表1. 鉄と鋼中の水素の定量のための方法: アルゴンガス運搬熱抽出法

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<tr>
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Determination of Hydrogen in Iron and Steel by the Argon Gas Carrier Hot-Extraction Method*

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Synopsis

An apparatus for a rapid determination of hydrogen in iron and steel was designed by applying the argon carrier gas hot-extraction method. The sample was heated at 950 ~ 1100 °C in the stream of pure argon at the flow rate of about 80 ml/min, and hydrogen extracted was sent together with argon into a hot palladium osmosis tube. After allowing hydrogen to diffuse into the vacuum through the tube, the hydrogen was collected in a manometer through a mercury diffusion pump and an automatic Toepler pump, by which the amount of hydrogen was determined within 25 min. The present method was applied to the determination of hydrogen in iron and steel samples and satisfactory results could be obtained.

I. Introduction

The determination of hydrogen in steel has usually been carried out by the volumetric, manometric or by the thermal conductometric method after extracting it by the vacuum fusion or the vacuum heating method. The vacuum fusion method requires various complicated procedures and a long time for degassing. In addition, the special heating source like a high-frequency furnace or a carbon spiral resisting furnace is required to obtain high temperatures above 1200°C. In foreign countries, attempts of the determination of hydrogen are being made by carrying out the fusion or the heating of the sample in an inert gas atmosphere instead of vacuum, the so-called argon gas carrier-palladium tube osmotic method.

The argon gas carrier method is simpler in the insertion of the sample than the conventional vacuum heating method and can be used to analyze samples consecutively. Furthermore, the apparatus can be made smaller and the analytical procedure becomes simpler.

From these circumstances, an apparatus was designed for a rapid determination of hydrogen in steel by applying the argon carrier hot-extraction method, and a satisfactory result was obtained.

II. Apparatus

1. Purification of argon gas

A schematic diagram of the newly devised apparatus is shown in Fig. 1. The

The purification of argon gas, especially the complete removal of moisture and oxygen, is effected by passing it through a washing bottle containing sulfuric acid, a U-tube filled with calcium chloride, five U-tubes filled with phosphorus pentoxide, a furnace filled with titanium sponge which is heated at 500–600°C, and again through a U-tube filled with phosphorus pentoxide by turns. Finally, the purified argon is sent into the reaction tube. The introduction of argon gas up to the reaction tube is made entirely through glass tubes. By applying this purification procedure, the blank hydrogen gas evolution was less than 0.5μg in 30 minutes, which is a negligible amount.

2. Reaction tube

At the beginning of the experiment the reaction tube, 50 mm in outer diameter and 170mm in length, was placed vertically to introduce the sample into a quartz crucible 32mm in internal diameter and 45 mm in height. Later, in order to maintain the volume of the reaction tube as small as possible, especially in the argon gas carrier method, and to enable the sample to be taken easily out of the reaction tube, a reaction tube tilted by 35° was constructed as shown in Fig. 2.

In Fig. 2, a tap A permits the sample to be loaded into the reaction tube. When the sample is introduced, the three-way tap (Fig. 1, 5) is closed. After loading the sample, the tap A is opened to the air and allow argon gas to escape for one minute, and then the three-way tap is turned back so as to be connected with the palladium osmosis tube. The tap A is then turned to let the sample slide into the center of the reaction tube. After finishing the determination of hydrogen, the tap C is turned to allow the sample to drop in to the sample holder D. The
sample stopper B is a quartz rod 5 mm in diameter and has some protrusions on both sides of the tip so as to facilitate the sliding of the sample when the tap is turned. The reaction tube is heated with silicon carbide heating elements.

![Fig. 2. Detail of reaction tube.](image)

3. Palladium osmosis tube

The palladium osmosis tube, shown in Fig. 3, is a 1000-mm one 1mm in internal diameter and 0.2mm in wall thickness. A 10-mm platinum tube is connected to the tip. The outside of the palladium tube is kept in high vacuum.

![Fig. 3. Palladium osmosis tube.](image)
and after allowing hydrogen to diffuse to the vacuum through the tube, the hydrogen is collected in a manometer through a mercury diffusion pump and a Toeppler pump.

4. Toeppler pump

A U-shaped automatic Toeppler pump shown in Fig. 1 was used. Many devices have been made for the Toeppler pump valve\(^{(1)(2)}\), and most of them are electrically operated. This makes it mechanically complicated and, especially when the pump is directly connected with the measuring system, the internal volume of the valve tends to become larger and it has a defect to decrease the sensitivity of the manometer. The new valve devised for the present work has a simple structure and is a special mercury valve, free from back-flowing of the collected gas, even at a high counter pressure. After complete collection of the gas, the three-way tap for measurement (Fig. 1, 9) is turned to close to isolate the rotary pump and mercury is allowed to rise into the valve by which mercury rises to the mark and stops there.

5. Other apparatus

The temperature of the palladium osmosis tube and the reaction tube is kept within \(\pm 1^\circ\mathrm{C}\) of the heating temperature by the automatic temperature regulator (Okura Electric Co.). The standardization of the amount of hydrogen was made with the gas sampler CGS-1 (Shimadzu's gas chromatographic calibration grade). For the measurement of the flow rate of argon gas, a soap-solution flowmeter was used.

III. Experiments

1. Relationship between flow rate of argon and amount of hydrogen collected in palladium osmosis tube

As a basic experiment, the examination was made to see whether faster flow rate of argon gas allowed the complete diffusion of hydrogen to the vacuum through the palladium osmosis tube. Electrolytic iron was chosen as the sample since it contained a comparatively large quantity of hydrogen and the liberation of hydrogen from the sample was rather rapid. The fine granules of electrolytic iron were wrapped in an iron foil, which was dehydrogenated by heating at 900\(^\circ\mathrm{C}\) in argon stream, and submitted to this analysis at various flow rates of argon. The pressure of hydrogen collected was read on a manometer and, as shown in Fig. 4, the values were constant at a flow rate of 45~150ml/min.

2. Time required for gas collection at various argon flow rates

With the same iron sample as used in the above experiment, the periodical change in the pressure of hydrogen collected was examined with varying flow rate of argon. As will be seen from Fig. 5, the collection of hydrogen is completed in

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(1) R. Lesser and H. Gruber, Z. Metallk., 51 (1960), 495.
(2) S. Suzuki, Japan Analyst, 7 (1958), 513; 11 (1962), 618.
15~20 minutes at the flow rate of 70~100 ml/min of argon, but this period tends to become longer at the flow rate below 40ml/min, probably due to the longer time required for the introduction of hydrogen into the palladium osmosis tube. At the flow rate of 37 ml/min of argon, it takes more than 30 minutes to complete the collection of hydrogen, 22~25 minutes is required at the flow rate of 55~73 ml/min and 15~20 minutes at the flow rate of 80~150 ml/min.

Fig. 4. Relation between flow rate of argon and amount of hydrogen collected by palladium osmosis tube.

Fig. 5. The time for collection of H₂ in various argon flow rate.

These results indicate that the flow rate of argon should be around 80 ml/min for the present apparatus.

3. Relationship between heating temperature of palladium osmosis tube and amount of hydrogen collected

The heating temperature of the palladium osmosis tube necessary for the diffusion of hydrogen to the vacuum has been reported differently as 350°C(3) and around 750°C(4). For the determination of the suitable temperature in the present experiment, it is necessary to consider the various conditions of the palladium osmosis tube itself, such as the thickness and the length of palladium osmosis tube, the degree of vacuum outside the tube and the degeneration of the diffusibility of hydrogen in a long-term use.

In the present experiment, the heating temperature of the palladium

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osmosis tube was varied, 0.5ml of hydrogen was added to argon carrier and the hydrogen pressure was measured. As shown in Fig. 6, the complete diffusion of hydrogen was effected at temperatures above 350°C.

Fig. 6. The recovery of hydrogen in various heating temperature of palladium tube.

4. Extraction rate of hydrogen in various samples

The liberation of hydrogen from iron and steel begins from around 500°C and the rate increases with increasing temperature, but the liberation of carbon monoxide also increases at the same time.

In the present series of experiments, it was found that a minute quantity of hydrogen was extracted at 800~900°C even after 25 minutes, and that the formation of methane was greater at lower temperatures. Considering the decomposition of hydrides, hydrogen was found to be completely extracted at 950~1100°C in 20~25 minutes as shown in Fig. 7.

Fig. 7. Extraction rate of hydrogen in various samples.
In the case of cast iron, the heating method is considered to give generally lower values than those by the vacuum fusion method. This is said to be due to the fact that the liberation of hydrogen from cast iron is more difficult than from steel, and that a part of hydrogen in the sample containing a large amount of carbon is converted into methane in palladium osmosis tube extraction method, where the recovery of hydrogen is not effected(5).

5. Relationship between heating temperature of palladium osmosis tube and yield of hydrogen in methane

As stated above, the lower determination value of hydrogen in the cast iron sample is considered to be due to the formation of methane and, therefore, the behavior of methane in the palladium osmosis tube was examined.

Fig. 8 shows the result obtained by sending 0.3ml of methane gas together with argon into the palladium osmosis tube, at various heating temperatures and by examining the amount of gas collected in the manometer. If hydrogen is generated by the formation of methane gas, this hydrogen will be collected in the manometer. The yield of hydrogen was deemed 100% when the volume of hydrogen collected was double that of methane gas. This examination proved that the recovery of hydrogen was effected in the palladium osmosis tube heated above 800°C even if methane gas was formed.

IV. Analytical results

Based on the results of the preliminary experiments mentioned above, analysis was carried out on several kinds of sample and the result was compared

with that by the vacuum fusion method, as shown in Table 1. In these experiments the samples were heated at 1000°C and the palladium osmosis tube was heated at 800°C in the case of cast iron sample and at 700°C for other samples.

Table 1. Results of the determination of hydrogen in iron and steel samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample taken</th>
<th>Press of $H_2$ collected</th>
<th>Amount of $H_2$</th>
<th>$H_2$ determined (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g)</td>
<td>(mmHg)</td>
<td>(µg)</td>
<td>Proposed method</td>
</tr>
<tr>
<td>C-Steel</td>
<td>6.0584</td>
<td>21</td>
<td>6.5</td>
<td>0.00011</td>
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<tr>
<td></td>
<td>6.0545</td>
<td>18</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>cast iron</td>
<td>5.5884</td>
<td>40</td>
<td>12</td>
<td>0.00021</td>
</tr>
<tr>
<td></td>
<td>5.5622</td>
<td>38</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>Fe-S</td>
<td>5.9690</td>
<td>250</td>
<td>74</td>
<td>0.0012</td>
</tr>
<tr>
<td>Fe-Fe-Si-S</td>
<td>5.9263</td>
<td>101.5</td>
<td>30</td>
<td>0.00051</td>
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<tr>
<td>White cast iron ER$^{3}$</td>
<td>7.3128</td>
<td>72</td>
<td>21.5</td>
<td>0.00029</td>
</tr>
<tr>
<td>White cast iron RG$^{3}$</td>
<td>7.2986</td>
<td>79</td>
<td>23.5</td>
<td>0.00032</td>
</tr>
</tbody>
</table>

Summary

1. In order to examine the argon carrier—palladium osmosis tube extraction method for the determination of hydrogen in iron and steel, an apparatus was designed and analyses were carried out on several samples after preliminary basic experiments.

2. The flow rate of argon gas should be around 80ml/min, but the diffusion of hydrogen to the vacuum through the palladium osmosis tube is complete even at the flow rate of 150ml/min.

3. The heating temperature above 300°C of the palladium osmosis tube effects the complete diffusion of hydrogen but such a low temperature results in a facile oxidation of palladium itself. In addition, the recovery of hydrogen is not complete in the sample which forms methane, like a cast iron. The heating of the palladium osmosis tube above 700°C is required to obtain a good result.

4. Procedures using this apparatus facilitate easy introduction and removal of the sample, and also continuous analyses of samples are possible. The whole procedure is very simple and easy.

5. Analyses of various samples with the size 7 mm in diameter and 20 mm in length showed that the extraction of hydrogen was completed in 20~25 minutes by heating them at 1000°C.