On the hardness of high carbon ferrous martensite

J Mola* and M Ren

Institute of Iron and Steel Technology, Technische Universität Bergakademie Freiberg, Leipziger St. 34, 09599 Freiberg, Germany

* e-mail: mola@iest.tu-freiberg.de

Abstract. Due to the presence of retained austenite in martensitic steels, especially steels with high carbon concentrations, it is difficult to estimate the hardness of martensite independent of the hardness of the coexisting austenite. In the present work, the hardness of ferrous martensite with carbon concentrations in the range 0.23-1.46 mass-% was estimated by the regression analysis of hardnesses for hardened martensitic-austenitic steels containing various martensite fractions. For a given carbon concentration, the hardness of martensitic-austenitic steels was found to increase exponentially with an increase in the fraction of the martensitic constituent. The hardness of the martensitic constituent was subsequently estimated by the exponential extrapolation of the hardness of phase mixtures to 100 vol.% martensite. For martensite containing 1.46 mass-% carbon, the hardness was estimated to be 1791 HV. This estimate of martensite hardness is significantly higher than the experimental hardness of 822 HV for a phase mixture of 68 vol.% martensite and 32 vol.% austenite. The hardness obtained by exponential extrapolation is also much higher than the hardness of 1104 HV based on the rule of mixtures. The underestimated hardness of high carbon martensite in the presence of austenite is due to the non-linear dependence of hardness on the martensite fraction. The latter is also a common observation in composite materials with a soft matrix and hard reinforcing particles.

1. Introduction
The high strength and toughness of martensitic steels make them suitable candidates for a variety of structural and engineering applications [1]. The higher strength of martensite compared to other constituents such as ferrite, austenite, pearlite, and bainite is the reason behind the increasing use of martensite-containing steels. For instance, low carbon dual-phase and hot stamping steels with partially and almost fully martensitic microstructures, respectively, are being increasingly used for structural automobile parts [2,3]. Medium and high carbon martensitic steels, on the other hand, are commonly used in engineering applications such as gears, shafts, and bearings [4,5]. The strength of ferrous martensite arises from factors such as dislocation hardening [6,7], grain boundary hardening as described by the Hall-Petch relation [8], and interstitial strengthening [9]. The strengthening effect of carbon has been proposed to be a consequence of the concurrent increase in the density of dislocations [6]. The dependence of hardness on the carbon concentration has been established in numerous investigations [4,10–12]. For low carbon steels, hardness values reported in various investigations are largely consistent and indicate significant strengthening of martensite by an increase in the solute carbon concentration [12]. The rate of increase in the hardness of martensite decreases as the carbon concentration increases [4,12]. The hardness may even decrease as the carbon content exceeds 0.8-1 mass-% [13]. The latter observation may be justified by the presence of large
quantities of austenite in the microstructure of as-quenched high carbon steels. Therefore, the hardness of martensite in high carbon steels cannot be estimated unless the softening effect of retained austenite is properly excluded. By adjusting martensitic-austenitic microstructures containing various retained austenite contents, the present work enables to determine the dependence of hardness on the fraction of martensite. Establishing an appropriate fitting and extrapolation scheme in turn enables to obtain a realistic estimation of the hardness of martensite, especially in the case of high carbon martensitic steels where the coexistence of high austenite fractions with the martensite is inevitable.

2. Experimental procedure

Ingots with an approximate weight of 300 g and chemical compositions as given in table 1 were prepared in a cold-crucible induction melting facility. Specimens with approximate thicknesses of 4.5-5 mm were austenitized at 1150 °C for 5 min and subsequently quenched to room temperature (RT) using brine (10 NaCl in water). Subsequently, various martensite fractions were adjusted by resumed cooling to temperatures as low as -196 °C, approximately 3 sec after brine quenching. To ensure the absence of decarburization and oxidation in hardened specimens, an outermost layer of specimens with an approximate thickness of 0.8 mm was removed by mechanical grinding. Bulk martensite fractions were then quantified by magnetic measurements at room temperature using a Metis MSAT device equipped with a Lakeshore 480 fluxmeter. For pure iron, the equipment returns a mass magnetization of 213.5 emu/g. Given that the mass magnetization of iron decreases by 1.18 emu/g per mass-% solute Mn [14], the expected magnetization of specimens in the fully martensitic condition ($\sigma_{\alpha'}$) was calculated using the following equation:

$$\sigma_{\alpha'} \text{ (emu/g)} = 213.5 - (1.18 \times C_{\text{Mn}})$$

(1)

Martensite fractions of ternary Fe–Mn–C steels were quantified by dividing measured magnetizations by the magnetization based on equation (1). To obtain hardness values representative of all phases, Vickers hardness measurements with a load of 98 N (HV10) were done using a Wolpert 430-SVD indenter. To estimate the hardness of austenite in the steel 1.4C, a small load of only 49 mN (HV0.005) was applied using a Shimadzu HMV-2000 indenter. To obtain reliable average hardness values, five indentations were performed per specimen. To minimize the occurrence of aging/tempering reactions prior to hardness measurements, the specimens were mounted using cold resin. Mechanical grinding was done using SiC papers with grit sizes between 220 and 2000. Subsequently, specimens were polished using diamond suspensions with particle sizes of 3 μm and 1 μm for a total duration of 20 min. Final polishing for 2 min was done using a suspension of colloidal silica with a particle size of 0.04 μm. The deformation-induced transformation of austenite during the polishing steps was minimized by grinding under the flow of water at 80 °C. Light optical microscopy examinations using unpolarised light were done using a Neophot 30 microscope.

Table 1. Chemical composition of ternary steels in mass-%.

| Steel ID | Mn  | C   | Fe  |
|----------|-----|-----|-----|
| 0.2C     | 1.49| 0.23| bal.|
| 0.6C     | 1.49| 0.64| bal.|
| 1.0C     | 1.33| 1.04| bal.|
| 1.4C     | 1.48| 1.46| bal.|

3. Results and discussion

Table 2 summarizes the martensite contents associated with various quench temperatures. The choice of low quench temperatures aimed to eliminate austenitic regions with a low stability at RT by
inducing their thermal transformation to martensite. In general, the highest quench temperature was raised as the carbon concentration increased. This reduced the likelihood of deformation-induced martensite formation during the surface grinding and polishing steps. For the 1.4C steel, RT was used as the highest quench temperature. Figure 1 shows light optical micrographs for the 1.4C steel quenched to three different temperatures, indicating the increase in the fraction of martensite at lower quench temperatures. To obtain at least two different martensite contents in each steel, quenching to RT was also done for the 0.2C steel. The fraction of retained austenite after cooling to RT was only 3.5 vol.%. The retained austenite was therefore present as film-like regions between martensitic laths. This retained austenite morphology is associated with a much higher mechanical stability compared to the blocky retained austenite present in steels with higher retained austenite contents [15]. Therefore, quenching to RT was also done for the 0.2C steel. Given the influence of C on the martensite start temperature [16]. As table 2 shows, the martensite fraction obtained by quenching to -196 °C decreased as the carbon concentration increased.

Table 2. Martensite fractions after quenching to indicated temperatures

| Steel ID | Martensite fractions after quenching, vol.% |
|----------|--------------------------------------------|
|          | 20 °C | 0 °C  | -50 °C | -100 °C | -196 °C |
| 0.2C     | 96.5  | -     | -      | -       | 98.6    |
| 0.6C     | -     | -     | 92.4   | 94.4    |
| 1.0C     | -     | 83.8  | 85.7   | 87.3    |
| 1.4C     | 8.1   | 30.2  | 54.3   | 64.9    | 68.4    |

Due to the presence of untransformed austenite in the microstructure of all steels even the 0.2C steel with the lowest carbon content, the true hardness of martensite cannot be determined independently of the hardness of austenite. A possible way of excluding the effect of austenite is to extrapolate hardness values for the specimens with various martensite contents. In figure 2, hardness values are plotted as a function of the martensite fraction. The hardness values were measured using an applied load of 98 N (10 kgf). Under this load, the mean diagonal length of indentations would be at least 136 µm for hardness values up to 1000 HV. Therefore, the indentations are large enough to ensure the contribution of both phases to the measured values. Linear extrapolation has been previously used to estimate the hardness of fresh and tempered martensites in the microstructure of a quenched and partitioned Fe–13Cr–0.3C stainless steel [17]. When martensite fractions are varied in a narrow range close to 100 vol.%, different extrapolation schemes lead to similar hardness approximations for martensite. Nevertheless, linear extrapolation of hardness to 0 vol.% martensite might lead to negative hardness values for austenite [17], indicating the inappropriateness of linear extrapolation. In the present case too, linear fitting to experimental hardness values for 0.2C, 0.6C, and 1.0C steels would lead to negative hardness values for austenite. To overcome this obvious drawback of linear fitting, a non-linear fit was made to the experimental data. Hardness values for the 1.4C steel with the broadest variation of martensite fraction indicate the appropriateness of an exponential fit to the data.

Figure 1. Microstructure of the 1.4C steel after quenching to the marked temperatures. Nital was used as etchant. Martensite and austenite appear bright and dark, respectively.
To enhance the regression analysis, the hardness of austenite in the experimental steels was approximated using the following procedure (figure 2, open symbols at 0% martensite). By indenting a large austenitic region with a small load of 49 mN (5 gf), the hardness of austenite in a specimen of 1.4C steel containing a low martensite fraction was determined to be 211 HV. The hardness of austenite in steels containing lower carbon concentrations was assumed to decrease linearly to that for an SUS316L austenitic stainless steel (140 HV) [18] which was assumed to also represent the hardness of interstitial-free austenite in the present steel. The effect of carbon concentration on the hardness of austenite in the experimental steels (HV$_\gamma$) was subsequently expressed using the following equation:

$$HV_{\gamma} = 140 + (48.6 \times \text{mass-\% C})$$  \hspace{1cm} (2)

The extrapolated hardness of martensite based on exponential fits to the hardness values is marked in figure 2 and summarized using the data denoted HV$_\alpha$'$_{\text{exponential}}$ in figure 3. The results reveal that the hardness of martensite is close to 1014 HV for the 0.6C steel and increases to 1271 HV and 1791 HV for the 1.0C and 1.4C steels, respectively. These hardness levels are significantly higher than the measured hardness values for the specimens quenched to -196 °C (HV$_{\alpha+\gamma}$ measured in figure 3). The hardness values denoted HV$_\alpha$'$_{\text{RoM}}$ in figure 3 represent the hardness of martensite if the softening effect of austenite is excluded by applying the rule of mixtures to the hardness values for the specimens quenched to -196 °C (HV$_{\alpha+\gamma}$ measured). This was done by means of the following equation:

$$HV_{\alpha}^{\text{RoM}} = \frac{HV_{\alpha+\gamma}^{\text{measured}} - (f_{\gamma} \times HV_{\gamma})}{1 - f_{\gamma}}$$ \hspace{1cm} (3)

where $f_{\gamma}$ denotes austenite fractions after quenching to -196 °C. The dependence of $f_{\gamma}$ on the carbon concentration is also represented in figure 3. The HV$_\gamma$ values were estimated from equation (2). As shown in figure 3, HV$_\alpha$'$_{\text{exponential}}$ values are well above the HV$_\alpha$'$_{\text{RoM}}$ values as well as the literature results in which the effect of austenite has been excluded by the rule of mixtures [13]. Consideration of the hardness values for metal-matrix composites with various fractions of hard reinforcing particles confirms the non-linearity of the relationship between the hardness and the second phase volume fraction [19–21]. In other words, plastic deformation due to indentation is mainly accommodated by
the soft matrix phase. In such cases, the measured hardness values remain below the straight line drawn between the hardness values for the soft and hard constituents.

![Figure 3. Austenite fraction ($f_\gamma$) and hardness of steels with various carbon contents after quenching to -196 °C ($HV^\text{measured}_{\alpha+\gamma}$). The extrapolated hardness of martensite based on exponential fits to the hardness values in the presence of various martensite fractions is marked $HV^\text{exponential}_{\alpha}$. The hardness of martensite estimated based on the rule of mixtures is marked $HV^\text{RoM}_{\alpha}$.](image)

Nano-indentation measurement have indicated that the hardness is almost equal for hardened steels containing 0.6 mass-% and 0.8 mass-% carbon [22]. Invalid assumptions on the material response, excessive surface roughness, and insufficient penetration depths are among common sources of error in nano-indentation experiments [23,24]. Although increasing the penetration depth during the nano-indentation of hardened steels with martensitic-austenitic microstructures leads to an enhanced reliability of derived hardness values, it increases the contribution of retained austenite to the estimated hardness values for martensite. The difficulty of excluding the effect of austenite without compromising the reliability of nano-indentation measurements emphasizes the usefulness of regression analysis for the estimation of the true hardness of martensite.

4. Conclusions
In summary, the dependence of hardness on the martensite fraction of hardened martensitic-austenitic steels with various phase balances was described using exponential fits to the hardness data. The hardness of martensite containing 1.46 mass-% carbon was estimated to be 1791 HV which is significantly higher than the measured hardness of 822 HV for the same steel containing nearly 68 vol.% martensite and the hardness of 1104 HV obtained after excluding the effect of austenite by the rule of mixtures.

5. References
[1] De Cooman B C and Speer J G 2011 Fundamentals of Steel Product Physical Metallurgy (Warrendale: Association for Iron and Steel Technology)
[2] de la Concepción V L, Lorusso H N and Svoboda H G 2015 Effect of Carbon Content on Microstructure and Mechanical Properties of Dual Phase Steels Procedia Mater. Sci. 8 1047–56
[3] Fan D W, Kim H S and De Cooman B C 2009 A Review of the Physical Metallurgy related to the Hot Press Forming of Advanced High Strength Steel Steel Res. Int. 80 241–248
[4] Krauss G 1999 Martensite in steel: Strength and structure Mater. Sci. Eng. A 273–275 40–57
[5] Bhadeshia H K D H 2012 Steels for bearings Prog. Mater. Sci. 57 268–435
[6] Kehoe M and Kelly P M 1970 The role of carbon in the strength of ferrous martensite Scr. Metall. 4 473–6
[7] Chilton J M and Kelly P M 1968 The strength of ferrous martensite Acta Metall. 16 637–56
[8] Hansen N 2004 Hall–Petch relation and boundary strengthening Scr. Mater. 51 801–6
[9] Grange R A, Hribal C R and Porter L F 1977 Hardness of tempered martensite in carbon and low-alloy steels Metall. Trans. A 8 1775–85
[10] Litwinchuk A, Kayser F X, Baker H H and Henkin A 1976 The Rockwell C hardness of quenched high-purity iron-carbon alloys containing 0.09 to 1.91% carbon J. Mater. Sci. 11 1200–6
[11] Ohmura T, Tsuzaki K and Matsuoka S 2001 Nanohardness measurement of high-purity Fe–C martensite Scr. Mater. 45 889–94
[12] Sherby O D, Wadsworth J, Lesuer D R and Syn C K 2008 Revisiting the Structure of Martensite in Iron–Carbon Steels Mater. Trans. 49 2016–27
[13] Galindo-Nava E I and Rivera-Díaz-del-Castillo P E J 2016 Understanding the factors controlling the hardness in martensitic steels Scr. Mater. 110 96–100
[14] Yamauchi H, Watanabe H, Suzuki Y and Saito H 1974 Magnetization of α-Phase Fe-Mn Alloys J. Phys. Soc. Jpn. 36 971–4
[15] Xiong X C, Chen B, Huang M X, Wang J F and Wang L 2013 The effect of morphology on the stability of retained austenite in a quenched and partitioned steel Scr. Mater. 68 321–4
[16] Grange R A and Stewart H M 1946 The Temperature Range Of Martensite Formation AIME Tech. Publ. 1996 1–24
[17] Mola J and De Cooman B C 2013 Quenching and Partitioning (Q&P) Processing of Martensitic Stainless Steels Metall. Mater. Trans. A 44 946–67
[18] Suzuki K and Shobu T 2010 Residual Microstress of Austenitic Stainless Steel Due to Tensile Deformation Mater. Sci. Forum 652 7–12
[19] Levin B F, DuPont J N and Marder A R 2000 The effect of second phase volume fraction on the erosion resistance of metal-matrix composites Wear 238 160–70
[20] Sambathkumar M, Navaneethakrishnan P, Ponappa K, Sasikumar K S K, Sambathkumar M, Navaneethakrishnan P, Ponappa K and Sasikumar K S K 2017 Mechanical and Corrosion Behavior of Al7075 (Hybrid) Metal Matrix Composites by Two Step Stir Casting Process Lat. Am. J. Solids Struct. 14 243–55
[21] Sivasankaran S and Alaboodi A S 2016 Structural Characterization and Mechanical Behavior of Al 6061 Nanostructured Matrix Reinforced with TiO2 Nanoparticles for Automotive Applications
[22] Ohmura T and Tsuzaki K 2003 Evaluation of matrix strength of Fe-C as-quenched and quench-tempered martensite using nanoindentation techniques J. Phys. IV Proc. 112 267–70
[23] Menčík J 2012 Uncertainties and Errors in Nanoindentation Nanoindentation in Materials Science (InTech)
[24] Šmešlova V, Schwedt A, Wang L, Holweger W and Mayer J 2017 Electron microscopy investigations of microstructural alterations due to classical Rolling Contact Fatigue (RCF) in martensitic AISI 52100 bearing steel Int. J. Fatigue 98 142–54

Acknowledgements
Support of the technical staff at the Institute of Iron and Steel Technology of TU Bergakademie Freiberg is gratefully acknowledged.