

An Investigation of Microstructural Change of Low Alloy Steel AISI 4150 by Seebeck Coefficient

Teerapong SAMRAN¹ and Preecha TERMSUKSAWAD^{2*}

¹School of Metallurgical Engineering, Institute of Engineering,
Suranaree University of Technology, Nakhon Ratchasima, 30000 Thailand
²Division of Materials Technology, School of Energy Environment and Materials,
King Mongkut's University of Technology Thonburi, Bangkok 10140 Thailand

Abstract

Low alloyed steels, whose hardness can be modified by heat treatment, have been widely used in various applications. After heat treatment, they are normally destructively characterized and tested by many approaches via optical microscope and hardness testing. It is useful to develop a non-destructive method relating to its properties and microstructures. The proposed non-destructive approach in this study is the Seebeck coefficient measurement. The materials in this study were carbon steels AISI 4150 rod with a diameter of 1.3 cm and length of 3 cm. The specimens were heat-treated at 900°C for 1 hour and were then cooled to room temperature in furnace and in various mediums: air, oil and water. In addition, one of the samples was cooled in salt bath at 350°C for 1 hour and then cooled in water. X-ray diffractometry (XRD) and optical microscopy (OM) were used to characterize their crystal structures and microstructures, respectively. The Seebeck coefficient was measured relative to that of copper. The result indicated that the Seebeck coefficients of the treated samples are negative and their magnitudes are inversely related to hardness. The Seebeck coefficient also tends to be related to the crystal structure. Microstructure investigation, in addition, revealed that the magnitude of the Seebeck coefficient increases with a decrease of grain size. In conclusion, the Seebeck coefficient measurement could possibly be applied to study the microstructure of low alloyed steels.

Key words: Seebeck coefficient, Low alloyed steel, Heat treatment, XRD, Microstructure

Introduction

Low alloyed steels are steels with small additions of alloying elements such as nickel, chromium and molybdenum. These alloying elements increase hardenability of the steels; as a result, the mechanical properties of these steels can be improved by heat treatment. Because these steels possess good mechanical properties, they have been widely used in many applications such as automobile parts, structural steel parts, pipelines, etc. After heat treatment, the microstructure of the steels is altered and their mechanical properties such as hardness and strength are improved. Typically, mechanical properties of heat-treated steels such as hardness and strength are examined by some destructive tests. Therefore, it is useful to develop a nondestructive technique to predict these properties. One of the candidates is Seebeck coefficient or thermoelectric power measurement, which measures the amount of induced voltage developed by temperature

difference, $S_{AB} = \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T}$.⁽¹⁾ The Seebeck coefficient or thermoelectric power is contributed by two components: diffusion and phonon-drag thermoelectric powers. The phonon-drag thermoelectric power is very small and can be neglected at room temperature or above. Diffusion thermoelectric power is a function of electrical conductivity and effective mass.⁽²⁾ Effective mass is defined as curvature of electronic structure at the Fermi level.⁽²⁾ The effective mass, m^* , is calculated by $m^* = \hbar^2 \frac{d^2 E}{dk^2}$, where \hbar^2 and $\frac{d^2 E}{dk^2}$ are Plank's constant and curvature of electronic structure at Fermi level, respectively. Both electrical conductivity and effective mass are functions of microstructure and electronic structure; consequently, the Seebeck coefficient depends on these structures as well. It should be noted that signs of Seebeck coefficient depend on types of carriers.⁽³⁾ If a carrier is an

electron, the Seebeck coefficient will be negative. In contrast, positive Seebeck coefficient is found when the hole is a carrier. The magnitude of the Seebeck coefficient depends on effective mass and difficulty of carrier transport. Effects of microstructure of carbon steel on Seebeck coefficient were studied by various research groups.⁽⁴⁻⁷⁾ The effect of annealing on thermoelectric power of low carbon steel containing 460 ppm aluminium and 74 ppm nitrogen was investigated by Brami, *et al.*⁽⁴⁾ In this study, thermoelectric power increased with amounts of AlN and carbon precipitation. For ultra low carbon steel, Seebeck coefficient decreases with increasing defect concentration or amount of dissolved elements in the matrix, and increases with the amount of precipitation.^(5,6) An increase of Seebeck coefficient due to the amount of carbide precipitates was also found in martensitic stainless steel.⁽⁷⁾ In addition, Caballero, *et al.* indicated that the Seebeck coefficient can be increased with increasing grain size of austenite due to a decrease of grain boundary concentration. In literature, therefore, it is possible to study the effect of heat treatment on microstructure and mechanical properties of low alloyed steel via Seebeck coefficient. The present study aims to investigate this relationship in order to further develop this concept as non-destructive testing for heat-treated steel.

Materials and Experimental Procedures

Low alloy steel grade AISI 4150 rods with a diameter of 1.3 cm and length of 3 cm were used in this study. The sample composition, analyzed by emission spectroscopy, is shown in Table 1. From this table, the main alloying elements in this steel are chromium and molybdenum; both increase the hardenability of the steel.

Table 1. Composition of sample, analyzed by emission spectroscopy (wt.%)

	C	Mn	P	S	Cr	Mo	Si
AISI 4150 (std.)	0.48-0.53	0.75-1.00	≤ 0.035	≤ 0.04	0.75-1.2	0.15-0.25	0.15-0.3
Sample	0.489	0.789	0.021	0.002	0.851	0.177	0.192

The samples were annealed at approximately 900°C for 1 hour and subsequently cooled in different media: in furnace, air, water and oil. In addition, one of the samples was cooled in salt bath at 350°C for 1 hour and then cooled in water. Three specimens of each treatment were prepared. Seebeck

coefficients of heat-treated samples, relative to Seebeck coefficient of copper, were measured. The configuration of the Seebeck coefficient apparatus is demonstrated in Figure 1. The Seebeck coefficient of the sample, S_R , relative to Seebeck coefficient of copper, S_{Cu} , was calculated by the equation:

$$S_R = \frac{\Delta V}{\Delta T} \quad (1)$$

where ΔV and ΔT are induced voltage difference (V) and temperature difference (K), respectively. The absolute Seebeck coefficient of the sample can then be calculated by:

$$S_a = S_R + S_{Cu} = \frac{\Delta V}{\Delta T} + S_{Cu} \quad (2)$$

The applied temperature at the cold side is set at 26°C, which is the room temperature. The temperature difference between hot and cold sides in this experiment was maintained at approximately 4°C. The temperature at the hot side was controlled by heater with temperature control unit. The Seebeck coefficient of copper at 300 K is 1.83 $\mu\text{V}/\text{K}$.⁽¹⁾

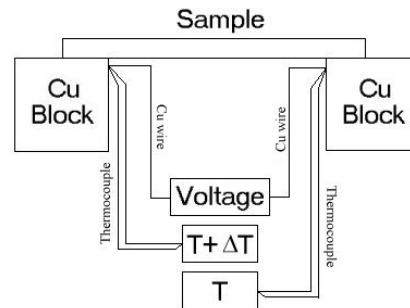


Figure 1. Diagram of Seebeck coefficient measurement apparatus

After Seebeck coefficient was determined, the hardness of the samples was measured by Rockwell scale C hardness testing machine with a loading of 150 kg; their microstructures were then investigated by optical microscope. The crystal structures of each sample were also examined by

D-8 Bruker X-ray diffractometer using Cu-K α as X-ray source, with step width of 0.02 degree and step time of 0.04 s.

Results and Discussion

Hardness and Seebeck Coefficient

Hardness and Seebeck coefficients of as-received samples and heat-treated low alloy steels after quenching with different media are shown in Figure 2. The negative Seebeck coefficient revealed that electron is a carrier responsible for thermoelectric power of the samples. According to Vedenikov⁽⁸⁾, Seebeck coefficient of pure iron at 300 K is approximately +12 $\mu\text{V}/\text{K}$. However, Seebeck coefficient of steel is perturbed by solute element in solid solution, microstructure, dislocation and precipitates.^(5,6) Among these contributions, contribution from solute atom is the greatest because solute atoms act as new diffusion centers for electrons.⁽⁵⁾ The contribution from solute atom to Seebeck coefficient, ΔS_i , obeys the linear law as shown by⁽⁶⁾:

$$\Delta S_i = \sum K_i C_i \quad (3)$$

where K_i and C_i are the specific thermoelectric power per weight percent of solute element i ($\mu\text{V}/(\text{K}\cdot\text{wt}\%)$) and amount of solute element i (wt.%), respectively.⁽⁶⁾ The value of K_i depends on various factors such as chemical composition, texture, grain size, etc.⁽⁶⁾ For example, the K_C varies from -20 to -52 $\mu\text{V}/\text{K}\cdot\text{wt}\%$ depending on carbon contents.⁽⁵⁻⁷⁾ The higher the carbon content, the lower is the K_C value. K_{Cr} and K_{Mn} were also reported as -0.30 and -3 $\mu\text{V}/\text{K}\cdot\text{wt}\%$, respectively.⁽⁷⁾ The change of the sign of Seebeck coefficient due to contribution from microstructure relies on the type of phase transformation. For example, an amount of retained austenite in martensitic stainless steel leads to a positive Seebeck coefficient with a specific thermoelectric power constant of +0.087 $\mu\text{V}/\text{K}\cdot\text{wt}\%$.⁽⁷⁾ It can be observed that the effect of the microstructure on thermoelectric power is smaller than that of solute atom in the order of magnitude; therefore, the negative Seebeck coefficient of steel is expected.

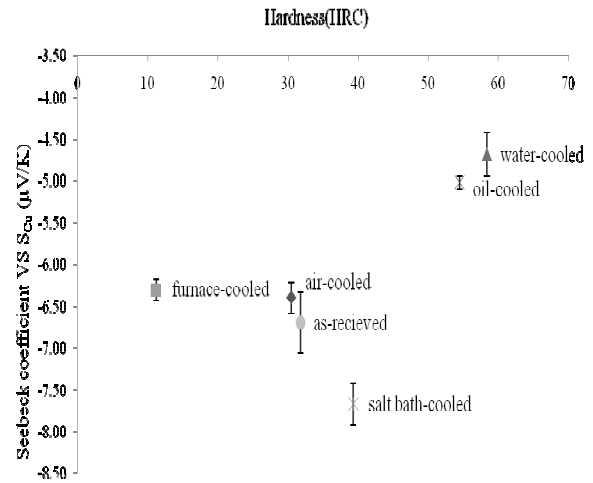


Figure 2. Hardness (HR_C) and Seebeck coefficients of as-received sample and heat-treated low alloy steels after quenching in different media

Figure 2 also demonstrates dependence of Seebeck coefficient on quenching media or cooling rate. When cooling rate is high, e.g. quenching in oil or water, the magnitude of Seebeck coefficient decreases and hardness increases. This phenomenon may be used to establish a relationship between Seebeck coefficient and hardness. It is well known that for fast cooling rate, carbon atoms do not have enough time to diffuse out of the austenite to form an equilibrium microstructure of pearlite. Consequently, depending on cooling rate, non-equilibrium structures such as bainite or martensite will form, and the hardness of the quenched sample increases. Hardness and Seebeck coefficients, relative to that of copper, of the samples quenched with low and moderate cooling rate are in the range of 10-40 HR_C and -6.2 to -8.0 $\mu\text{V}/\text{K}$, respectively. These values are significantly lower than those of samples quenched at a high cooling rate. From this point of view, Seebeck coefficient may be used as qualitative gauge to indicate range of hardness of the quenched steel. The relationship between cooling rate, hardness and Seebeck coefficient will be explained by crystal structure and microstructure as discussed later.

XRD-Result

The effect of the cooling rate on crystal structure can be seen by X-ray diffraction pattern demonstrated in Figures 3 and 4. These figures illustrate that crystal structures of quenched samples can be sorted into two groups: 1) samples quenched at low and moderate cooling rate and 2) samples quenched at high cooling rate. Figure 3

indicates that crystal structure of sample with low cooling rate is body center cubic with diffracted planes of (110), (200) and (211). In addition, (200) and (211) peaks tend to disappear when cooling rate is high. When considering (110) peak (Figure 4), (110) peaks of water-quenched and oil quenched samples are shifted from those of the other samples. In addition, they are broader than those of samples quenched at low and moderate cooling rate. The broader peaks indicate an occurrence of lattice distortion during fast cooling. During rapid cooling, carbon atoms cannot diffuse from austenite to form cementite and ferrite, but they are trapped in the octahedral sites of a body-centered cubic structure. As a result, a new phase, martensite, is formed.⁽⁹⁾ This type of transformation is diffusionless and results in lattice distortion. As shown in Figure 2, the magnitudes of Seebeck coefficients of oil-cooled and water-cooled samples are lower than those of other samples. The reduction of the magnitude of Seebeck coefficient may be due to lattice distortion. The distortion obstructs electron movement; consequently, the magnitude of Seebeck coefficient decreases. This explanation can also be applied when the Seebeck coefficients and X-ray diffraction patterns of only oil-quenched and water-quenched samples are related. However, crystal structure and chemical composition are not the only factors affecting the Seebeck coefficient. To explain the variation of Seebeck coefficients of as-received, furnace-cooled, air-quenched samples and of samples quenched in salt bath, a microstructural analysis is needed.

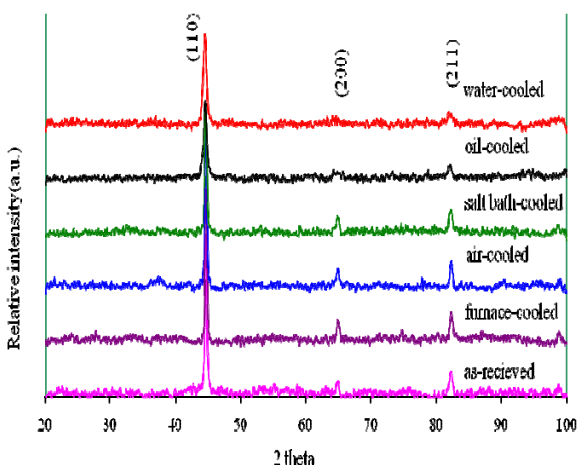


Figure 3. X-ray diffraction pattern of as-received sample and quenched samples

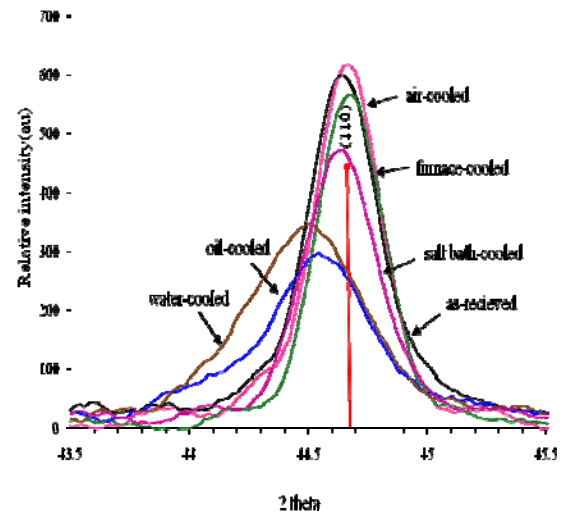


Figure 4. (110) peak of as-received sample and quenched samples

Microstructure

The microstructure of each sample is shown in Figure 5. This figure demonstrates that microstructures of oil-quenched and water-quenched samples are martensite with some ferrite. This microstructure is consistent with lattice distortion as indicated by XRD result. It is well known that the dislocation density of samples quenched at high cooling rate is very high. Accordingly, increase of hardness is expected. Not only does the dislocation increase hardness, it also impedes electron transport. Therefore, rather than the effect of lattice distortion, magnitudes of Seebeck coefficients of oil-quenched and water-quenched samples are reduced by the existing dislocation. Figure 5 also indicates the presence of ferrite and pearlite in samples cooled at low and moderate cooling rate. Unlike the microstructure of the furnace-cooled sample, the ferrite and cementite of the other samples are not owing to lamellar order as illustrated in Figure 6. The non-lamellar array of ferrite and cementite is classified as bainite.⁽⁹⁾ In addition, cementite in as-received, air-cooled and salt bath-cooled samples disperses all over the microstructure. Consequently, hardness of these samples is higher than that of the furnace-cooled sample. Although the microstructure of the furnace-cooled sample is different from microstructures of as-received and air-quenched samples, the Seebeck coefficients of all three samples are insignificantly different. The reason for this may be that the phases (ferrite and cementite) present in these samples are the same. However, this is not conclusive and more investigation is needed. As has been distinguished before from Seebeck coefficient and XRD result, the magnitude of Seebeck coefficient of the sample

quenched in salt bath is slightly higher than magnitudes of the other samples, although microstructures of as-received sample and of samples quenched in air and salt bath are all bainite. The higher magnitude of the Seebeck coefficient may be due to larger grain size. Theoretically, grain boundary behaves as an obstacle for electron transport. Increasing magnitude of Seebeck coefficient due to increasing grain size was also found by Caballero, *et al.*⁽⁷⁾

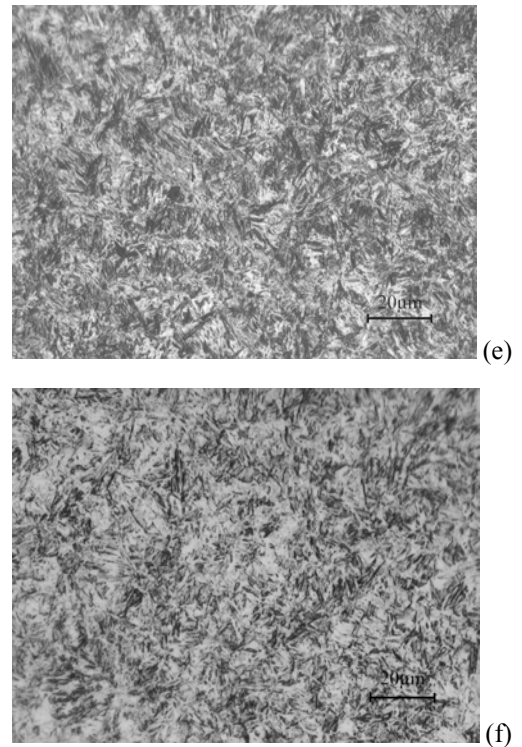
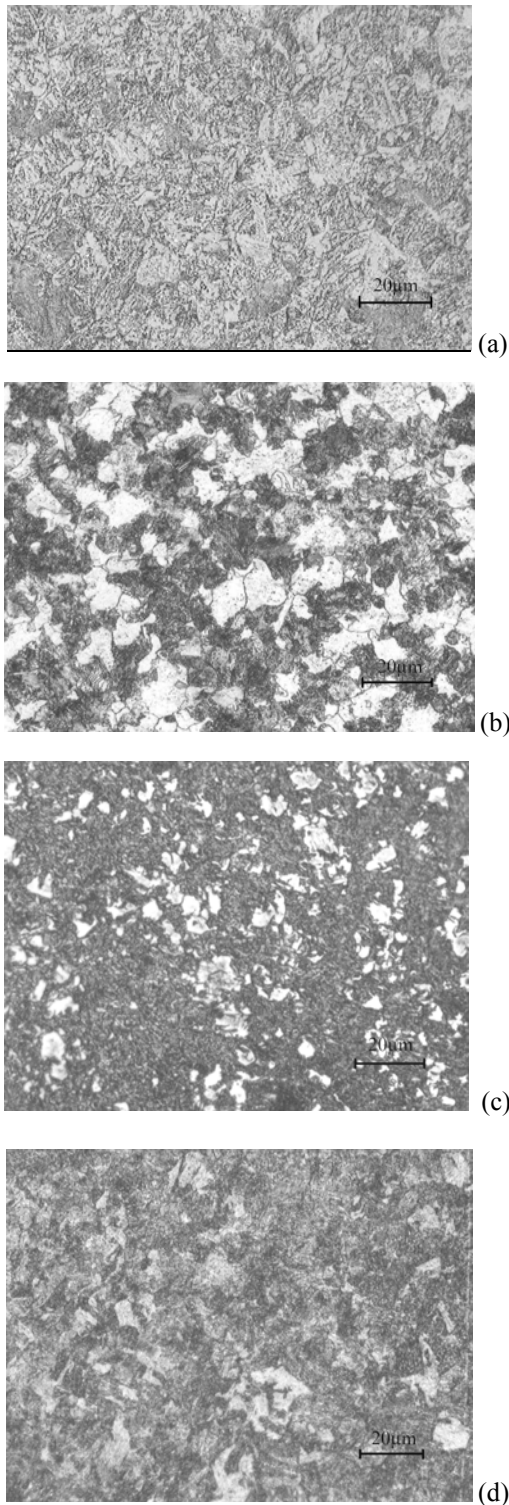


Figure 5. Microstructures of samples: a) as-received, and heat-treated samples with different quenching media: b) furnace, c) air, d) salt bath, e) oil and f) water at magnification of 500x

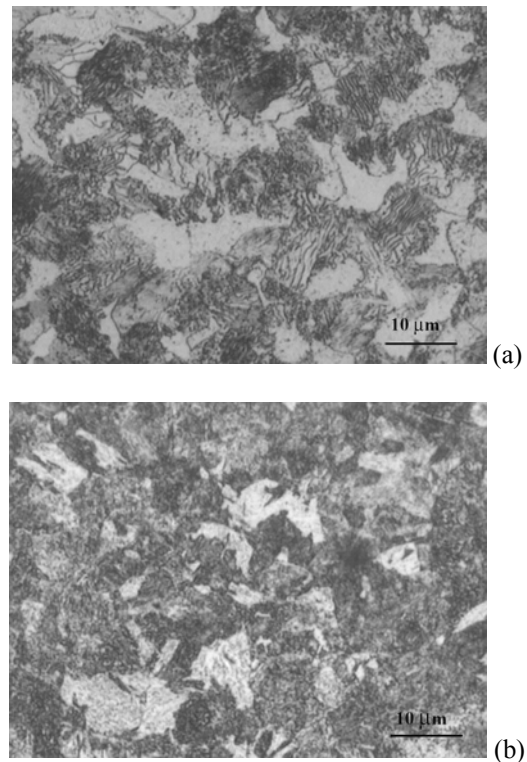


Figure 6. Microstructures of samples cooled in a) furnace and b) salt bath at magnification of 1000x

Conclusions

This research proposes an attempt to apply Seebeck coefficient measurement as a non-destructive test method. Seebeck coefficients and hardness of low alloy steels AISI 4150, after subject to various heat treatments, were measured. Negative Seebeck coefficient indicated that electron is a carrier. The Seebeck coefficients of the treated samples can be grouped into two groups: 1) samples treated at low and medium cooling rates and 2) sample treated at high cooling rate. The magnitudes of the Seebeck coefficients decreased with increasing cooling rate. Seebeck coefficient of the quenched samples is affected by crystal structure and microstructure. Although Seebeck coefficients of the treated samples are not linearly related to hardness, they can be used to identify which samples possess high hardness. Therefore, Seebeck coefficient can be used as a qualitative gauge for high hardness steel. To extend this technique to other ferrous alloys, the Seebeck coefficient of those alloys must be measured with various treatments; then the Seebeck coefficient-hardness-composition diagram of ferrous alloys may be developed.

References

1. Blatt, F.J., Schroeder, P.A., Foiles, C.L. and Greig, D.L. 1976. Thermoelectric power of metals, New York : Plenum press : 310.
2. Mott, N.F. and Jones H. 1936. The theory of the properties of metals and alloys. New York: Dover Inc.
3. Kasap, S. 1996. *Thermoelectric effects in metals: Thermocouples*. (Online). Available: <http://www.materials.usask.ca/samples/Thermoelectric-Seebeck.pdf> [September 9, 2009].
4. Brahma, A. and Borrelly, R. 1997. Study of aluminium nitride precipitation in pure Fe-Al-N alloy by thermoelectric power measurements. *Acta Mater.* **45(5)** : 1889-1897.
5. Lavaire, N., Merlin, J. and Sardoy, V. 2001. Study of ageing in strained ultra and extra low carbon steels by thermoelectric power measurement. *Scr. Mater.* **44(4)** : 553-559.
6. Massardier, V., Lavaire, N., Soler, M. and Merlin, J. 2004. Comparison of the evaluation of the carbon content in solid solution in extra-mild steels by thermoelectric power and by internal friction. *Scr. Mater.* **50(12)** : 1435-1439.
7. Caballero, F.G., Capdevila, C., Alvarez, L.F. and García de Andrés, C. 2004. Thermoelectric power studies on a martensitic stainless steel. *Scr. Mater.* **50(7)** : 1061-1066.
8. Vedemikov M.V. 1969. The thermoelectric powers of transition metals at high temperature. *Adv. Phys.* **18(74)** : 337-370.
9. Krauss, G. 1990. *Steel: Heat treatment and processing principles*. ASM international. Ohio : U.S. 78.