



## Quantifying the dependency of uniform corrosion of structural steel on grain size

Maryam Soleimani, Hamed Mirzadeh\*, Changiz Dehghanian

School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, Tehran, Iran.

Received: 19 November 2019; Accepted: 9 December 2019

\* Corresponding author email: [hmirzadeh@ut.ac.ir](mailto:hmirzadeh@ut.ac.ir)

### ABSTRACT

The dependency of uniform corrosion of structural steel on the average grain size ( $D$ ) should be quantified for design purposes. In the present work, a spectrum of grain sizes was obtained by simple heat treatment routes in st37 structural steel. It was revealed that the corrosion current density ( $i_{corr}$ ) increased by grain refinement, which was related to the increased density of grain boundaries. The data on the plots of hardness and  $i_{corr}$  versus  $1/\sqrt{D}$  were successfully fitted by a straight line and an exponential function, respectively. Therefore, the mechanical response was rationalized by a Hall-Petch type relationship with a slope of  $237.8 \text{ MPa}/\mu\text{m}^{0.5}$ . Moreover, the obtained simple relationship between  $i_{corr}$  and  $1/\sqrt{D}$  can be used for prediction of the dependency of uniform corrosion on the average grain size.

**Keywords:** Structural steel; Corrosion resistance; Grain size; Hall-Petch law.

### 1. Introduction

A general consensus regarding the grain size effect on corrosion resistance of ferrous alloys is not available. If the coarse grained sample shows an active behavior in an electrolyte, then grain refinement likely will make the surface more active. However, when it shows passive behavior, grain refinement will likely results in a more stable protective film [1]. The energies of grain boundaries and triple junctions are higher than that of the bulk and there is an enhanced electron activity and diffusion rates, and hence, grain refinement can significantly enhance the reactivity of the surface [2].

The mechanical performance of metallic materials is largely determined by the average grain size, where finer grain sizes are favorable for room-temperature mechanical properties and this relationship can be expressed by the Hall-Petch type law [3]. The application of this law for mild

steel has been verified by Hall [4]. For mild steel with submicron grains, Liu et al. [5] proposed relationships of  $\sigma_y \text{ (MPa)} = 272.15 + 236.66/\sqrt{D(\mu\text{m})}$  and  $H \text{ (GPa)} = 2 + 0.67/\sqrt{D(\mu\text{m})}$  for yield stress and hardness, respectively. Based on these works, the dependency of the mechanical strength can be successfully expressed by the Hall-Petch type relationships. It should be noted that fine grain sizes are not recommended at high temperatures when creep deformation becomes pronounced [6].

However, due to the higher energy and chemical activity of grain boundaries, a high density of these boundaries increases the reactivity of the surface through increased electron activity and diffusion [1,2], and hence, it can affect the corrosion resistance. Higher corrosion resistance results in longer service of the steel structures [7]. Therefore, studying the effect of grain size on the corrosion resistance of low carbon steel is an important

subject. Accordingly, the effect of grain size on the corrosion resistance of low carbon steel will be studied in the present work, where a spectrum of grain sizes will be obtained by simple heat treatment routes that can be applied in the industrial practice.

## 2. Experimental details

Sheets of 0.12C-1.11Mn-0.16Si (wt%) st37 steel were austenitized at 1050 °C for the holding times of 1, 120, and 240 min followed by air cooling (normalizing) or furnace cooling (full annealing) as shown in Table 1. After etching in the 2% Nital solution, optical micrographs were taken and the average grain size was obtained based on the standard intercept method (ASTM E112 - 13). Vickers hardness test was based on the loads of 5 kg. A Solartron potentiostat (Model SI 1287)

operating at the scanning speed of 2 mV/s was used for corrosion tests in a 3.5 wt% NaCl solution at room temperature, which was based on the three electrode configuration (saturated calomel and platinum as counter and reference electrodes, respectively). These corrosion tests were repeated twice and it was found that the reproducibility of the results was in the valid range.

## 3. Results and discussion

The representative microstructures are shown in Figure 1 and the obtained grain sizes are summarized in Table 1. It can be seen that the samples have ferritic-pearlitic microstructures, which is consistent with the microstructure of similar steels [8,9]. By increasing the holding time at the austenitization temperature, the

Table 1- Details of the considered samples in the present work

Sample	Austenitization time (min)	Annealing method	Average grain size (μm)
D1	1	Normalizing	11.5 ± 1.5
D2	120	Normalizing	28.0 ± 1.2
D3	120	Full annealing	47.7 ± 1.7
D4	240	Full annealing	70.0 ± 2.1

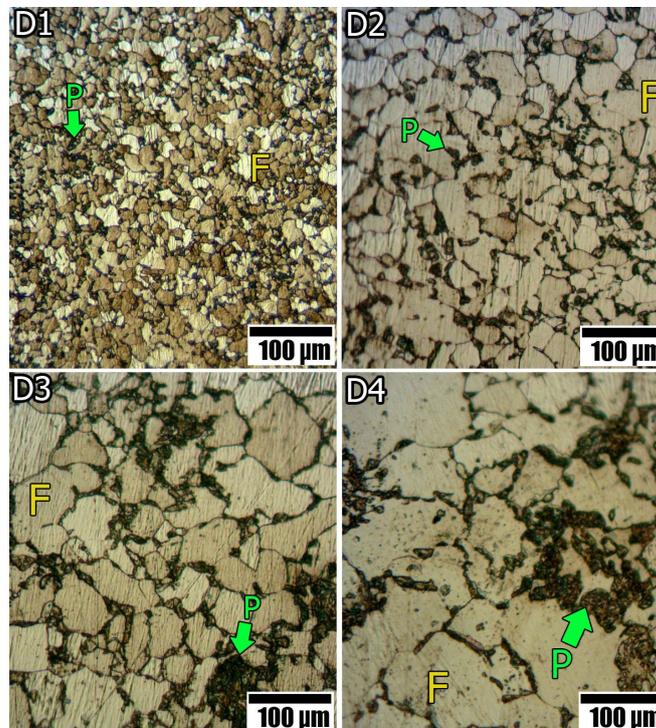


Fig. 1- Micrographs of the processed samples, where F and P denote the ferrite grains and pearlite colonies, respectively.

microstructures became coarser. This is related to the effect of austenitization time on the grain growth of austenite, and hence, coarser grain sizes were obtained during decomposition of austenite as also shown in previous works [10,11]. It can be also seen that grains of the fully annealed samples are coarser than that of the normalized ones. For instance, compare the grain size at the austenitization time of 120 min for the D2 and D3 samples. The measured hardness values of the samples are shown in Figures 2, where it is seen that, by increasing the grain size, the hardness falls rapidly, which was an expected result based on the Hall-Petch strengthening law as discussed by Armstrong [3].

Representative polarization curves are shown in Figures 3, where the corrosion current density ( $i_{corr}$ ) was obtained by the Tafel extrapolation method [12] according to the anodic and cathodic extrapolation lines. The results are summarized in Figures 4, where by grain refinement, it can be seen that  $i_{corr}$  increased significantly. This can be directly

related to the effect of grain boundaries [7]. Due to the higher energy and chemical activity of grain boundaries, a high density of these boundaries increases the reactivity of the surface through increased electron activity and diffusion [1,2].

Based on Figure 3,  $E_{corr}$  is in the range of -0.7 V to -1 V. For NaCl solution with pH of 7, the Pourbaix diagram of iron in Figure 5 [13] predicts that the metal does not form a stable coating of an oxide, and hence, passivation does not occur.

Figure 6 shows the dependency hardness and  $i_{corr}$  on  $D^{-0.5}$ , where D is the average grain size. It can be seen that the hardness data can be fitted by straight line, and hence, the hardness data follows a Hall-Petch type relationship. This reveals that the mechanical response can be judged by Hall-Petch type relationships, which can be used for design purposes. On the other hand, the  $i_{corr}$  data can be fitted by an exponential function. As a result, the following relationships were obtained for the dependency of hardness and uniform corrosion on the average grain size:

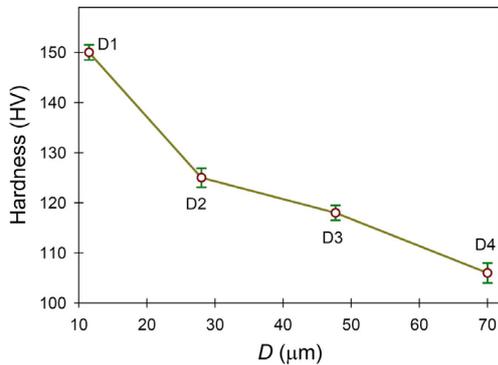


Fig. 2- Hardness versus average grain size.

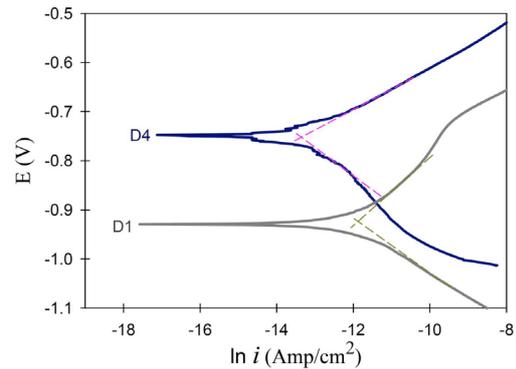


Fig. 3- Representative polarization curves.

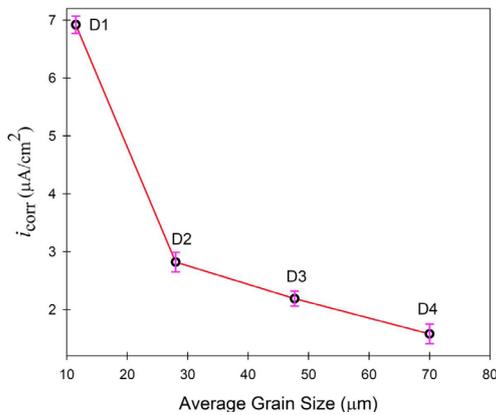


Fig. 4- Values of  $i_{corr}$  versus average grain size.

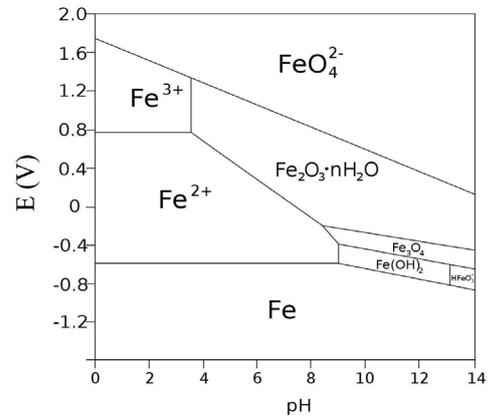


Fig. 5- Pourbaix diagram (simplified potential-pH) of iron [13].

$$H(HV) = 80.27 + 237.8/\sqrt{D} \quad (\text{eq. 1})$$

$$i_{\text{corr}}(\mu\text{A}/\text{cm}^2) = 0.62\exp(8.16/\sqrt{D}) \quad (\text{eq. 2})$$

For the hardness relationship, the intercept (80.27 HV) represents the intrinsic hardness of the crystal (lattice friction) regardless of the grain size [6]. This value is comparable to the reported hardness of ferrite (80 HB [14]). It should be noted that  $80.27 \text{ HV} \approx 76.25 \text{ HB}$  ( $1 \text{ HB} \approx 0.95 \text{ HV}$  [15]). This reveals that the Hall-Petch type relationship for hardness is valid, and hence, the Hall-Petch slope of  $237.8 \text{ MPa}/\mu\text{m}^{0.5}$  is reasonable. The  $i_{\text{corr}}$  relationship predicts the  $i_{\text{corr}}$  of  $0.62 \mu\text{A}/\text{cm}^2$  for the single-crystal iron. By decreasing grain size, and increasing grain boundary area, the corrosion rate increases exponentially as predicted by Equation 2.

#### 4. Conclusions

In summary, a spectrum of grain sizes was obtained by simple heat treatment routes in st37 structural steel and the variation of hardness and corrosion current density ( $i_{\text{corr}}$ ) with grain size were studied. The following conclusions can be drawn:

1. It was revealed that the corrosion current density increased by grain refinement, which was related to the increased density of grain boundaries.
2. The data on the plot of hardness versus  $1/\sqrt{D}$  was successfully fitted by straight line, and hence, the mechanical response can be judged by Hall-Petch type relationship of  $H(HV) = 80.27 + 237.8/\sqrt{D}$ .

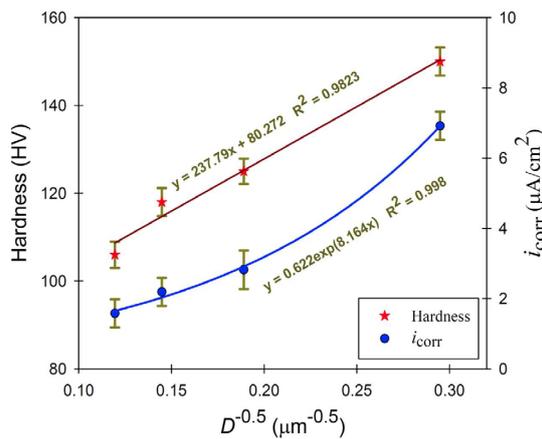


Fig. 6- Dependency of hardness and  $i_{\text{corr}}$  on average grain size.

The intercept (80.27 HV) as the intrinsic hardness of the crystal was comparable to the reported hardness of ferrite (80 HB), which revealed that the Hall-Petch slope of  $237.8 \text{ MPa}/\mu\text{m}^{0.5}$  was reasonable.

3. The  $i_{\text{corr}}$  data versus  $1/\sqrt{D}$  was fitted by an exponential function of  $i_{\text{corr}}(\mu\text{A}/\text{cm}^2) = 0.62\exp(8.16/\sqrt{D})$ , which predicts the  $i_{\text{corr}}$  of  $0.62 \mu\text{A}/\text{cm}^2$  for the single-crystal iron. By decreasing grain size, and increasing grain boundary area, the corrosion rate increases exponentially.

#### References

1. Ralston KD, Birbilis N, Davies CHJ. Revealing the relationship between grain size and corrosion rate of metals. Scripta Materialia. 2010;63(12):1201-4.
2. Ralston KD, Birbilis N. Effect of Grain Size on Corrosion: A Review. CORROSION. 2010;66(7):075005--13.
3. Armstrong RW. 60 Years of Hall-Petch: Past to Present Nano-Scale Connections. MATERIALS TRANSACTIONS. 2014;55(1):2-12.
4. Hall EO. The Deformation and Ageing of Mild Steel: III Discussion of Results. Proceedings of the Physical Society Section B. 1951;64(9):747-53.
5. Liu MY, Shi B, Wang C, Ji SK, Cai X, Song HW. Normal Hall-Petch behavior of mild steel with submicron grains. Materials Letters. 2003;57(19):2798-802.
6. Paupler P. G. E. Dieter. Mechanical Metallurgy. 3rd ed., Mc Graw-Hill Book Co., New York 1986. XXIII + 751 p., DM 138.50, ISBN 0-07-016893-8. Crystal Research and Technology. 1988;23(2):194-.
7. Chen YT, Zhang KG. Influence of Grain Size on Corrosion Resistance of a HSLA Steel. Advanced Materials Research. 2012;557-559:143-6.
8. Soleimani M, Mirzadeh H, Dehghanian C. Phase transformation mechanism and kinetics during step quenching of st37 low carbon steel. Materials Research Express. 2019;6(11):1165f2.
9. Cabrera JM, Ponce J, Prado JM. Modeling thermomechanical processing of austenite. Journal of Materials Processing Technology. 2003;143-144:403-9.
10. Kumar S, Aashranth B, Samantaray D, Davinci MA, Borah U, Bhaduri AK. Influence of nitrogen on kinetics of dynamic recrystallization in Fe-Cr-Ni-Mo steel. Vacuum. 2018;156:20-9.
11. Lin YC, Chen M-S, Zhong J. Microstructural evolution in 42CrMo steel during compression at elevated temperatures. Materials Letters. 2008;62(14):2132-5.
12. Mandal S, Ummadi R, Bose M, Balla VK, Roy M. Fe-Mn-Cu alloy as biodegradable material with enhanced antimicrobial properties. Materials Letters. 2019;237:323-7.
13. Fontana MG. Corrosion Engineering, 3rd edition: McGraw-Hill; 1987.
14. Nag P, Tripathi K, Pawar C. Basic Mechanical Engineering. McGraw-Hill, New York; 2009.
15. Hosford WF. Mechanical behavior of materials: Cambridge university press; 2010.