

Table II. The CH₄ and H₂ Emission during the Fracture in Arbitrary Units and the Percentage of Brittle Fracture Measured on the SEM Images

Sample	CH ₄ Emission (Arb. Unit)	H ₂ Emission (Arb. Unit)	Percentage of Brittle Fracture
No. 1	110	7	70
No. 2	130	12	70
No. 3	180	35	75
No. 4	20	17	0
No. 5	8	8	5

H₂O emission were not observed, while the CH₄ emission was always significant. The H₂ emission was less pronounced than the CH₄ emission. Typical results for the embrittled regions are shown in Figure 1. The partial pressures vs time curves for CH₄ and H₂ are presented in Figure 1. Both curves are normalized to the pressure before fracture. The fracture occurred at time zero. The results for a sample taken from the region that was not embrittled are presented in Figure 2. If the fracture time is much less than the decay of the gas emission signal (less than 0.1 second), the area under the peaks can be used as a relative measure of the gas emission during fracture. Table II summarizes some typical results of the gas emission and SEM measurements. Sample numbers 1 to 3 were cut from the embrittled part of the tube while sample numbers 4 and 5 were taken from the part of the tube which was not embrittled. The methane emission for sample numbers 4 and 5 and the hydrogen emission for all samples (except number 3) are given to characterize the noise level of the system. It is clear from Table II that the samples studied can be divided into two groups: ductile samples (percentage of brittle fracture less than 15 pct) and brittle samples (percentage of brittle fracture is in the range of 70 to 80 pct). Thus, a function connection, reflecting the correlation, between the brittleness and methane emission could not be established. Table II, however, demonstrates clearly that only the brittle fracture is associated with methane emission; thus, we conclude that the formation of methane filled bubbles, cracks, etc. may be primarily responsible for the brittleness of these evaporator tubes.

In summarizing, we conclude that this simple measurement technique is suitable to identify the gas content of the cracks, bubbles, etc. revealed by the fracture.

REFERENCES

1. L. Weiner: *Corrosion*, 1961, vol. 17, pp. 137-43.
2. P. G. Shewmon: *Metall. Trans. A*, 1976, vol. 7A, pp. 279-86.
3. R. Pishko, M. McKimpson, and P. G. Shewmon: *Metall. Trans. A*, 1979, vol. 10A, pp. 887-94.
4. T. J. Hakkarainen, J. Wanagér, and Che-Ju Li: *Metall. Trans. A*, 1980, vol. 11A, pp. 2035-36.
5. J. P. Hirth: *Metall. Trans. A*, 1980, vol. 11A, pp. 861-89.
6. T. G. Nieh and W. D. Nix: *Acta Met.*, 1980, vol. 28, pp. 557-67.

Hydrogen Traps, Repellers, and Obstacles in Steel; Consequences on Hydrogen Diffusion, Solubility, and Embrittlement

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It is now a well-established fact that hydrogen may be more or less reversibly trapped at particular defect sites in steel; direct evidence such as that obtained by autoradiography techniques,¹ or indirect evidence as in permeation experiments,² are numerous. These results even have allowed the drawing of various classifications of possible traps in steel, e.g., References 1, 3, 4, 5, 6.

The aim of this communication is to propose an additional classification of defects that have the opposite effect of trapping, i.e., that *repel hydrogen*. As will be shown, such "hydrogen repellers" are numerous in steel; furthermore, some of their effects may be mistaken for those of trapping. Hence, we will also indicate how to distinguish between "traps" and "repellers".

Identification of hydrogen traps, repellers, and obstacles in steels. In a recent classification,³ several reasons were given to explain trapping of hydrogen by a particular defect in steel. These reasons were sufficient to distinguish between two main types of traps, as shown in Figure 1: attractive traps and physical traps. In a more elaborate manner (see Reference 3 for details), one may say that:

Attractive traps are a region of the lattice where hydrogen atoms are subjected to an attractive force of various origins: it may be electronic (atoms and other defects introducing electron vacancies will attract hydrogen when it is present as a screened proton⁷); it may be due to the existence of a tensile stress field,^{8,9} of a thermal gradient, or to the non-ideal part of a chemical potential gradient.¹⁰ These reasons allowed the identification of various attractive traps; in the case of atomic size traps, for instance, elements on the left

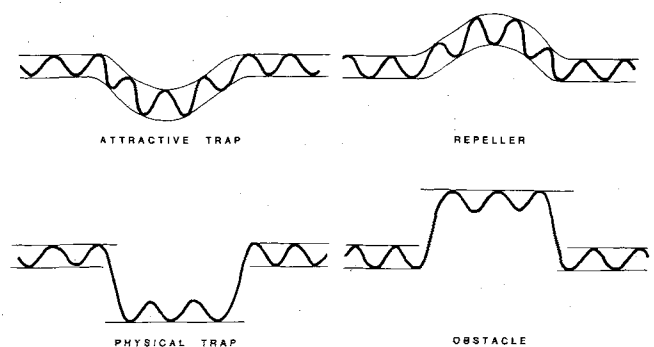


Fig. 1—Schematic of attractive and physical traps (from Ref. 3) vs repellers and obstacles. Note that diffusion of hydrogen through a repeller may be possible, although less probable than in the lattice; on the contrary, diffusion through the obstacle may be downright improbable (too much energy needed in only one jump). In fact, repellers and obstacles may be considered as the antithesis of attractive and physical traps, respectively.

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Table I. Possible Hydrogen Traps, Repellers, and Obstacles in Steel. In the Case of Atomic Size Defects, the Ranking Is of Increasing Interaction When Going Down along the Column; Underlined Elements Mean That Contradictory Information Exists; Only Elements with Varying Electrons in the 3d and 4d Shells Were Considered for the Ranking Based upon the Position vs Iron in the Periodic Table.

Type	Traps				Repellers—Obstacles				
	Elements at the Left of Iron		Elements with a Negative ϵ_H^i		Elements at the Right of Iron		Elements with a Positive ϵ_H^i		
Atomic Size	Mn	Tc	<u>Ni</u>	Mn	Co	Rh	Cu	<u>Ni</u>	
	Cr	<u>Mo</u>	Mn	Cr	<u>Ni</u>	Pd	<u>Mo</u>	Cu	
	V	Nb	Cr	<u>Mo</u>	<u>Cu</u>	Ag	Co	Pt	
	Ti	Zr	V	<u>Nb</u>	Zn	Cd	H	Co	Cd
	Sc	Y	Nb	V			W	Ag	In
			Ce	Ta			Sn	Au	
			Ti	Zr			S	Ga	(Ref. 12)
			<u>O</u>	Ti			Pd	<u>O</u>	
			La	(Ref. 13)			P	S	
			Ta				Al	P	
			Nd	(Ref. 11)			Rh	As	
							Ge	Sb	
							B	N	
							Si	Al	
							C	B	
						(Ref. 11)	Sn		
							C		
							Ge		
							Si		
							(Ref. 13)		
		Vacancy							
Linear	Edge Dislocation Core. Intersection of three grain boundaries				—				
Bi-dimensional	Interfaces (inclusions, particles, grain boundaries, clean internal surface (void))				Interfaces, grain boundaries, or internal surfaces with adsorbed repellers (segregations, <i>e.g.</i>)				
Volumic	Voids Cracks Particles dissolving hydrogen				Inclusions, particles, phases that: — do not dissolve hydrogen — induce compressive stresses in the surrounding matrix				

of iron in the Periodic Table should attract hydrogen⁷ (electronic force), as should elements with a negative first order interaction coefficient,¹⁰ ϵ_H^i , or substitutional atoms of a smaller size than iron.

Physical Traps are due to a physical discontinuity of the parent lattice, where it is more energetically favorable for hydrogen to stay. Also, the term "mixed trap" was coined to designate those traps with both an attractive and physical character.³ Now, the exact counterpart of these reasons may be taken to identify hydrogen repellers and obstacles in steels:

A *hydrogen repeller* will be the opposite of an attractive trap (Figure 1), *i.e.*, a region of the lattice where a repulsive force exists. Among hydrogen repellers, one should find: (1) atoms on the right of iron in the Periodic Table, as long as they introduce (as hydrogen does) excess electrons to the collective (3d band) electron gas of the metal; (2) elements, *i.*, with a positive first order interaction coefficient: $\epsilon_H^i > 0$; (3) substitutionals of a larger size than iron that introduce a compressive stress field in the lattice; (4) defects introducing a compressive stress field in the lattice, *e.g.*, some particles, inclusions, and the extra-plane region of an edge dislocation; and (5) regions of a specimen that are cooler, or that are submitted to a compressive stress.

A *hydrogen obstacle* will be the opposite of a physical trap (Figure 1), *i.e.*, a physical discontinuity of the lat-

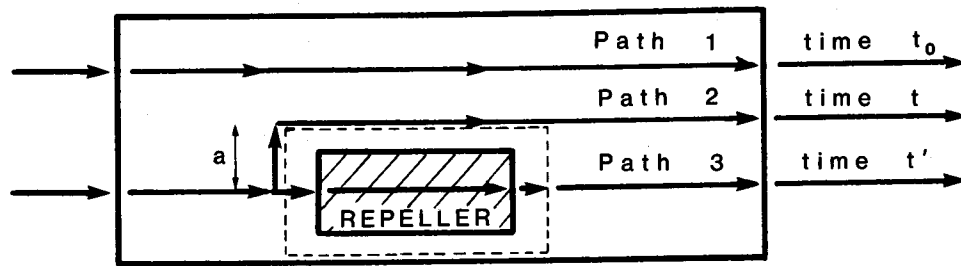
tice through which hydrogen cannot diffuse. For instance, this could be a coherent precipitate that does not dissolve hydrogen.

Table I gives examples of defects that should act as repellers or obstacles. The following remarks are in order:

Most generally, an element located on the left of iron in the Periodic Table exhibits a negative ϵ_H^i , while elements on the right of iron have a positive ϵ_H^i . Two exceptions are molybdenum and nickel. In this last case, the most recent table on ϵ_H^i ¹¹ gives a very slightly negative ϵ_H^{Ni} (-0.05) while an older one¹³ gave it a null value; as for molybdenum, contradictory information exists, since ϵ_H^{Mo} is given as being negative¹³ (-0.5) or positive¹¹ (0.15). Since both elements are not too far from iron in terms of electronic outer shells ($4d^5$ for Mo, $3d^8$ for Ni instead of $3d^6$ for iron), other effects may be important (*e.g.*, the ionic radius of Ni^{2+} is smaller than Fe^{2+} : 0.72 \AA instead of 0.76). In fact, ϵ_H^i sums up the result of several attractive forces (electronic, size, temperature, *etc.*).

Contradictory ϵ_H^i values also exist for oxygen; however, the ϵ_H^O value of the most recent reference¹¹ is much greater than that of the older one¹³ (-12 instead of 1.1), and probably more realistic.

Surprisingly, some elements that were (indirectly) suspected as hydrogen traps appear to be promising repellers: such is the case for C and N.¹⁴ In the same way, the slightly positive value of ϵ_H^H ¹¹ (1.0) should rule out the formation of

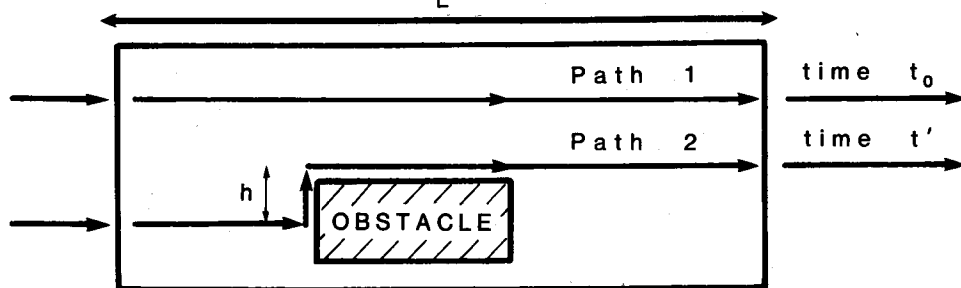


• Simple diffusion : $t_0 \simeq L^2 / D_0$

• With repeller : $t \simeq t_0 + a^2 / D_0 = L^2 / D_a$

and $D_a \simeq \left(\frac{L^2}{L^2 + a^2} \right) \cdot D_0 < D_0$

(a)



• Simple diffusion : $t_0 \simeq L^2 / D_0$

• With obstacle : $D'_a \simeq \left(\frac{L^2}{L^2 + h^2} \right) \cdot D_0$

$D_a < D'_a < D_0$

(b)

Fig. 2—Schematic of diffusion with repellers and obstacles. (a) t_0 : time to diffuse through “L”, without repeller, path ‘1’. D_0 : diffusion coefficient in perfect lattice. t : time to diffuse when hydrogen goes around the repeller, path ‘2’. t' : time to diffuse when hydrogen goes over the repeller (or inside its interaction zone), path ‘3’. a : width of the zone where the repulsive force is exerted. D_a : apparent diffusion coefficient with repeller. (b) Same as (a), with obstacle. h : width of obstacle.

H-H pairs in iron,* inasmuch as the sign of ϵ_H^i will not

*This would also be in agreement with the fact that the electronic force between H atoms should be repulsive, since each H atom introduces an excess electron in the 3d band of iron.⁷

change with temperature.

Finally, one should note that these considerations are valid for lone atoms in a perfect iron matrix. It is difficult to presume, say, the repelling role of the metalloids in Table I (P, S, As, Sb) when these preferentially segregate on grain boundaries. On the other hand, when the above condition holds, several experimental results do verify the predictions of Table I. For instance,¹⁵ Me-H complexes (where Me is a transition metal) were found in Fe-Ti and Fe-Zr alloys, while none was detected in Fe-Ni, Fe-Co, and Fe-Pd alloys (according to Table I, Ni, Co, and Pd should be repellers).

Consequences on Hydrogen Diffusion. Numerous trapping theories, e.g., Reference 22 and experimental data, e.g., Reference 2, have demonstrated that in the presence of traps, the diffusion coefficient of hydrogen through α -iron is lowered. This has often been demonstrated² using permeation experiments through a metallic membrane, in which the time of crossing is delayed by traps compared to a purer specimen.

However, it can easily be shown that if repellers or obstacles are present, the same delaying effect should be obtained. This is schematically shown in Figure 2. In Figure 2(a), the hydrogen atom may go round the repeller, and the path ‘2’ is increased by “a”, a distance proportional to the repulsive force. The hydrogen atom may also go over the repeller as in path ‘3’ (see also Figure 1). The same considerations hold for the obstacle (Figure 2(b)), but this

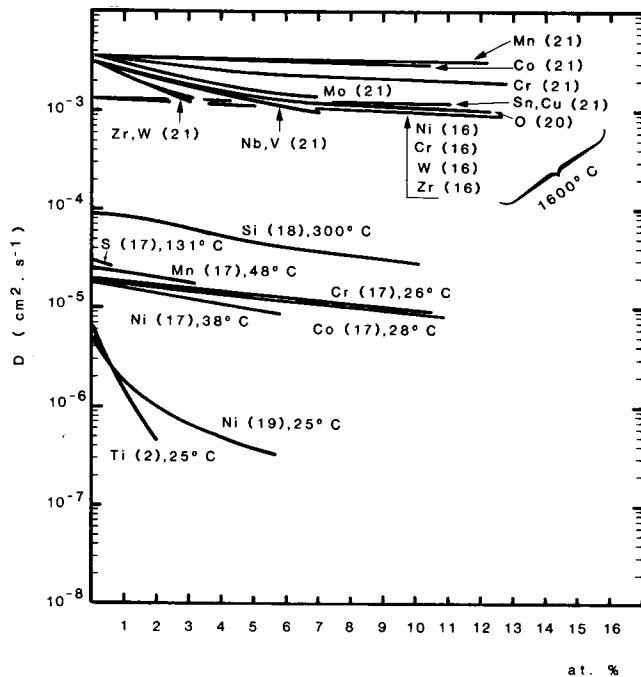


Fig. 3—Diffusion coefficients of hydrogen in iron alloyed with various elements vs temperature. References are between parentheses.

time the only possible path is to go around the obstacle. The diffusing path being increased, the diffusion coefficient should decrease by a factor that is roughly proportional to the dimensions of the defect and to the strength of the repulsive force.

The important thing here is that the sole measure of a decrease in the diffusion coefficient is not sufficient to conclude that trapping is responsible: repellers and obstacles may act the same way.

Figure 3, drawn from several references in the literature, stresses this point: cobalt, tin, copper, nickel, and silicon that are tabulated as repellers (Table I) decrease the diffusion coefficient, as well-known traps do (Ti, Zr, Nb, . . .).

Consequences of Hydrogen Solubility. Since a repeller or an obstacle physically suppresses possible interstitial sites for hydrogen, the solubility of hydrogen in steel should decrease with increasing repellers and/or obstacle concentrations. This can readily be demonstrated for elements with a positive ϵ_H^i ,* and is a well-known experimental fact

*At constant given temperature and pressure, one has the equilibrium: $H_2 \rightleftharpoons 2H$ (dissolved) with: $a_H = k\sqrt{pH_2} = \text{constant}$. Since¹⁰ $a_H = \text{activity of } H = \gamma_H X_H$ and since $\ln \gamma_H = \ln \gamma_H^0 + \sum_{i=2}^n \epsilon_H^i X_i$, with $\gamma_H^0 = \text{activity coefficient}$ and $X_i = \text{atom fraction of element "i" added to steel}$, one gets in the case of only one element "i" added: $a_H = \gamma_H^0 \cdot \exp(\epsilon_H^i X_H) \cdot X_H = \text{constant}$; and if $\epsilon_H^i < 0$, an increase in X_i must result in an increase of X_H to keep a_H constant. If $\epsilon_H^i > 0$, an increase in X_i will result in a decrease of X_H . The greater the value of ϵ_H^i , the greater the effects.

whenever compressive stresses are present. On the contrary, hydrogen solubility should increase with trapping.

The above conclusions are well illustrated in Figure 4, from Reference 13: elements with a positive ϵ_H^i (repellers) decrease hydrogen solubility, while elements with a negative ϵ_H^i (traps) increase it. Similar data may be found elsewhere, at lower temperature.^{25,26}

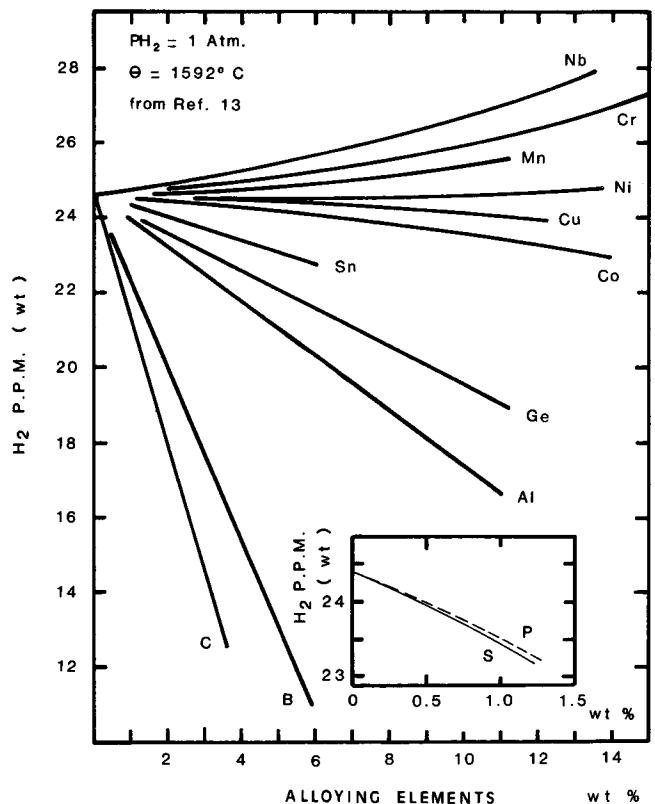


Fig. 4—Solubility of hydrogen in liquid iron vs alloy content (from Ref. 13).

Hence, it becomes imperative, when performing trapping experiments using such techniques as the permeation technique, to add solubility measurements before concluding about a trapping effect.

Consequences on Hydrogen Embrittlement. Inasmuch as a repeller or an obstacle will both delay hydrogen diffusion through steel and reduce its solubility, one could expect a beneficial effect of these defects on hydrogen embrittlement.

Indeed, it is remarkable that many elements called herein repellers have been recognized^{23,24} as "beneficial additions" when trying to establish correlations between hydrogen embrittlement and chemical composition; this is the case for silicon, aluminum, cobalt, palladium, gold, platinum, silver, and sometimes copper.

On the other hand, other elements classified as repellers (Table I) have been recognized or suspected as detrimental: carbon and various metalloids, for instance (S, P, As, Sb . . .). However, it can be argued in this case that these elements rarely exist as lone atoms in the matrix, and may not act as predicted; indeed, they readily form particles (carbides), inclusions (sulfides), or segregate to interfaces and boundaries (*i.e.*, they are not dissolved in the matrix: P, As, Sb . . .).

In any case, the addition of repellers is worth trying as a solution to hydrogen embrittlement.

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REFERENCES

1. M. Aucouturier, G. Lapasset, and T. Asaoka: *Metallography*, 1977, vol. 10, p. 133.
2. G. M. Pressouyre and I. M. Bernstein: *Metall. Trans. A*, 1978, vol. 9A, p. 1571.
3. G. M. Pressouyre: *Metall. Trans. A*, 1979, vol. 10A, p. 1571.
4. R. Gibala: *Trans. TMS-AIME*, 1967, vol. 239, p. 1574.
5. C. A. Wert: *Hydrogen in Metals II*, 1978, Springer-Verlag, New York, NY, p. 305.
6. J. P. Hirth: *Metall. Trans. A*, 1980, vol. 11A, p. 861.
7. J. Friedel: *Ber. Bunsenges. Ges.*, 1972, vol. 76, p. 828.
8. J. C. M. Li, R. A. Oriani, and L. S. Darken: *Zeitschrift für Physik Chemie Neue Folge*, 1966, Bd. 49, Heft 314, p. 271.
9. M. Shibata and K. Ono: *Mat. Sci. Eng.*, 1978, vol. 34, p. 131.
10. C. H. P. Lupis and J. F. Elliott: *Acta Met.*, 1967, vol. 15, p. 265.
11. G. K. Sigworth and J. F. Elliott: *Metal Science*, 1974, vol. 8, p. 298.
12. P. J. Depuydt and N. A. D. Parlee: *Metall. Trans.*, 1971, vol. 2, p. 612.
13. M. Weinstein and J. F. Elliott: *Trans. TMS-AIME*, 1963, vol. 227, p. 382.
14. J. Au and H. K. Birnbaum: *Scripta Met.*, 1981, vol. 15, p. 941.
15. H. Kronmüller: *Phil. Mag. B*, 1978, vol. 37, p. 569.
16. G. W. Hong, J. Y. Lee, and B. T. Lee: *Arch. Eisenhüttenwes.*, 1982, vol. 53, p. 259.
17. K. W. Lange and H. J. Köning: in *2nd Int. Conf. on Hydrogen in Metals*, P. Azou, ed., Pergamon Press, 1977 (Paris), Paper No. 1A5.
18. V. I. Saliy, R. A. Ryabov, and P. V. Gel'd: *Fiz Metal. Metalloved.*, 1973, vol. 35, p. 119.
19. W. Dresler and M. G. Froberg: *JISI*, 1973, vol. 211, p. 298.
20. I. V. Gavrilin, G. S. Ershov, and V. M. Bychev: *Steel in the USSR*, 1973, p. 494.
21. G. S. Ershov and A. A. Kasatkin: *A. N. SSSR, Metall.*, 1977, p. 82.
22. G. M. Pressouyre: *Acta Met.*, 1980, vol. 28, p. 895.
23. See *Proceedings of First International Conference on Current Solutions to Hydrogen Problems in Steels*, C. G. Interrante and G. M. Pressouyre, eds., November 1982, Washington, DC, ASM, Metals Park, OH, pp. 18 and 159.
24. B. E. Wilde, C. D. Kim, and J. C. Turn, Jr.: *Corrosion NACE*, 1982, vol. 38, p. 515.
25. B. T. Lee, J. Y. Lee, and S. H. Hwang: *Arch. Eisenhüttenwes.*, 1982, vol. 53, p. 71.
26. W. Beck, J. O'M. Bockis, M. A. Genshaw, and P. K. Subramanyan: *Metall. Trans.*, 1971, vol. 2, p. 883.