

**BI-MONTHLY REPORT-I**

**[OCTOBER 1- DECEMBER 31, 2004]**

**PROGRESS REPORT**

***Thermoelectric Power Coefficient Assessment of Hydrogen in Pipeline Steels***

**1. ABSTRACT**

The preliminary investigation was performed to measure and monitor the diffusible hydrogen content using rapid electronic property measurement technique. To measure the hydrogen content in pipeline steel, low temperature thermoelectric power (TEP) measurement was used for hydrogen charged HSLA steel samples. The measurement of as-received HSLA steel sample shows a negative slope and decreases with time within two minutes as the specimen warms up from liquid nitrogen temperature to room temperature. The thermoelectric power coefficient of the corresponding hydrogen-charged specimen increases with time as it warms up from liquid nitrogen to room temperature. The large difference in the thermoelectric power coefficient at the low temperature range (about  $-140\text{ }^{\circ}\text{C}$ ) between uncharged and charged specimens was observed. This result indicates that the thermoelectric power coefficient can be amplified at low temperatures, resulting in accurate measurement in the thermoelectric power coefficient for the hydrogen-charged HSLA steel. Also, the TEP coefficient measurement of HSLA steel welded with hydrogen containing shielding gas was performed as a function of specimen temperature and time. The instantaneous amounts of diffusible hydrogen for weld metal can be obtained by recording both the TEP coefficient value and specimen temperature for diffusible hydrogen measurement practice. The TEP coefficients of fixed sample temperature, such as  $-60$  and  $-40\text{ }^{\circ}\text{C}$ , show linear relationship with different diffusible hydrogen content as a function of diffusible hydrogen content. In addition, the TEP coefficient measurement results as a function of time results can be used to curve fit a standard plot to determine the resulting diffusible hydrogen content for steel weld metal by using the error function. These preliminary experimental results show potential use of TEP coefficient measurement technique to assess the hydrogen content in pipeline steel.

**2. INTRODUCTION**

Through the utilization of modern physics concepts, a portable non-destructive thermoelectric power device has been designed for determination of hydrogen content in HSLA steels. The thermoelectric power coefficient is extremely sensitive to microstructural changes, and with careful correlation to standards it can be used as a rapid, non-destructive technique to assess the alloy composition and microstructural variations before potential loss of integrity in the HSLA steel specimen. The HSLA steel specimens have been charged to various hydrogen contents and then the thermoelectric power coefficient monitors the change in

hydrogen content with time as the hydrogen diffuses out of the HSLA steel specimen. Different conditions in the thermoelectric power measurement procedure were investigated to determine if increased sensitivity could be achieved in by making measurements at liquid nitrogen temperature relative to room temperature. This practice was performed since we know that low temperature TEP measurements are much more sensitive.

The second effort of this study was devoted to measure TEP coefficient at low temperature to measure the diffusible hydrogen content for ferritic or martensitic steel welds. The TEP coefficient was measured as a function of time and temperature for different diffusible hydrogen content in HSLA steel welds. The TEP coefficient measured as a function of time can be used to find initial hydrogen content using error function. It is very important to notice that there is a large TEP coefficient at low temperature and much smaller coefficient at the room temperature range. This result indicates that TEP signal could be amplified at low temperature.

This report consists of three sections: theory section, preliminary experiments section, cryogenic Seebeck measurement section, and dynamic Seebeck measurement section.

### 3. THEORY

The thermoelectric power coefficient is a function of the electron concentration, the effective mass of the electrons, the electronic scattering behavior in an alloy, which are all influenced by the solute content, lattice strain, microstructural changes, material processing, and time-dependent phase changes. In metallic alloys, the value and the sign of the thermoelectric power coefficient are dependent upon the electronic features in the vicinity of the Fermi energy level, the effective mass tensor, the density of electronic states, and the dominating scattering mechanism [1]. In turn, the Fermi energy value (Fermi energy surface in the k-space) changes with electronic filling in the conduction band due to the electron donation by hydrogen atoms. For example, with the high degeneracy of the free electron gas, the resulting thermoelectric power coefficient,  $Z$ , is related to the electron theory through the following expression where the degeneracy of the electron gas is for high carrier concentrations:

$$Z = \left( \pm \frac{\bar{k}}{e} \right) (27.1) \left( r + \frac{3}{2} \right) \left( \frac{m_e}{h^2} \right) \left( \frac{\bar{k}}{kTn} \right)^{\left( \frac{2}{3} \right)} \quad [1]$$

where  $r$  is the scattering parameter determined by the dominating scattering mechanism, and  $h$  is Planck's constant,  $\bar{k}$  is Boltzmann's constant,  $n^*$  is the electron concentration, and  $m_e$  is the effective mass. From the free electron model, the electron concentration is directly related to the Fermi energy. The

electronic effective mass defines the rate of Fermi energy change with increasing electron concentration [1]. The effective mass can be described as:

$$m_e = \hbar^2 \left( \frac{d^2 E}{dk^2} \right)^{-1} \quad [2]$$

where  $k$  is the wave number. The effective mass,  $m_e$ , describes the shape of the s, p, and d bands that are in contact with the Fermi energy level. The shape of the bands at the contact position offers a characteristic indication that can be measured with changes in the Fermi energy level due to electron donation from the hydrogen addition.

To observe thermoelectricity, it is necessary to have a circuit composed of two different materials, and the net difference between their thermoelectric properties can be measured. The electromotive force (emf) produced under these conditions is the relative Seebeck emf. The potential difference between the hot end and the cold end as illustrated at Figure 1. The developing voltage of each element is dependent upon the Seebeck coefficient difference between two metals  $Z_{AB}$ . The emf between the two metals,  $V_{AB} = \Delta V_A - \Delta V_B$  can be expressed by:

$$V_{AB} = \int_{T_0}^T (Z_A - Z_B) dT = \int_{T_0}^T Z_{AB} dT \quad [3]$$

where  $Z_{AB} = Z_A - Z_B$  is defined as thermoelectric power for the thermocouple A-B. The absolute Seebeck coefficient (ASC) of the alloy material,  $Z_a$ , can be determined from measurements as:

$$Z_a = \frac{V}{\Delta T} - Z_{Cu} \quad [4]$$

where  $V$  is the Seebeck voltage measured between alloy material and reference copper electrode,  $\Delta T$  is the temperature difference, and  $Z_{Cu}$  is the well-calibrated Seebeck coefficient for copper. One copper probe is maintained at room temperature and the other one at a temperature higher by 10 °C. The temperature difference can be varied, but it must remain constant for all tests.

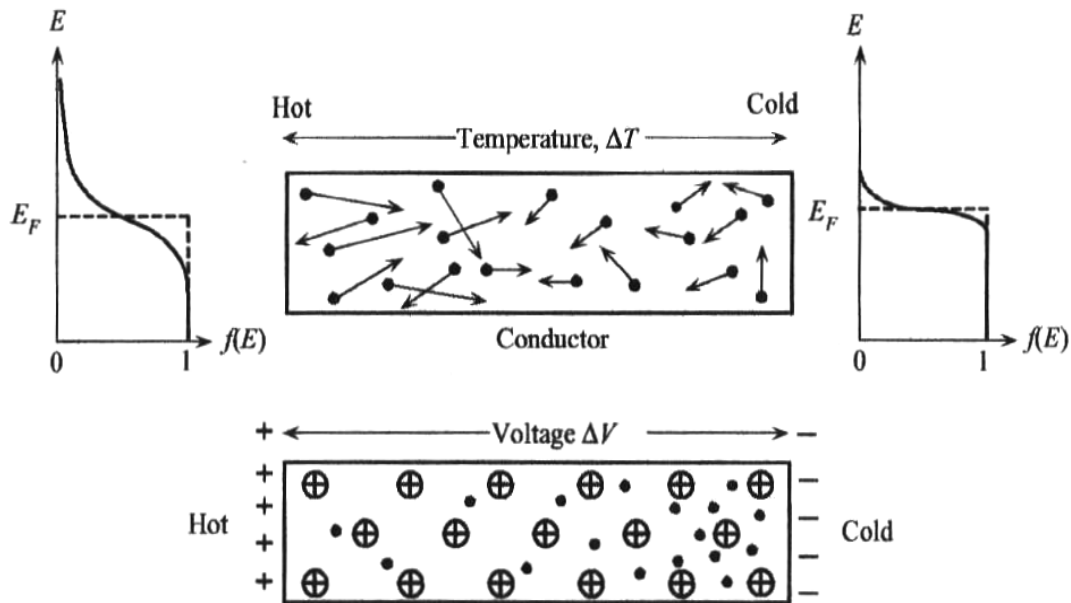


Figure 1. A temperature gradient ( $\Delta T$ ) gives rise to a potential difference ( $\Delta V$ ), which is the Seebeck effect [2]. Free carriers in the picture are electrons (N-type material).

#### 4. PRELIMINARY EXPERIMENTS

##### *Thermoelectric Power Coefficient Measurement Scheme*

For the determination of hydrogen content using thermoelectric power, a non-destructive Seebeck measurement device has been developed. The Seebeck apparatus consists of a Keithley Nano-voltmeter 2182, two Watlow temperature controllers and read-outs, two type T and two type K thermocouples, two heating cartridges, and two copper (or iron) reference probes. The thermoelectric power set-up used for hydrogen charged HSLA steel specimen consisted of two reference copper blocks (or iron) as shown in Figure 2(a). HSLA steels welded sample with hydrogen containing shielding gas is shown in Figure 2(b). A total of four different thermoelectric power measurement set-ups were used to maximize the measuring sensitivity.

Pure copper and iron are both used as reference materials in the thermoelectric power measurement set-up dependent upon the material being tested. The use of a pure iron reference is utilized to determine if there will be an increase in the resolution of the thermoelectric power measurement on HSLA steel specimens [3]. Copper has been used in most cases for thermoelectric power measurements because of its high thermal and electrical conductivity. It has been reported that pure iron reference materials can increase thermoelectric power measurement

sensitivity on HSLA steel specimens, which is due to the similarity in chemical composition.

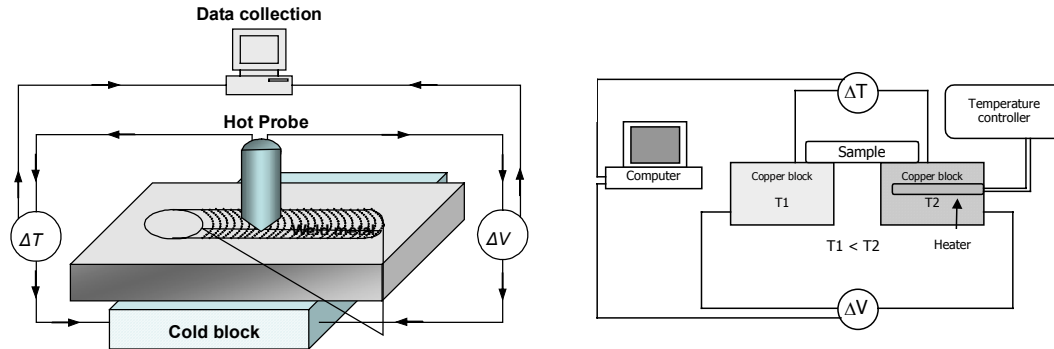


Figure 2. Schematic drawing of a) TEP measurement system used for hydrogen measurement of HSLA steel weldments and b) TEP coefficient measurement setup for hydrogen charged HSLA steels.

## 5. PRELIMINARY RESULTS: Cryogenic Seebeck Measurements

HSLA steels have a ferritic (body-centered cubic) microstructure, in which hydrogen has a diffusion coefficient that is orders of magnitude higher than in austenitic (face-centered cubic) microstructure. Because hydrogen has a high mobility, the transfer of steel specimens from the hydrogen charging system to the thermoelectric power measurement system requires a special procedure. The HSLA steel specimens are put into liquid nitrogen was used to immobilize the diffusible hydrogen in these specimens until the TEP coefficient measurements began. Preliminary hydrogen content results on HSLA steels are shown and discussed below.

The hydrogen content of the as-received HSLA steel specimen was 0.52 ppm (Leco Hydrogen Determinator). This as-received HSLA steel specimen was then charged with hydrogen at 1123 K (850 °C) for 48 hours at a pressure of 200 psig. A continuous thermoelectric power measurement of hydrogen content was conducted for a series of specimens in a time interval of 250 minutes. Between the first and second measurements, a large reduction of total hydrogen content (about 13 ppm hydrogen) occurred in the specimen in a period of less than ten minutes (Figure 3), giving direct evidence that the hydrogen distribution in the specimen is not uniform and a large amount of hydrogen is in solution near the surface. The hydrogen trapped on the surface area can easily and quickly diffuse out after the specimens are taken out of the liquid nitrogen. After ten minutes from the start of the measurement, the rate of hydrogen evolution began to slowly decrease and then became constant at a particular value. The rate of hydrogen evolution began to slow down because more diffusion time is necessary for

hydrogen to travel from the middle of the specimen to the surface. It is not reasonable to conclude that the remaining hydrogen is all trapped because the specimens were not baked, and a small amount of diffusible hydrogen could still remain in the specimens after a waiting time of 250 minutes.

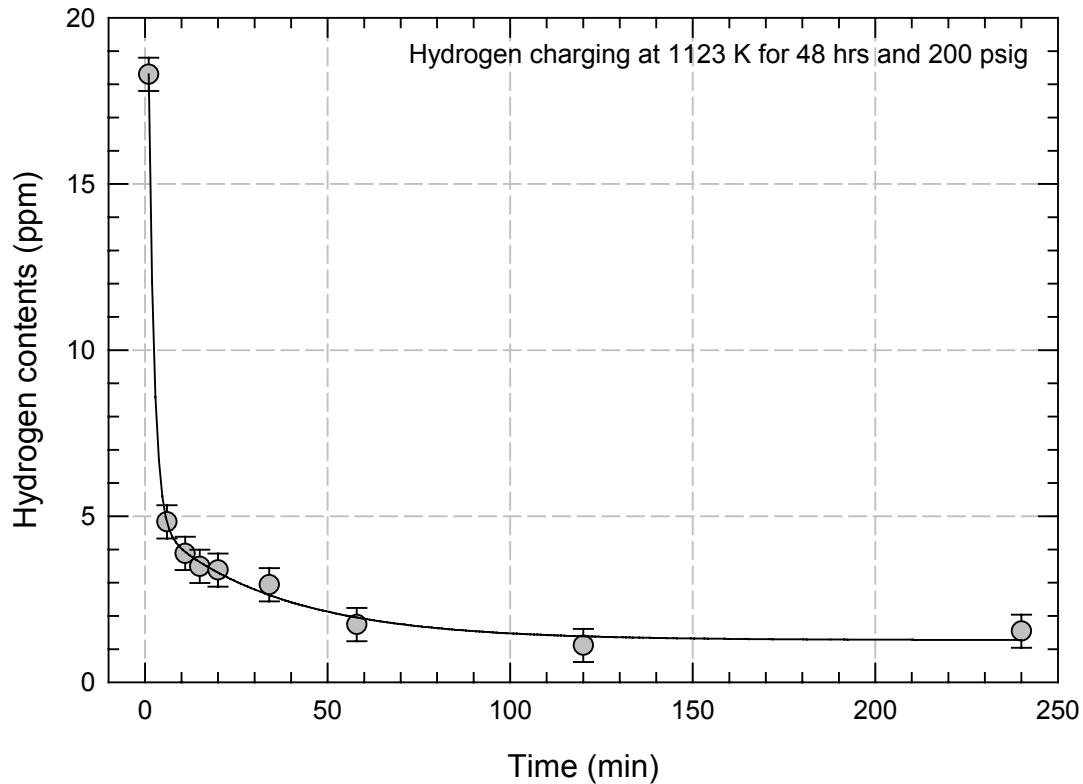
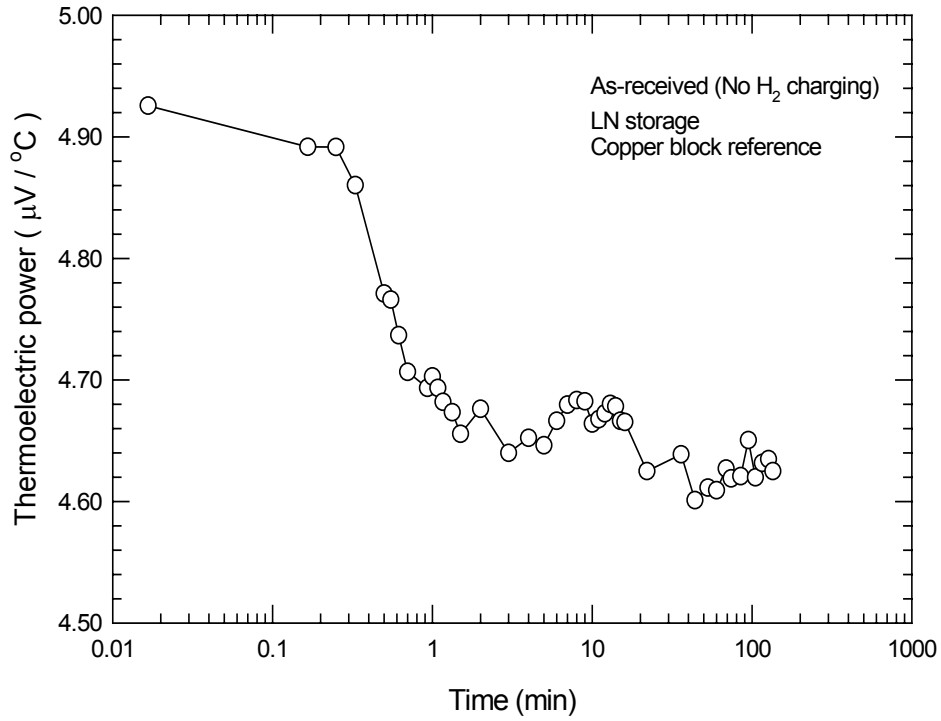


Figure 3. Experimental hydrogen evolution curves measured by the LECO RH-404 hydrogen determinator. All of the specimens were taken out from the liquid nitrogen at the same time and placed in air until the hydrogen content measurements began.

The thermoelectric power coefficient results for the as-received and the liquid nitrogen quenched HSLA steel specimens (without hydrogen charging) are shown in Figure 4(a). The thermoelectric power coefficient quickly decreases from 4.9 to 4.6 ( $\mu\text{V}/^\circ\text{C}$ ) in one minute. After one minute, no significant changes in the thermoelectric power coefficient are observed up to a time span of 200 minutes. The large changes in the first minute is mainly due to specimen temperature changes because the specimen was held in liquid nitrogen and then the temperature began to rise to room temperature.

a)



b)

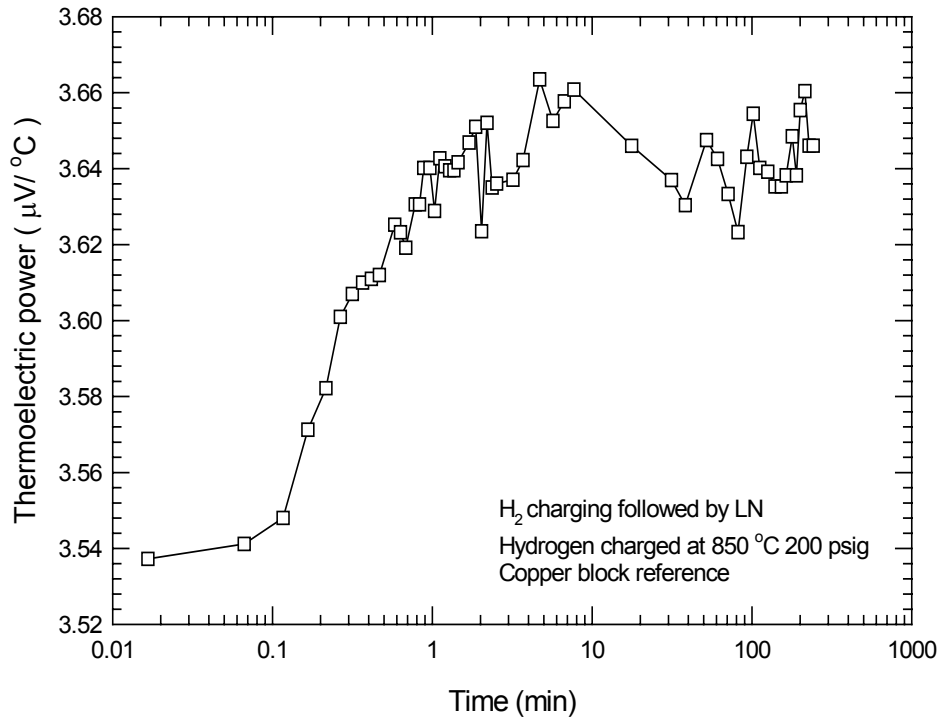


Figure 4. TEP coefficient measurement for HSLA steel (a) as received specimen (b) hydrogen charged specimen. : LN = Liquid Nitrogen

Figure 4(b) shows the thermoelectric power coefficient of the hydrogen-charged HSLA steel specimen. The main difference between the as-received (Figure 4 (a)) and the hydrogen-charged (Figure 4 (b)) thermoelectric power plots are the slope of the curves. The as-received (without hydrogen-charging) curve has a negative slope and decreases with time within two minutes as the specimen warms up from liquid nitrogen to room temperature. The thermoelectric power coefficient of the corresponding hydrogen-charged specimen is positive and increases with time as it warms up from liquid nitrogen to room temperature. There is a huge difference in the thermoelectric power coefficient in the very low temperature range (about  $-140^{\circ}\text{C}$ ) between uncharged and charged specimens. It is very important to notice that there is a large thermoelectric power coefficient difference at low temperature, even though no variation is observed at the room temperature range. This result indicates that the thermoelectric power coefficient can be amplified at low temperatures, resulting in a large deviation in the thermoelectric power coefficient corresponding to the hydrogen-charged HSLA steel.

Figures 4 (a) and (b) show that the thermoelectric power coefficient at room temperature is different between the as-received and the hydrogen charged specimens. This result could be caused by the hydrogen charging process because the specimens were heated to  $850^{\circ}\text{C}$  and then were quenched, which results in microstructural changes. In addition, trapped hydrogen in the HSLA steel specimen may also contribute to small changes in the thermoelectric power coefficient.

The thermoelectric power coefficient of the as-received HSLA steel specimen without hydrogen charging is shown in Figure 5 (a). This measurement was made using an iron reference probe to see if there would be an increase in the sensitivity in the thermoelectric power measurement. The thermoelectric power coefficient is constant for a time span of 100 minutes. The result of the thermoelectric power coefficient for the as-received and the liquid nitrogen quenched HSLA steel specimen (no hydrogen charging) is shown in Figure 5(a). The thermoelectric power coefficient result are not much different utilizing a iron reference probe as compared to the copper reference probe in the above measurements. The low temperature curve shows a negative slope and decreases with time within two minutes. The thermoelectric power coefficient of the corresponding hydrogen charged specimen is positive and increases with time (Figure 5(b)). There was no direct evidence of any advantages in using an iron reference material rather than copper reference material. Also, the sensitivity at room temperature does not appear to be improved significantly.

This observation suggests that a practice of cooling a small spot on the pipe and measurement of the thermoelectric power coefficient systematically as the spot warms up will allow an assessment of the hydrogen content in pipe. This will require extensive hydrogen charging and measuring to correlate the thermoelectric power measurement and methodology for future hydrogen assessment on pipe.



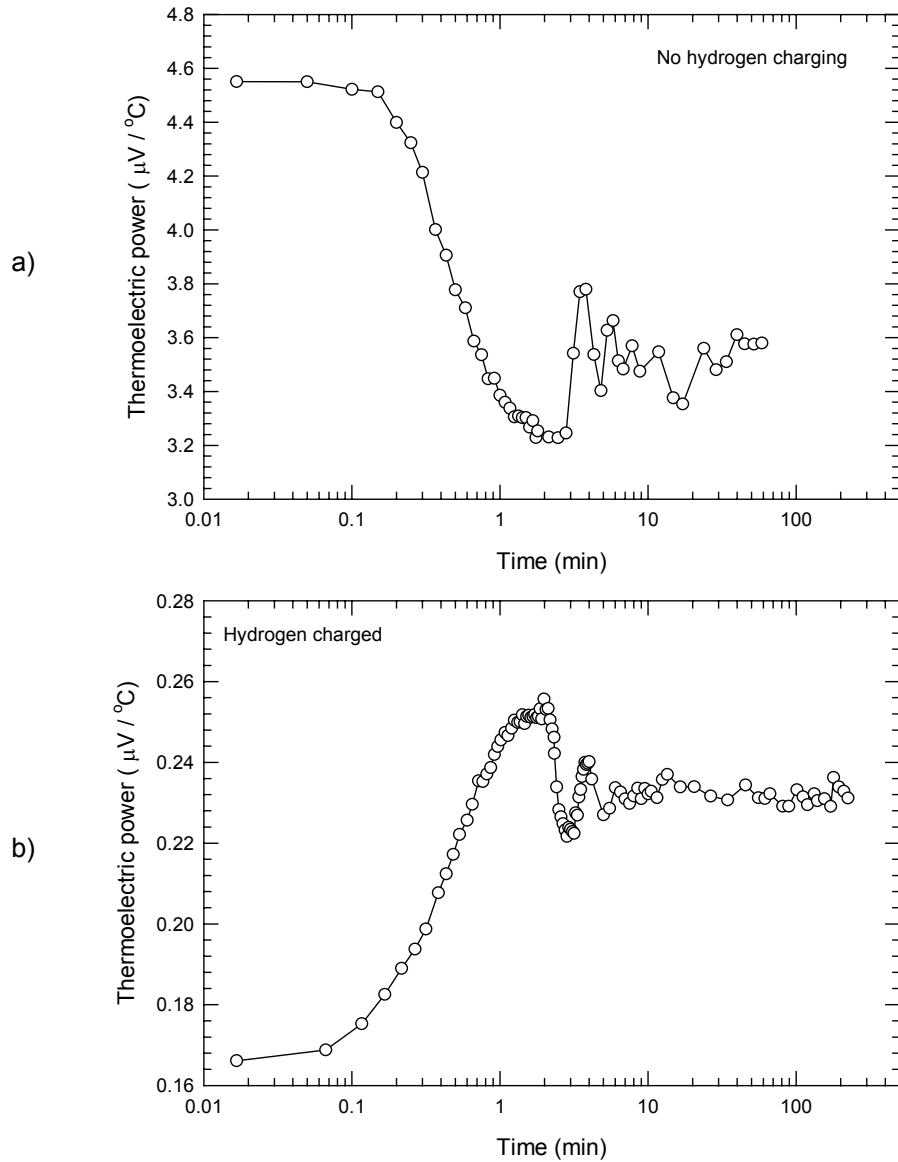


Figure 5. The TEP coefficient measurement for a) as-received and b) hydrogen charged HSLA steel with iron block reference. Hydrogen was charged at 1123 K (850 °C) for 48 hours at pressure of 200 psig.

## 6. PRELIMINARY RESULTS: Dynamic Seebeck Measurements

To correlate TEP coefficient values with various hydrogen content levels in HSLA steel welds, measurements of actual diffusible hydrogen of welded HSLA steel with increasing hydrogen concentration in shielding gas were conducted according to standard procedures. The hydrogen content of the argon shielding gas was increased

to a level of 6 percent by volume. The welding parameters were kept same as described in experimental procedures. Other hydrogen contents, 1, 3, and 5 vol. pct. in shielding gas, were welded, and TEP coefficient measurements were conducted to correlate with diffusible hydrogen content. The probe type TEP measurement system was used and temperature difference between two probes were maintained around 10 °C. The welded sample was quenched in the liquid nitrogen right after welding, then the measurement was started before temperature reached -100°C.

The results of TEP coefficient measurements of these welded specimens are shown in Figure 6. As diffusible hydrogen content increases, each TEP coefficient curve move to lower level, systematically. These results suggest that the plot of TEP coefficient as a function of either time can be used to curve fit a standard plot to determine the resulting diffusible hydrogen content for steel weld metal.

An attempt can be made to correlate the slope of the TEP coefficient curve to the initial diffusible concentration in the sample. The steady state portion of the curve could be assumed to be proportional to the flux of hydrogen from the weld metal. To investigate this possibility, theoretical curves will be generated using an equation derived from the error function  $erf(x)$  as shown in Equation 5. The error function is a mathematical formula associated with a normal Gaussian distribution and occurs often in engineering applications.

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-w^2} dw \quad [5]$$

The diffusion was assumed to occur from a semi-infinite plane sheet with a uniform initial concentration  $C_0$  throughout and a constant surface concentration of zero. For this case, the solution for the error function equation takes the form:

$$M_t = 2C_0 \left( \frac{Dt}{\pi} \right)^{1/2} \quad [6]$$

where  $M_t$  is the amount of hydrogen,  $D$  is the diffusion coefficient for hydrogen in a particular medium,  $C_0$  is the initial concentration and  $t$  is time. Solutions can be generated for different initial concentrations as a function of time.

By using this approach, field practitioners may take the TEP coefficient measurement device and measure the TEP coefficient value of actual welds in low temperature by recording a specimen temperature. The measured TEP coefficient value can be compared with a plot of the TEP coefficient as a function of time, and basically indicates the hydrogen content in the welds. This approach using TEP coefficient measurement at low temperature makes diffusible hydrogen content measurement much easier and faster. The time required for measurement is about thirty times faster as compared to conventional standard diffusible hydrogen measurement methods.

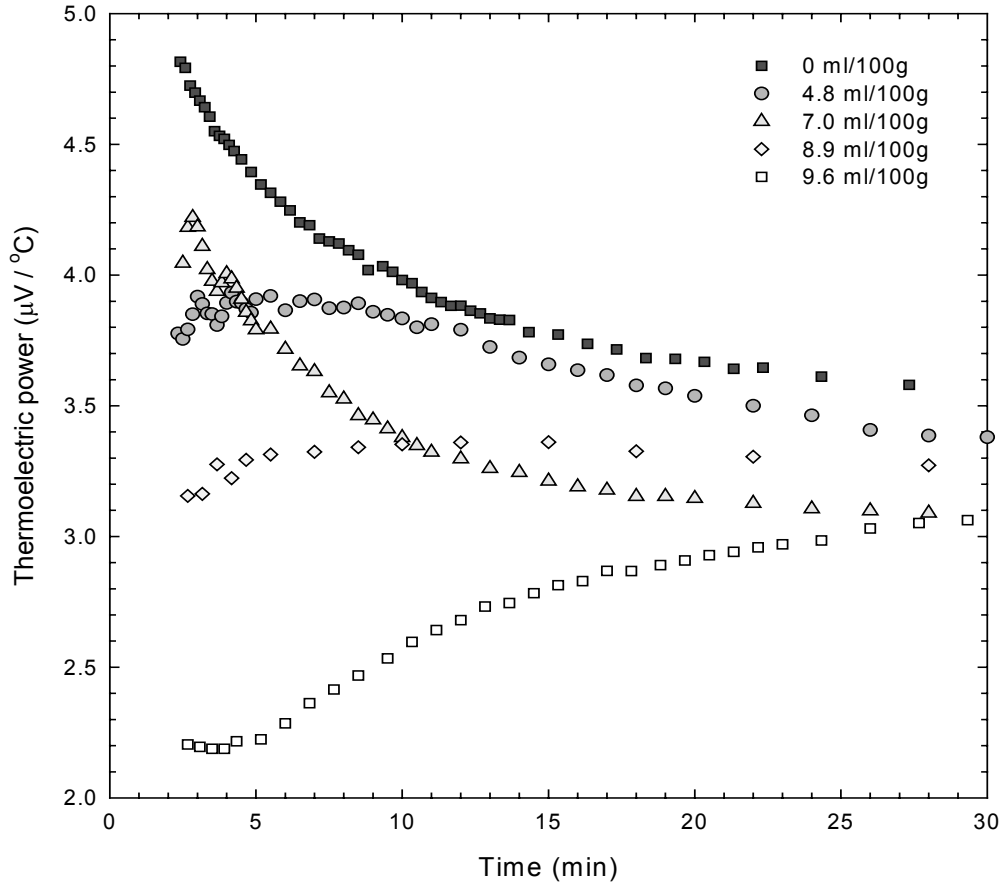


Figure 6. Measured TEP coefficient of welded HSLA steel with five different hydrogen content levels (0, 1, 3, 5, and 6 vol. pct.) in shielding gas for thirty minutes. Actual diffusible hydrogen content is shown in legend. Welding condition: 120 Amps, 1 mm/s travel speed, ice water quenching, and liquid nitrogen storage.

Figure 7 presents the measured TEP coefficient as a function of specimen temperature. Each curve shows linear relationship between the TEP coefficient and the sample temperature when TEP coefficient was plotted as a function of sample temperature. These results indicate that each TEP coefficient curve represents amount of diffusible hydrogen in HSLA steel welds. Therefore, by recording both the TEP coefficient value and specimen temperature for diffusible hydrogen measurement practice, instantaneous amounts of diffusible hydrogen for weld metal can be obtained. The TEP coefficients of fixed sample temperature, such as -60 and -40 °C, were taken and plotted as a function of diffusible hydrogen content. The results are shown in Figure 8a and b. The results indicate that TEP coefficient is relatively linear with amount of diffusible hydrogen in welded HSLA for both sample temperature of -60 and -40 °C.

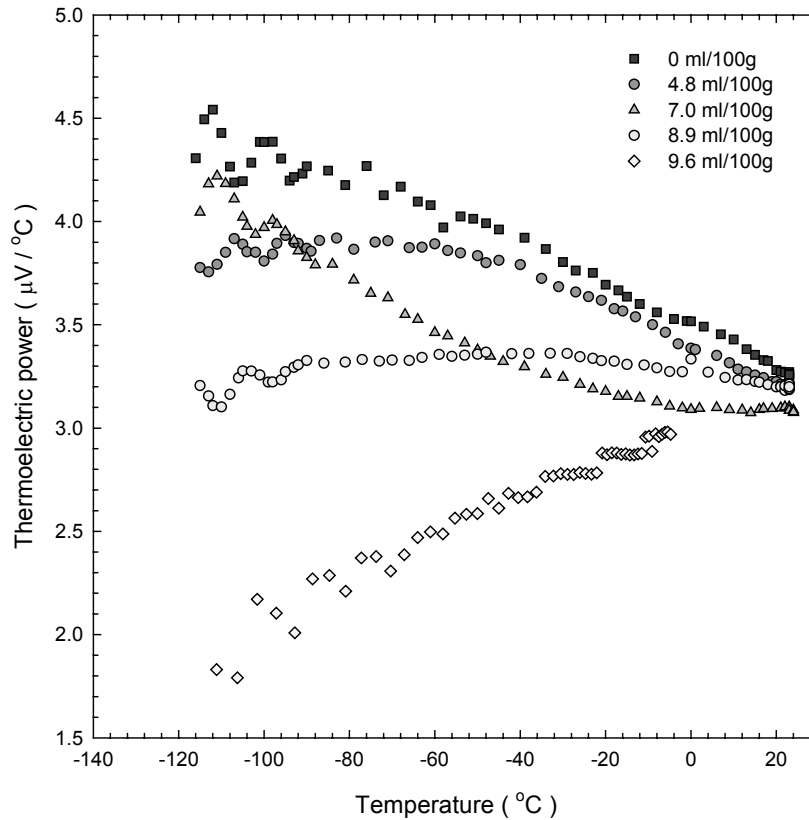


Figure 7. Measured TEP coefficient as function of specimen temperature for all five welded HSLA steel specimens.

Experimental difficulties appear to create poor reproducibility of test results. Because the liquid nitrogen quenched specimen is placed in a measurement set-up, the temperature controllers are immediately trying to maintain the differential temperature (10 °C), and it takes approximately 5-10 minutes to achieve the stable differential temperature of 10 °C. Also, the contact probe pressure on specimens is found to be a very critical issue at low temperatures.

Other approaches include making TEP coefficient measurements comparing specimens welded with zero hydrogen in shielding gas and those with 3, 5, and 6 vol. pct. hydrogen in argon shielding gas was taken to correlate with the diffusible hydrogen content at several temperature. The difference in TEP coefficient between each curve at fixed temperature can be directly correlated to the amount of diffusible hydrogen or initial hydrogen content of sample. As shown in Figure 9, TEP coefficient was increased with increasing diffusible hydrogen content.

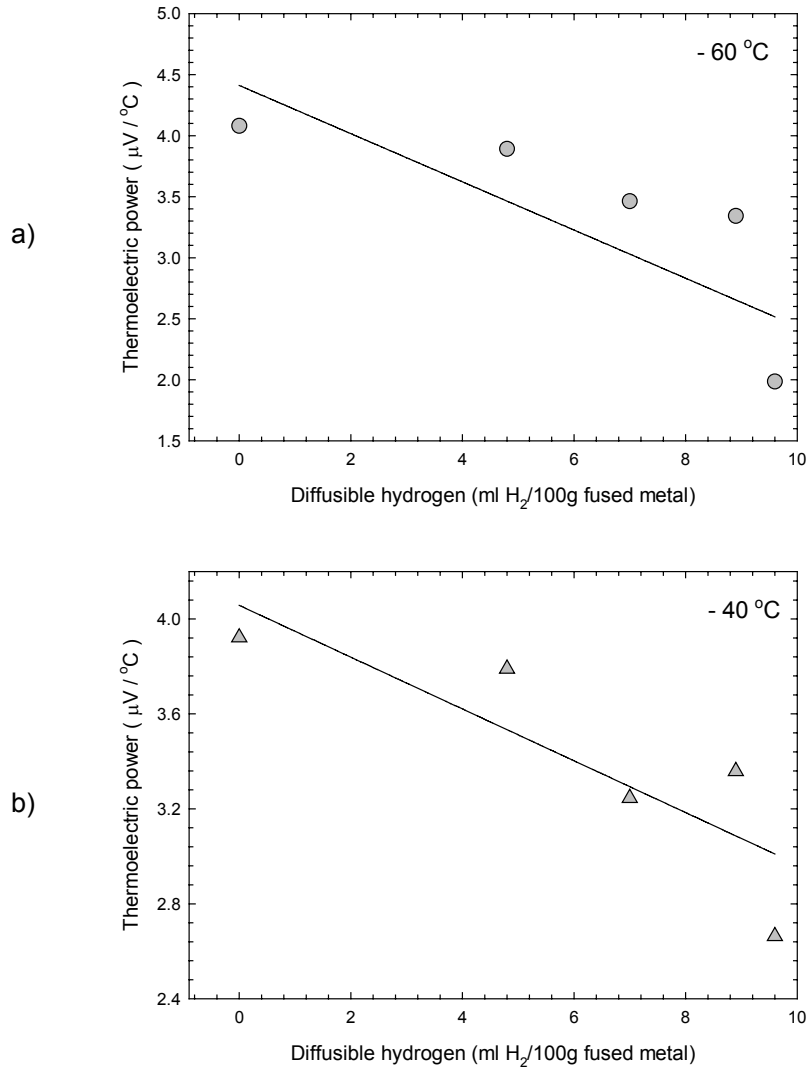


Figure 8. Measured TEP coefficient as a function of hydrogen content vol. pct. in shielding gas at specimen temperature of a) -60 and b) -40 °C.

## 7. POTENTIAL UTILIZATION

These are preliminary results that suggest that thermoelectric power can potentially be used to assess hydrogen on line pipe, but further work needs to be done to work out a practice and to qualify this practice as a measuring technique to assess hydrogen.

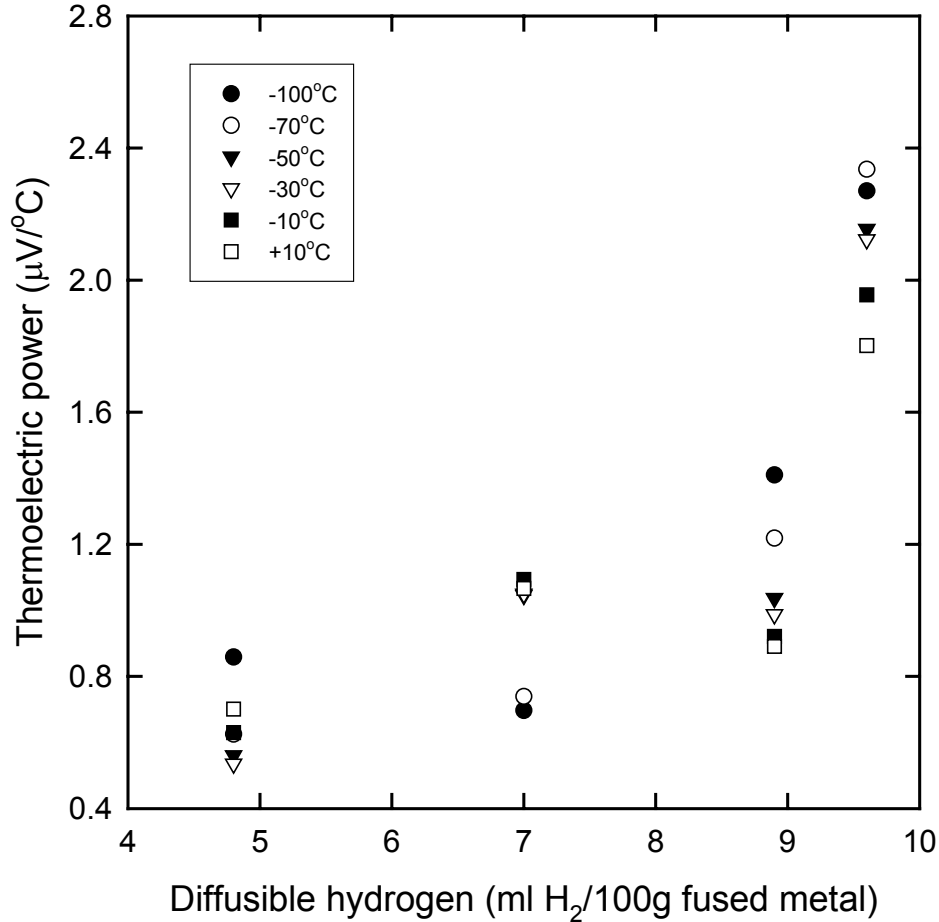


Figure 9. Measured TEP coefficient as a function of diffusible hydrogen content. The TEP coefficient shown in plot was differential values subtracted from TEP coefficient of zero diffusible hydrogen samples.

## 8. REFERENCES

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