MASTER

AN INTRODUCTION TO HYDROGEN IN ALLOYS

by

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23	ABSTRACT	FIRST LINE OF TEXT (FIRST PAGE)		23
24	<p>Substitutional alloys, both those that form hydrides and those that do not, are discussed, but with more emphasis on the former than the latter. This overview includes the following closely related subjects: 1) the significant effects of substitutional solutes on the pressure-composition-temperature (PCT) equilibria of metal-hydrogen systems, 2) the changes in thermodynamic properties resulting from differences in atom size and from modifications of electronic structure, 3) attractive and repulsive interactions between H and solute atoms and the effects of such interactions on the pressure dependent solubility for H, 4) "H trapping" in alloys of Group V metals and its effect on the terminal solubility for H (TSH), 5) some other mechanisms invoked to explain the enhancement (due to alloying) of the (TSH) in Group V metals, and 6) "H-impurity complexes" in alloys of the metals Ni, Co, and Fe. Some results showing that an enhanced TSH may ameliorate the resistance of a metal to hydrogen embrittlement are presented. Recent studies of resistivity and of elastic constants are summarized as just two examples of the important effects that interstitial hydrogen can have on the properties of metals and their alloys. Finally, a potential hydrogen storage material, ZrNi, is considered. From empirical rules, predictions are made regarding both the particular sites that can be occupied by hydrogen in this intermetallic compound and the resultant stoichiometries.</p>			24
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50	*Work supported by the U.S. Department of Energy.			50
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As the title of this contribution suggests, it is meant to introduce the reader to a few aspects of the behavior and effects of hydrogen in alloys. Because of space considerations, it could not be a comprehensive review; some properties and some theories and experimental techniques have not even been mentioned. The list of references is by no means complete either. Those that are given here, however, refer to many others, and the interested reader may use the present list as a nucleus for subsequent growth.

PCT EQUILIBRIA

AUTHORS' NAMES

For the study of metal-hydrogen (M-H) systems, one of the most useful diagrams is that showing pressure-composition-temperature (PCT) equilibria. Figure 1 is a schematic representation of such a diagram for Zr-ZrH₂. At low H concentrations, the isotherms are shown as straight-lines in accord with Sieverts' Law (Equation 1).

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$$P^{1/2} = K^{-1} n,$$

(1)

where $n \equiv H/M$ (hydrogen to metal ratio). K is the equilibrium

Fig. 1

Fig. 2

Fig. 1. Schematic pressure-composition isotherms for the Zr-ZrH₂ system.

Fig. 2. Temperature dependence of hydrogen solubility in various V-Co alloys.

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3	constant for the reaction $1/2 H_2(g) \rightleftharpoons H(in\ solution\ in\ metal)$			3
4	and is given by			4
5				5
6	$K = n_s \exp(-\Delta\bar{H}/RT) \exp(\Delta\bar{S}/R) .$			6
7				7
8	Here, n_s is the maximum value of n derived from the crystal			8
9	structure of the solvent, $\Delta\bar{H}$ is the relative partial molar			9
10	enthalpy of solution of hydrogen in the metal, and $\Delta\bar{S}$ is the			10
11	relative partial molar entropy of solution. For a given isochore			11
12	(a, for example), one can plot $\ln K$ vs $1/T$ to obtain $\Delta\bar{H}$ from the			12
13	slope and $\Delta\bar{S}$ from the intercept.			13
14				14
15	The points b, c, and d in Fig. 1 represent the terminal			15
16	solubilities for hydrogen (TSH) at three different temperatures.			16
17	A plot of $\ln(TSH)$ vs $1/T$ yields $\Delta\bar{H}_s$, the heat of solution of the			17
18	hydride phase in the solid solution. The compositions of the two			18
19	phases are given by the respective extremities of the plateau.			19
20	For an isochore such as e, one can obtain $\Delta\bar{H}_f$ (the heat of			20
21	formation of the hydride phase from the saturated solid solution)			21
22	from the slope of a plot of $\ln P^{1/2}$ vs $1/T$.			22
23	FIRST LINE OF TEXT (FIRST PAGE)			23
24	The value of K (in Equation 1) changes with the addition of			24
25	alloying elements. Examples are shown in Figs. 2 ² and 3 ³ for V-Co			25
26	and Mo-Ti alloys, respectively. For these experiments $P = 1\ atm.$,			26
27	so the numerical value of K is the same as the solubility, n . In			27
28	Fig. 2, if we use the isotherm at $1000^\circ K$, we obtain the open			28
29	triangular symbols shown in the top half of Fig. 4. With the			29
30	addition of Co to V and the concomitant increase in e/a ratio, the			30
31	value of K decreases. Similar behavior is observed with the			31
32	addition of Fe and Cr to V. Addition of Ti, a group IV element,			32
33	however, increases the value of K . The way these changes			33
34	affect $\Delta\bar{H}$ is shown at the bottom of Fig. 4. Obviously, $\Delta\bar{H}$ becomes			34
35	more negative with decreasing values of e/a and less negative with			35
36	the addition of elements that increase the value of e/a . Figure 5			36
37	shows that the variation of $\Delta\bar{S}$ with e/a is relatively small, but			37
38	certainly significant. For both $\Delta\bar{H}$ and $\Delta\bar{S}$, these are the same			38
39	qualitative trends reported by Lynch et al. ⁴ for V-Cr alloys.			39
40				40
41	Burch and Mason ⁵ have calculated the contributions of the			41
42	enthalpies of lattice expansion and of electronic effects to the			42
43	relative partial molar enthalpy of hydrogen in body-centered cubic			43
44	metals. They found that the enthalpy due to lattice expansion			44
45	falls in the range 50-100 kJ per g-atom of H, while the electronic			45
46	contribution is roughly $-1500\ kJ(g\text{-atom})^{-1}$. If we take the V-Cr-H			46
47	system as an example, we would conclude that the observed changes			47
48	in $\Delta\bar{H}$ are effected primarily by modification of electronic			48
49	structure and not by the 5% difference in atom size between V and			49
50	Cr. A similar explanation would seem to be fitting for the			50
51	observed ^{3,6-8} changes in $\Delta\bar{H}$ for the Nb-Mo-H system.			51
52				52

Fig. 3. Temperature dependence of hydrogen solubility in various Mo-Ti alloys.³

Fig. 4. Top: Dependence of the hydrogen solubility at 1000°K on the electron to atom ratio for various alloys of vanadium.² Bottom: Dependence of the relative partial molar enthalpy for solution of H in vanadium alloys on the electron to atom ratio.²

Fig. 5. Dependence of the relative partial molar entropy for solution of H in vanadium alloys on the electron to atom ratio.²

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Fig. 6

Fig. 7

Fig. 6. Variation of the relative partial molar enthalpy for solution of H with electron to atom ratio in Nb-Mo⁸, Mo-Ti³ and V-Co² alloys.

Fig. 7. Pressure-composition isotherms for the $\text{Nb}_{0.3}\text{Ta}_{0.7}\text{-H}$ system.⁹

Fig. 8. van't Hoff plots for the $\text{Nb}_{0.3}\text{Ta}_{0.7}\text{-H}$ system⁹. One isochore for Nb and two for Ta are shown for comparison.^{10a}

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3 The case of Mo-Ti alloys shown in Fig. 3 is an especially 3
4 interesting one. At low concentrations of Ti, plots of $\ln K$ vs 4
5 $1/T$ have negative slope meaning, of course, that ΔH is 5
6 endothermic. At 19.8 at.% Ti ($e/a = 5.60$), the slope approximates 6
7 zero, and it becomes positive for higher Ti concentrations. The 7
8 variation of ΔH with e/a is shown in Fig. 6³. The four triangles 8
9 (from Fig. 4) are for the V-Co system² and the dashed line is for 9
10 the Nb-Mo system⁸. Obviously, for given e/a ratios, the values 10
11 of ΔH for the three systems are similar. Eguchi and Morozumi³ 11
12 have shown that ΔS remains constant in Mo-Ti alloys for 12
13 $5 \times 10^3 \text{ cal/deg-atom}$ 6. TITLE 13

14
15 PCT results for the $\text{Nb}_{0.3}\text{Ta}_{0.7}\text{-H}$ system⁹ are shown 15
16 in Fig. 7. For comparison, we show that the isotherm at 371°C 16
17 falls between those^{10a} for the pure metals Ta and Nb. This 17
18 collection of isotherms yields the van't Hoff plots shown in 18
19 Fig. 8, from which we obtain the values of ΔH and ΔS shown in 19
20 Figs. 9 and 10, respectively. Obviously, both ΔH and ΔS remain 20
21 virtually unchanged in this alloy system for which the apparent 21
22 e/a ratio remains constant at 5. 22

Fig. 9

Fig. 10

Fig. 9³ & 10. Relative partial molar enthalpies and entropies for 50
various hydrogen concentrations in $\text{Nb}_{0.3}\text{Ta}_{0.7}$ (o) 51
compared with published ranges for Nb, Ta, and V. 52

Similar studies of metals like Fe and Ni and of their alloys are made more difficult by the fact that the pressure dependent solubilities for H are very low. For example, in a study of the Fe-Ni-H-system¹¹, the solubilities (H/M) at 1 atmosphere H₂ pressure were less than 5×10^{-4} . As a result, the thermodynamic data obtained in such studies show considerable experimental scatter.

TERMINAL SOLUBILITY FOR HYDROGEN

In recent years, the terminal solubility for hydrogen (TSH) in V, Nb, and Ta has been studied by several techniques: resistometry¹², differential thermal analysis¹³, optical metallography¹⁴, internal friction¹⁵, and others. For a given temperature T, the TSH represents the H concentration of the α phase of a metal when it is in equilibrium with the hydride phase. In other words, a plot of T vs. TSH is the solvus of the metal-metal hydride phase diagram. At 273°K, the TSH is 100 H/(M+H) $\approx$ 1.5 at.% for V, $\sim$ 2.5 at.% for Nb and $\sim$ 9 at.% for Ta.

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Only recently were any attempts made to determine the influence of alloying on the TSH^{9,16-20}. Two factors that could

Fig. 11

Fig. 12

- Fig. 11. Terminal solubilities for H in α -phase Nb-Ta alloys at 250°K.⁹
Fig. 12. Temperature dependence of the terminal solubilities for H in various V-Ti alloys.¹⁹

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3	be important are electronic structure and atomic volume. As an			3
4	initial step in differentiating between these, Westlake and			4
5	Miller ⁹ undertook the investigation of Nb-Ta alloys. These two			5
6	metals were selected because their Goldschmidt atomic diameters			6
7	differ by only 0.06% and they are isovalent. Both the lattice			7
8	parameter ⁹ and the electron density-of-states at the Fermi			8
9	surface ²¹ are linear functions of composition in the Nb-Ta			9
10	system. Because of the simplicity of this system, it was			10
11	anticipated that the TSH would increase monotonically with			11
12	additions of Ta to Nb, thereby providing a base line for			12
13	Subsequent measurements on other alloys in which e/a and atomic			13
14	volume would be allowed to vary, one at a time. In fact, however,			14
15	the TSH exhibits a maximum at all temperatures for the alloy			15
16	Nb _{0.3} Ta _{0.7} . The results at 250°K are shown in Fig. 11.			16
17				17
18	In the preceding section, it was pointed out that			18
19	both ΔH and ΔS for the solution of H in Nb _{0.3} Ta _{0.7} are nearly the			19
20	same as those for the pure metals. Thus, the observed enhancement			20
21	of TSH does not seem to be attributable to changes in the			21
22	thermodynamic properties of the solid solutions. Variations in			22
23	the elastic properties of the alloys and in the mechanical			23
24	constraint to hydride formation could conceivably affect the TSH,			24
25	but their roles have been minimized ⁹ .			25
26				26
27	Before further discussion of the mechanisms for enhancement			27
28	of the TSH, let us consider some of the other systems that have			28
29	been investigated. Titanium additions have important effects on			29
30	both V ¹⁹ and Nb ²⁰ , as shown in Figs. 12 and 13, respectively. The			30
31	linear relationship in Fig. 12 allows the calculation of ΔH_s , the			31
32	heat of solution of the hydride phase in the saturated solid			32
33	solution. For V, $\Delta H_s = 12.3$ kJ/g-atom H, in agreement with Ref.			33
34	12, and the addition of Ti to V causes ΔH_s to decrease.			34
35				35
36	It is from solvi such as those shown in Fig. 13, that we			36
37	obtain isothermal values of TSH for an alloy system. Our results			37
38	at 250°K for Nb-V alloys are presented in Fig. 14 and compared			38
39	with the results for Nb-Ta alloys (shown also in Fig. 11). While			39
40	the enhancement of TSH in Nb-Ta alloys is very significant, it			40
41	appears small relative to that in the Nb-V system. The TSH in			41
42	Nb _{0.5} V _{0.5} at 250°K is unknown but apparently very high; this alloy			42
43	was charged to 30 at.% H and slowly cooled all the way to 77°K			43
44	without the initiation of hydride precipitation. A few			44
45	measurements have been made on Nb-Mo alloys, also ^{18,20} . Figure 15			45
46	compares the TSH's in the four different Nb alloy systems at			46
47	230°K. For the enhancement of TSH, at all concentrations, Ta is			47
48	the least effective solute in Nb. At low concentrations, V is the			48
49	most effective, but Mo becomes most effective at a solute			49
50	concentration of 10 at.%. 2			50
51				51
52				52

Fig. 13. Partial phase diagrams (hydrogen solvi) for Nb-Ti-H alloys.²⁰

Fig. 14. Terminal solubilities for hydrogen at 250°K in Nb-V and Nb-Ta alloys.²⁰

Fig. 15. Effect of metal solutes in Nb on the terminal solubility for hydrogen at 230°K.²⁰

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3	Several explanations for the observed enhancement of TSH are			3
4	conceivable, and it seems likely that there may be more than one			4
5	mechanism involved. Matsumoto et al. ¹⁶ suggested an attractive			5
6	interaction between one solute atom and one H atom arising from			6
7	the elastic strain around an undersized solute atom. One can			7
8	rationalize H "trapping" at oversized solutes, also. For V-Ti			8
9	alloys with less than 4% Ti, Tanaka and Kimura ¹⁹ reported that H			9
10	is bound to single Ti atoms with an energy of 0.15 eV. After			10
11	studying the effects of several solutes on H diffusivity in V,			11
12	however, they have concluded that trapping does not correlate well			12
13	with atom-size and that the binding may be of electronic origin.			13
14	Moreover, they have shown that the apparent binding energy between			14
15	Ti and H in a V solvent increases for Ti concentrations greater			15
16	than 3.9 at.%, and this correlates well with the onset of Ti			16
17	segregation that they observe in this alloy system. Further			17
18	evidence that "one-on-one" H-solute interactions cannot be the			18
19	only mechanism involved in the enhancement of TSH is obvious in			19
20	Figs. 13 and 14. At solute concentrations greatly in excess of			20
21	10 at.%, the TSH continues to increase rapidly with solute			21
22	additions, despite the fact that, at these concentrations, even in			22
23	a random solid solution, very few solute atoms would not have at			23
24	least one other solute atom for a nearest neighbor.			24
25				25
26	The literature contains other reports of clustering and			26
27	short-range order in bcc solid solutions. Rudman ²² used x-ray			27
28	diffuse scattering to show that, in Nb, Ti solute atoms cluster			28
29	moderately ($\alpha_1 \approx 0.10 \pm 0.05$, where α_1 is the short range order			29
30	parameter for the first coordination sphere), a phenomenon he			30
31	attributed almost wholly to the valence difference between Nb and			31
32	Ti, because he considered the atom-size difference so small as to			32
33	be nearly negligible. He quoted from other sources that			33
34	clustering occurs in Mo-W alloys, also, and short range order			34
35	(SRO) occurs in Ti-Mo alloys. With the limited information			35
36	available to him, he postulated, for bcc alloys of these			36
37	transition metals, "a general tendency toward clustering with the			37
38	superposition of a size-difference driving force toward			38
39	ordering". Later studies, in which the same experimental			39
40	technique was used, seem to support the postulate. In			40
41	Nb _{0.50} Ta _{0.50} , with the atom size difference less than 0.06%,			41
42	clustering has been reported ²³ , and in Nb _{0.50} V _{0.50} and			42
43	Ta _{0.50} V _{0.50} , for which the atom-size difference is nearly 8%, SRO			43
44	has been reported ²⁴ . Investigations of the electronic structures			44
45	of Nb alloys have recently been reported ^{25,26} and it could be			45
46	fruitful to try to correlate these with studies of local order and			46
47	with the enhancement of TSH. Abell ²⁷ , in a theoretical treatment,			47
48	has invoked a d-band resonance state localized on the			48
49	nearest-neighbor metal atoms of an interstitial H, to explain			49
50	distortion of the cubic lattice, hydrogen diffusion and excess			50
51	partial entropy. He suggests that, within the framework of his			51
52	model, the enhancement of TSH due to alloying is expected.			52

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3	As one tries to rationalize the observations, an important			3
4	fact to bear in mind is that the TSH is a point on the solvus of			4
5	the metal-metal hydride phase diagram. It is, therefore, a			5
6	function of the properties of the hydride as well as the			6
7	properties of the metal alloy. One may not be able to fully			7
8	comprehend the mechanism of enhanced TSH's without investigating			8
9	the properties of the relevant ternary hydrides. Stalinski and			9
10	Nowak ²⁸ have determined crystal structures and lattice parameters			10
11	for the hydrides of Nb-Ti alloys, but little else is known about			11
12	any of the properties of other alloy hydrides discussed in this			12
13	section.			13
14	SECTION OF TITLE			14
15	HYDROGEN TRAPPING			15
16	AUTHORS' NAMES			16
17	There is ample evidence that H can be "trapped" by other			17
18	interstitial impurities in Nb metal. Chen and Birnbaum ²⁹ have			18
19	discussed some of the published reports and also presented their			19
20	results from internal friction and stress-relaxation			20
21	measurements. One O atom, occupying an octahedral interstice,			21
22	traps one H atom, and the observed relaxations are due to			22
23	stress-induced hopping of the H around the O. They were not able			23
24	to ascertain the sites occupied by the H or the jump paths. For a			24
25	different case, that of an O-H pair in V metal, Ozawa et al ³⁰ used			25
26	channeling of ³ He ⁺ ions to show that the H and the O occupy			26
27	nearest-neighbor octahedral interstices.			27
28				28
29	As mentioned in the preceding section, the enhancement of TSH			29
30	in both Nb-V and Nb-Mo alloys has been attributed to H trapping by			30
31	the substitutional solutes ¹⁶⁻¹⁸ . The binding energies for V-H			31
32	and Mo-H pairs have been estimated to be 0.2 eV ¹⁸ and 0.07 eV ¹⁶ ,			32
33	respectively. These values, however, are now being contested.			33
34	Pick and Welch ³¹ have developed a theoretical model for the Nb-V-H			34
35	system from which they predict the pressure-composition isotherm			35
36	for 423°K shown in Fig. 16. For Nb _{0.94} V _{0.06} , their calculated			36
37	isotherm (423°K) deviates in a positive sense, from the calculated			37
38	isotherm for pure Nb ^{10a} when the V-H binding energy is taken to be			38
39	0.2 eV. At this temperature, their experimental plot does not			39
40	exhibit a positive deviation from Sievert's law, as did their			40
41	calculated plot, but this does not allow one to conclude that			41
42	there is no trapping at lower temperatures. They have concluded,			42
43	however, that, if trapping occurs, the binding energy of the V-H			43
44	complex must be considerably less than the assumed 0.2 eV. From			44
45	other measurements of PCT, they have estimated that the critical			45
46	temperature for the $\alpha + \alpha'$ phase field is reduced from 443°K to			46
47	slightly less than 418°K by the addition of 6 at.% V, and this			47
48	allows them to calculate a binding energy of ~ 0.07 eV. This is			48
49	in reasonably good agreement with the value 0.09 eV obtained from			49
50	NMR measurements by Matsumoto ¹⁷ and with 0.095 eV obtained from			50
51	quasielastic neutron scattering measurements ³² . If we use their			51
52	values of the pressure for H/M = 0.05 and T = 418, 433, and			52

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Fig. 16

Fig. 17

Fig. 16. Experimental pressure-composition diagram for the $\text{NbV}_{0.94}\text{V}_{0.06}\text{-H}$ system at 423°K ³¹ compared with calculated plots for the Nb-H^{10a} and $\text{Nb}_{0.94}\text{V}_{0.06}\text{-H}^{31}$ systems.

Fig. 17. Temperature dependence of hydrogen diffusivity in Nb-Ti alloys.³³

473°K , we can estimate that the value of $\bar{\Delta H}$ is roughly -44 kJ/g-atom H compared with -36.7 kJ/g-atom H for pure Nb^{10a} . The increase in enthalpy is consistent with trapping.

As was mentioned earlier, Inoue et al.⁶ reported that $\bar{\Delta H}$ for the solution of H in Nb becomes less negative as e/a is increased by the addition of Mo. They conclude from this that the interaction between Mo and H must be repulsive, a contradiction to the trapping model^{16,18} for Nb-Mo-H alloys.

The occurrence of H trapping in Nb-Ti alloys has been inferred from studies of diffusion. Measurement of the Gorsky effect in Nb-Ti-H alloys has produced the plots of H diffusivity shown in Fig. 17.³³ The apparent activation energy for H diffusion increases with increasing Ti concentration. The word apparent is used because, in this case, a given value does not represent the activation energy for just one type of jump.

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3	Instead, each H atom makes at least four distinguishable types of			3
4	jump ³⁴ : from one host lattice site to another, from a host lattice			4
5	site to a Ti trap site, from one trap site to another, and from a			5
6	trap site to a host lattice site. From their determination of D			6
7	as a function of Ti concentration, Cannelli and Cantelli ³³ have			7
8	estimated a Ti-H binding energy $\Delta E_B > 0.06$ eV. In their studies			8
9	of internal friction ³⁵ , for a given concentration of H, the			9
10	addition of 2 at.% Ti to Nb caused the hydride precipitation			10
11	temperature to be markedly lower. In Nb with 4.2 at.% H, they			11
12	observed hydride precipitation at about 300°K, but, with a similar			12
13	H concentration in Nb _{0.95} Ti _{0.05} , they could not detect the			13
14	formation of any hydride down to 50°K. It was concluded that the			14
15	partial removal of H from solid solution in a trapped state was			15
16	the cause of the effective increase in terminal solubility.			16
17				17
18	Krönmüller et al. ³⁶ have measured the magnetic after-effect			18
19	in Ni, Co, and Fe alloyed with transition metals and charged with			19
20	H. This proves to be a highly sensitive technique for detection			20
21	of Snoek-type relaxations arising from the interaction between			21
22	"metal-hydrogen (M-H) complexes" and domain walls. They found			22
23	that, in bcc binary alloys, M-H complexes were formed if the			23
24	substitutional solute atom has a smaller number of d-electrons			24
25	than the host metal. Thus, in an Fe host, Ti and Zr solutes			25
26	formed M-H complexes, but Ni, Co, and Pd solutes did not. In all			26
27	fourteen of the Ni-based fcc alloys that they studied, M-H			27
28	complexes were formed, regardless of the number of d-electrons in			28
29	the solute atom.			29
30				30
31	In the body centered lattice, the reorientation process of			31
32	M-H complexes has been modeled ³⁶ as shown in Fig. 18. In a			32
33	tetragonal configuration, sites 1, 2, and 3 are nearest neighbor			33
34	octahedral interstices for the solute (Ti) atom, whereas sites 4-9			34
35	are next nearest neighbors. Two jump frequencies, indicated on			35
36	the energy diagram, are involved as the H occupies the two types			36
37	of site, alternately. For a monoclinic configuration (Fig. 18b)			37
38	also, there would be two jump frequencies, one for the			38
39	tetrahedral-tetrahedral (t-t) jumps in a single (100) plane and			39
40	another for t-t jumps out of that plane. Magnetic after-effect			40
41	measurements cannot distinguish between the two configurations.			41
42				42
43	In a face-centered lattice (Fig. 19), a M-H complex in a			43
44	tetragonal configuration would reorient by the motion of H ⁺ from			44
45	one nearest neighbor octahedral site to another (1,2,3, or 4) ³⁷ .			45
46	The jump path, however, would probably be through a tetrahedral			46
47	site, so, two jump frequencies would be involved in this lattice,			47
48	also.			48
49				49
50	Hohler and Krönmüller ³⁷ have shown that Q, the activation			50
51	energy for the reorientation of M-H complexes in Ni, is not			51
52	correlated with the number of outer (d + s + p) electrons, but is			52

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Fig. 18a

Fig. 18b

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Fig. 18. M-H complexes in b.c.c. alloys.²⁶ (a) H in octahedral interstices. Jumps of the type 1 + 6 and 6 + 2 occur with frequencies v_1 and v_2 , respectively. (b) H in tetrahedral interstices. Diagram indicates the 12 different orientations of the M-H axis.

Fig. 19

Fig. 20

Fig. 19. M-H complexes in f.c.c. alloys.³⁷ Reorientation of the M-H axis would occur by diffusion of H^+ from the occupied octahedral site to one of the four numbered, unoccupied sites.

Fig. 20.⁴ Dependence of the activation energy Q for the reorientation of M-H complexes in Ni on Δa , the lattice expansion caused by a 2% concentration of the indicated solute.³⁷

Fig. 22. Variation of the shear and bulk moduli in Nb-Ta single crystals with Ta concentration (298°K). Results for C' and C_{44} deviate only slightly from linear plots.³⁸

Fig. 23. Deviation from elastic isotropy ($C_{44}/C' = 1$) in Nb-Ta alloys at 298°K.³⁸

Fig. 24. Variation of the ratio C_{44}/C' with Nb concentration in V-Nb alloys at 298°K.³⁸

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correlated with isotropic elastic behavior, i.e., $C_{44}/C' = 1$. Instead, Fisher et al.³⁸ have shown that elastic isotropy occurs in the alloy containing about 54 at.% Ta. They have found, also, that introduction of H shifts isotropy to even lower Ta concentrations. In a similar study³⁸ of Nb-V single crystals, it was found that C_{44}/C' increased monotonically, but not linearly, from 0.492 for Nb to 0.778 for V (Fig. 24). There seems, therefore, to be no correlation between elastic properties and the enhancement of TSH shown in Figs. 11 and 14.

SECOND It has been known^{40,41} for several years that, in V, Nb, and Ta metals, H reduces C' , increases C_{44} and effects little change in K. Only recently have the effects of H been studied in alloys. For the Nb-Ta system, Figs. 25 and 26 show, respectively, the relative changes in C' and C_{44} normalized to 1 at.% H. For one particular alloy, Nb₃₃Ta₆₇, the changes effected in the moduli at 298°K by increasing concentrations of H or D are shown in Fig. 27. The analogous results for one alloy in the Nb-V system are reproduced in Fig. 28. Some possible explanations for the isotope effect have been developed³⁸, but these will not be presented here. FIRST LINE OF TEXT (FIRST PAGE)

Alberts et al.⁴² have discussed the existing controversy over whether the effect of H on C' can be interpreted as a Snoek relaxation resulting from a tetragonal distortion around the interstitial atom. The change in C' , according to the Snoek

Fig. 25

Fig. 26

Fig. 25. Variation of the relative change in C' (normalized to 1 at.% H) with Ta concentration in Nb-Ta alloys at 298°K.³⁸

Fig. 26. Variation of the relative change in C_{44} (normalized to 1 at.% H) with Ta concentration in Nb-Ta alloys at 298°K.³⁸

Fig. 27. Plots of normalized elastic constants versus hydrogen or deuterium concentrations in $Nb_{0.33}Ta_{0.67}$.
Fig. 28. Plots of normalized elastic constants versus hydrogen or deuterium concentrations in $Nb_{0.18}V_{0.82}$.

Fig. 29. Variation of the relative change in C_{44} (normalized to unit hydrogen concentration) with metal solute concentration in V-Nb and Nb-Ta alloys at 298°K.

1	EVEN	RUNNING HEAD	ODD	1
2				2
3	model, is given by:	LINE OF TEXT (OTHER THAN FIRST PAGE)		3
4				4
5		$\Delta C'/C' = - [2 N(V_0 C')/3 kT](\lambda_1 - \lambda_2)^2,$		5
6				6
7		where N is the mole fraction of interstitial atoms, V_0 is the		7
8		atomic volume of the bcc lattice, λ_1 is the strain along one cube		8
9		axis and λ_2 is the strain along the two orthogonal axes. Any		9
10		change in C_{44} cannot be attributed to a Snoek mechanism.		10
11		FIRST LINE OF TITLE		11
12		Alberts et al. ⁴² argue that, under increased hydrostatic		12
13		pressure, the tetragonal distortion parameter $(\lambda_1 - \lambda_2)$ should		13
14		become larger. Accordingly, $\Delta C'$ should also be larger. They		14
15		measured the elastic constants of both pure and hydrogenated		15
16		crystals of V and Nb ₅₃ Ta ₄₇ and found that the value of $\Delta C'$ for		16
17		unit concentration of H became larger by 1.4% for V and by 2.0%		17
18		for Nb ₅₃ Ta ₄₇ when the pressure was increased from 0 to 3 kbar.		18
19		They have considered other contributions but have concluded that		19
20		the largest must arise from the effect of pressure on $(\lambda_1 - \lambda_2)$.		20
21		In both materials, the value of ΔC_{44} was unaffected by pressure.		21
22		These observations are consistent with the Snoek model.		22
23		FIRST LINE OF TEXT (FIRST PAGE)		23
24		The increase in C_{44} due to solute H has been attributed to		24
25		electronic effects ³⁸ . Figure 29 shows the variation in the		25
26		relative change in C_{44} per unit H concentration for the V-Nb and		26
27		Nb-Ta systems. The maximum occurs for Nb and, thus, coincides		27
28		with the maximum in the density of electron states at the Fermi		28
29		surface.		29
30				30
31		RESISTIVITY DUE TO HYDROGEN		31
32				32
33		Many of the values of TSH in alloys have been determined		33
34		resistometrically ^{9,12,16,18,20} . By careful examination of the		34
35		contribution made by solute H to the resistivity, ρ , of transition		35
36		metal alloys ⁴³ , one can gain considerable insight regarding the		36
37		types of interaction involved.		37
38				38
39		Matthiessen's rule states that, in a given temperature range,		39
40		dp/dT for a metal remains unchanged by the addition of solute		40
41		atoms. Westlake and Miller ⁴³ have shown that, for H solute in		41
42		Nb-V, Nb-Ti and Nb-Mo alloys, Matthiessen's rule is not obeyed.		42
43		While there are many possible causes for failure to conform to		43
44		this rule, their results lend support to some electronic and		44
45		trapping effects.		45
46				46
47		The behaviors of Nb-Mo-H and Nb-Ti-H alloys are shown in		47
48		Figs. 30a and 30b. The addition of Mo to Nb causes dp/dT to		48
49		decrease and addition of H to the Nb-Mo alloy causes a		49
50		continuation of the same decreasing trend. Addition of Ti to Nb		50
51		decreases dp/dT , also, but the effect of H in these Nb-Ti alloys		51
52		is an enhancement of dp/dT . Within the approximation of a rigid		52

Fig. 30. (a) Temperature derivative of the resistivity in Nb-Mo-H alloys for $240 < T < 300^\circ\text{K}$. (b) Temperature derivative of the resistivity in Nb-Ti-H alloys for $295 < T < 340^\circ\text{K}$.

Fig. 31. Temperature derivative of the resistivity in Nb-V-H alloys for $295 < T < 350^\circ\text{K}$.

1	EVEN	RUNNING HEAD	ODD	1
2				2
3	band model, these observations seem to suggest that the values			3
4	of dp/dT are related to the density of electron states at the			4
5	Fermi level. The density is at or near a maximum for Nb and would			5
6	be reduced by the addition of Ti, Mo or H, but for Nb-Ti alloys,			6
7	it would be increased by solute H.			7
8				8
9	Hydrogen trapping may also make a significant contribution to			9
10	some of the observed deviations from Matthiessen's rule.			10
11	According to Pfeiffer and Wipf ⁴⁴ , the fraction of H atoms that are			11
12	weakly trapped by nitrogen atoms in Nb increases with decreasing			12
13	temperature, and, in the trapped state, $\Delta\rho_H$ (the contribution of H			13
14	to the resistivity) is reduced by 40%. Thus, in Nb-N-H			14
15	alloys, $\Delta\rho_H$ decreases with decreasing temperature. Such behavior			15
16	makes dp/dT greater for a hydrogenated alloy than for a			16
17	hydrogen-free alloy.			17
18	AUTHORS' AFFILIATION			18
19	Figure 31 shows that dp/dT decreases slightly as V is added			19
20	to Nb, but then increases for V concentrations greater than			20
21	10 at.%. Solute H causes dp/dT to increase, just as it did in			21
22	Nb-Ti alloys. In Ta metal and in Nb-Ta alloys, the change			22
23	in dp/dT due to additions of H were small, and maybe			23
24	insignificant. These observations seem to suggest that trapping			24
25	may occur in Nb-V and Nb-Ti alloys, but not in Nb-Mo alloys, and			25
26	maybe not in Nb-Ta alloys. Attractive interactions might be			26
27	expected to arise from the size difference (~8%) between Nb and V			27
28	and from, the effective valence difference between Nb and Ti. On			28
29	the other hand, Nb and Ta are isovalent and have virtually the			29
30	same atom size. The possible repulsive interaction between Mo and			30
31	H in Nb was discussed earlier. Further evidence against a			31
32	trapping model for the Nb-Mo-H system arises from the following			32
33	comparison: for $H/M = 0.05$, the values of $\Delta\rho_H$ at room temperature			33
34	in Nb, $Nb_{0.9}V_{0.1}$, $Nb_{0.9}Ti_{0.1}$ and $Nb_{0.9}Mo_{0.1}$ are, respectively,			34
35	3.10, 2.45, 2.45, and 3.95 $\mu\Omega$ cm. Thus, the presence of either V			35
36	or Ti solute atoms reduces $\Delta\rho_H$, an effect that is consistent with			36
37	a trapping mechanism, but the presence of Mo solute atoms			37
38	anomalously increases $\Delta\rho_H$.			38
39				39
40	HYDROGEN EMBRITTLEMENT			40
41				41
42	The topic of hydrogen embrittlement may be somewhat outside			42
43	the scope of this NATO Advanced Study Institute on Metal			43
44	Hydrides. On the other hand, the problem of reduced ductility in			44
45	hydrogenated transition metals and their alloys is so closely tied			45
46	to the nucleation and growth of hydride particles, that it seems			46
47	to be deserving of at least a short discussion here. The			47
48	phenomenon of stress-induced hydride precipitation ⁴⁵⁻⁴⁷ , which is			48
49	essential to the generalized model we proposed for hydrogen			49
50	embrittlement ⁴⁸ , has now been demonstrated experimentally ^{49,50} .			50
51	Because of this phenomenon, the brittle hydride phase is nucleated			51
52	at one or more structural inhomogeneities during mechanical			52

1	EVEN	RUNNING HEAD	ODD	1
2				2
3	testing. In all cases, therefore, the temperature for the onset			3
4	of H embrittlement during cooling is a few degrees higher than the			4
5	temperature for initiation of hydride precipitation in an			5
6	unstressed specimen. We know now that we can lower this latter			6
7	temperature by alloying, and this could very well be accompanied			7
8	by increased resistance to H embrittlement.			8
9				9
10	In Fig. 15, we can see the relative importance of Ta, V, Ti,			10
11	and Mo for enhancement of the TSH in Nb. Sasaki and Amano ¹⁸ have			11
12	measured the reduction in area (R.A.) as a function of temperature			12
13	in Nb, Nb _{0.95} V _{0.05} , Nb _{0.95} Mo _{0.05} , Nb _{0.97} Ta _{0.03} , and in each of			13
14	these materials with 1 at.% H. The effect of Ta was minimal, as			14
15	might be expected from the small change in TSH due to 3 at.% Ta			15
16	(Fig. 11). The addition of V, however, lowered the embrittlement			16
17	temperature by at least 50°K, as shown in Fig. 32a. The small			17
18	arrows indicate the temperatures for initiation of hydride			18
19	precipitation in the unstressed materials. The recovery of the			19
20	ductility below 140 K can be attributed to the fact that trapping			20
21	reduces the effective diffusivity of H. In Fig. 32b, the arrows			21
22	indicate the considerable lowering of the temperature for the			22
23	initiation of hydride precipitation when 5% Mo was added to Nb,			23
24	but the temperature for the onset of hydrogen embrittlement			24
25	remained essentially, and anomalously, unchanged.			25
26				26
27	Tanaka and Kimura ⁵¹ have measured the total strain to			27
28	fracture in hydrogenated V-Ti alloys. In Fig. 33, their results			28
29	for V-3.9 at.% Ti (with and without 0.55 at.% H) are compared with			29
30	the analogous results for unalloyed V. Obviously, the enhancement			30
31	of TSH ¹⁹ due to the addition of Ti to V is accompanied by			31
32	appreciably increased resistance to H embrittlement.			32
33				33
34	For the Nb and V alloys discussed above, the reaction with H ₂			34
35	is exothermic and the hydride phase formed is relatively stable.			35
36	It is now becoming realized, however, that hydride formation may			36
37	play a role in the hydrogen embrittlement of some metals and			37
38	alloys, under certain conditions, even if the hydride is quite			38
39	unstable. One example is that of Ni-base superalloys, which are			39
40	candidates as structural materials in the hostile chemical			40
41	environments of sour-gas wells. Baranowski ⁵² has shown that it			41
42	requires a H ₂ pressure in excess of 6 kbar to bring about the			42
43	formation of NiH at 298°K. Yet, in a recent study of Hastelloy			43
44	Alloy C-276 (~55% Ni) ⁵³ , it was found that a fcc hydride was			44
45	formed on the surface during electrolytic charging. Obviously			45
46	then, these are conditions of very high H fugacity. The hydride			46
47	formed on this alloy had the same structure as NiH, but its			47
48	lattice parameter was somewhat different. Like NiH, it was an			48
49	unstable hydride in that it decomposed completely in 20 h at room			49
50	temperature. Decomposition left the surface covered with a			50
51	network of cracks. Because local cathodic conditions and high H			51
52	fugacities can exist at the tips of microcracks and surface flaws			52

Fig. 32. The effects of hydrogen additions on the ductility of niobium below room temperature, with and without solute V(a) or Mo(b).

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Fig. 33. The effects of hydrogen on the total strain to fracture of vanadium below room temperature, with and without solute titanium.

1	EVEN	RUNNING HEAD	ODD	1
2				2
3	even in anodically polarized specimens ⁵⁴ , it seems that the role			3
4	of hydride formation in the hydrogen embrittlement of such alloys			4
5	warrants further study.			5
6				6
7	HYDRIDES OF INTERMETALLIC COMPOUNDS			7
8				8
9	All of the materials being seriously considered as media for			9
10	the chemical storage of hydrogen are alloys and, therefore, fall			10
11	within the purview of the title for this contribution. On the			11
12	other hand, many of the properties of these particular alloys have			12
13	been discussed as separate topics by other researchers at this			13
14	NATO Advanced Study Institute. On the subject of the hydrides of			14
15	intermetallic compounds, therefore, we shall limit our remarks to			15
16	our recently completed consideration of the stoichiometries and			16
17	the sites occupied by H in the hydrides of ZrNi ⁵⁵ .			17
18	SEVERAL POSSIBLE CRITERIA			18
19	Several possible criteria have been considered by different			19
20	researchers to be useful in the prediction of H site occupation			20
21	and the resulting hydride stoichiometry. Lundin et al. ⁵⁶ , for			21
22	example, reported a correlation between the radii of tetrahedral			22
23	holes and the stability of both hexagonal AB ₅ and cubic AB			23
24	intermetallic compounds. Another suggestion of the importance			24
25	of hole size was made by Thompson et al. ⁵⁷ for a solution of			25
26	deuterium in the α phase of FeTi. Only octahedral sites			26
27	coordinated by two Fe atoms and 4 Ti atoms are occupied by D. In			27
28	a hard-sphere model, this colinear Fe site can accommodate an atom			28
29	of radius $r = 0.31 \text{ \AA}$, whereas the analogous Ti site would limit r			29
30	to $0.09 \text{ \AA}$.			30
31				31
32	A phenomenological model was proposed by Jacob et al. ⁵⁸ for			32
33	pseudobinary Laves phase compounds to explain the capacity for			33
34	absorption of hydrogen on the basis of nearest-neighbor-atom			34
35	species. The same criterion is essential to another model ^{59,60}			35
36	used to predict the sites to be occupied by H in AB ₂ Laves phases			36
37	(both hexagonal and cubic) from the values of $\Delta H'$ assigned to each			37
38	site. $\Delta H'$ is the sum of the enthalpies of formation of elementary			38
39	(imaginary, binary) hydrides formed by the A and B atoms			39
40	surrounding a given site, and these enthalpies are calculated from			40
41	the theory of Miedema (references listed) ⁵⁹ .			41
42				42
43	From theoretical considerations, Switendick ⁶¹ has concluded			43
44	that, in a stable hydride, H-H interatomic distances can be no			44
45	shorter than about $2.1 \text{ \AA}$. In accord with this, Didisheim et			45
46	al. ^{62,63} have suggested that, in hexagonal and cubic Laves phases,			46
47	H's do not occupy nearest neighbor tetrahedral (t) sites			47
48	($1.3 \text{ \AA}$ apart), but do occupy next nearest neighbor t sites, which			48
49	are about $2.0 \text{ \AA}$ apart. Shoemaker and Shoemaker ⁶⁴ considered two			49
50	particular AB ₂ Friauf-Laves phases and were led to postulate the			50
51	operation of the following exclusion rule: "two tetrahedra having			51
52	a triangular face in common may not both accommodate hydrogen			52

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atoms at their centers. In these phases, the centers of such tetrahedra are less than 1.6 Å apart, while for tetrahedra not sharing a face the distance is at least 2.2 Å.

What we have chosen to study⁵⁵ is the ZrNi-H system with its orthorhombic metal sublattice (space group Cmc₂m). Figure 34 shows this rather complex structure and a sampling of the possible sites for H. Using only the criteria of interstitial-hole size and H-H interatomic distance, we have sorted through these sites and combinations of sites to make predictions of occupancy and the resultant stoichiometries. As an example, let us consider the case of ZrNiH₃.

From the estimated, expanded lattice parameters of ZrNiH₃, we have calculated the H-H distances and hole radii listed in Table 1. One can see that, for ★ and ● sites, the hole radius, is just that which seems to be minimum for typical stable hydrides (0.37-0.39 Å)⁵⁴. The radii of the other three sites, however are even larger. One can eliminate the ⊙ sites from further consideration, because the H-H distance for nearest neighbor ⊙ sites is only 1.07 Å.

A combination of ★ and ◆ would give the correct number of sites and the respective hole radii, 0.39 and 0.72 Å, are acceptable. The ◆ - ◆ and the ◆ - ★ distances are more than adequate, but the ★ - ★ distance is somewhat less than Switendick's⁶¹ minimum value of 2.1 Å, so let us consider other possibilities.

Fig. 34. Structure of ZrNi with examples of the interstitial sites possibly available for occupation by hydrogen shown as solid symbols. The symbols ○ and □ represent zirconium and nickel, respectively. As an aid in perspective, four face-centers are shown as ⊙.

EVEN		RUNNING HEAD						ODD	
1. Hole sizes and H-H nearest-neighbor distances for H in designated interstitial sites in ZrNiH ₃ .									
Site	No. Sites Per Zr Atom	Hole Radius in Å	H-H distance in Å						
1	1	0.72	2.87	1.61	1.43	2.67	2.23		
		0.55	1.61	2.58	2.46	1.52	2.39		
		0.50	1.43	2.46	2.08	2.21	1.30		
		0.39	2.67	1.52	2.21	1.97	1.38		
2	2	0.38	2.23	2.39	1.30	1.38	1.07		

AND ADDRESS

There is only one $\blacklozenge$ site per Zr atom, so, if it is occupied in ZrNiH₃, then some other sites must be occupied, as well. We note, however, that the distances $\blacklozenge - \blacktriangle$ and $\blacklozenge - \blacktriangledown$ are only 1.61 and 1.43 Å, respectively. We submit, therefore, that occupation of $\blacklozenge$ would preclude occupation of either $\blacktriangle$ or $\blacktriangledown$ sites.

Examination of Table 1 reveals that a combination of $\blacktriangle$ and $\blacktriangledown$ yields just the required number of sites, and both hole sizes and H-H distances are well above the minima for stable hydrides. The resulting prediction of full occupancy of $\blacktriangle$ and $\blacktriangledown$ sites in ZrNiH₃ is in complete agreement with experimental observations (references listed).⁵⁵ Using analogous rationales for several stoichiometries, we have made the following predictions:

1. A monohydride, ZrNiH, should exist with H occupation of either $\blacklozenge$ or $\blacktriangle$ sites.
2. ZrNiH₂ probably does not occur.
3. Little, if any, H solubility is to be expected in ZrNiH₃ because of the short H-H distances ($\blacktriangle - \blacklozenge$, $\blacktriangle - \star$, $\blacktriangledown - \blacklozenge$, $\blacktriangledown - \bullet$).
4. The compound ZrNiH_{4-x} may exist at high H₂ pressures with occupancy of $\blacktriangledown$ and $\star$ sites.

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1	EVEN	RUNNING HEAD	ODD	1
2				2
3	CONCLUSIONS	FIRST LINE OF TEXT (OTHER THAN FIRST PAGE)		3
4				4
5		In general, when Group V metals (V, Nb, Ta) are alloyed with		
6		other metals, for each alloy the logarithm of the hydrogen		
7		solubility is linear with reciprocal temperature. The resulting		
8		relative partial molar values of both enthalpy and entropy become		
9		less negative as e/a (electron to atom ratio) increases. For a		
10		given alloy system, the isothermal hydrogen solubilities decrease		
11		monotonically with increasing values of e/a.		
12				
13	SECOND	The terminal solubilities for hydrogen in Group V metals are		
14		enhanced markedly by the addition of solute atoms from Groups IV,		
15		V or VI. No single explanation for the enhancement is universally		
16		accepted, and it may very well be that more than one mechanism is		
17		operative.		
18		AUTHORS' AFFILIATION		
19		One of the phenomena possibly influencing the terminal		
20		solubility for H in alloys is "hydrogen trapping" or the formation		
21		of "M-H complexes" between H and the metal solute atom. There is		
22		considerable evidence that such complexes do exist in alloys		
23		whether the relative partial molar enthalpy is negative, as it is		
24		for Nb, or positive, as it is for Ni. In Ni, apparently, the		
25		elastic and the electronic contributions to the binding energy of		
26		M-H complexes are of the same order of magnitude.		
27				
28		In alloys of Group V metals, the principal shear moduli vary		
29		almost linearly with solute concentration, and there are no		
30		anomalies in elastic properties to which one can attribute the		
31		observed enhancements in terminal solubility for hydrogen. The		
32		addition of H to alloys, as well as to pure metals of Group V,		
33		causes important decreases in C' and increases in C ₄₄ . Whether		
34		Snoek relaxation is responsible for the effect of H on C' is still		
35		contested, but the change in C ₄₄ apparently arises from electronic		
36		effects.		
37				
38		The contribution of H to the resistivity of Nb alloys does		
39		not obey Matthiessen's rule. Such nonconformity is common and has		
40		many possible causes, but the behavior of both Nb-V and Nb-Ti		
41		alloys is consistent with the formation of M-H complexes.		
42				
43		Group V metals containing H are known to be embrittled by the		
44		precipitation of a hydride phase. Some alloying elements with		
45		demonstrated capacity for impeding hydride formation in such a		
46		metal have been shown to enhance its resistance to		
47		embrittlement. On the other hand, the addition of Mo to Nb		
48		anomalously increases the terminal solubility for H without any		
49		improvement in ductility. Unstable hydrides can be produced even		
50		in some metals and alloys not usually thought of as hydride		
51		formers when conditions of very high H fugacity exist. Because in		
52		many practical situations high H fugacities do exist at crack tips		

1	EVEN	RUNNING HEAD	ODD	1
2				2
3	or surface flaws, the rôle of hydride formation in the hydrogen			3
4	embrittlement of such materials should be reassessed.			4
5				5
6	A number of models and criteria have been used in the past to			6
7	explain the observed stoichiometries and H-site occupations in			7
8	hydrides of various intermetallic compounds. Presently, an			8
9	examination of the structure of ZrNiH ₃ has shown that one can make			9
10	predictions agreeing with experimental observations using only			10
11	empirical rules regarding the sizes of occupied interstices in			11
12	stable hydrides and a theoretically determined minimum H-H			12
13	distance. Predictions made here regarding other stoichiometries			13
14	for hydrides of ZrNi require experimental verification.			14
15				15
16	REFERENCES			16
17				17
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