Experimental Determination of the Accuracy of Hydrogen Measurement in Liquid Steel with HYDRIS ®System

R.P. Stone, Electro-Nite Company
E.T. Turkdogan, Consultant
D. Vensel, Armco Research and Technology

Introduction

Depending on the steelmaking process, melt shop and ladle refining practices, the hydrogen content of non-degassed liquid steel varies over a wide range from 3 to 12 ppm H. Casting problems are often encountered at high concentrations of hydrogen. Also, there is the well known hydrogen induced flaking and cracking in the steel processing of heavy sections, e.g. HSLA heavy plates, seamless tubes, rails and so on.

Because of these adverse effects of hydrogen on steel casting and processing, the steel industry is keenly aware of the practical importance of in situ determination of hydrogen in liquid steel at various stages of ladle refining and in the tundish. The in situ determination of hydrogen in liquid steel with an immersion probe called HYDRIS is based on the same principle as that developed by Ransley et al in the late 1950's for the determination of hydrogen in liquid aluminum. The principle of the hydrogen measurement with the HYDRIS system is as follows. A given volume of an inert gas (commercial grade) is bubbled into the melt, recaptured by the porous ceramic bell and recirculated through the measuring system in a closed circuit having a volume of about 200 ml. The time of every gas recycle is about 4 seconds. The hydrogen is transferred from liquid steel to the circulating gas until the partial pressure of H_2, measured by a thermal conductivity detector (katharometer), is that approaching the equilibrium value for the concentration of hydrogen in the liquid steel.

Theoretical Approach to Experimental Work

Based on theoretical considerations, three types of critical tests can be made with the HYDRIS system to evaluate the degree of absolute accuracy of the hydrogen readings.

1. LIQUID STEEL SATURATED WITH H_2 AT KNOWN PRESSURE: If the P_{H2} measured by the HYDRIS system is close to that used in saturating the melt, then the measurement would be considered to be accurate within the limits of reproducibility of the results.

2. HYDRIS READINGS WITH 100% N_2 AND 15% H_2-N_2 FLUSH GASES IN THE GAS CIRCULATION SYSTEM: Usually, commercial grade nitrogen is used to flush the gas circulation system; this is then followed by hydrogen pick up from the melt until the final reading is obtained. With a flush gas containing a relatively high concentration of H_2, upon gas circulation during the measurement, the partial pressure of H_2 in the circulation gas will decrease, ultimately approaching that which is in equilibrium with concentration of hydrogen in the melt. If the consecutive hydrogen readings obtained with these two types of flush gases are in close agreement, one would then surmise the HYDRIS reading to be accurate.

3. HYDRIS READINGS AT DIFFERENT DEPTHS OF PROBE IMMERSION IN THE MELT: The microprocessor of the HYDRIS system is programmed to convert the concentration of H_2 in the circulating gas at a total pressure P', to the partial pressure of $H_2(P_{H2})$ at 1 atm (1013 mbar) total pressure of the H_2+N_2 mixture. This HYDRIS reading of P_{H2} should be adjusted for the total pressure P at the probe tip, determined by the depth of probe immersion in the melt, thus

$$P_{H2}\ (\text{adj't}) = P_{H2}(\text{HYDRIS reading}) \times \frac{P(\text{mbar})}{1013}$$

which gives for the adjusted hydrogen concentration:

$$\text{ppm H(adj.)} = \text{ppm}_{H}\ (\text{HYDRIS}) \times \left(\frac{P(\text{mbar})}{1013}\right)^{\frac{1}{2}}$$

That is, the apparent P_{H2} and ppm H readings by HYDRIS should decrease with an increasing depth of immersion, in accord with the above theoretical relations.

For the average liquid steel and slag densities of 7.0 and 3.1 g/cm³ respectively and Z cm thick slag layer, the total gas pressure at the probe tip at Y cm depth of immersion in liquid steel would be:

$$P(\text{bar}) = \frac{145.69\ P_O + (Y + 0.443 \times Z)\ (\text{cm})}{145.69}$$

where P_0 is the ambient barometric pressure in bar.

Laboratory Experiments and Plant Tests

The experimental programs (1) and (2) outlined above on theoretical basis, were put to test in the R & D Laboratory of Electro-Nite Co. in Philadelphia. Inductively heated 180-kg melts of various compositions were used. N_2 + H_2 gas mixtures of certified compositions (6, 9, 12 and 15 wt% H) were employed in controlling the hydrogen content of the liquid steel. The gas mixture was blown onto the surface of the melt at the rate of about 100 Nl/min, such that there was local turbulence of the melt in the area of impingement of the gas stream. Several duplicate measurements were made both with HYDRIS and dual-wall sampling (DWS) to evaluate the reproducibility of the results. As part of the test program, consecutive HYDRIS readings were taken with 100% N_2 and 15& H_2 - N_2 mixture as the flush gas.

Program (3), the effect of depth of probe immersion on the HYDRIS reading, was investigated by taking a series of measurements in the tundish of Gary Caster No. 2 (USS) on three consecutive heats. In these plant tests, consecutive HYDRIS readings were taken also with 100% N_2 and 15% H_2 - N_2 mixture as the flush gas.

Experimentation with High Alloy Steels

Measurements in induction furnace and ARMCO/AMC were made in high alloy heats to determine the validity and accuracy of the HYDRIS system.

Using argon carrier gas and nitrogen carrier gas, duplicate tests were made to verify the theoretical considerations described below.

1.CALIBRATION OF HYDRIS FOR H_2& AR MIXTURES
The thermal conductivity of argon is lower than nitrogen, therefore for a given concentration of H_2 the TCD will give a higher PH_2 for the H_2 + Ar carrier gas. The experimental ratio of Ar vs N_2 carrier gas was verified as follows:

$$\frac{10\%\ H_2 - Ar}{10\%\ H_2 - N_2} = 1.18$$

2.HYDRIS TESTS WITH HYDROGENATED STAINLESS STEEL MELTS
Stainless steel melts were saturated with hydrogen at a known level. If the PH_2 measured with the HYDRIS system is close to the level of gas used to saturate the melt, then the measurement would be considered to be accurate within the limits of reproducibility of the results.

Results

The results obtained in the hydrogenation experiments, using a low alloy steel, are plotted in Fig. 1. The dotted lines give the equilibrium contents of hydrogen in liquid steel at indicated melt temperatures and hydrogen contents of the gas mixture which were blown on the melt surface for about 50 minutes. It is seen that the measurements taken a few minutes before changing the gas composition, gave results in close agreement with the equilibrium values for the gas mixture that was blown on the melt surface. Similar results were obtained in the measurements made with two other steel melts. Most of the data points are within $\pm$ 5% of the calculated equilibrium values for the H_2 + N_2 mixtures used in saturating the melt with hydrogen.

An example is given in Fig. 2 of the HYDRIS tracing with 100% N_2 and 15% H_2 - N_2 flush gas. The results of these numerous measurements with the 180-kg melts and with 50-tonne steel in the tundish of the Gary Caster No. 2 are summarized in Fig. 3, where the HYDRIS measurement of ppm H with the 15% H_2 - N_2 flush gas is plotted against that with the 100% N_2 flush gas. In these consecutive tests, it was found that the ppm H recorded by HYDRIS using the 15% H_2 - N_2 mixture, as the flush gas, was invariably 0.1 to 0.5 ppm H higher than that measured with the 100% N_2 flush gas. This small difference, in the right direction, is indeed as one would expect from the kinetics of the gas-metal reactions with the gas phase having initially a higher and lower concentration of the reactant.

The data in Fig. 3 are represented by

$$\text{ppm H}(15) = 1.08 \times \text{ppm H}(0)$$

where (15) and (0) indicate respectively 15% H_2 - N_2 and 100% N_2 flush gas. In practice, it is convenient to use commercial grade N_2 as the flush gas; recognizing that there is always an asymptotic approach to saturation of the circulating gas with H_2 that is in equilibrium with the hydrogen dissolved in the steel.

In three caster heats, HYDRIS measurements were made with 100% N_2 and 15% H_2 - N_2 flush gases at immersion depths of 10 to 45 cm. As seen from the data in Fig. 4 (top diagram), the HYDRIS reading of the apparent ppm H decreases with an increasing depth of probe immersion in the steel. The adjusted ppm H in the lower diagram is seen to be independent of the depth of probe immersion. These findings are in complete accord with the theoretical prediction discussed earlier.

Conclusions

The results obtained from various tests in this investigation, and the theoretical interpretation thereof, lead to the conclusion that, the HYDRIS system gives accurate readings of hydrogen content of liquid steel and iron alloys. The degree of accuracy of the measurement corresponds to an uncertainty of about ± 5% of the true hydrogen content of the liquid steel.

Figure 1

Hydrogen contents of 180-kg low alloy steel as measured by the HYDRIS system, which gives readings close to the equilibrium values for indicated melt temperatures and gas compositions.

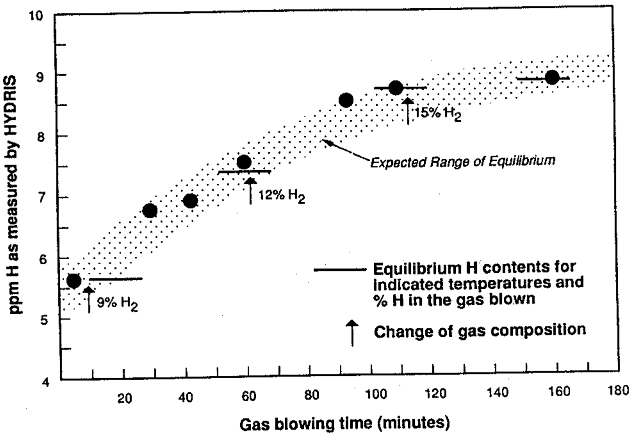

Figure 2

HYDRIS reading with 100% N_2 flush gas (6.7 ppm) and 15% H_2 - N_2 flush gas (7 ppm) in 50-tonne capacity tundish.
(Measurement screens are enhanced for clarity.)

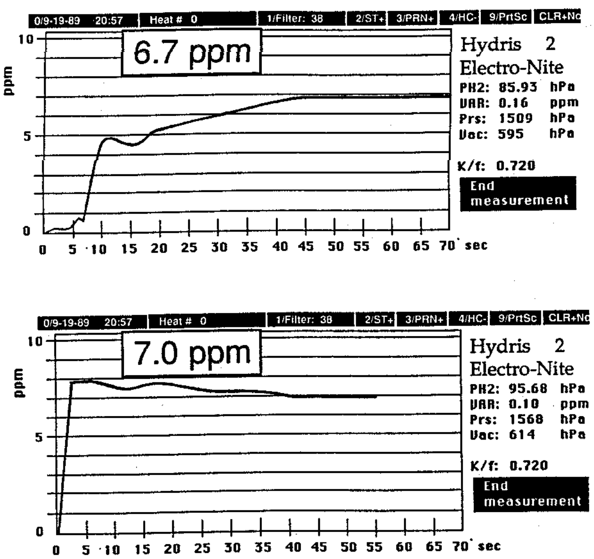

Figure 3

Comparison of HYDRIS readings with 100% N_2 and 15% H_2 - N_2 flush gas.

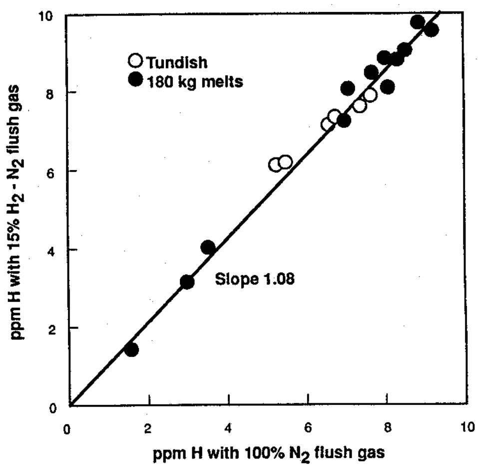

Figure 4

HYDRIS measurements at different depths of probe immersion in the tundish, substantiating the expected depth effect on HYDRIS reading and theoretical correction thereof.