

which was not rotated, showed an increase of only  $4.4 \times 10^{14} \text{ cm}^{-3}$ . At intermediate rotation rates, the depth of the skin at the crystal surface, which remained unchanged by annealing at  $475^\circ\text{C}$ , increased rapidly with decreasing rotation rates.

The cause of the above described changes in resistivity is not at present understood. It is evident that the effect is intimately associated with the crystal growing process, but whether it involves lattice defects or impurities or both must await further work.

C. S. FULLER  
J. A. DITZENBERGER  
N. B. HANNAY  
E. BUEHLER

Bell Telephone Laboratories  
Murray Hill, New Jersey

#### References

1. H. C. Theuerer and J. H. Scaff, *J. Metals* **191**, 59 (1951).
2. C. S. Fuller and J. D. Struthers, *Phys. Rev.* **87**, 526 (1952).
3. G. K. Teal and J. B. Little, *Phys. Rev.* **78**, 647 (1950).
4. G. L. Pearson, Private communication.

\* Received June 21, 1954.

### The Diffusion of Hydrogen in Iron and Ferritic Steels\*

The evolution of hydrogen from iron and ferritic steels has been reported by many investigators<sup>1,2,3</sup> to differ markedly from the behavior predicted by the usual diffusion laws. Mathematical descriptions of the evolution rate have been found to require at least two distinct rate constants differing from each other by several orders of magnitude. In some cases the hydrogen diffusing at the lower rate is termed "residual" to distinguish it from the more mobile "diffusible" hydrogen, and its rate constant is approximated as zero.<sup>2</sup> Some authors have suggested essentially that the "residual" hydrogen is partially converted into "diffusible" hydrogen on heating, but that it does not disappear completely until after traverse of the alpha-gamma transformation.<sup>1</sup>

This nonconformity of the evolution rate with diffusion theory is apparently responsible in large measure for the widespread past use of strictly empirical expressions for representing the rate of hydrogen evolution from steel. Slowly diffusing or "residual" hydrogen has not always been detected, however, and in these cases the evolution rate appears to conform satisfactorily with the theory. Thus Sykes, Burton and Gegg<sup>4</sup> reported that both their own evolution rate data and those of Andrew *et al*<sup>5</sup> are consistent with the diffusion laws, despite the substantial quantity of "residual" hydrogen postulated by the latter authors as necessary in mathematical representations of their data. More recently the diffusion laws have been applied to hy-

drogen in steel by Demarez, Hock and Meunier,<sup>6</sup> who, like Sykes *et al*, have dismissed the apparent presence of slowly diffusing hydrogen as a natural consequence of the manner in which the evolution rate theoretically varies with time.

We have investigated the evolution of hydrogen from 99.9 per cent pure iron by several experimental methods including that described by Demarez, Hock and Meunier.<sup>6</sup> Suitable solutions of Fick's equation for finite cylinders were obtained from Carslaw and Jaeger.<sup>7</sup> For a cylinder of length  $a$  and diameter  $b$  the solution of present interest is

$$\bar{C}/C_0 = \psi(a, t)\chi(b, t) \quad (1)$$

in which  $\bar{C}$  is the average concentration,  $C_0$  is the initial concentration and  $\psi(a, t)$  and  $\chi(b, t)$  are the respective functions for the time dependence of  $\bar{C}/C_0$  in an infinite slab of thickness  $a$  and an infinitely long cylinder of diameter  $b$ , respectively. Thus

$$\begin{aligned} \bar{C}/C_0 = & \frac{32}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-(2n+1)^2 \pi^2 Dt/a^2] \\ & \times \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \exp[-4\beta_n^2 Dt/b^2] \quad (2) \end{aligned}$$

in accordance with the derivation of Demarez *et al*.

After a relatively short initial diffusion period  $t_0$ , Eq. (2) reduces to

$$\log \bar{C}/C_0 = \log g - Dt \left( \frac{4.29}{a^2} + \frac{10.05}{b^2} \right) \quad \text{for } t > t_0 \quad (3)$$

in which  $g$  is 0.56 for finite cylinders.

As was pointed out by Demarez *et al*, the precise form of Eq. (2) is never obtained experimentally from small specimens examined at elevated temperatures because of the unavoidable hydrogen losses that occur during heating of the specimen to the experimental temperature. The diffusion coefficient  $D$ , however, is readily evaluated from the slope of the final  $\log \bar{C}$  versus  $t$  plot under a variety of conditions including those in which zero time is not precisely known and the initial concentration  $C_0$  is not uniform throughout the specimen.

The experimental evaluation of  $g$  in Eq. (3) may be approached in several ways, of which that employed by Demarez *et al*, viz., minimizing the time of heating the specimen to the experimental temperature, is one. The same effect is obtained by conducting the experiment at a sufficiently low temperature to make the heating time negligible in comparison with the total period of diffusion. In this connection we have found that extractions conducted at room temperature yield curves of theoretical form over their entire length.

The principal reason for attempting to establish agreement between experimental and theoretical values of  $g$  is apparently to validate the application of diffusion

theory. Any departure from Eq. (2) would probably result, however, from (1) non-uniformity of the initial concentration  $C_0$ , (2) control of the evolution rate by processes at the specimen surface rather than by diffusion, or (3) variation of  $D$  with concentration. The first effect does not alter the apparent or measured value of  $D$  and hence need not be considered further. The last effect can be considered to include the possible co-existence of rapidly and slowly diffusing hydrogen.

The effect of slow surface processes has been shown by Dünwald and Wagner<sup>8</sup> to be detectable from the manner in which the evolution rate varies with specimen dimensions. According to Eq. (2) the time required for evolution of a given fraction of the hydrogen from specimens of equal shape should vary directly with the square of the diameter when the evolution rate is diffusion controlled. When the rate is surface-controlled, on the other hand, this time is proportional to only the first power of the diameter. Both Derge *et al*<sup>5</sup> and Andrew *et al*<sup>5</sup> have reported in effect that the time for a given degree of hydrogen removal is proportional to the square of dimensions in specimens larger than 3/8 inch and at temperatures down to 25°C. Our own data confirm this finding, indicating that the evolution rate is entirely diffusion controlled under the conditions specified.

To permit close examination of the possible variation of  $D$  with concentration, we have employed a modified experimental procedure based on a relationship given by Geller and Sun,<sup>9</sup> of which the following form applies to finite cylinders:

$$\log(-\partial\bar{C}/\partial t) = \text{const.} - Dt \left( \frac{4.29}{a^2} + \frac{10.05}{b^2} \right) \quad (4)$$

The evolution rate  $-\partial\bar{C}/\partial t$  is actually proportional to the flow rate of hydrogen from the specimen into the collecting volume of the measuring apparatus. Hence  $D$  may be evaluated directly from the slope of a plot of  $\log$  (flow rate) versus time. This method is more precise than that involving the measurement of pressures in the collecting volume, in that  $D$  is obtained directly from a plot of the experimental data themselves rather than of small differences between large quantities.

The initial experiments were on 9/32 to 3/4 inch diameter iron specimens prepared by "thermal charging," a method of introducing reproducible quantities of hydrogen that consists of saturating in a hydrogen atmosphere at from 1000 to 1350°C, and then quenching in cold water to prevent hydrogen losses during cooling. Although the quench through the transformation is known to have caused internal stresses, the subsequent evolution of hydrogen into a vacuum appeared to be normal in all respects, yielding reproducible values of  $D$  with mean deviations of from  $\pm 10$  to  $\pm 20$  per cent. Hydrogen analysis of replicate specimens by both graphite crucible and tin vacuum fusion methods indicated, moreover, that the hydrogen had been quantita-

tively evolved from these specimens at single values of  $D$  in less than one hour at 300 to 650°C. Thus no slowly diffusing or "residual" hydrogen was evident in any of these "thermally charged" specimens.

Subsequent experiments on specimens of the same material that had been hydrogen charged by a different method have indicated, however, that slowly diffusing or "residual" hydrogen is unmistakably present in specimens of less severe thermal history than those described above. Such specimens were prepared by "pressure charging," which consists of saturating with hydrogen at 650°C under a hydrogen gas pressure of up to 75 atm. The apparatus for this purpose was patterned after that described by Hobson and Sykes.<sup>10</sup> Although quenching from the saturation temperature was employed here as well as in the previous charging method, a considerably less severe internal stress level was assured by the fact that the material remained ferritic throughout the heating and quenching cycle.

The evolution of hydrogen from the "pressure charged" specimens at 385 to 575°C exhibited a behavior that departed radically from that observed in the "thermally charged" specimens. Early in the process the evolution rate decreased in the expected exponential manner and at essentially the same rate as that observed in the thermally charged specimens. After a period corresponding to the extraction of from 80 to 90 per cent of the hydrogen in the previous specimens, however, the plot of  $\log$  (flow rate) versus time became nonlinear, indicating a decrease in the rate of change of  $\log(-\partial\bar{C}/\partial t)$ . Subsequent heating to 850°C, moreover, invariably resulted in a rapid evolution of additional hydrogen amounting to 20 to 50 per cent of the amount previously extracted in from 1½ to 19 hours at the lower temperature. The conditions and results of five of these experiments are listed in Table I, which indicates (1) that the quantity of hydrogen that is not evolved during several hours heating in vacuum de-

TABLE I. Vacuum extraction of hydrogen from 0.75 inch diameter  $\times 0.75$ -inch iron cylinders prepared by pressure charging.

Specimen Preparation: Hours at 650°C, 62-67 atm. H <sub>2</sub> pressure	18	18	14	14	21	21
Initial extraction: Temp., °C	385	480	575	575	575	990
Extraction time, hours	2.0	2.5	1.5	1.5	3.0	1.5
Hydrogen extracted, RV*	0.60	0.62	0.68	0.78	0.57	0.84
Additional extraction time, hrs.	—	—	—	—	16	—
Additional H <sub>2</sub> extracted, RV*	—	—	—	—	0.03	—
Final extraction at 850°C						
Extraction time, hrs.	1.3	1	0.75	0.75	1	—
Additional H <sub>2</sub> extracted, RV*	0.30	0.25	0.16	0.18	0.13	—
Total H <sub>2</sub> extracted, RV*	0.90	0.87	0.84	0.96	0.73	0.84

\* RV = Relative Volume = 12.72 ml/100 g = 0.00114 wt.%,

creases with increasing temperature, and (2) that continuation of vacuum treatment at 575°C for more than two hours is apparently ineffective in removing much additional hydrogen.

That slowly diffusing or "residual" hydrogen is not characteristic of "pressure-charged" specimens alone is indicated by numerous previous reports of a similar behavior in electrolytically charged steel<sup>11</sup> as well as in as-trepanned samples from massive sections of commercial steel.<sup>2</sup> If anything, "pressure-charged" specimens should be more representative of the interiors of thick steel sections containing hydrogen than any other specimens that can be prepared in the laboratory.

Although much information on slowly diffusing or "residual" hydrogen remains to be learned, the following conclusions are indicated by the data collected thus far:

1. Slowly diffusing or "residual" hydrogen is not a consequence of the theoretical time dependence of the diffusion rate but a real component or effect detectable only after the removal of the rapidly diffusing or "diffusible" hydrogen.

2. The amount of "residual" hydrogen appears to decrease as the specimen temperature is increased from 400 to 900°C.

3. The amount of slowly diffusing or "residual" hydrogen appears to depend on thermal history. Prominent quantities of this component were found in small iron specimens quenched from 650°C after heating in a high pressure hydrogen atmosphere, but not in specimens rapidly quenched from hydrogen atmosphere treatment above 1000°C. The amount of "residual" hydrogen present in commercial steel might therefore be expected to be appreciable in hot-rolled or forged heavy sections, but not in rapidly cooled materials such as weld metal deposits.

E. W. JOHNSON  
M. L. HILL

Westinghouse Research Laboratories  
East Pittsburgh, Pennsylvania

\* Received June 30, 1954.

#### References

1. G. A. Moore and D. P. Smith, *Trans. A.I.M.E.* **135**, 255 (1939).
2. G. Derge, W. Peifer, and J. H. Richards, *Trans. A.I.M.E.* **176**, 219 (1948).
3. J. Bleton, S. Mischonsniky, G. Coin, and P. Bastien, *Rev. Metall.* **48**, 471 (1951).
4. C. Sykes, H. H. Burton, and C. C. Gegg, *J. Iron Steel Inst.* **156**, 155 (1947).
5. J. H. Andrew, H. Lee, A. K. Mallick, and A. G. Quarrell, *J. Iron Steel Inst.* **153**, 67 (1946).
6. A. Demarez, A. G. Hock, and F. A. Meunier, *Acta Met.* **2**, 214 (1954).
7. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press (1947).
8. H. Dünwald and C. Wagner, *Z. Phys. Chem.* **B24**, 53 (1934).
9. W. Geller and T. H. Sun, *Arch. Eisenhüttenwesen* **21**, 423 (1950).
10. J. D. Hobson and C. Sykes, *J. Iron Steel Inst.* **169**, 209 (1951).
11. J. B. Seabrook, N. J. Grant, and D. Carney, *Trans. A.I.M.E.* **188**, 1317 (1950).

#### Electron Microscope Study of Slip Bands in Radiation-Damaged Aluminum Crystals\*

Jamison and Blewitt<sup>1</sup> studied the effect of radiation damage on copper, using light micrographs of the surface. The phenomenon studied was the density and spacing of slip lines. They showed that the density of slip lines was greater in damaged copper, other things being the same. Heidenreich and Shockley<sup>2</sup> studied slip bands in pure aluminum with the electron microscope and demonstrated that a single band may have a fine structure of several closely spaced bands which cannot be resolved by the light microscope. In the experiment reported here, the anode-oxide replication process as described in the latter paper was used to study the fine structure of slip bands in both irradiated and unirradiated aluminum.

The aluminum samples were 99.996 per cent pure. After heat-treating to increase the grain size they were abraded, electro-polished, and etched, using the procedure given by Heidenreich and Shockley.

The irradiated and the control samples were strained to produce slip lines. The usual method of strain was simple bending, carried out at room temperature, -78°C, and -196°C. The time of bending was a few seconds, and the amount was such as to produce a strain of 5 to 10 per cent at the surface. The strain was computed crudely by estimating the radius of curvature of the central part of the specimen and assuming the central plane to remain unchanged in length. Because the microscopic strains vary widely from the macroscopic strain, particularly from crystal to crystal within the polycrystalline specimen, it was felt that any effort to measure strain precisely would not be profitable at this time.

The damaged samples were obtained by alpha bombardment in the Berkeley 60-inch cyclotron. The damage was produced by 39.6-Mev alpha-particles. The average bombardment was 8  $\mu$ ah/cm<sup>2</sup>, which is equal to  $9 \times 10^{16}$  alpha-particles/cm<sup>2</sup>. The samples were kept below -100°C during and after the bombardment to prevent annealing of the damage. The temperature of one of the samples was recorded continuously by means of a thermocouple imbedded in it.

Twenty-five samples were observed, of which six had been bombarded. Each sample provided two or three replica squares, each having 50 meshes observable in the microscope. Thus the number of fields observed in the microscope was about 3000, not including faulty replicas. Of these 200 were photographed.

On the basis of the electron-microscope studies and observations with the light microscope, it is believed that irradiation at temperatures near the liquid-nitrogen point followed by straining at the liquid-nitrogen point increases the amount of slip which takes place on a given plane. The opinion is based upon the qualitative observations of many photographs similar to those in Fig. 1. Similar observations indicated no noticeable