ATOMIC HYDROGEN OCCLUDED IN IRON NITRIDE.

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Introduction. Since Savart(1) first studied in 1828 the action of ammonia gas upon iron at elevated temperature, numerous investigations on iron nitride have been reported. In 1923, A. Fry(2) invented the so-called nitriding process. By this process, or by treating the chrome aluminium steel with ammonia he obtained the hardest substance ever known in metallurgical products. This invention has stimulated the study of iron nitride. The equilibrium diagram of iron and nitrogen was partially determined by Fry,(2) B. Sawyer(3) and O. Eisenhut and E. Kaupp.(4) As the results of X-ray studies conducted by G. Hägg,(5) A. Osawa and S. Iwaizumi(6) and Eisenhut and Kaupp,(4) the existence of the compounds Fe_2N and Fe_4N was ascertained.

While investigating(7) (8) iron nitride, the author discovered the existence of atomic hydrogen in nitrided iron and the formation of so-called porous iron by the action of ammonia on compact iron. The details of the investigation are shown in the following pages.

In 1880, A. H. Allen(9) first reported the existence of hydrogen in iron nitride and in 1911 J. H. Andrew(10) also admitted the existence of the occluded hydrogen in iron nitride. In 1913, W. Herwig(11) found that the nitrogen content in molten iron did not increase when it was treated with nitrogen but increased due to the action of the mixture of nitrogen and hydrogen. But in 1929, Hägg(12) reported that he could find no traces of hydrogen in iron nitride.

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(1) Savart, *Ann. chim. phys.*, [2] **37** (1828), 326.

(2) A. Fry, *Stahl u. Eisen*, **43** (1923), 1271.

(3) B. Sawyer, *Am: Inst. Mining Met. Eng.*, **4** (1923), 356.

(4) O. Eisenhut und E. Kaupp, *Z. Elektrochem.*, **36** (1930) 392.

(5) G. Hägg, *Nova acta regiœ societates scientiarum Upsaliensis*, Ser. IV, Vol 7, No. 1.

(6) A. Osawa and S. Iwaizumi. *Z. Krist.*, **69** (1928), 26.

(7) S. Satoh, *Rev. métal.*, **26** (1929), 248.

(8) S. Satoh, *Tetsu to Hagane*, **16** (1930), 79.

(9) A. H. Allen, *J. Iron Steel Inst.*, **1** (1880), 181.

(10) J. H. Andrew, *Carnegie Schol. Memo.*, **3** (1911), 236.

(11) W. Herwig, *Stahl u. Eisen*, **33** (1913), 1721.

(12) Hägg, loc. cit.

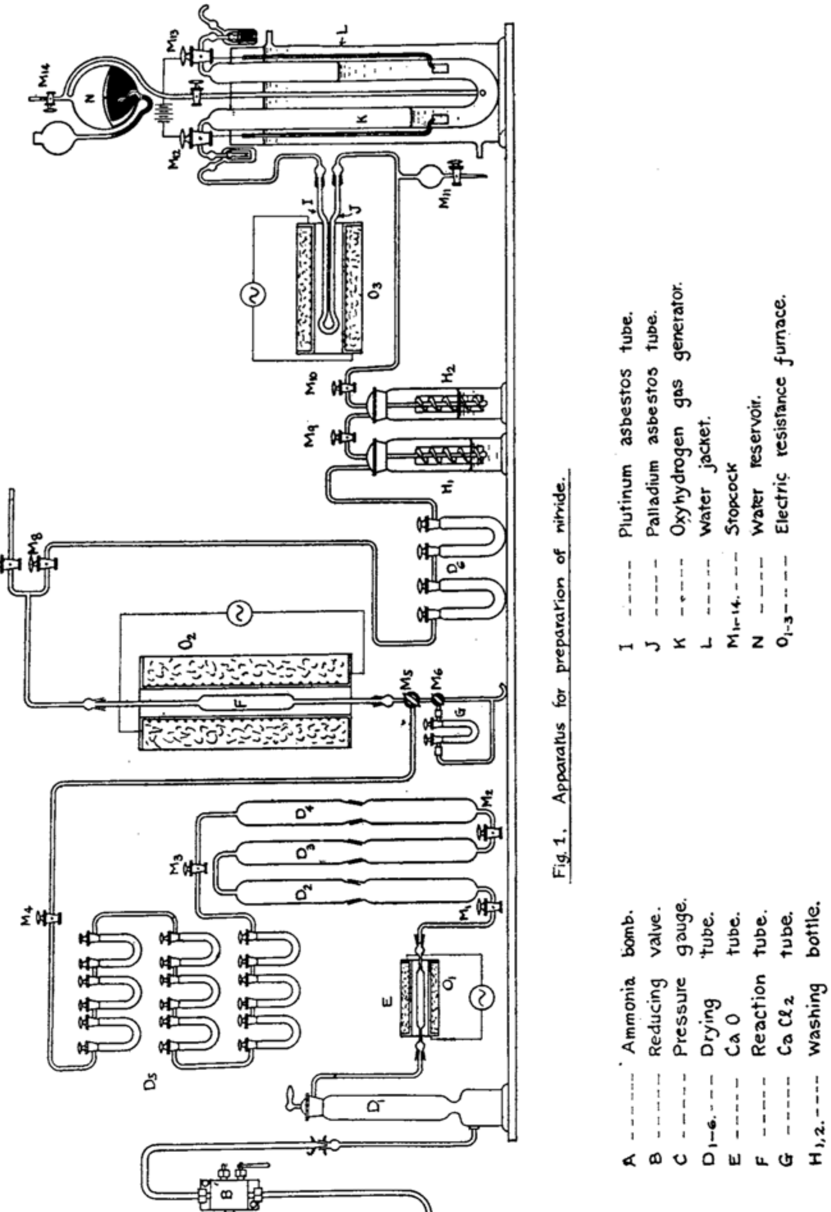
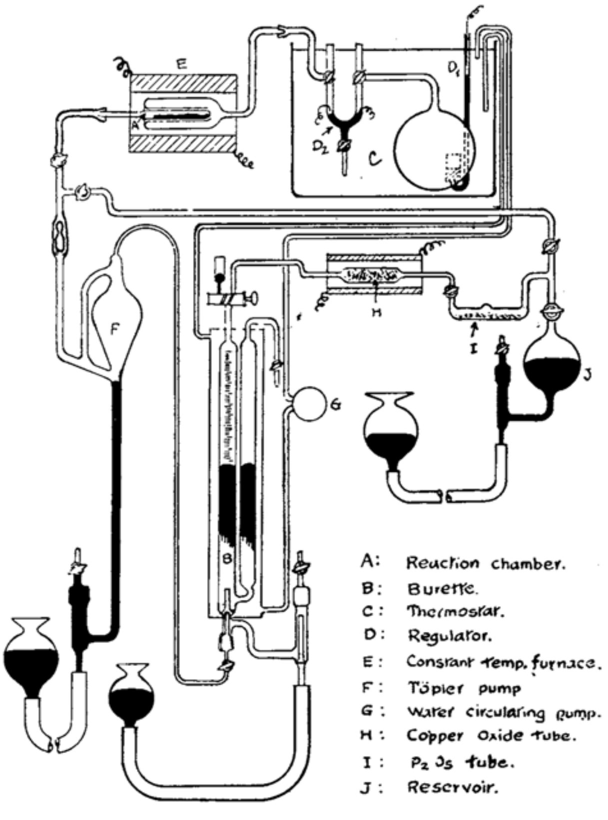


Fig. 1. Apparatus for preparation of nitride.

Fig. 1.

Hydrogen Occluded in Iron Nitride. With the object of ascertaining the existence of hydrogen in nitrided iron, the author prepared iron nitride by the use of the apparatus shown in Fig. 1. Iron oxide, which he obtained by igniting iron oxalate, was put in F and reduced with electrolytic hydrogen. Pure iron thus obtained was treated with ammonia gas at 450°C. for 250° hrs. Iron nitride which was formed in this way and which contains 9.796% nitrogen, was decomposed at 430°C. and 450°C. and analysed by means of the apparatus shown in Fig. 2. These two different degrees were chosen in order to ascertain the decomposition temperature of iron nitride and at the same time the existence of hydrogen, as Fry⁽¹⁾ re-



Apparatus for Hydrogen Determination.

Fig. 2.

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(1) Fry, loc. cit.

ported that the decomposition temperature of Fe_2N was 440°C. when he made his rapid decomposing experiment. 15.36 gr. of iron nitride was put in A and heated at 430°C. The evolved gas was analysed. Again the specimen was heated at 450°C. and the same process was repeated. The temperature was measured by means of the Pt-PtRh thermocouple standardized by the melting points of zinc and aluminium and kept constant within the range of ±0.6° by the method used by J. H. Haughton and D. Hanson.(1) The decomposed gas was collected by means of the Töpler pump into the burette B corrected with mercury at every 2 c.c. The collected gas passed backwards and forwards through the red heated copper oxide tube and phosphorus pentoxide tube by means of the mercury reservoir J. The gas thus treated was again collected into the burette B by the use of the Töpler pump and the amount of hydrogen was determined by the change of volume. The result is shown in Table 1.

Table 1.

Analysis of Gas Evolved by Heating Nitrided Iron.

Temp.	Heating time	Decomposed volume (N_2+H_2) (0°, 760 mm.)	Volume after combustion (N_2) (0°, 760 mm.)	Volume of hydrogen (0°, 760 mm.)	Volume of hydrogen per 1 gr. of sample
430°C.	97.5	23.76	22.63	1.08	0.0703
450°C.	49.0	27.10	27.03	0.02	0.0013

As may be seen from Table 1, iron nitride contains hydrogen and decomposes below 430°C.

Atomic Hydrogen Occluded in Iron Nitride. By the above experiment the author has confirmed the existence of hydrogen in iron nitride. But how hydrogen is occluded is unknown. According to Richards(2) the iron may occlude atomic hydrogen by quenching it from 1000°C. into water or by depositing it electrolytically. But nobody has ever mentioned the existence of atomic hydrogen in iron nitride. The author has confirmed the existence of atomic hydrogen in iron nitride by the following experiments.

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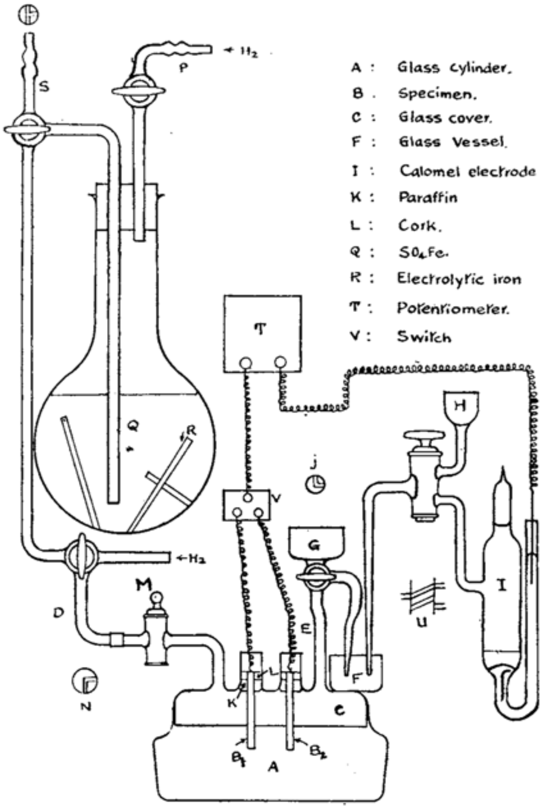
(1) J. H. Haughton and D. Hanson, *National Phys. Lab. Collected Res.*, **55** (1920), 51.

(2) T. W. Richards and G. E. Behr jr., *Z. physik. Chem.*, **58** (1907), 301.

(a) *Single Potential of Iron Nitride.* Reduced pure iron above mentioned is compressed in the form of a cylinder and nitrided at 500°C. for 4 hrs. The nitride thus formed is quickly immersed in 0.988 normal ferrous sulphate solution and the potential difference between the nitride and the deci-normal calomel electrode is measured with the Leeds and Northrup potentiometer. A deci-normalc alomel electrode was prepared by calomel, potassium chloride from Kahlbaum and mercury which has been distilled several times *in vacuo*.

The ferrous sulphate solution was prepared according to the method adopted by Richards.⁽¹⁾ Definite quantity of ferrous sulphate (Merck) was



Apparatus for Potential Determination in $FeSO_4$ Solution.

Fig. 3.

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(1) Loc. cit.

dissolved in distilled water which had been boiled *in vacuo* in the atmosphere of hydrogen. The solution, to which was added a definite quantity of sulphuric acid and pieces of electrolytic iron, was kept for about 100 days in the flask filled with hydrogen gas and covered with black paper to keep off light. The concentration of the solution was 0.988 normal which the author determined by titrating it with potassium permanganate standardized with sodium oxalate.

The measurement was carried out with the apparatus indicated in Fig. 3, which is an improved one of the apparatus reported by C. Benedicks and R. Sundberg(1): an enclosed glass cylinder A covered with black paper and containing the electrode, was filled with hydrogen gas through the tube M and then the solution of ferrous sulphate was poured in it through the tube D until it fills the vessel F. The deci-normal calomel electrode was dipped into the vessel F and the potential difference between the electrode and the deci-normal calomel electrode was measured, and as soon as the measurement was finished the deci-normal calomel electrode was taken out of the solution. As ferrous sulphate solution in the vessel F is oxidized by air, the fresh solution was poured into F through the funnel G at the beginning of each experiment. Between the vessel F and the cylinder A a glass cock was attached. By opening this cock the measurement was carried out and then the cock was closed to prevent the solution in A from being oxidized.

The deci-normal potassium chloride solution was poured now and then into the vessel H to drive away the solution mixed with ferrous sulphate at the end of the calomel electrode. In this way, the change of voltage in relation to time was measured at room temperature (24–32.7°C.) until the constant voltage was obtained. The results obtained are shown in Table 2 and graphically in Figs. 4, 5 and 6.

The author calculated the single potential differences referring to one normal ferrous sulphate solution according to the equation :—

$$\epsilon_c = \epsilon_{c.0} + 2.3026\frac{RT}{nF}\log\frac{C}{C_0}$$

where $n=2$, $T=303$, $C_0=0.988$, $C=1$. But the correction was found negligible.

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(1) C. Benedicks and R. Sundberg, *J. Iron Steel Inst.*, **44** (1926), 177.

Table 2.

Potential Measurement of Iron, Nitrided or Not, in Ferrous Sulphate.

Time in ferrous sulphate hr. m.	Nitrided iron powder (curve 1) (29.8°∼32.3°C.) volt.	Nitrided iron powder dipped in O_2 free water (curve 4) (28.3°∼31.3°C.) volt.	Nitrided iron powder dipped in water (curve 3) (29.3°∼31.7°C.) volt.	Nitrided wrought iron (curve 5) (24.0°∼26.5°C.) volt.	Wrought iron (curve 6) (29.3°∼31.7°C.) volt.
0	—	–0.3 —	—	—	—
.01	—	—	—	—	–0.7510
.02	–0.7886	—	—	—	—
.03	—	—	–0.5071	–0.8079	–0.7540
.10	–0.8470	—	—	—	—
.25	—	–0.9370	—	—	—
.40	—	—	–0.6990	—	—
1.00	—	–0.9542	—	—	—
1.23	—	—	—	–0.8544	—
1.35	–0.9023	—	—	—	–0.7683
2.00	–0.9000	—	—	—	—
2.25	—	—	–0.8295	—	—
2.40	—	—	—	—	—
4.35	—	–0.9393	—	—	—
5.10	—	—	–0.8390	–0.8486	–0.7694
17.45	–0.8481	—	—	—	—
21.50	—	–0.9279	—	–0.8465	—
22.25	—	—	–0.8403	—	–0.7681
29.00	—	–0.9326	—	—	–0.7688
42.	–0.8353	—	—	—	—
46.	—	–0.9258	–0.8383	–0.8410	—
70.	—	–0.9324	–0.8361	–0.8344	–0.7634
76.	—	—	—	—	–0.7628
94.	—	–0.9311	–0.8297	—	–0.7646
100.	–0.8028			—	—
122.	—			–0.8201	–0.7665
141.	—			–0.8122	–0.7672
168.	—			–0.8005	–0.7675
191.	—			–0.7964	–0.7630
216.	—			–0.7926	—
236.	–0.7852			—	–0.7665
289.				–0.7882	–0.7663
460.				–0.7889	

In Fig. 4, the time voltage curves of nitrided iron powder (curve 1) and of iron powder quenched into water (curve 2 quoted from the paper of Richards⁽¹⁾) show minima at their beginning. According to Richards this

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(1) Loc. cit.

minimum voltage was caused by atomic hydrogen occluded in iron, therefore it will be certain that nitrided iron powder is loaded with atomic hydrogen.

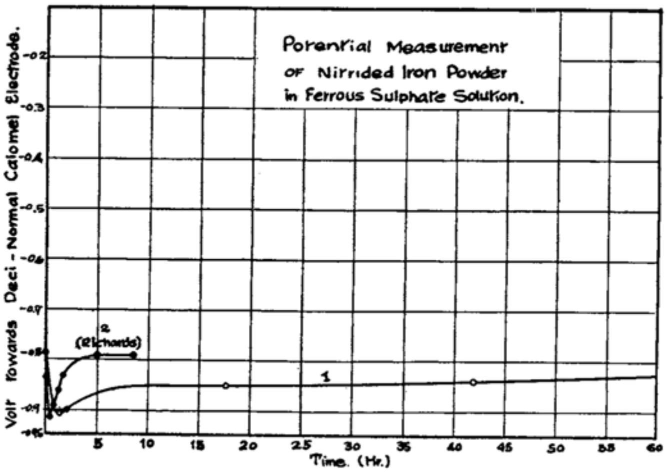

Fig. 4.

Richards[1] states that atomic hydrogen occluded in iron vanishes rapidly in ferrous sulphate solution and slowly in water. The author tested how atomic hydrogen occluded in iron nitride vanishes by the action of

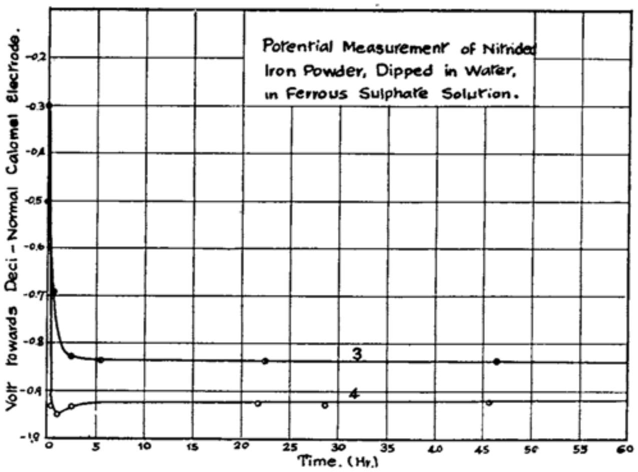

Fig. 5.

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[1] Loc. cit.

oxygen in water. For this purpose nitrided iron powder was on the one hand immersed in the oxygen free distilled water for 118 hrs. and the other in the distilled water for 90 hrs. Both of them were dried by absolute alcohol and quickly immersed in the ferrous sulphate solution and their single potentials were measured. The results obtained are indicated in Table 2 and Fig. 5. As may be seen from Fig. 5, the nitrided iron powder immersed in oxygen free distilled water (curve 4) shows minimum at the beginning, while that immersed in distilled water (curve 3) does not show it. From the above fact it may be confirmed that atomic hydrogen is oxidized by the oxygen contained in distilled water. The nitrided iron becomes black and never rusts to form red hydroxide of iron in distilled water and moreover it retains its silver white surface in oxygen free distilled water. L. Guillet and M. Ballay⁽¹⁾ reported that the nitrided special steel has great corrosion resistance in the water of the Seine.

(*b*) *Reducing Property towards Potassium Ferricyanide.* With the object of ascertaining the existence of atomic hydrogen in iron nitride, the author immersed nitrided iron in the 5% potassium ferricyanide solution after nitriding it, and after 48 hrs. he; by adding ferric chloride solution, noticed the formation of Prussian blue. This reaction takes place equally in the dark place. The reaction :

$$K_3Fe(CN)_6 \rightarrow K_4Fe(CN)_6$$

occurs due to atomic hydrogen occluded in nitrided iron. Iron loaded with atomic hydrogen by quenching it from a high temperature into water also reduces the potassium ferricyanide solution, but ordinary iron powder never reduces it. And it was observed that more Prussian blue is formed with the iron nitride immersed in the potassium ferricyanide solution directly after being nitrided than with the iron nitride which is dipped in distilled water before being immersed in the potassium ferricyanide solution.

Surface Change of Iron due to Nitriding. The results of the potential measurements of wrought iron (C=0.045%, Si=0.02%, Mn= trace, P= 0.047%, S=0.004%) and of that nitrided at 500°C. for 30 hrs. are shown in Table 2 and Fig. 6. As may be seen in Fig. 6, the time voltage curve of nitrided iron (curve 5) shows minimum due to atomic hydrogen at its beginning and remains constant finally (−0.7889 volt). This final potential difference is about 0.023 volt lower than that of iron not nitrided (curve 6). In 1913, F. Hanaman⁽²⁾ measured the single potential difference of steel that had been treated with ammonia at above 650°C. and obtained the result :

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(1) L. Guillet and M. Ballay, *Compt. rend.*, **189** (1929), 957.

(2) F. Hanaman, Dissertation Berlin, 1913.

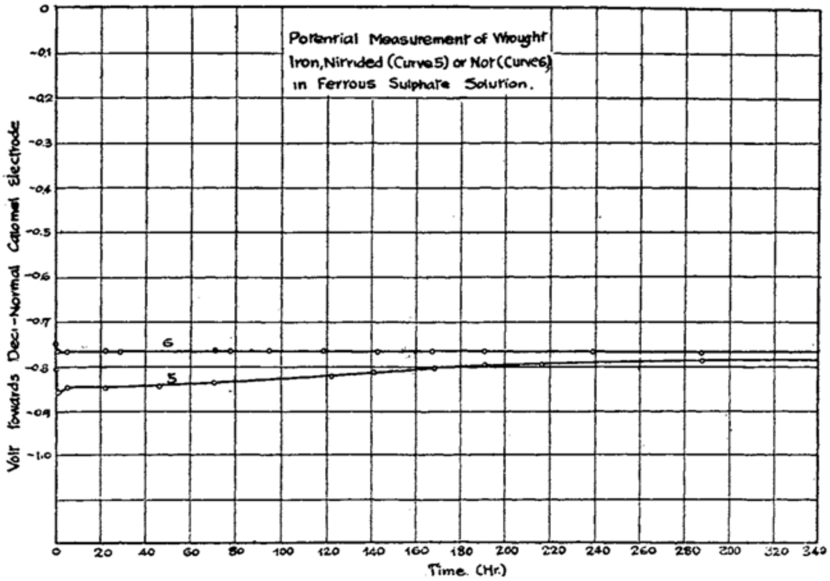


Fig. 6.

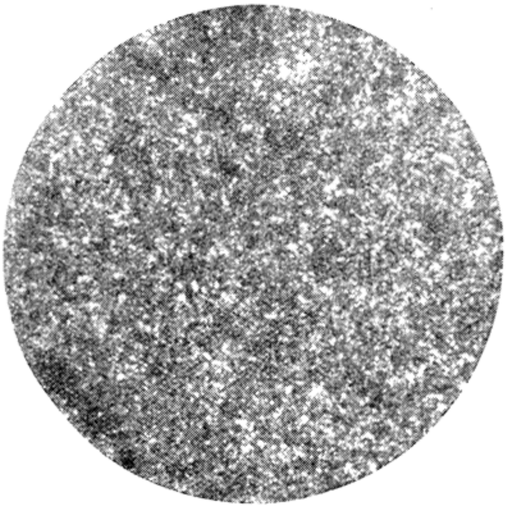
$\epsilon_h=0.51$ volt for the iron nitride. For this reason the above mentioned potential of −0.7889 volt is not that of the iron nitride but that of the porous iron which contains nitrogen as a solid solution, and therefore the potential

Table 3.

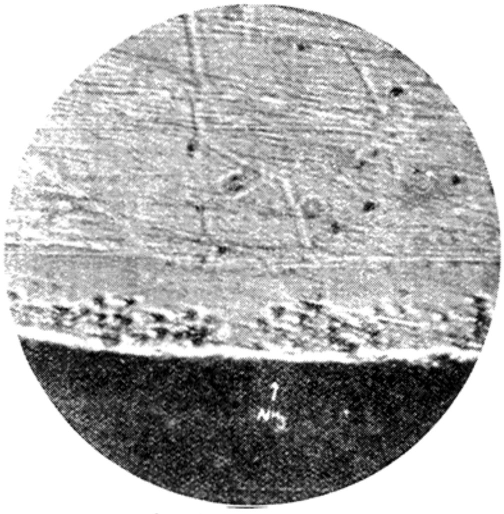
ϵ_h Values of Various States of Iron.

	T. W. Richards and G. E. Behr. (20°C.)	C. Benedicks and R. Sundberg (16°±2°C.)	Author (28°±2°C.)
Purest iron melted *in vacuo*.	−0.423	—	—
Technical pure iron.	−0.427	−0.422	−0.429
Purest porous iron containing hydrogen reduced at high temperature.	−0.442∼−0.456	—	—
The same, reduced at low temperature.	−0.458∼−0.462	—	—
Iron loaded with atomic hydrogen by quenching in water or by electrolysing.	−0.602∼−0.562	—	—
Iron loaded with atomic hydrogen by nitriding.	—	—	−0.565
Technical pure iron nitrided.	—	—	−0.452
Iron powder nitrided.	—	—	−0.448

difference of 0.023 volt would correspond that between compact iron and porous iron reported by Richards,(1) i.e., the compact iron would trasfer into porous iron by the action of ammonia. This is clearly seen by the photomicrograph shown in Fig. 7.



Surface ×500



Section (unetched). ×500

Photomicrograph of Nitrided Wrought Iron.

Fig. 7.

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(1) Loc. cit.

The author calculated the single potential differences of nitrided iron, referring to hydrogen electrode according to the equation :

$$\epsilon_h=\epsilon_c+0.337.$$

The calculated values are shown in Table 3 together with ϵ_h values of the various states of iron reported by Richards.(1)

Influence of Light on the Single Potential of Iron Nitride. The photo-cells are known for silver, copper, tin and stainless steel(2) but, so far as is known, not for iron nitride. The author constructed a photo-cell by means of two plates of nitrided iron, immersed in a ferrous sulphate solution to determine whether it is light-sensitive or not. In Fig. 8, A and B are armco iron plates (C=0.011%, Mn=0.017%, P=0.008%, S=0.030%, Si=trace, Cu=0.025%) nitrided at 500°C. for 23 hrs. Illuminating a nitrided plates through the window C, the author observed the change of single potential of both plates but found that light produces no marked photo-chemical effect upon them.

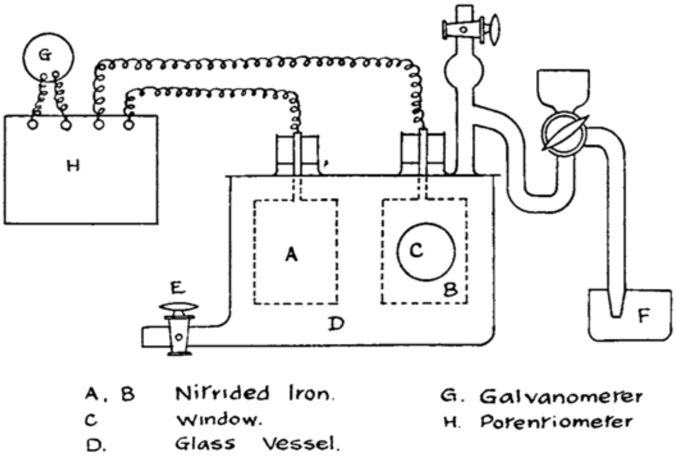

Photo-cell Made of Nitrided Iron.

Fig. 8.

Summary.

The author confirms the existence of atomic hydrogen in iron nitride :

(1) By the presence of hydrogen when heating iron nitride above 430°C. at which iron nitride is found to decompose slowly.

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(1) Loc. cit.

(2) Benedicks and Sundberg, loc. cit.

(2) By the measurement of the single potential of iron nitride in the normal ferrous sulphate solution.

(3) By the oxidation of atomic hydrogen due to oxygen in the water in which iron nitride is immersed.

(4) By the transformation of potassium ferricyanide into potassium ferrocyanide by atomic hydrogen occluded in iron nitride.

By measuring the single potential of nitrided iron, he observed the change of compact iron into porous iron by nitriding.

The influence of light on the single potential of iron nitride was tested and it was found that light produces no marked photo-chemical effect upon it.

In conclusion, the author expresses his cordial thanks to Professor M. Katayama for his valuable advice and suggestion. Thanks are also due to Mr. Hoshi and Mr. Shinozuka for their assistance in the experimental work.

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