10^{-2} bar). Such difference between absorption and desorption pressures at the first cycle and between absorption pressures of the first and subsequent cycles are quite unusual for hydride systems. Structural investigations are currently in progress in order to analyze this phenomenon.

The μ phase in the Nb–Ni system was synthesized at the nominal composition $Nb_{51.5}Ni_{48.5}$. Microprobe analysis confirms the composition and homogeneity of the alloy. Pycnometric measurement gives a density of 8.84 g/cm^3, which, considering the lattice parameters, leads to a composition of 52 at.% Nb, also in good agreement with the nominal composition. The structure is confirmed to be of the W_6Fe_7 type [7] ($R\bar{3}m$, *hR13*). Rietveld analysis including refinement of the atomic positions and of the mutual occupancies of each site by Nb and Ni has been performed and will be the subject of another communication.

Hydrogenation occurs also for this phase but reaches only 0.10 H/M under 50 bar at the first cycle. After

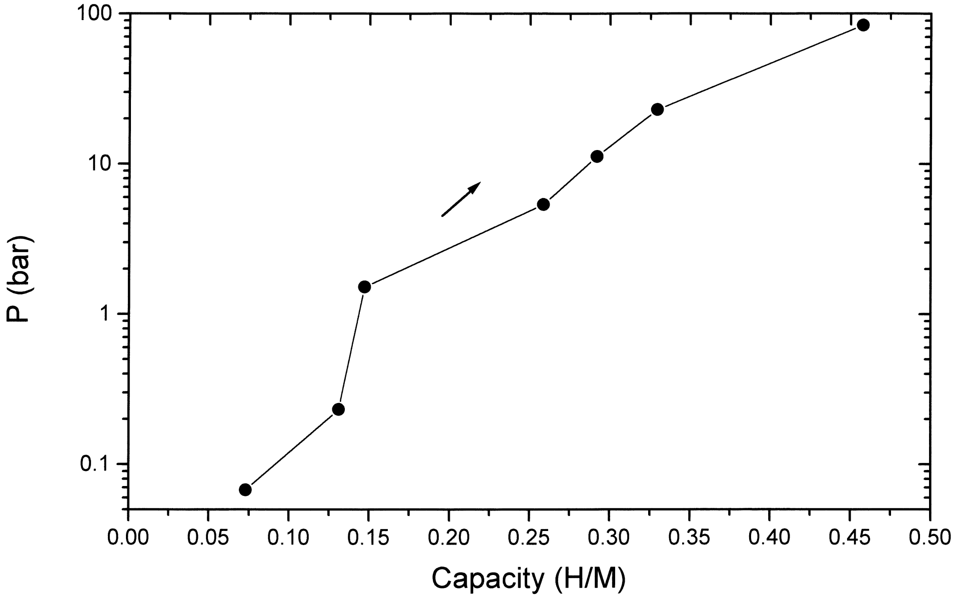

Fig. 1. Pressure–composition isotherm (absorption) for σ phase (nominal $V_{75}Ni_{25}$) at 25°C at the third hydrogenation cycle after desorption under primary vacuum at 200°C.

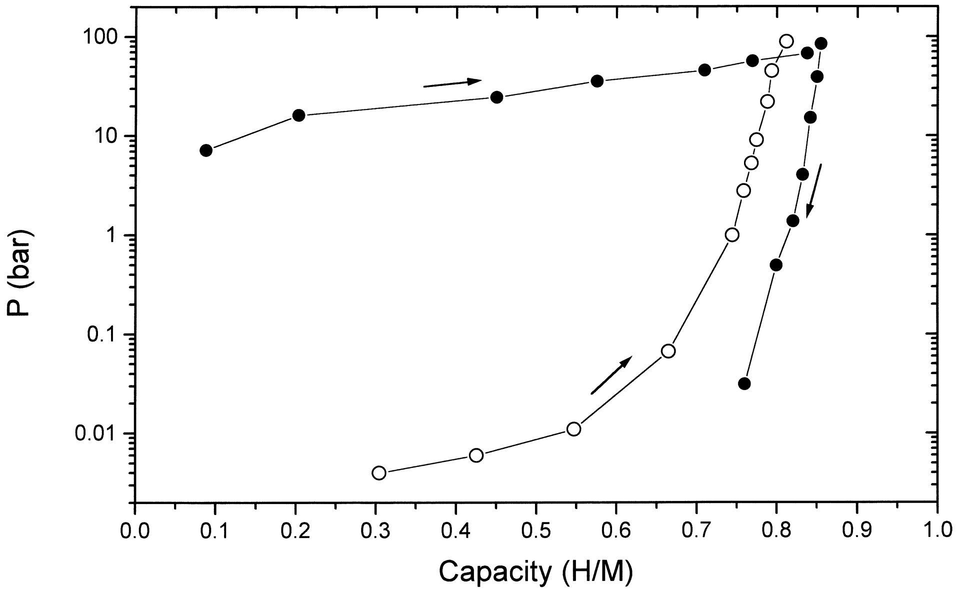

Fig. 2. Pressure–composition isotherms for A15 phase (nominal $V_{80}Ni_{20}$) at 25°C at the first hydrogenation cycle (absorption and desorption, solid symbols) and at the third hydrogenation cycle (absorption, open symbols) after desorption under primary vacuum at 80°C.

desorption under vacuum at 25°C, the *P–C* curve was measured and is shown in Fig. 3.

3.2. Ternary compounds

Considering the interesting properties of, at least, the σ V–Ni and A15 V–Ni phases, respectively, various substitutions were considered in order to increase the hydrogen capacity of the binary compounds and modify the stability of the hydrides. The method investigated was to substitute V by more electropositive elements, that also present stronger affinity for hydrogen: La, Zr, Nb and Ti. The results of the alloy characterization are shown in Table 1.

The substitution by La was first considered. Two alloys were synthesized in the ternary system: $V_{70}La_5Ni_{25}$ and $V_{80}La_5Ni_{15}$ equilibrated at 1000°C and 850°C, respectively, to obtain σ and A15 phases. La does not substitute in any phase, which appear to have no ternary extension. For $V_{70}La_5Ni_{25}$, EPMA measurements indicate that La content in the σ phase is inferior to 0.1 at.%. La precipitates as LaNi phase (BCr structure type) with a V content also lower than 0.1 at.%. In $V_{80}La_5Ni_{15}$, three phases are

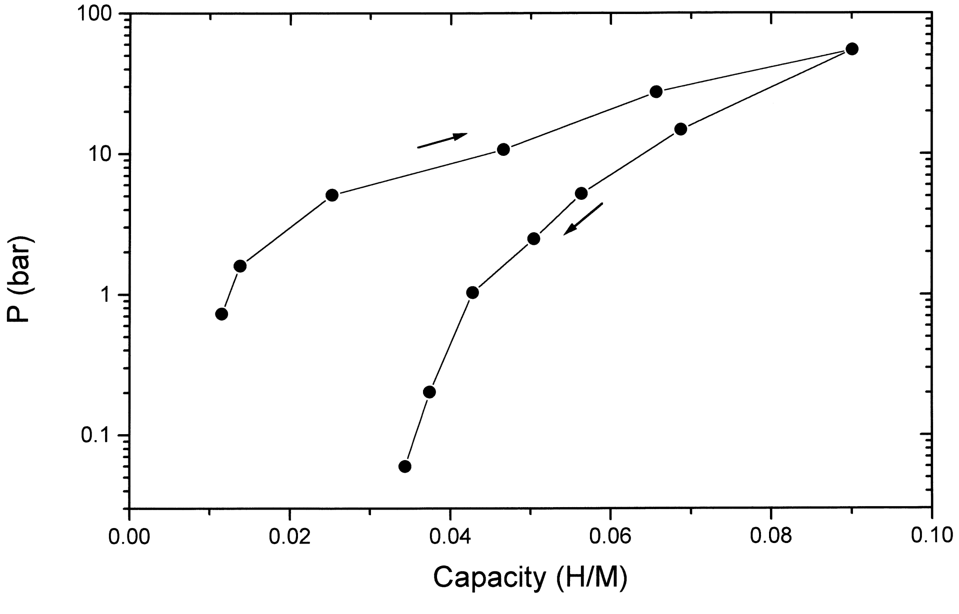

Fig. 3. Pressure–composition isotherm (absorption and desorption) for μ $Nb_{51.5}Ni_{48.5}$ phase at 25°C at the third hydrogenation cycle after desorption under primary vacuum at 25°C.

Table 1
Metallurgical characterization of the alloys. Phase compositions are from EPMA measurements, lattice parameters and phase ratios are refined by the Rietveld method. General standard deviation on the lattice parameters and cell volumes is 1 unit of the last digit

Nominal composition (at.%)	Annealing treatment	Phase type	Phase composition (at.%)	*a* (Å)	*b* (Å)	*c* (Å)	Cell volume (Å^3)	Phase ratio (wt.%)
$V_{75}Ni_{25}$	32 days 850°C	σ	$V_{72(1)}Ni_{28(1)}$	9.083		4.693	387.2	93%
		A15	[a]	4.709			104.4	7%
$V_{78}Ni_{22}$	35 days 850°C	A15	$V_{77.5(6)}Ni_{22.5(6)}$	4.708			104.3	82%
		σ	$V_{73.2(3)}Ni_{26.8(3)}$	9.095		4.698	388.6	16%
		bcc	[a]	3.007			27.2	2%
$Nb_{51.5}Ni_{48.5}$	31 days 1000°C	μ	$Nb_{51.8(9)}Ni_{48.2(9)}$	4.915		26.761	559.9	100%
$V_{70}La_5Ni_{25}$	19 days 1000°C	σ	$V_{72.0(4)}La_{0.07(1)}Ni_{27.9(4)}$	9.080		4.692	386.8	97%
		BCr	$V_{0.04(3)}La_{50.3(1)}Ni_{49.6(2)}$	3.92	10.81	4.39	185	3%
$V_{80}La_5Ni_{15}$	31 days 850°C	A15	$V_{78.6(7)}La_{0.2(4)}Ni_{21.2(3)}$	4.711			104.5	Not given
		bcc	$V_{92.0(4)}La_{0.1(2)}Ni_{7.9(3)}$	3.007			27.2	
		BCr	$V_{2.1(3)}La_{49.4(4)}Ni_{48.5(3)}$	3.91	10.79	4.40	186	
$V_{70}Zr_5Ni_{25}$	12 days 1000°C	σ	$V_{74(1)}Zr_{0.6(6)}Ni_{25(1)}$	9.105		4.700	389.6	68%
		C15	$V_{24(1)}Zr_{27.4(6)}Ni_{48.0(5)}$	7.030			347.4	22%
		bcc	[a]	2.998			26.9	10%
$V_{70}Zr_5Ni_{25}$	12 days 1000°C + 31 days 850°C	A15	$V_{80(2)}Zr_{0.10(3)}Ni_{20(2)}$	4.709			104.4	5%
		σ	$V_{74.8(4)}Zr_{0.17(2)}Ni_{25.0(4)}$	9.109		4.703	390.2	61%
		C15	$V_{21.5(6)}Zr_{29.7(3)}Ni_{48.7(4)}$	7.041			349.1	20%
		bcc	$V_{91.6(3)}Zr_{0.03(2)}Ni_{8.4(3)}$	3.005			27.1	14%
$V_{75}Nb_5Ni_{20}$	30 days 850°C	σ	$V_{67(2)}Nb_{6(2)}Ni_{27(2)}$	9.162		4.736	397.6	83%
		bcc	[a]	3.017			27.5	14%
		C14	[a]	[a]			[a]	2%
$V_{75}Ti_5Ni_{20}$	42 days 850°C	σ	$V_{68.5(5)}Ti_{6.1(1)}Ni_{25.4(4)}$	9.138		4.717	393.8	81%
		bcc	$V_{90(1)}Ti_{1.7(3)}Ni_{8(1)}$	3.009			27.2	19%
$V_{70}Ti_5Ni_{25}$	33 days 1000°C	σ	$V_{68.1(8)}Ti_{5.0(7)}Ni_{26.8(3)}$	9.123		4.711	392.0	100%

[a] Present in too small a quantity to be accurately determined.

observed: A15 phase with La content inferior to 0.5 at.%, bcc V-based solid solution with La content again inferior to 0.5 at.% and LaNi with substitution of vanadium in the amount of ~2 at.%.

In the ternary V–Zr–Ni system, one composition was investigated but at two different annealing temperatures. $V_{70}Zr_5Ni_{25}$ equilibrated at 1000°C (i.e. above the decomposition temperature of A15 phase) shows three phases: C15 Laves phase derived from ZrV_2 by high Ni substitution for V, bcc V-based solid solution and σ phase in agreement with the partial phase diagram reported in Ref. [8]. In none of those two later phases is Zr content significant. The alloy annealed at 850°C shows only partial peritectoid transformation into A15 phase, but clearly the V substitution in this latter phase appears again to be negligible.

Ternary $V_{75}Nb_5Ni_{20}$ annealed at 850°C leads to a three-phase equilibrium involving σ, bcc and C14 phases in agreement with the isothermal section at 1050°C as determined by Eremenko et al. [9]. This shows that the extension of A15 phase in the ternary equilibrium diagram is very limited. On the contrary, Nb substitution in σ phase occurs and its effect on the hydrogenation properties can be studied. The absorption capacity of this alloy at the first cycle is 0.52 H/M under 23 bar. The *P–C* curve measured after desorption at 80°C is drawn in Fig. 4.

Finally, substitution by titanium was also investigated. As for the V–Nb–Ni system, the A15 phase is clearly absent in an alloy of composition $V_{75}Ti_5Ni_{20}$ annealed at 850°C. Ternary extension of the A15 phase is therefore very limited. On the contrary, ternary extension of the σ phase appears to be non-negligible as described by Eremenko et al. [10]: $V_{70}Ti_5Ni_{25}$ is synthesized as a single σ phase. The modification of the hydrogenation properties of this phase by titanium substitution could therefore be investigated. The measured hydrogenation *P–C* curve at the first cycle is presented in Fig. 4. The capacity reached under 90 bar is 0.59 H/M.

4. Discussion

Solubility in σ V–Ni phase occurs only with elements electronically close and forming extended bcc solid solutions with vanadium, i.e. Nb and Ti. As no change of the nickel stoichiometry is observed, it can be concluded that those elements come in replacement of vanadium. The substitution leads to significant increase of the cell volumes (+1.2% for Ti, +2.7% for Nb substitution) in agreement with increased atomic radii as compared to vanadium. However, even for those elements, no signifi-

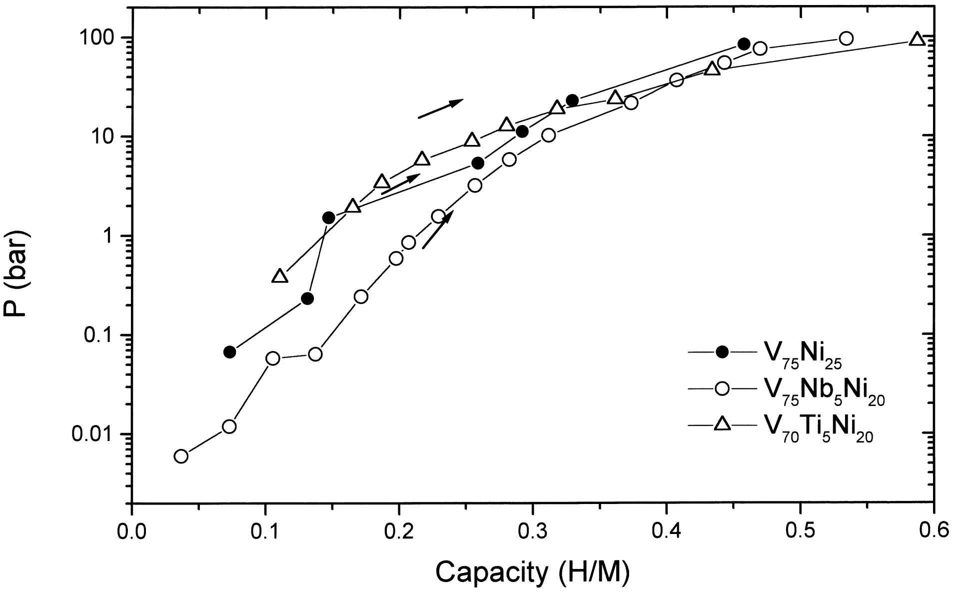

Fig. 4. Pressure–composition isotherms at 25°C for binary σ $V_{75}Ni_{25}$ phase (absorption, third cycle after desorption at 200°C), σ $V_{75}Nb_5Ni_{20}$ (absorption, third cycle after desorption at 80°C) and σ $V_{70}Ti_5Ni_{25}$ (absorption, first cycle).

cant replacement of vanadium in A15 V–Ni phase occurs. This seems to be due to peculiar instability of this phase.

Hydrogenation properties are reported here for phases (A15 V–Ni) and structural types (σ and μ) which, to our knowledge, were never reported to absorb hydrogen. In all cases the hydrogenation occurs without any difficulty at room temperature. The absorption in μ Nb–Ni (52 at.% Nb) is poor as compared to well known absorbing intermetallic compounds like $ZrCr_2$ or $LaNi_5$ which absorb ~1 H/M. Substitutions on Nb or Ni sublattices in order to increase the capacity has not yet been experimented with but will hardly allow us to obtain such values. Absorption in σ V–Ni (72 at.% V) seems to be more interesting, though the hydrogen capacity could not be increased substantially by Nb or Ti substitutions except, perhaps only under high pressures (100 bar). In $LaNi_{5-x}M_x$ (M= Mn, Al . . .) systems, cell volume increase induced by substitution is known to cause decrease of the absorption pressure in the order of 0.5 pressure decade per percent increase of cell volume. Contrary to what is expected, the influence of Nb and Ti substitution, though leading to significant changes in the lattice parameters, seems nearly ineffective to change neither the shapes of the *P–C* curves, which remains typical of a solid solution behaviour of hydrogen in the intermetallic compound, nor the stability of the hydrides.

Finally, the most interesting compound as regard to hydrogen absorption is A15 V–Ni (78 at.% V) phase. Its hydrogen capacity reaches 0.85 H/M which represents 1.63 wt.% compared to 1.4 wt.% for $LaNi_5H_6$ and 1.8 wt.% for $ZrCr_2H_{3.5}$. However, this capacity is absorbed only under high pressure and desorbed under low pressure with a strong memory effect which needs to be further explained. In addition any attempt to substitute vanadium by other elements failed up to now.

5. Conclusion

Hydrogen absorption properties of topologically close-packed compounds in V–Ni and Nb–Ni systems were systematically investigated. All the phases are shown to absorb hydrogen without activation at room temperature. A15 V–Ni (78 at.% V) phase absorbs up to 0.85 H/M, σ V–Ni (72 at.% V) 0.46 H/M, μ Nb–Ni (52 at.% Nb) 0.10 H/M. The hydrogen capacity depends strongly on the concentration of the most electropositive element (V or Nb). The compounds investigated here show that among the topologically close-packed structures, not only the Laves phases absorb hydrogen. Absorption seems to be favoured by the exclusive presence of tetrahedral interstices in those phases combined with a high quantity of elements presenting strong affinity for hydrogen.

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