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Microstructure Characterization in Martensitic Steels Using Thermoelectric NDE

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Summary

This project is part of a collaborative EPRI research program aimed at assessing candidate nondestructive evaluation (NDE) techniques that can identify undesirable material microstructures in tempered martensitic steels with high chromium content. Specifically, an NDE technique is sought that is capable of distinguishing between Grade 91/92 steels with microstructural characteristics that lead to acceptable and poor performance in service. The objective of the UC study reported here was to evaluate the feasibility of thermoelectric (TE) NDE for this purpose. TE NDE is highly sensitive to certain microstructural changes in metal alloys and, at the same time, uniquely insensitive to the geometrical features of the components under test, therefore could potentially be used for industrial manufacturing quality control and later to assess the condition of installed components. Sixteen small-diameter thin-wall tube and eight large-diameter thick-wall pipe section specimens made of Grade 91/92 martensitic steel were tested in this study. These specimens represented eight heat treatment conditions used to control the microstructure of the samples resulting in Vickers hardness levels between 147 and 428 HV. These specimens were characterized by a high-precision automated four-point thermoelectric power (TEP) measurement system developed at the University of Cincinnati (UC). Compared to commercially available two-point TEP measurement devices, this novel thermoelectric NDE technique offers higher repeatability and absolute accuracy without the need for empirical calibration. Four-point TEP measurements were conducted in the temperature range of 36-40°C on the smaller tube specimens and 31-35°C on the larger pipe sections. All measured TEP values were temperature compensated to the same reference temperature of 38°C using the linear temperature coefficient of TEP determined on the same specimen by linear regression of the experimental data. Thermoelectric measurements conducted on both tubes and pipe sections exhibited the same trend of decreasing TEP in the 10.8−13.2 μV/°C range with increasing hardness. The main conclusion of this investigation is that the normalized and heat affected zone microstructures of Grade 91/92 martensitic steels, which produce significantly elevated hardness levels, can be easily identified by TEP measurements. In addition, the over tempered microstructure, which does not exhibit significantly elevated hardness level, could also be identified in the two tube specimens, but not in the single pipe specimen tested in this study.

1. Introduction

A significant portion of failures in creep-resistant martensitic Grades 91 and 92 steels have been attributed to microstructural variations caused by high production variability. It has been established that the long-term creep strength of such ferritic-martensitic steels might be compromised by microstructural instability at elevated temperature. Figure 1 illustrates schematically that effective stabilization of the microstructure is particularly important in the medium-stress regime (M) where the creep properties are highly susceptible to changes in the chemical composition, heat treatment condition and microstructure [1]. The objective of this project is to assess candidate NDE techniques that can identify undesirable material microstructure in tempered martensitic steels with high chromium content with special focus on the detection and quantitative assessment of the presence of ferrite grains in the tempered martensitic matrix. For this purpose, an NDE technique is sought that is capable of distinguishing between Grades 91 and 92 steels with microstructural characteristics that lead to acceptable and poor performance in service. It is anticipated that such an NDE technique could potentially be used for manufacturing quality control and later to assess the condition of installed components. EPRI is pursuing a multi-modal approach involving various NDE methods in order to achieve the required sensitivity and selectivity for different microstructures. The TEP measurements conducted by UC in this project were aimed at nondestructively characterizing the microstructure of martensitic Grades 91 and 92 steels after various heat treatments. TEP measurements were selected for this study because, in sharp contrast with most NDE methods, TEP measurements are sensitive only to material property variations but completely insensitive to geometrical features such as variations in size and shape.

Table 1 lists the eight heat treatment conditions used to control the microstructure of the samples. The conditions identified as normalized and heat affected zone (HAZ) produced Vickers hardness above 400 HV, while the rest of the microstructural conditions exhibited much lower average hardness between 147 and 220 HV. Table 2 lists the geometrical dimensions of the tube and pipe section samples provided by EPRI for this investigation. In total, sixteen small-diameter thin-wall tubes and eight large-diameter thick-wall pipe specimens were tested. The 12”-long tubes were of full cross section, while the 9”-long pipes were sectioned into $\approx 60°$ segments. All twenty-four samples were characterized using a precision four-point TEP inspection system developed at UC in collaboration with Imperial College of London and EPRI specifically for such applications that allows absolute TEP measurement without any need for empirical calibration [2].

Table 1 List of sample microstructure conditions.

ID	Condition	Heat Treatment	Target Hardness (HV 5.0)	Actual Median Hardness
1	As received	None	215	220
2	Normalized	1050°C/0.5h/AC	425	428
3	Normalized+Tempered	1050°C/0.5h/AC + 775°C/2h/AC	215	208
4	Tempered	790°C/2h/AC	195	207
5	Over-Tempered	790°C/10h/AC	185	198
6	Fully Ferritic	950°C/0.5h + cool to 760°C/3h/AC	160	147
7	HAZ	900°C/1m/AC	300	405
8	HAZ+Tempered	900°C/1m/AC + 775°C/2h/AC	215	170

Table 2 List of sample geometries.

Sample	Quantity	Outer Diameter (in)	Wall Thickness (in)	Axial Length (in)	Angular Section
Tubes	16	2	0.165	12	360°
Pipe Sections	8	18	1.5	9	$\approx$60°

In in Section 2, first the four-point TEP measurement procedure will be described and then the obtained TEP results will be presented. Finally, Section 3 summarizes the conclusions drawn from these results.

2. TEP Measurements

This project relied on TE sensing of microstructural changes in creep-resistant martensitic steel tubes and pipes. Essentially all existing TE NDE techniques are based on the well-known Seebeck effect that is commonly used in thermocouples to measure temperature at the junction between two different conductors. Ideally, regardless of the temperature difference between the junctions, only thermocouples made of materials of different thermoelectric power will generate a thermoelectric voltage. This inherently differential nature makes TE inspection one of the most sensitive material discriminators used in NDE. TE techniques can be used to monitor corrosion, thermal and radiation embrittlement, plasticity, anisotropic texture, inhomogeneity and residual stresses and can be also exploited for nondestructive characterization of structural nuclear reactor components [3]. TE measurements require only the simplest possible access in the form of some sort of forced heating or cooling and two contact electrodes for the measurement of the resulting temperature and thermoelectric voltage differences while the material itself is used as the sensing element. Since the absolute accuracy and relative reproducibility of conventional TE measurements are adversely affected by imperfect electric and, especially, thermal contact imperfections between the reference electrodes and the specimen under test [4], a recently developed four-point thermoelectric inspection technique was used in this project that introduces heating remotely from the voltage sensing electrodes and has been shown to be essentially insensitive to surface conditions [2].

Generally, four-point TEP measurements are far more accurate and reproducible than conventional two-point TEP measurements. The reason for this difference is that in the case of two-point measurements external heating is applied through the interface between the hot electrode and the specimen and the required substantial heat conduction through this inherently imperfect interface produces a significant uncertainty in the difference between the measured temperature and the specimen's local temperature [4]. This is the same issue why four-point electric resistance measurements are significantly more accurate and reproducible than simpler two-point resistance measurements.

2.1 Four-point TEP Measurement Procedure

Thermoelectric power measurements were conducted using a custom-built four-point TEP measurement system that separates heat injection from the temperature and electric potential difference measurements [2]. Figure 2 shows a schematic diagram of the experimental arrangement. Two thermocouples are attached to the specimen to be tested at two points separated by a large enough distance to assure that under natural or artificial heating/cooling conditions a sufficient temperature difference $\Delta T = T_2 - T_1$ arises between them for accurate TE voltage difference measurement. In addition to measuring the voltages generated by these two thermocouples to determine the local temperatures T_1 and T_2, two additional voltage differences, ΔV_{N+} and ΔV_{N-}, are measured between the two positive and two negative thermocouple wires, respectively, of the two thermocouples. The subscripts N indicate that N-type thermocouples are used in this case. These two voltage differences are

$$\Delta V_{N+} = (S_S - S_{N+}) \Delta T \tag{1}$$

and

$$\Delta V_{N-} = (S_S - S_{N-}) \Delta T , \tag{2}$$

where S_{N+} and S_{N-} denote the known absolute thermoelectric power of the positive (Nicrosil) and negative (Nisil) wires of the N-type thermocouple, respectively, and S_S denotes the unknown absolute thermoelectric power of the specimen under test. Finally, the sought TEP can be calculated from

$$S_S = \frac{1}{2}\left(\frac{\Delta V_{N+}}{\Delta T} + \frac{\Delta V_{N-}}{\Delta T} + S_{N+} + S_{N-} \right). \tag{3}$$

For the purposes of heating, two 15 Ω/10 W power resistors were clamped on the specimens. The two heating resistors were driven by a Two-Channel Stanford Research Systems CTC100 Temperature Controller that produced harmonically changing out-of-phase outputs of 6 W peak power superimposed on a 6 W baseline power. The period of the excitation was chosen to be 30 minutes for the small-diameter tubes and 60 minutes for the large-diameter thick-wall pipe sections to allow for the much larger heat capacity of the latter. The specimens were simultaneously tested at two locations referred to as A and B by two pairs of high-precision "special limits of error" N-type thermocouples embedded in small copper pads. The temperature and electric potential differences between the sensing pads were monitored by an eight-channel Pico TC-08 Thermocouple Logger. Figure 3 shows a screen shot of the data acquisition and processing LabView software used for four-point TEP measurements (tube specimen T1, as received). The sampling rate was set to 1 Hz and a new TEP reading was calculated and recorded in every 30 minutes, i.e., based on 1,800 sampling point. The measurements were run over 12-48 hours resulting in a minimum 24 measurement points at both locations. Figure 4 shows a typical example of 72 readings at two locations (A and B) of tube specimen T1 with $\overline{S} = -12.95 \mu\text{V/°C}$ average TEP, $S_\sigma = 0.03 \mu\text{V/°C}$ standard deviation, and $\Delta S = \pm 0.09 \mu\text{V/°C}$ estimated measurement error indicated by error bars. It should be pointed out that on the tube specimens the four-point TEP measurements were conducted in the temperature range of 36-40°C, but all the results were temperature compensated to the reference temperature of 38°C. In contrast, because of their significantly higher thermal capacity, on the pipe specimens the four-point TEP measurements were conducted in the slightly lower temperature range of 31-35°C and all the results were temperature compensated to the same reference temperature of 38°C. All TEP measurements were compensated using the linear temperature coefficient of TEP determined on the same specimen by linear regression of the experimental data.

2.2 Four-point TEP Measurement Results

Figure 5 shows the results of four-point TEP measurements conducted on 16 steel tubes. The microstructural conditions of these samples were listed in Table 1 and their geometrical dimensions were listed in Table 2. EPRI provided two identically heat treated samples for each condition; one with the temper identified (T) and one blind specimen without identification (B). Accordingly, the specimen IDs used in Figure 5 were constructed from letters T and B followed by the ID numbers previously listed in the first column of Table 1. Two tests were conducted on each sample; each test yielded measurements at two locations and the tests were repeated approximately ten days later after remounting the sensing electrodes. No special measures were taken to polish or clean the surfaces since repeatability tests indicated that the surface conditions did not exert a significant influence on the measurement results. The symbols in Figure 5 indicate the average of these four measurements and the error bars represent measurement uncertainty levels calculated from the random variation of the measurements and the estimated ±0.07 μV/°C systematic error of the absolute TEP of the copper pads. Five specimens from both the identified (T) and unidentified (B) series exhibited essentially the same thermoelectric power of 12.93 ±0.05 μV/°C. These specimens could not be distinguished from each other by TEP measurements. However, three specimens from both batches exhibited very similar TEP values that indicated that they must have the same microstructural condition. These assumed pairs are indicated by dashed lines in Figure 5. The three identified pairs were T2-B4 (normalized), T5-B8 (over tempered), and T7-B6 (HAZ).

Figure 6 shows the four-point TEP measurement results versus Vickers hardness provided by EPRI for eight steel tubes with identified microstructures. The symbols represent measured data and the solid line is the best fitting linear regression line. There is an overall trend of decreasing TEP with increasing hardness with a fairly high coefficient of determination of $R^2 = 0.90$. However, this overall trend is followed closely only by the two fully hardened specimens, namely T2 (normalized) and T7 (HAZ), while the other specimens form a fairly tight cluster.

Interestingly, even specimen T5 (over tempered), which had a distinctly lower TEP value than the other five specimens, exhibited a hardness level of 198 HV that put it squarely in the middle of the group of five specimens of high TEP and low hardness values.

Figure 7 shows the four-point TEP measurement results obtained from eight steel pipe sections. The microstructural conditions of these samples were listed in Table 1 and their geometrical dimensions were listed in Table 2. The specimen IDs used in Figure 7 were constructed from letter P for pipe sections followed by the ID numbers previously listed in the first column of Table 1. Like in the case of tube specimens, two tests were conducted on each sample; each test yielded measurements at two locations and the tests were repeated approximately ten days later after remounting the sensing electrodes and no special measures were taken to polish or clean the surfaces since repeatability tests indicated that the surface conditions did not exert a significant influence on the measurement results. The operational parameters were also the same as before, with the exception of the period of the heating cycle that was increased from 30 to 60 minutes to compensate for the higher thermal capacity of these specimens. Again, the symbols indicate the average of these four measurements and the error bars represent measurement uncertainty levels calculated from the random variation of the measurements and the estimated ±0.1 μV/°C systematic error of the absolute TEP of the copper pads. Six specimens exhibited essentially the same thermoelectric power of 13.12 ±0.07 μV/°C and could not be distinguished from each other by TEP measurements. However, two of the previously identified microstructural conditions, namely P2 (normalized) and P7 (HAZ) exhibited significantly lower TEP values than the other specimens. This observation indicated that their microstructural condition could be identified by TEP measurements on the pipe sections as well. Importantly, the over tempered microstructural condition represented by pipe section P5, which could be separated by TEP measurements conducted on tube specimens, could not be separated from the rest of the pipe sections.

Figure 8 shows four-point TEP measurement results versus Vickers hardness values provided by EPRI for the eight microstructural conditions listed in Table 1. Symbols represent measured data and the solid line is the best fitting linear regression line. There is an overall trend of decreasing TEP with increasing hardness with the same fairly high coefficient of determination of $R^2 = 0.90$ as it was found in the case of martensitic steel tubes. The reason for the similar R^2 value found in this case is that the tempered specimen (P5) fits the linear trend line much better, while the two pipe sections with normalized (P2) and HAZ (P7) microstructures exhibited larger deviation from it. However, it should be pointed out that this relatively high R^2 value is mainly due to the fact that the TEP values fell in one of two clusters well separated from each other and this fact should not be construed as an evidence of linear relationship between hardness and TEP.

Finally, Figure 9 shows a comparison of four-point TEP measurement results between tubes and pipe sections. Symbols represent measured data and the solid line represent perfect correlation. Most of the data points are actually above this ideal line because the TEP values measured on the pipe segments were on the average 0.3 μV/°C higher than those measured on the tubes. The physical cause of this difference could not be determined within the technical and scheduling limitations of this project. However, it should be pointed out that both the average temperatures and the temperature gradients were rather different during testing of the small-diameter thin-wall tubes and large-diameter thick-wall pipe specimens and this might have introduced a systematic difference due to imperfect temperature corrections. More importantly, the chemical compositions of the tubes and pipe segments might have been different and, because the high sensitivity of absolute TEP measurements to chemical composition variations, could have caused the observed small but detectable discrepancy between their absolute TEP values in similar microstructural conditions.

3. Conclusions

This project was part of a collaborative EPRI program aimed at identifying an NDE technique or a combination of complementary NDE techniques capable of distinguishing between Grades 91 and 92 martensitic steels with microstructural characteristics that lead to acceptable and poor performance in service. The objective of the UC study reported here was to evaluate the feasibility of a recently developed four-point thermoelectric inspection technique for this purpose. Four-point TE instruments introduce heating remotely from the voltage sensing electrodes and therefore are much less sensitive to surface conditions than commercially available two-point TEP devices. Sixteen small-diameter thin-wall tubes and eight large-diameter thick-wall pipe sections made of Grade 91/92 martensitic steel were tested in this study. These specimens were exposed to eight different heat treatment procedures that were applied to control the microstructure of the samples resulting in Vickers hardness levels between 147 and 428 HV. Four-point TEP measurements were conducted in the temperature range of 36-40°C on the smaller tube specimens and 31-35°C on the larger pipe sections. All measured TEP values were temperature compensated to the same reference temperature of 38°C using the linear temperature coefficient of TEP determined on the same specimens by linear regression of the experimental data. Thermoelectric measurements conducted on both tube and pipe specimens indicated the same basic pattern of decreasing TEP over the 10.8−13.2 μV/°C range with increasing hardness. The main conclusion of this investigation is that the normalized and heat affected zone microstructures of Grade 91/92 martensitic steels, which produce significantly elevated hardness levels, can be easily identified by TEP measurements.

Specifically, the identified (T2) and blind (B4) tube specimens in normalized condition (428 HV) exhibited TEP values of 10.78 ±0.02 μV/°C while the identified (T7) and blind (B6) tube specimens in HAZ condition (405 HV) exhibited TEP values of 11.02 ±0.02 μV/°C. In addition, the identified (T5) tube specimen in over tempered condition (198 HV) and blind tube specimen (B8) exhibited statistically indistinguishable TEP values of 12.28 ±0.02 μV/°C, therefore have been tentatively identified as having the same microstructural condition. The remaining five microstructural conditions all exhibited significantly higher TEP values of 12.78 ±0.05 μV/°C, but further identification of these blind tube specimens was not possible based on TEP measurements only. All local variations of the TEP value measured using the high-precision four-point TE technique were within the ±0.02 μV/°C standard uncertainty of this technique on small-diameter thin-wall tubes when the peak temperature difference is around 10 C°.

Somewhat less accurate results were obtained from the eight pipe section specimens, mainly because only 5-6 C° peak temperature differences could be reached with the existing four-point TEP measurement system due to the much higher heat capacity of these larger specimens even with cycle times increased from 30 to 60 minutes. In this case only specimens P2 in normalized and P7 in HAZ conditions exhibited low enough TEP values of 10.82 ±0.01 μV/°C and 11.68 ±0.08 μV/°C, respectively, to positively distinguish them from the remaining six microstructural conditions that all exhibited TEP values of 13.10 ±0.07 μV/°C and were statistically indistinguishable from each other. Comparing the results of the four-point TEP measurements conducted on the identified tube and pipe section specimens yielded a strong correlation but with ≈0.3 μV/°C higher absolute TEP values for the pipe sections than for the tubes. Although the physical cause of this statistically significant difference could not be determined within the technical and scheduling limitations of this project, it is likely that the chemical compositions of the pipe segments and the tubes were slightly different and, because of the intrinsically high sensitivity of TEP measurements to chemical composition variations, likely caused the observed small but detectable discrepancy between their absolute TEP values in similar microstructural conditions. In spite of this discrepancy in the measured absolute values, a least mean square fit to the TEP data of the pipe sections versus those of the tubes yielded a linear regression of fairly high coefficient of determination of $R^2 \approx 0.90$.

The main conclusion one can draw from these results is that four-point TEP measurements can be used to positively identify the normalized and heat affected zone microstructures of Grade 91/92 martensitic steels that produce significantly elevated hardness levels, but, with the possible exception of the over tempered condition, other microstructures of lower hardness levels cannot be distinguished by TE NDE alone.

4. References

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[2] J. Corcoran, S. Raja, and P. B. Nagy, "Improved thermoelectric power measurements using a four-point technique," *NDT&E Int.* **94**, 92-100 (2018).

[3] P. B. Nagy, "Non-destructive methods for materials' state awareness monitoring," *Insight* **52**, 61-71 (2010).

[4] J. Hu and P. B. Nagy, "On the role of interface imperfections in thermoelectric nondestructive materials characterization," *Appl. Phys. Lett.* **73**, 467-469 (1998).

5. Figures

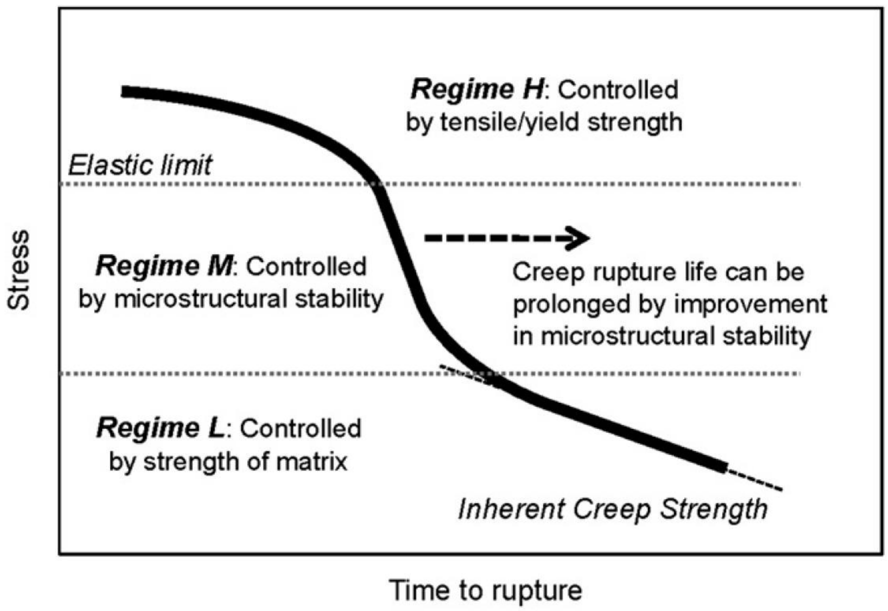

Figure 1 Schematic illustration of creep strength vs rupture time in the high-, medium-, and low-stress regimes of Grade 92 steel [1].

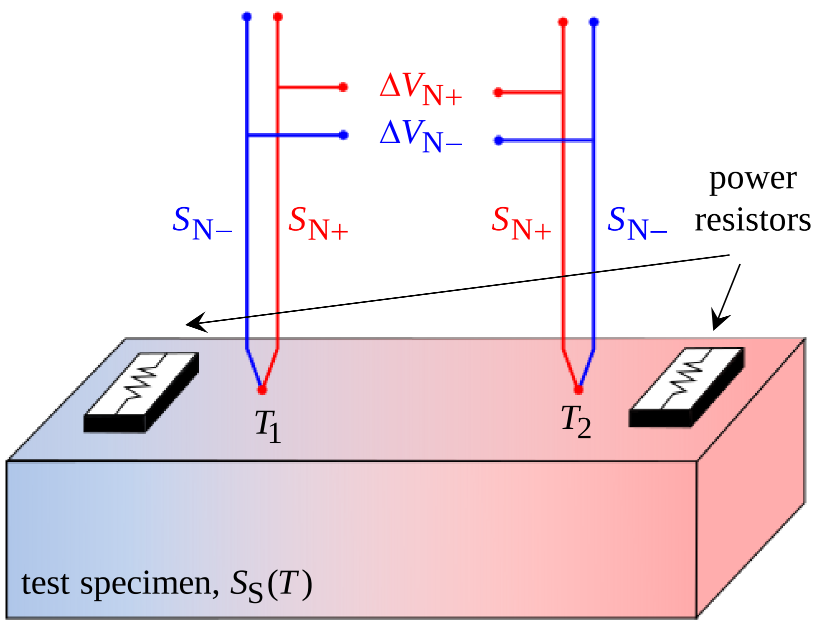

Figure 2 Schematic arrangement of the four-point TEP measurement.

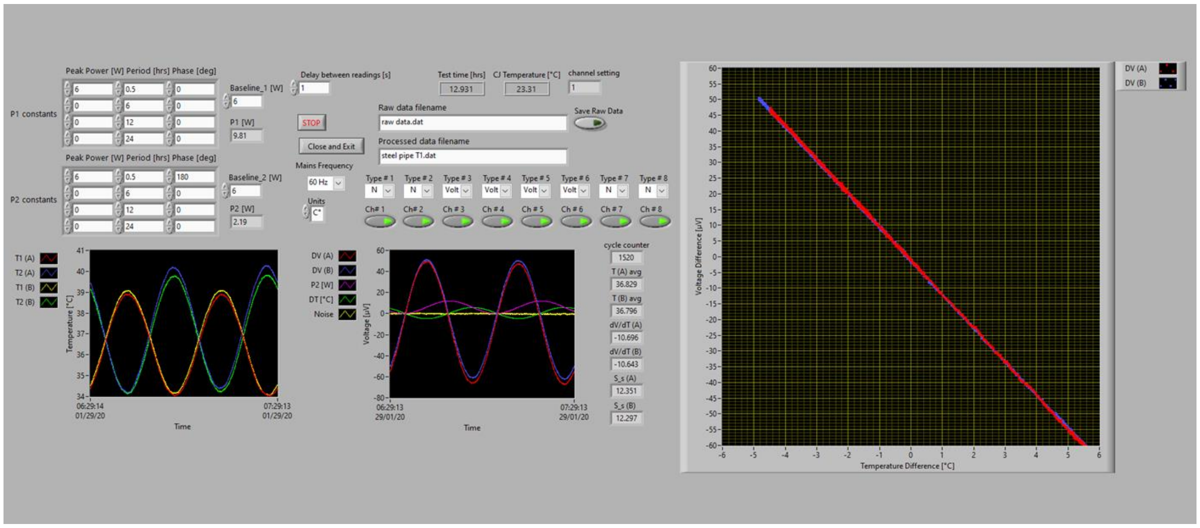

Figure 3 Data acquisition and processing LabView software used for four-point TEP measurements (tube specimen T1, as received).

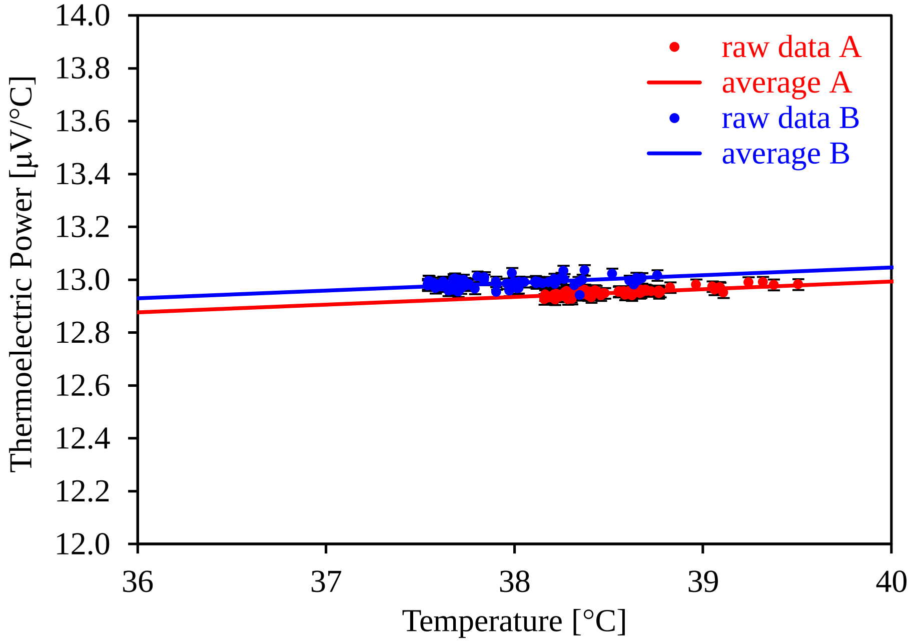

Figure 4 A typical example of TEP readings at two measurement locations from tube specimen T1 of as received condition.

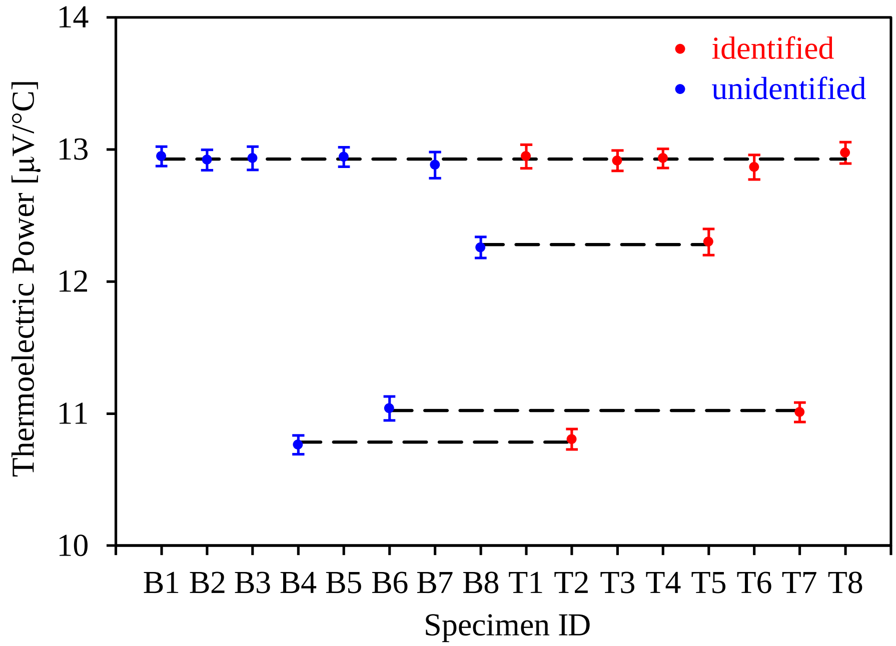

Figure 5 Four-point TEP measurement results obtained from sixteen steel tubes (specimens marked with B are unidentified while those marked with T are identified).

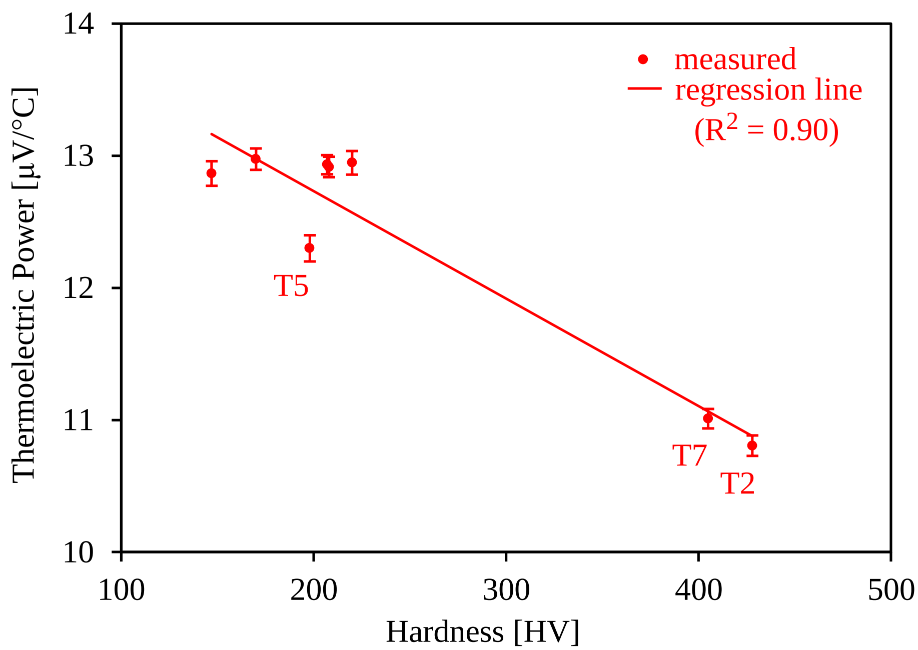

Figure 6 Four-point TEP measurement results versus Vickers hardness provided by EPRI for eight steel tubes with identified microstructures.

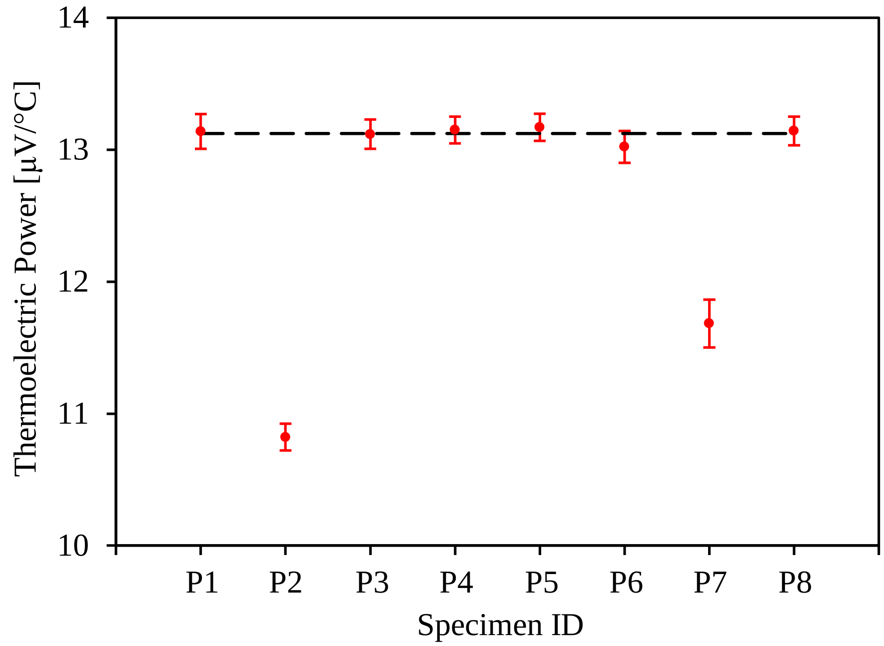

Figure 7 Four-point TEP measurement results obtained from eight steel pipe sections.

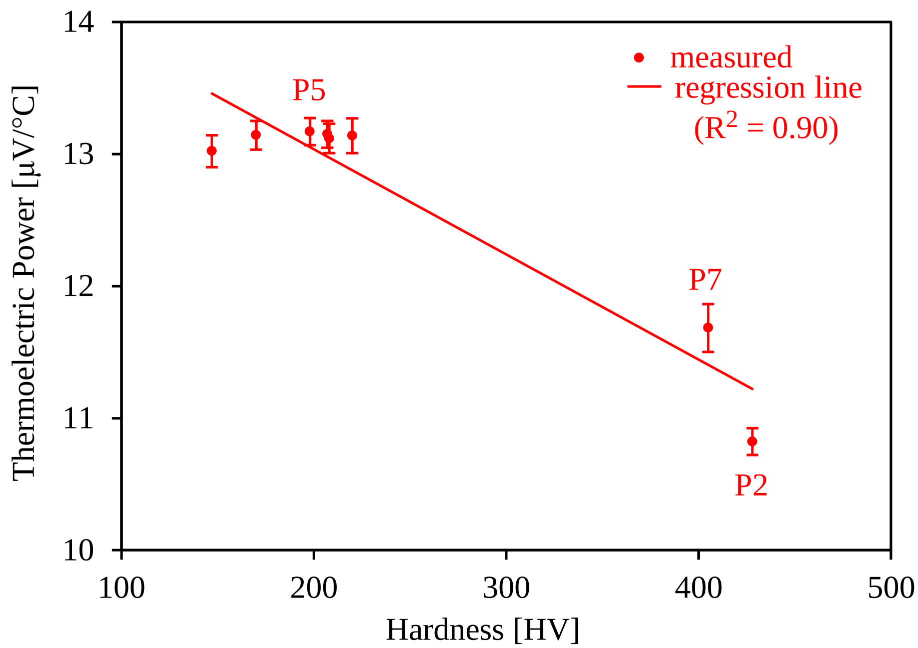

Figure 8 Four-point TEP measurement results versus Vickers hardness provided by EPRI for eight steel pipe sections with identified microstructures.

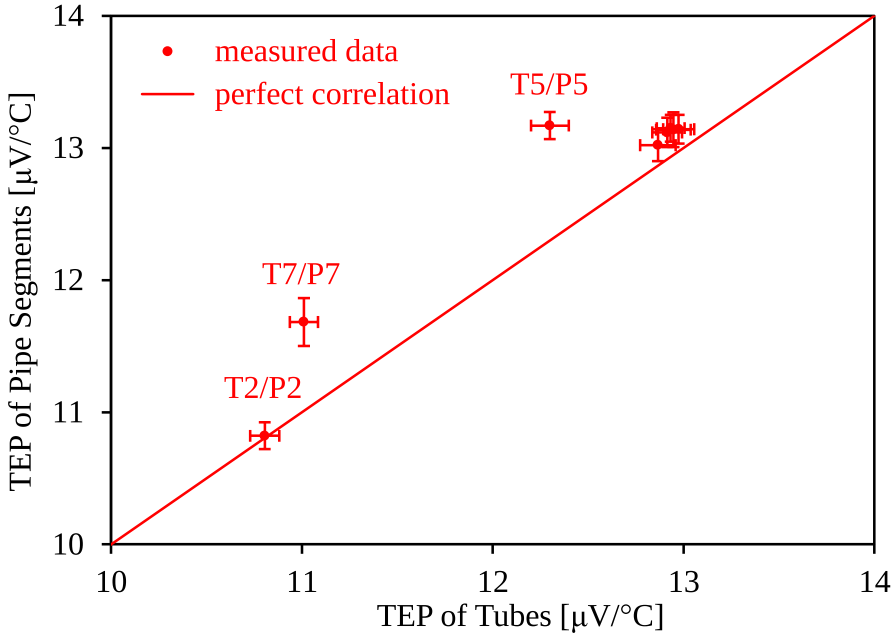

Figure 9 Comparison of four-point TEP measurement results for tubes and pipe sections.