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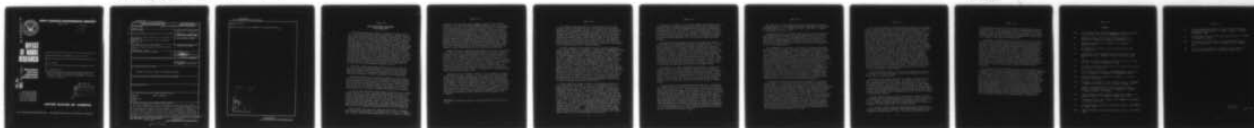
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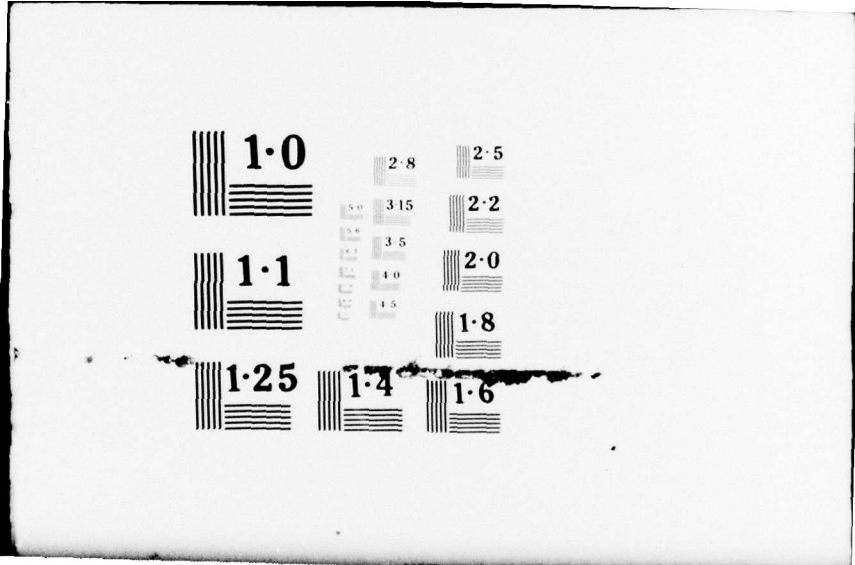
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HYDROGEN-IN-METALS CONFERENCE, PARIS, JUNE 1977
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21 SEPTEMBER 1977

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Second International Congress on Hydrogen in Metals was held in Paris, 6-10 June 1977. This report presents a review of a few important papers. Most of the papers were related to applied problems. In particular, problems of H-related damage to engineering alloys were treated extensively. In addition to work on H in pure metals such as Pd, Nb, and other transition metals, some work was also reported on H in alloys such as Nb-Ti, Pd-Ag and various steels. Storage of H in intermetallic compounds such as FeTiH _x or LaNi ₅ H _x was of great		

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interest because of their importance as energy converters.

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HYDROGEN-IN-METALS CONFERENCE,
PARIS, JUNE 1977

The Second International Congress on Hydrogen in Metals, held in Paris from 6 through 10 June 1977, was very much an international affair, with several countries making important contributions. With 200 papers and over 300 attendees, the Conference also reflected the vast increase in interest in the problem of hydrogen in metals, especially from the point of view of the basic research groups. Slightly over half the papers presented were related to applied problems, especially H-related damage to engineering alloys, and the rest of the papers were concerned with various aspects of unraveling the structural and dynamical characteristics of metal-hydrogen systems. While the majority of basic work reported was done on H in pure metals, such as Pd, Nb, and other transition metals, some work was also reported on H in alloys such as Nb-Ti, Pd-Ag, and steels. Intermetallic compounds, in particular FeTiH_x and LaNi_5H_x , were of immense interest because of their importance for H storage for use in H-based energy converters. The basic research problems receiving the most attention were associated with the location of the interstitial H, the way in which the H modified the metal lattice, and the diffusive behavior of the H.

There were several review papers on the use of H as a fuel, and they reflected a well-balanced analysis of the virtues and vices of H-fuel with emphasis on the fact that H represents an excellent fuel that poses relatively few technical problems and can easily compete with storage batteries, although not gasoline, as an energy source.

The following part of this review will consist of a brief discussion of a few of the papers to give the reader some idea of the topics of current interest to specialists in this field. No attempt has been made to evaluate the work critically, in part because even the specialists are not in total agreement on many of the ideas. At the end of this review there is a list of titles and authors that will give additional insight into the types of problems associated with H in metals.

One of the most interesting metal-hydrogen systems consists of metals such as Pd, Nb, V, Ta, etc., into which large amounts of H can be dissolved. The H-atoms occupy interstitial sites in the metals and, as a first approximation, the system is much like a lattice gas where the particles move about from cell to cell in the lattice. At lower temperatures the lattice gas undergoes phase transitions which are analogous to gas-liquid-solid phase transitions. The phase diagrams of the pure-metal-with-H systems are fairly well established, but the physical reasons for the phase diagram's characteristics are still not understood.

Several papers criticized the "widely-accepted" model of Brodowsky that suggested that the limit of H-solubility in Pd is due to a combination of ideal configurational entropy effects plus an increase in chemical

potential as the electrons from the added H tend to fill the d-band of the host Pd. W.A. Oates and R. Ramanathan (2A11*, Univ. of Newcastle, Australia) preferred to use a model in which the filling of the Pd d-band is not essential and the configurational entropy effects are primarily responsible for the characteristics of H in Pd or in Pd alloys with Ag, a case where the Brodowsky model fails. R.B. McLellan (2A7, Rice Univ., US) also criticized the Brodowsky model on the grounds that the diffusive behavior of H in Pd did not show any marked changes when the d-band supposedly became full, and McLellan also proposed to explain the system's behavior solely on the characteristics of a configuration where H simultaneously occupied octahedral and tetrahedral interstitial sites. This model was not, however, able to explain all of the thermodynamic properties of the Pd-H system such as the strong variation of the partial enthalpy of H with H concentration at very low-solute concentrations.

Examining the same problem from a different point of view, R. Griessen *et al* (2C7, Vrije Univ., the Netherlands and Univ. of Toronto, Canada) presented data on the de Haas-van Alphen effect in Pd-H alloys where they proposed to have measured the changes in the Fermi surface of Pd as H was added. They interpreted their data to show that the addition of H did not alter the part of the Fermi surface associated with the Pd d-band, and thus they concluded as false the concept of having the Pd d-band filled as H is added, i.e., an important aspect of the Brodowsky model. These ideas are not completely new, but they represent a growing amount of evidence that does not agree with the rigid-band model of the Pd-H system, which features electrons from the H contributing to the mainly d-like states near the Fermi energy in Pd.

The problem of the electronic structure of the H impurity in a metal is seemingly very simple because H is such a simple atom; however, there seems to be no complete and comprehensive description of the electronic structure of H in metals that explains the results of the wide variety of experiments which measure some features of the electron density around the H impurity. Briefly the problem is related to whether the electron-charge density is highly localized around the H, or whether it is delocalized to the extent that the charge density from the H contributes to the band states of the host metal. The situation is complicated by the fact that most of the cases of interest have transition-metal hosts where the s-like and d-like bands are quite different in their response to the H impurity.

*The label in parentheses refers to the paper listed at the end of this review.

An excellent review was given by P. Langlart (M2, Univ. of Lille, France) in which he discussed the case of H in metals and the equally important case of H on metal surfaces. His conclusion was that the H-in-metals case is solved and the H-on-metal surfaces is not. Not all participants agreed that the problem was completely solved for H-in-metals, although this could represent a naturally cautious attitude since the problem had supposedly been "solved" earlier, albeit not in any quantitative detail. Current models take into account the s- and d-bands of transition metals and are also able to explain the fact that rare-earth metals behave quite differently toward H than do transition metals because of the localized state for H in rare-earth metals.

The phase diagrams for pure materials with H seem well established except for some details. For example, T. Schober (1D2, Festkörperforschung Jülich, Germany) presented a Ta-H phase diagram based on differential thermal analysis, and he suggested some new features such as a tetragonal or pseudotetragonal so-called ϵ phase between 10°C and 50°C and 40 and 60 at.% H. Presumably there is a second low-temperature phase around 75% with a nominal composition of Ta₄H₃. The DTA phase diagram also suggests the existence of a TaH-like low-temperature phase between 0° and -60°C. The highest concentrations obtained were around 82 at.%, and a TaH₂ phase was not observed, although dihydride phases are readily observed in Nb and V. J.M. Welter *et al* (1D3, Festkörperforschung, Jülich, Germany) presented a revised Nb-H phase diagram which represented improvements in the phase boundary locations, and they also noted a low-temperature NbH-like phase as was reported for the Ta-H system. Welter *et al* discussed the α and α' phases, both of which have the bcc structure and differ only in lattice parameter according to the various H concentrations. They claimed the α - α' phase transition is now understood very well on the basis of the elastic interaction between disordered H interstitials via their long-range elastic displacement field.

In most cases only a small fraction of the interstitial sites in a metal are actually occupied by H. There is considerable interest in learning which sites are occupied and how the crystal structure is affected when certain types of sites are fully occupied. H. Asano and M. Hirabayashi (1D6, Tohoku Univ., Japan) discussed their recent neutron diffraction work on β -VH_x ($0.4 \leq x \leq 0.8$) and β -V₂D where they have concluded that H atoms do indeed locate at Z-type octahedral sites in β -V₂H as had already been verified for β -V₂D. It is not a straightforward matter to assume the location of D in the deuteride is the same as the location of H in the hydride because the phase diagrams do have significant differences. J. Hauck (1D1, Festkörperforschung, Jülich, Germany) had examined the V-H and V-D systems and offered an explanation for the substantial differences in the phase diagrams for the two systems: The electrons near the D-atoms are better localized because of the smaller thermal motion, thus their concentration near the D-atom is increased. These effects and others were quantified and used to discuss the thermodynamic stability of the various phases of V-H and V-D.

E.T.C. Ho *et al* (2B3, Univ. of Toronto, Canada) had examined the problem of hydride precipitation, and they reported on electron microscope studies of the $\beta \rightarrow \alpha$ phase transformations in Pd-H down to temperatures of approximately 85 K. (The α phase is a low H-concentration solid solution of H in Pd, and the β phase is a similar structure having a higher H concentration and a larger lattice constant.) By carefully controlling the purity of their thin foils, they were able to estimate the position of the coherent phase boundary to be ~ 160 K below the incoherent phase boundary.

Because of H-storage applications, there was considerable interest in the properties of intermetallic compounds, especially FeTi. O. de Pous and H.M. Lutz (1E8, Battelle, Switzerland) correlated the occurrence of hydride formation with interatomic distances and electron density that are characteristic of the structure and the stability of the initial intermetallic compound. The existence of binary and ternary hydrides could be predicted. However, a good material for H-storage must absorb and desorb H at convenient temperatures, typically a few degrees above room temperature, and the rates of absorption-desorption must be high. These characteristics were not dealt with, and they represent a much more difficult problem than predicting the formation of hydrides. However, empirical models such as that of de Pous and Lutz are important initial steps at predicting which materials are best for certain applications.

E. Lebsanft *et al* (1E10, Festkörperforschung, Jülich, Germany) discussed FeTi properties strictly from the point of view of a practical H-storage material, and they described a commercially available H-storage container which can be charged at 60 bar and features important safety aspects such as a low operating pressure of 5 to 30 bar and slow release of the H if the vessel is ruptured. Their 1.8 liter storage vessel contained 1.5 Mm³ of H₂ at STP. They also emphasized that the selective solubility for H of the FeTi resulted in a very high purity of desorbed H₂ gas.

The rate at which an H-storage material will absorb H is determined by a complex blend of dissociation rate for H₂ \rightarrow 2H, particle size, and bulk diffusion rate for the H. Materials such as FeTi and LaNi₅ typically become very brittle and expand due to absorption of H so that the initial hydrogenation produces a powder which contains a large number of particles, thus facilitating H absorption. This powdering and the complications of surface effects make it difficult to measure the diffusion coefficient of H in storage materials by using conventional methods. A variety of techniques were used to measure H diffusions. G. Busch *et al* (1D7, Lab. für Festkörperphysik, Switzerland) used neutron inelastic scattering to study the dynamics of the H-atoms in LaNi₅H₆, but they had no explanation as to why their value of 2×10^{-6} cm²/sec for the diffusion coefficient of H at room temperature was an order of magnitude faster than observed by other researchers using NMR techniques.

H.C. Carter *et al* (1F12, National Bureau of Standards, US) reported on NMR measurements of H in FeTiH_x and concluded the diffusion coefficient was rather low at $D \lesssim 10^{-11} \text{ cm}^2/\text{sec}$ in the $x = 1$ and the $x = 2$ phases at temperatures from 130 to 320 K.

The diffusion of H in pure metals such as Nb, Ta, and V has attracted considerable attention because of the very rapid diffusion (10^{15} times more rapid than O, N, or C at room temperature for H in V and Nb!), the possibility of quantum mechanical effects on diffusion (especially in Nb), the very curious change in activation energy of diffusion at about 250 K for Nb, and the nonclassical relationship between the observed diffusion of H as compared to D.

H.K. Birnbaum *et al* (1B1, Univ. of Illinois, US) presented diffusion data for H, D, and T in Nb. They used the Gorsky effect where the diffusion coefficient is determined from the time response of a sample of metal to an applied strain gradient. (This technique is very popular for studying H diffusion because it avoids problems associated with the transport of H across solid-gas interfaces.) The ratio of the diffusion coefficients for deuterium and tritium was very close to the classically expected ratio of $\sqrt{3}/2$ and both isotopes exhibited the same activation energy. The \sqrt{m} behavior was not observed when comparing the diffusion of H with respect to D and the activation energy for H was 0.08 eV compared to 0.13 eV for D and T. Birnbaum *et al* interpreted these results as unambiguous evidence for quantum effects. They went on to discuss the possible geometry of the H motion where they envisioned that at low temperatures the H interstitial tunnels from site to site in a ring of tetrahedral and trigonal sites. Actual bulk diffusion corresponds to a phonon-assisted tunneling between rings which have a tetrahedral site in common. They suggested that the ring-to-ring motion corresponds to quantum-mechanical diffusive motion described by the Flynn-Stoneham calculation.

In recent years there has been controversy regarding the existence of a deviation in the diffusion coefficient of H in Nb at a temperature of about 250 K. It has recently been suggested that other interstitials such as oxygen and nitrogen play an important part in trapping H-interstitials and greatly altering their diffusive behavior. F.M. Mazzolai and R. Franco (2C1, CNR, Italy) studied the effects of oxygen doping on the diffusion of H in Nb, a project which complements earlier work by Alefeld and co-workers, who found that N-impurity levels higher than 0.29 at.% suppressed the deviation in H-diffusion behavior at 250 K. Quite surprisingly, Mazzolai and Franco found that oxygen concentrations as high as 0.76 at.% did not result in suppression of the deviation. They also noted that for most of their data the deviation from Arrhenius behavior occurred at temperatures higher than the solvus temperature so that it could reasonably be inferred that the deviation is not associated with hydride precipitation. Hydride precipitation has been frequently used as a possible explanation for the unusual diffusive behavior of H in Nb.

One of the most important engineering problems related to H in metals is that of metal fracture which is enhanced by the presence of H. Hydrogen induces embrittlement in various kinds of nonferrous metals and their alloys by forming hydrides which are soft and brittle as compared to the matrix material. Hydrogen-embrittlement appears in steel and iron alloys frequently as the H-induced delayed fracture, in which no hydride formation is observed and with a very low-average concentration of H. F.W. Fujita (2B10, Osaka Univ., Japan) presented a theory of H-induced delayed fracture of steel that started from the electronic structure, bonding nature, and other related properties of the H and Fe system. The theory was based on platelet clustering of H, similar to what is known to happen for carbon and nitrogen, which form platelet-like clusters and precipitates associated with dislocation loops. The carbides or nitrides resist crack initiation; however, the H-cluster, according to the model, could be a crack initiator. Fujita suggested that a cluster of H can be formed in the lattice with the aid of applied tensile stress, for example, at the tip of an existing crack. He then suggested that the conduction electrons must be repelled more or less from the cluster region because of lattice expansion and bonding level formation. The H-atoms in the cluster region would then closely resemble adsorbed H-atoms. The repulsion of conduction electrons from the cluster region would diminish the iron lattice bonding to a considerable extent. In addition, a more severe reduction in the lattice cohesion could be expected by the conversion of s-type H-adatoms to r-type H-adatoms.

Apparently H-embrittlement is still not well understood on the atomic scale, and Fujita's work represents a step in the right direction, but further work is certainly needed.

There were several papers reporting the effects of H-bearing environments on various engineering materials. For example, A. Ikeda *et al* (4A7, Sumitomo Metal Ind., Ltd., Japan) examined pipeline steel under wet hydrogen sulfide. They observed that the addition of a small amount of copper prevents the absorption of H. They also observed that sulfide-stress-corrosion-cracking hardly occurs in steels free of hydrogen-induced-cracking; on the other hand, hydrogen-induced-cracking, which could cause failure without external stress, frequently occurs in steel free of sulfide-stress-corrosion-cracking.

P. Mayer and D.P. Dautovich (4A10, Ontario Hydro, Canada) discussed a method for measuring the H-permeability of several steels used in nuclear reactor systems. They were particularly interested in the case where the H is dissolved in water, and they concluded that the steels were less permeable to H from water because of an oxide formation.

C.S. Kortovich and P.A. Clarking (3B11, TRW and Office of Naval Research, US) dealt with the problem of inhibiting H-embrittlement in steels by adding rare-earth metals Ce or La. Their results indicated that an

order-of-magnitude reduction in crack growth could be obtained in high rare-earth steel. It is important to note that maximum improvement was obtained only at the high rare-earth levels (e.g., 0.16 wt.%) for both elements. There was little difference in the performance of Ce compared to La additions, and there was a slight (4%) decrease in strength properties because of the high rare-earth additions.

Daimler-Benz in Germany and the city of Provo, Utah, US have demonstrated that metal-hydride storage systems will work for bus applications. K.D. Beccu (6Bl, Battelle, Switzerland) discussed the requirements of automotive and stationary hydrogen-storage applications such as for off-peak energy storage from large power sources. He concluded that while there is no chance to substitute H for gasoline, metal-hydride energy storage is considerably better than batteries: energy storage densities are much higher with metal hydrides than with even the most advanced storage batteries, the capital cost of a H/metal hydride power system would be below that of even the low-cost Pb/PbO₂ storage batteries, the running costs for H-powered cars would be below that of battery-powered cars because of lower charges of capital cost amortization, and Beccu also claimed the H-system to be more flexible than battery power because of the variety of ways of generating H, either electrolytically or chemically.

The general tone of the Conference was that there are many interesting and practical aspects of the H-metal system to be explored and explained. To emphasize this, two more H-in-metal conferences were announced, 1978 in Japan and 1979 in the US, and a representative of the US National Bureau of Standards made a request that copies of all H-in-metal papers be sent to the NBS to aid in their compilation of a H-in-metals data summary. There will also be a H-in-metals conference in Oslo in August 1977 that represented competition with the Paris meeting in a sense, and the preliminary information on the Oslo meeting indicates it will also be well attended—especially by the basic research groups—although there will be some duplication. It is certainly obvious that the H-in-metals problem is receiving a large share of attention by metals scientists and that considerable progress is being made toward achieving an understanding of the various metal-H systems. The 10-volume *Proceedings of the 2nd International Congress* will be published soon by Pergamon Press.

APPENDIX

- 2A11 On the interpretation of the thermodynamic properties of hydrogen in Pd-Ag alloys. W.A. OATES, R. RAMANATHAN - Australia
- 2C7 De-Haas-van Alphen effect in palladium-hydrogen alloys. R. GRIESSEN, W.J. VENEMA, J.K. JACOBS, F.D. MANCHESTER - FRG
- M2 Structure électronique de l'hydrogène dans les métaux. P. LANGLART - France
- 1D2 The TaH-system: structures, phase diagram and morphologies. T. SCHOBBER - FRG
- 1D3 Investigations on the phase diagram of the Nb-H system. J.M. WELTER, M.A. PICK, T. SCHOBBER, J. HAUCK, H.J. FENZL, H. WENZL - FRG
- 1D6 Hydrogen (deuterium) location and tetragonal distortion in βVH_x and $\beta\text{V}_2\text{D}$. H. ASANO, M. HIRABAYASHI - Japan
- 1D1 About the different structural behaviour of hydrogen and deuterium in vanadium. J. HAUCK - FRG
- 2B3 The P \rightarrow J phase transformation in palladium-hydrogen alloys. E.T.C. HO, H.A. GOLDBERG, G.C. WEATHERLY, F.D. MANCHESTER - Canada
- 1E8 Hydrogen absorption on intermetallic compounds. O. de POUS, H.M. LUTZ - Switzerland
- 1E10 Properties of Fe-Hydrides used for hydrogen storage. E. LEBSANFT, G. ARNOLD, K.H. KLATT, M.A. PICK, J. TOPLER, H. WENZL - FRG
- 1D7 Hydrogen in La-Ni compounds: Localization and diffusion. G. BUSCH, L. SCHLAPBACH, W. THOENI, TN. v WALDKIRCH, P. FISCHER, A. FURRER, W. HAELG - Switzerland
- 1F12 Nuclear magnetic resonance studies of diffusion in FeTiH_x . R.C. BOWMAN, A. ATTALLA, G.C. CARTER, Y. CHABRE - USA, France
- 1B1 Hydrogen mobility in B.C.C. metals. H.K. BIRNBAUM, G. MATUSIEWICZ, C.G. CHEN, P. ZAPP - USA
- 2C1 On the diffusion coefficient of hydrogen in niobium. F.M. MAZZOLAI, R. FRANCO - Italy
- 2B10 Theory of hydrogen induced delayed fracture of steel. F.W. FUJITA - Japan

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- 4A7 On the hydrogen-induced cracking of line pipe steel under wet hydrogen-sulfide environment. A. IKEDA, Y. MORITA, F. TERASAKI, M. TAKEYAMA - Japan
- 4A10 Hydrogen entry into alloys from high temperature water. P. MAYER, D.P. DAUTOVICH - Canada
- 3B11 The effect of rare-earth additions on hydrogen embrittlement in high-strength steel. DR. C.S. KORTOVICH, DR. P.A. CLARKING - USA
- 6B1 The use of metal hydrides for hydrogen storage in automotive and stationary applications. K.D. BECCU - Switzerland

END

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