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Effect of substitution on hysteresis in some high-pressure AB₂ and AB₅ metal hydrides

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Abstract

Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8-x}V_x-H₂ ($x=0, 0.05$ or 0.1), Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8-y}Co_y-H₂ ($y=0, 0.1$ or 0.2) and Ce_{0.8}La_{0.2}Ni_{5-z}Co_z-H₂ ($z=0, 0.5, 1.0$ or 1.5) systems were studied experimentally in order to (a) find suitable alloys for high-pressure applications, and (b) gain insight into the reasons for the hysteresis and its reduction due to certain partial substitutions. A special volumetric pressure–composition isotherm (PCI) measurement technique at high pressures (up to 400 bar in this case), pressure differential scanning calorimetry (PDSC), and X-ray diffractometry (XRD) of both starting alloys and SO₂- (or air-) poisoned high-pressure hydrides were applied. Practically hysteresis-free high-pressure alloy–hydrogen systems with good PCI plateau properties were found, e.g. Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.75}V_{0.05}-H₂. Furthermore, it was shown that an intermediate hydride phase in the Ce_{0.8}La_{0.2}Ni_{3.5}Co_{1.5}-H₂ system exists, which explains the remarkably reduced hysteresis compared to the less or non-substituted systems. Finally, an experimental correlation between hysteresis and discrete unit cell volume expansion between coexisting phases was displayed. It suggests that the volume expansion is a major reason for the hysteresis, but more experimental data needs to be collected. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hysteresis; Intermediate hydride phase; High-pressure hydrides; Discrete volume expansion

1. Introduction

Metal hydrides based on TiMn₂ and CeNi₅ intermetallic compounds are promising for various high-pressure applications because of their high dissociation pressure, high capacity, and flat pressure–composition isotherm (PCI) plateaus. Unfortunately, these hydrides are characterized by a large hysteresis effect [1,2] which renders them useless if the temperature interval of operation is narrow. However, even if the working temperatures are not the limiting factor, the hysteresis is of great importance, especially in cyclic devices, because it results in large energy and efficiency losses and, thus, makes thermally driven hydride devices less attractive alternatives to existing electricity-powered solutions.

In order to improve the hydriding properties of high-pressure alloys for applications with strict thermal boundary conditions, e.g. self-sufficient solar hydrogen energy systems [3], we earlier studied the effect of partial substitutions [4–6]. The thermodynamical behaviour of Ce_{1-a}La_aNi_{5-b}M_b-H₂ (M=Al, Sn or Co) [5] and Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.7}M_{0.1}-H₂ (M=Mn, Fe, Co or V) [6]

systems was investigated by PCI measurements at 20 and 60°C, and the crystal structure of the alloys by X-ray diffraction (XRD). A rich diversity of both wanted and unwanted effects was observed. In the present study, we concentrated on the three most promising substitution series: Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8-x}V_x ($x=0, 0.05$ or 0.1), Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8-y}Co_y ($y=0, 0.1$ or 0.2), and Ce_{0.8}La_{0.2}Ni_{5-z}Co_z ($z=0, 0.5, 1.0$ or 1.5). Especially, we investigated reasons for the various effects of partial substitutions on PCI properties and, in particular, on the hysteresis. The role of lattice expansion due to hydrogenation in the hysteresis behaviour was studied by determining the structure parameters of selected alloys and their high-pressure hydrides. We considered this an interesting approach because the discrete unit cell volume expansion between the α - (solid solution) and the β - (hydride) phase may be a major reason not only for poor (electrochemical) cycling stability of alloys [7], but also, more fundamentally, for the very phenomenon of hysteresis.

Pressure Differential Scanning Calorimetry (PDSC) was used to study thermal sorption of Co-substituted AB₅-H₂ systems which showed single or double PCI plateau, depending on the Co content. In the previous study [5], it

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was observed that increasing the Co content resulted in gradually decreasing hysteresis, but also that an assumed intermediate hydride phase (double PCI plateau) appeared only at the highest studied Co content ($z=1.5$). Because the existence of an intermediate hydride phase can be used to explain the reduction of the hysteresis, which was significant already at $z=1.0$, we wanted to find out whether such a phase does exist already at $z=1.0$, in spite of the single PCI plateau. We considered it possible that the PCI curves do not support the existence of an intermediate hydride phase due to very close plateau pressures. But because PDSC is a very sensitive means, it should give a double thermal sorption peak as an indication of a two-step sorption process if an intermediate hydride phase existed.

2. Experimental details

The volumetric high-pressure (up to 2000 bar) apparatus for PCI measurements, as well as the PDSC equipment were described earlier [8,9]. The latter was modified by wrapping the pressure cell with insulating material. In addition, an air gap was left between the cell and the insulator to facilitate internal convective cooling induced by an ice-filled steel cylinder on the top of the pressure cell. This construction enabled us to cool the PDSC cell sufficiently uniformly to avoid leakages and to reach a steady-state temperature below room temperature (around 10–15°C), which was necessary to fully hydrogenate the high-pressure hydrides.

Unfortunately, XRD spectra of high-pressure hydrides cannot be obtained in-situ with existing equipment. To circumvent this problem, the fully hydrogenated samples were quenched with liquid nitrogen, and then passivated with SO_2 (AB_5 samples) or air (AB_2 samples). After the treatment, during the slow leaking of hydrogen through the poisoned hydride surface, the XRD spectra were taken in

air at various hydrogen concentrations. The remaining hydrogen content was measured by simultaneous high-temperature vacuum extraction (HTVE) using samples that had gone through identical treatment, because an XRD sample is too small to be used for a direct determination.

Two new AB_2 samples were prepared as before [6] from pure (99.98+%, except for V: 99.7%) elements by melting in an arc furnace under an argon atmosphere of 1 bar. After remelting three times, the samples were annealed at 1000°C for 10 days in a vacuum of 10^{-2} mbar to enhance homogeneity.

3. Results

The PCIs of $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.8-x}\text{V}_x$, $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.75}\text{V}_{0.05}$ and $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.6}\text{Co}_{0.2}$ - H_2 systems at 20 and 60°C show that substituting Mn partially either with V or Co reduces hysteresis compared to the non-substituted base system (Figs. 1–3). This is particularly evident at 20°C, while at 60°C the hysteresis has practically disappeared in all cases. In order to make the comparison with similar systems [6] easier, PCIs of both substitution series ($\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.8-x}\text{V}_x$, $x=0, 0.05$ or 0.1 , and $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.8-y}\text{Co}_y$, $y=0, 0.1$ or 0.2) at 20°C were plotted in Figs. 4 and 5, respectively. Fig. 4 shows that substituting Mn partially with a small amount of V ($x=0.05$) is most advantageous. Fig. 5 does not provide such a clear optimum for the Co substitution.

Fig. 6 shows the PCIs of the $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{5-z}\text{Co}_z$ - H_2 system ($z=0, 0.5, 1.0$ or 1.5) [5]. Hysteresis reduction is clear already at $z=0.5$ and 1.0 , but the double plateau (the assumed intermediate hydride phase) appears only at $z=1.5$. Evidence obtained from PDSC runs (Fig. 7) shows that the thermal desorption curves of the Co-substituted system at $z=1.0$ and $z=1.5$ correspond very well with the

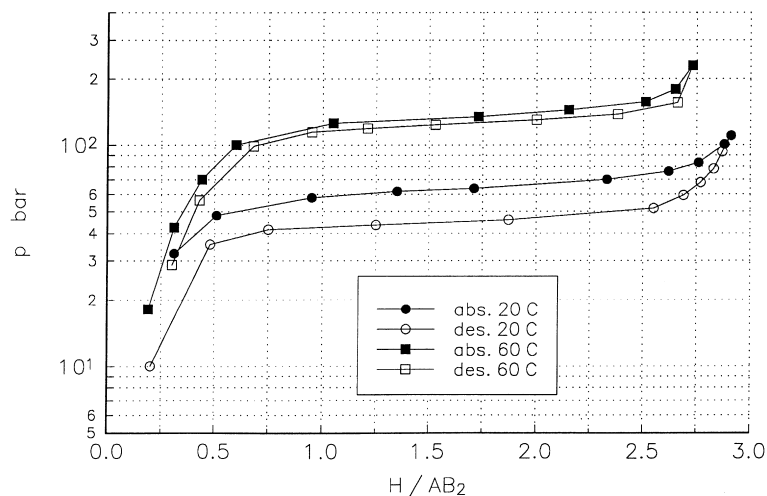


Fig. 1. PCIs of the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.8}$ - H_2 system at 20 and 60°C.

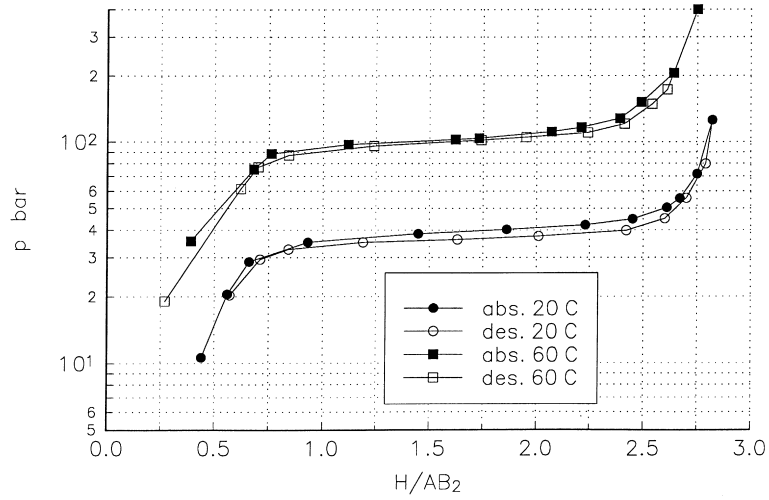


Fig. 2. PCIs of the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.75}\text{V}_{0.05}\text{-H}_2$ system at 20 and 60°C.

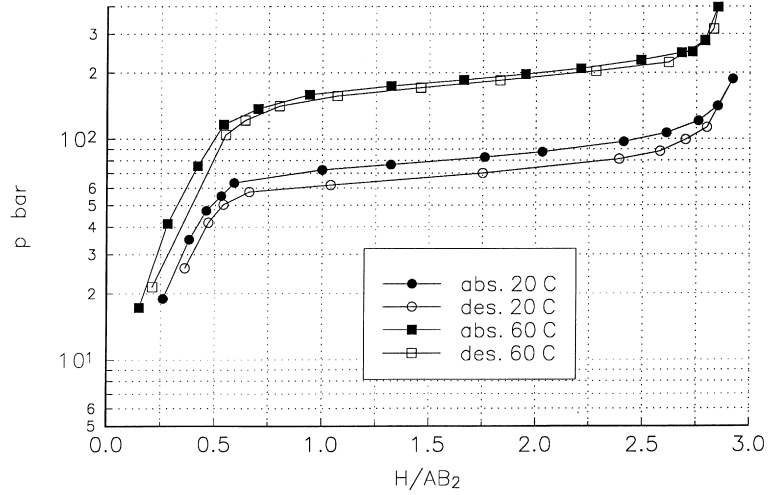


Fig. 3. PCIs of the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{-H}_2$ system at 20 and 60°C.

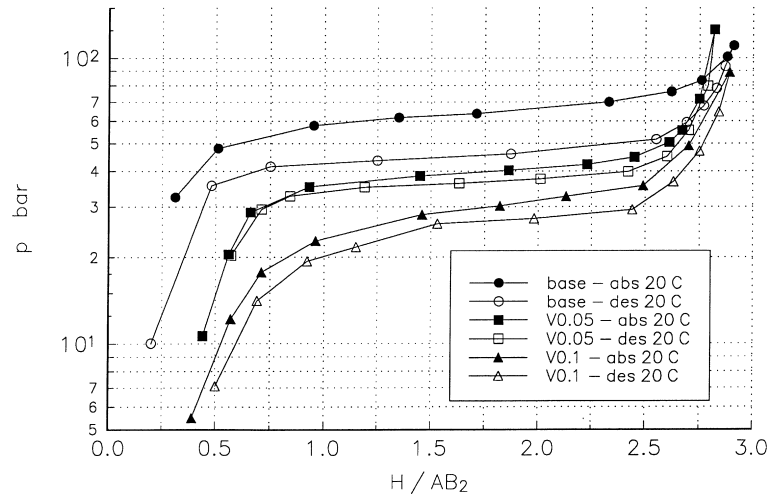


Fig. 4. PCIs of the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.8-x}\text{V}_x\text{-H}_2$ system at 20°C ($x=0, 0.05$ or 0.1).

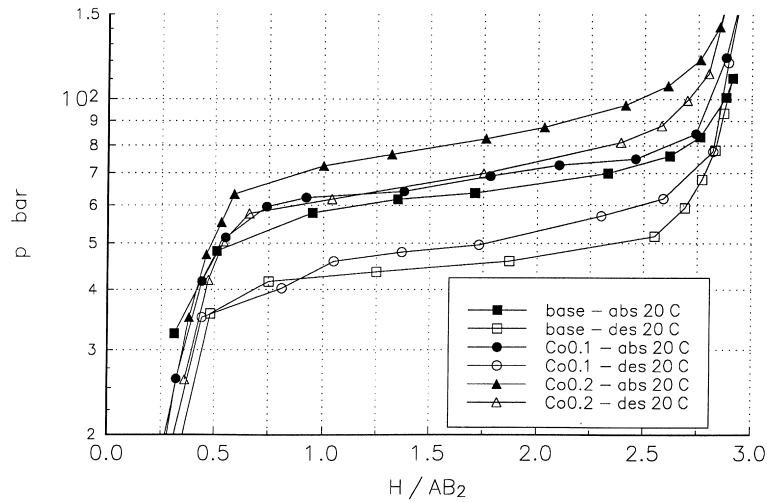


Fig. 5. PCIs of the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.8-y}\text{Co}_y\text{-H}_2$ system at 20°C ($y=0, 0.1$ or 0.2).

PCIs: the thermal counterpart of a single, sloping PCI plateau ($z=1.0$, desorption) is a single, asymmetric thermal desorption peak. Similarly, in the case of a double PCI plateau ($z=1.5$), the PDSC curve shows a double peak. Thus, the PDSC curves suggest the same as the PCIs: the intermediate hydride phase exists at $z=1.5$, but not at $z=1.0$. Additionally, careful comparison of the PCI and PDSC curves reveals that the kinetics of the desorption reaction is somewhat slower for $z=1.5$ (the tails of the PDSC peaks).

The XRD analysis of the partially decomposed high-pressure hydrides showed that, indeed, an intermediate hydride phase exists in the $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{3.5}\text{Co}_{1.5}\text{-H}_2$ system, but not in any other of the studied systems (Table 1). The structure parameters and the hysteresis values were calculated approximately at the middle of the PCI plateaus ($\text{H}/\text{AB}_2=1.5$ and $\text{H}/\text{AB}_5=3.0$, except for the $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{3.5}\text{Co}_{1.5}\text{-H}_2$ system: $\text{H}/\text{AB}_5=1.3$ and 4.5).

The discrete unit cell volume expansion (dv_{discr}) between coexisting phases during hydrogenation was calculated as a relative difference: $(v_{\beta}-v_{\alpha})/v_{\alpha}$ or $(v_{\beta 2}-v_{\beta 1})/v_{\beta 1}$.

4. Discussion

Fig. 8 indicates that the discrete unit cell volume expansion during hydrogenation is an important factor when trying to understand the complicated phenomenon of hysteresis. Even though our experimental data is limited, the general trend is clear: the larger the difference in the unit cell volume between the coexisting phases, the larger the hysteresis. This is understandable because the deformation strains and stresses in the host lattice are undoubtedly increased with increasing difference in the lattice parameters of the two coexisting phases. Applying this reasoning further to one-phase solid solution regions (α or β), the

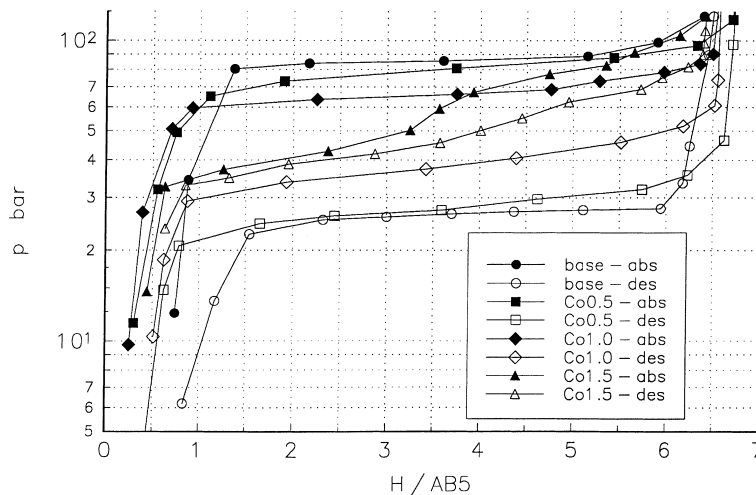


Fig. 6. PCIs of the $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{3-z}\text{Co}_z\text{-H}_2$ system at 20°C ($z=0, 0.5, 1.0$ or 1.5).

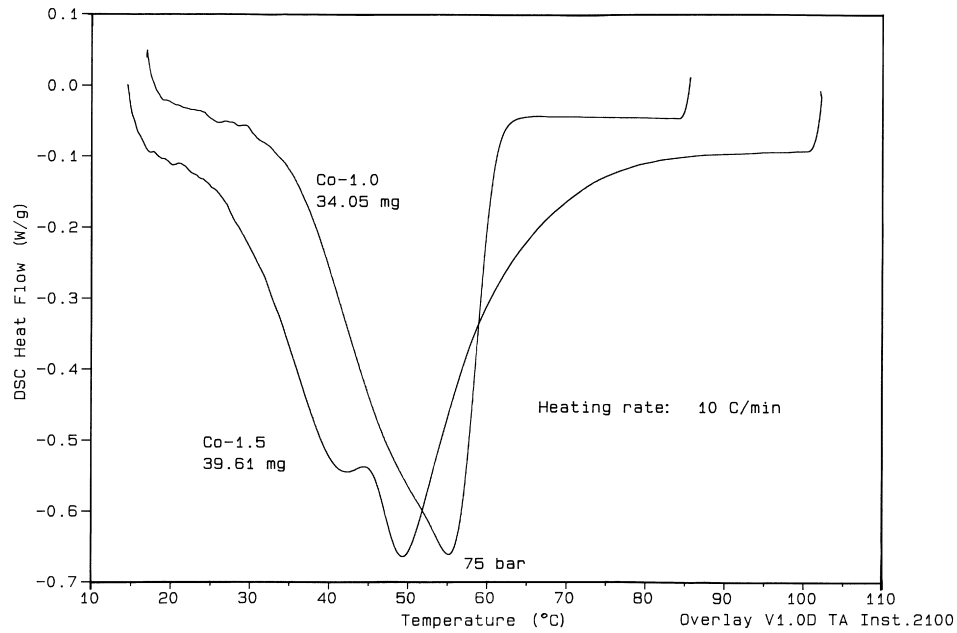


Fig. 7. Typical thermal desorption curves in the $\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{5-z}\text{Co}_z\text{-H}_2$ system ($z=1.0$ or 1.5) at 75 bar (PDSC curves).

Table 1
XRD analysis results and hysteresis values calculated from PCI data

Alloy composition	Phase	Structure	Parameters	v (\AA^3)	dv_{discr} (%)	Hysteresis ^a $\ln(p_{\text{abs}}/p_{\text{des}})$
		a (\AA)	c (\AA)			
$\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.8}$	Alloy α and β	4.875	7.995	164.55	18.1	0.34
		4.900	8.035	167.1		
		5.183	8.480	197.3		
$\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.75}\text{V}_{0.05}$	Alloy α and β	4.876	7.996	164.66	17.2	0.07
		4.903	8.049	167.58		
		5.167	8.495	196.43		
$\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.7}\text{V}_{0.1}$	Alloy	4.882	7.992	164.94		0.10
$\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.7}\text{Co}_{0.1}$	Alloy	4.867	7.973	163.59		0.30
$\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{1.2}\text{Mn}_{0.6}\text{Co}_{0.2}$	Alloy α and β	4.859	7.965	162.9	21.4	0.17
		4.888	7.995	165.4		
		5.215	8.523	200.8		
$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_5$	Alloy α and β	4.915	4.000	83.68	28.1	1.19
		4.913	4.011	83.85		
		5.399	4.253	107.4		
$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.5}\text{Co}_{0.5}$	Alloy α and β	4.913	4.003	83.68	26.5	1.07
		4.904	4.002	83.34		
		5.366	4.228	105.43		
$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{4.0}\text{Co}_{1.0}$	Alloy α and β	4.917	4.002	83.79	24.9	0.58
		4.953	4.045	85.93		
		5.396	4.254	107.3		
$\text{Ce}_{0.8}\text{La}_{0.2}\text{Ni}_{3.5}\text{Co}_{1.5}$	Alloy ^b	4.920	3.999	83.8		
	Alloy ^c	4.903	3.992	83.1		
	α and β_1	4.919	4.000	83.8	9.9	0.07
		5.120	4.059	92.1		
	β_1 and β_2	5.131	4.066	92.7	13.2	0.29
		5.368	4.205	104.9		

^a At 20°C.

^b Starting intermetallic compound.

^c Fully dehydrogenated sample.

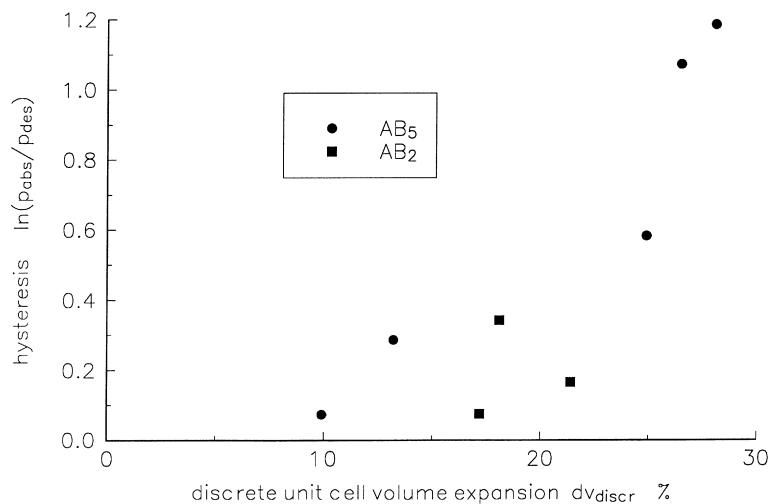


Fig. 8. Experimental correlation between the hysteresis and the discrete unit cell volume expansion.

negligible hysteresis can also be understood since the discrete volume expansion does not occur. Instead, the lattice enlarges continuously due to continuous increase of hydrogen concentration.

The correlation between the discrete volume expansion and the hysteresis does not seem to be linear — very low hysteresis values can be achieved even with a discrete volume expansion of about 20%. This might be explained by differences in the elastic modulus: if the host material is soft, it may exhibit both low hysteresis and relatively large volume expansion. Unfortunately, the elastic moduli of fine-grained alloy and hydride powders are extremely difficult to study experimentally.

In the studied AB_2-H_2 systems, the discrete volume expansion is insufficient to explain the differences in the observed hysteresis behaviour (Table 1 and Fig. 8). But because the applied partial substitutions, V or Co for Mn, nevertheless reduce hysteresis, softening of the lattice due to decreased elastic modulus of the substituted alloy may be partially responsible, at least in the case of V (elastic moduli: Mn-20*, Co-20* and V-13* 10^{10} N/m²). Cobalt, on the other hand, reduced hysteresis significantly only at $y=0.2$ (Fig. 5). At the same time, unfortunately, the plateau slope increased, which may be due to slight inhomogeneities of the starting alloy. This makes it difficult to draw conclusions on the origin of the hysteresis reduction.

The existence of an intermediate hydride phase in the $Ce_{0.8}La_{0.2}Ni_{3.5}Co_{1.5}-H_2$ system explains the remarkable hysteresis reduction: when a single phase transformation, with a large difference in the hydrogen concentration (and unit cell volume) of the coexisting phases, is divided into two separate steps, the discrete volume expansion per step decreases (Table 1). This explanation leaves, however, an open question: why is the hysteresis significantly reduced already at minor Co-substitutions, especially at $z=1.0$,

when there is no XRD evidence of an intermediate hydride phase? The decreased discrete unit cell volume expansion is probably an answer, but only a part of it. Softening of the alloy due to partial Co substitution does not seem likely because the elastic moduli of Ni and Co are the same. A possible explanation lies in the unique ability (among rare earths) of Ce atoms to assume either 3+ or 4+ valency states [10]. The suggested change of valency on hydrogenation, considered to be responsible for the large hysteresis in the $Ce_{0.5}La_{0.5}Ni_{5-x}Co_x-H_2$ system (if $0 \leq x < 1$) [10], may be avoided by sufficient ($z \geq 1$) Co substitution.

5. Conclusions

It has been shown that V and Co as substitution elements in $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.8-x}M_x-H_2$ and $Ce_{0.8}La_{0.2}Ni_{5-z}M_z-H_2$ systems, respectively, reduce hysteresis effectively. Generally, a major reason for hysteresis effects appears to be the discrete unit cell volume expansion between the coexisting phases. However, this hypothesis requires further experimental evidence. Other factors, such as elastic moduli or electronic structure of the alloys, may play an equally or even more important role, depending on the case.

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