Thermodynamic property of hydrogen in high nitrogen martensitic stainless steel melts

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Hydrogen in steel products may cause serious defects such as hydrogen embrittlement and hydrogen flake. Similarly, seasonal pinhole defects of stainless steel have been often considered to be related to excess hydrogen in molten steel. Hence, reliable information on hydrogen in molten steel is extremely important. However, it should be noted that reliable information of hydrogen in stainless steel is not sufficient. Moreover, there has been significant uncertainty in hydrogen content among previously reported data due to difficulty in measurement.
In the present study, it was aimed to determine the hydrogen solubility of molten stainless steel. Particularly, the influence of Cr content on the hydrogen solubility was focused. Metal samples were equilibrated under controlled hydrogen partial pressure at 1823K and quenched by dropping them into liquid nitrogen. Then the activity coefficient of hydrogen in molten stainless steel with varying Cr content could be determined based on following equation.

$$\log K = \log \frac{f_H[\%H]}{\sqrt{P_{\mathrm{H}_2}}} \qquad \log f_{\mathrm{H}} = \sum_i e_H^i[\%i]$$

Additionally, relatively convenient method for estimating H content in molten steel using hydroxyl capacity of slags and the equilibrium relation among gas-slag-metal was also investigated. To verify the tentatively suggested the measurement method, the measurement of diffusional hydrogen at the moderately elevated temperature was attempted using a gas chromatograph.

KEYWORDS: STAINLESS STEEL, HYDROGEN SOLUBILITY, CR CONTENT, ACTIVITY COEFFICIENT;

INTRODUCTION

As the conventional structure of global industries quickly shifts towards hydrogen economy, the demands of metallic materials suitable for the storage and the transportation of highly compressed hydrogen or liquid hydrogen are drastically increasing. Since stainless steel can be a good candidate for hydrogen-related applications owing to its superior characteristics and phase stability even in very low temperatures, it is greatly important to understand the properties of hydrogen for its proper control.

Hydrogen in steel products may cause serious defects such as, hydrogen embrittlement and hydrogen flake.[1] Similarly, seasonal pinhole defects of stainless steel have been often considered to be related to excess hydrogen in molten steel. Typical examples of the pin hole defects

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in stainless steel product are present in Fig. 1. Although reliable information on of hydrogen in molten steel is extremely important, there has been significant uncertainty in hydrogen content among previous studies due to difficulty in measurement. Therefore, the aim of the present study is to determine the hydrogen solubility of molten stainless steel with high nitrogen content and propose simpler way of estimating hydrogen content of molten steel.

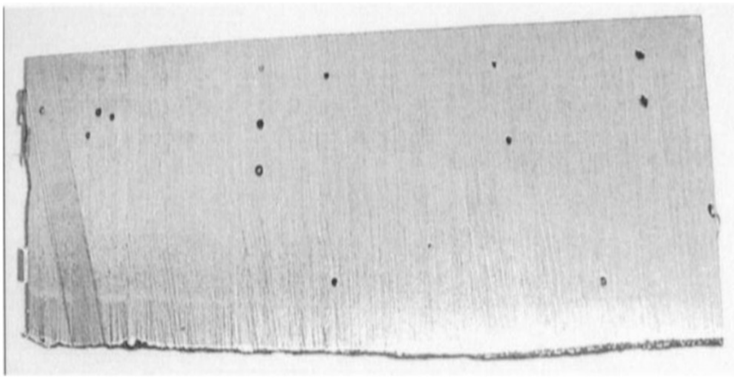

Fig.1 - Photograph of pin-hole defect just under the surface of martensitic stainless steel product.

EXPERIMENTAL

In order to determine the hydrogen content of molten steel, an electric resistance tube furnace, with which a molten steel sample can be quenched, was used. An alumina crucible holding the sample was hanged with Mo or Pt wire to be located at the even temperature zone. After 8 hours equilibration at 1823K with Ar+H2 mixture gases (3%, 6.5%, 10%H2), the sample was instantaneously dropped into liquid nitrogen, which was placed at the bottom of the furnace. The experimental apparatus is schematically described in Fig. 2.

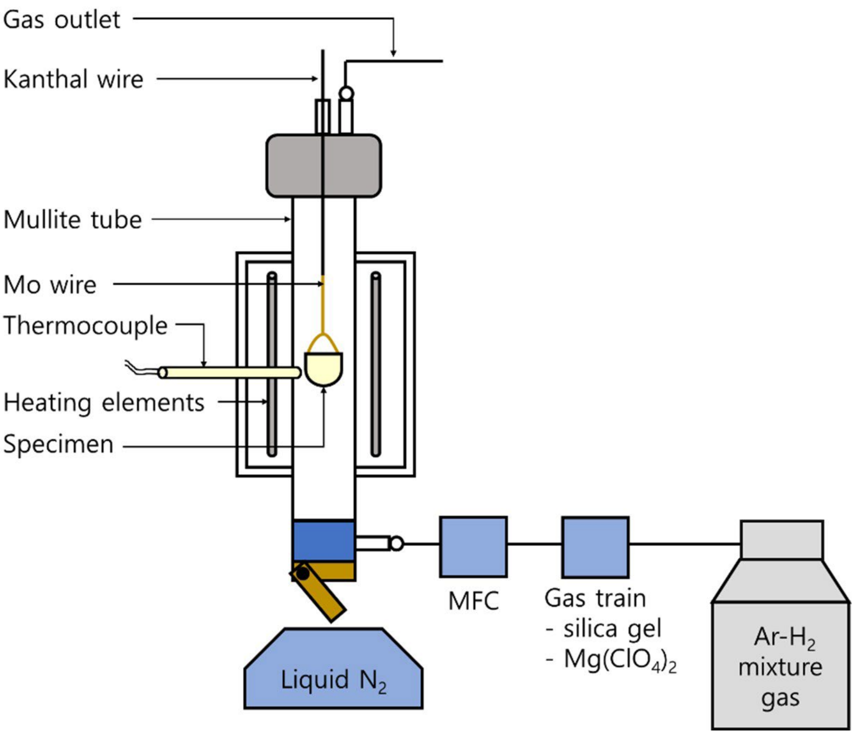

Fig.2 - Schematic presentation of experimental apparatus for hydrogen solubility measurements.

And the dissolution of water vapor into molten stainless steel was also investigated. Water vapor generated at 303K was introduced into the furnace, in which molten steel samples were prepared, along with Ar+H_2 mixture gas. After the equilibration with the same conditions to those described earlier, the sample was quenched in similar manner using liquid nitrogen. Hydrogen and oxygen contents in the steel samples for hydrogen solubility and water vapor dissolution were measured by N/O/H determinator (ONH2000, ELTRA GmbH, Haan, Germany).

RESULTS AND DISCUSSION

Hydrogen solubility in high nitrogen stainless steel

The relationship with H_2 partial pressure and hydrogen content in molten stainless steel is presented in Fig. 3. As H_2 partial pressure increases, hydrogen content increases. A good linearity between the hydrogen content and square root of H_2 partial pressure indicates hydrogen in stainless steel obeys Sievert's law. From the value of slope, moreover, the activity coefficient of hydrogen in molten stainless steel could be determined to with respect to infinite dilute solution, in which the activity coefficient of hydrogen is unity. It can be inferred that the difference between the activity coefficient in stainless steel to unity is caused by the existence of other elements, such as, Cr, C and Si. This relationship can be expressed as Eq. [1]. Based on obtained results about hydrogen dissolution, the hydrogen solubility in molten stainless steel was evaluated to be 9.7 ppm, which is slightly smaller than that in pure Fe.

$$\log f_{\mathrm{H}} = \sum_i e_{\mathrm{H}}^i [\%i] = 0.38 \qquad [1]$$

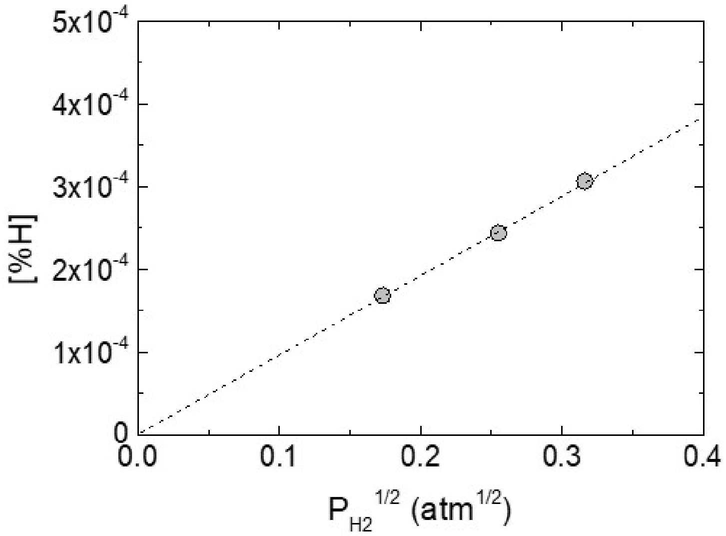

Fig.3 - Relationship with H2 partial pressure and hydrogen content in molten stainless steel.

Dissolution of water vapor in high nitrogen stainless steel

Since water vapor dissolves into molten steel as elemental hydrogen and oxygen as following reaction [2], the equilibrium content of hydrogen is supposed to be inversely proportional to that of oxygen at constant temperature.

$$\mathrm{H_2O}(g) = 2[\mathrm{H}] + [\mathrm{O}] \qquad [2]$$

Based on the equilibrium contents of hydrogen and oxygen at 1823K, the equilibrium constants of water dissolution into stainless steel could be estimated to be 5.47×10^{-7}, which is one order less than the case of pure Fe.[2] This difference in the equilibrium constant is consistent with the tendency of the hydrogen solubility of stainless steel and pure Fe, as explained the previous section.

Estimation method hydrogen content in steel

The accurate determination of hydrogen in steel has been known to be extremely difficult, due to its extraordinarily high diffusivity and the readiness of surface adsorption. There is also high possibility that hydrogen diffuses out during sample preparation and contaminates from environmental moisture. Compared to the case in steel, on the other hand, the hydrogen content in slag may be measured more correctly, because hydrogen is more tightly bound to oxygen by covalent bond in slag structure. Therefore, it can be proposed to estimate the hydrogen content in steel from the direct measurement of the hydrogen content in the slag, equilibrated with the steel.

In order to derive the hydrogen content in steel from that in slag, the partition ratio of hydrogen, which can be expressed using hydroxyl capacity of slag and the equilibrium constant of water vapor dissolution into steel, are required. Since the activity coefficient of hydrogen and the equilibrium of water dissolution were already discussed, the hydrogen content in steel can be deduced from oxygen activity in steel and hydroxide content in slag whose hydroxyl capacity is known, as shown in Eq. [3],

$$[\%\mathrm{H}] = \frac{(\%\mathrm{OH})}{L_\mathrm{H}} = (\%\mathrm{OH}) \cdot \sqrt{\frac{K_{GM}}{a_\mathrm{O}}} \cdot \frac{1}{C_{\mathrm{OH}^-} \cdot f_\mathrm{H}} \qquad [3]$$

Here, f_H and a_O are the activity coefficient of hydrogen and the activity of oxygen in molten steel, while C_{OH^-} and K_{GM} stand for hydroxyl capacity of the slag and the equilibrium constants of water dissolution into steel, respectively.

Finally, useful relationship to predict the hydrogen concentration in the metal from that in molten slag, using hydroxyl capacity of the slag and the activity of oxygen in the steel. Conclusively, relatively convenient method for estimating hydrogen in molten steel could be suggested.

SUMMARY

Experimental investigation on the influence of hydrogen on the pinhole defect in high nitrogen stainless steel was carried out. The hydrogen solubility and the equilibrium constant of the dissolution of water vapor (K_{GM}) in stainless steel were experimentally determined using liquid nitrogen quenching. Hydrogen solubility as well as the equilibrium constant of the dissolution of water vapor turned out to be lower in stainless steel than in pure Fe.

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