The Influence of Martensite on Line Broadening in Neutron Diffraction Spectra of a DP Steel

R. FILIPPONE, J. ROOT,1) P. JACQUES2) and S. YUE

Department of Mining and Metallurgical Engineering, McGill University, 3610 University St., Montreal, Quebec, H3A 2B2, Canada. 1) National Research Council of Canada, Chalk River Laboratories, Chalk River, Ontario, K0J 1J0, Canada. 2) Université Catholique de Louvain, Laboratoire PCIM, Place Sainte Barbe, 2, B-1348 Louvain-la-Neuve, Belgium.

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Neutron diffraction experiments were performed on dual-phase steels to determine the feasibility of measuring the martensite volume fraction through ferrite peak broadening. Mechanical properties were also investigated to determine if a correlation exists with ferrite peak broadening. Results indicate that the correlation between martensite volume fraction and ferrite peak broadening is carbon dependent. Furthermore, two mechanisms regarding the nature of the ferrite peak broadening in dual-phase steels are proposed. Tensile testing demonstrated that a correlation between peak broadening and mechanical properties exists for dual-phase steels.

KEY WORDS: martensite; neutron diffraction; dual-phase steels; ferrite peak broadening; mechanical properties.

1. Introduction

In modern multiphase steels, small amounts of martensite could play a major role in contributing to mechanical properties. In terms of microstructural characterization, the difficulty with martensite is that there exists peak overlap with ferrite due to the similarity in crystal structures (body centered cubic for ferrite, body centered tetragonal for martensite). This means for every ferrite peak, two martensite peaks will be present at slightly offset scattering positions (Fig. 1). Previous work1) done on martensite characterization using neutron diffraction showed that the martensite/ferrite peak remains unresolvable, due to the inherently broad nature of the martensite structure. However, it was shown that martensite causes the ferrite peak to broaden with increasing martensite volume fractions.

This study examines the relationship between martensite volume fraction and ferrite peak broadening. Furthermore, a correlation between line broadening and mechanical properties is also investigated.

2. Experimental Details

The chemistries of the steels investigated are listed in Table 1.

The steels are all plain low carbon grades and were chosen to facilitate the formation of dual-phase microstructures with varying amounts of martensite. All specimens underwent a solutionizing heat treatment at 1 200°C for 30 min and were furnace cooled to room temperature. Cold rolling (30% reduction) was then done to refine the initial grain structure. Specimens approximately 10 mm × 10 mm × 15 mm were cut and subjected to intercritical annealing at temperatures ranging from 750 to 900°C in 25°C increments, followed by a water quench after hold times of 10, 20, and 40 min at each temperature. One specimen for each steel chemistry was re-solutionized at 1 200°C and furnace cooled to room temperature to serve as a strain free, martensite-free reference for the neutron diffraction testing.

Martensite volume fractions were first determined by image analysis. Samples were etched using nital and sodium metabisulfite to improve contrast in the martensitic structures.2) Neutron diffraction experiments were conducted at the NRU reactor at Chalk River Laboratories. Neutron diffrac-

Fig. 1. Schematic diagram showing ferrite (α) overlap by martensite (M) and resulting convoluted peak (C).

Table 1. Steel chemical compositions (in wt%).

| Steel | C   | Mn | P  | S  | Si | Cr | Ni | Cu | Co |
|-------|-----|----|----|----|----|----|----|----|----|
| A     | 0.079| 0.426| 0.009| 0.012| 0.062| 0.041| 0.069| 0.033| 0.024|
| B     | 0.180| 0.470| 0.006| 0.011| 0.140| 0.059| 0.070| 0.039| 0.040|
| C     | 0.170| 0.700| 0.007| 0.001| 0.210| 0.060| 0.070| 0.048| 0.040|
tion was selected over X-ray diffraction due to its superior penetration, and consequent increased sampling volume. A triple-axis spectrometer equipped with a variable-width single-wire position sensitive detector was used to measure the (110) and (101) diffraction peaks of martensite and the (110) ferrite peak. The (110) diffraction was selected since it has the greatest peak intensity. Using a wavelength ($\lambda$) of 0.232 nm and a pyrolytic graphite filter to remove $\lambda/2$ and $\lambda/3$ wavelengths ensured that there would be no contamination of the diffraction pattern from higher ordered ferrite peaks. Sampling volume was limited to 2 mm × 2 mm × 15 mm to maximize the resolution to intensity ratio, and to ensure the sampling volume was completely inside the specimen. Restricting the sampling volume to be entirely within the specimen volume prevented the specimen position from affecting the scattering geometry, and thus the instrumental resolution. Instrumental resolution, determined as outlined by Cagliotti et al., was 0.44 degrees.3)

Diffraction patterns were fitted with Gaussian distributions and peak breadths were measured as the full width at half the maximum peak intensity (FWHM). Peak broadening is then calculated as the difference in peak breadth between the dual-phase sample and the reference, martensite is then calculated as the difference in peak breadth between the dual-phase sample and the reference, martensite peak broadening trends for the steels are illustrated in Figs. 5–7.

3.1. Correlation of Line Broadening to Microstructure

The slow cooling rate used to generate the reference samples resulted in microstructures as observed in Figs. 4(a)–4(c). The different ferrite morphology between steels A and steels B and C is believed to be a result of the increased fraction of pearlite, which may prevent the ferrite grains from growing into polygonal structures.

Figures 4(d)–4(f) compare the microstructures of the three steels following the intercritical anneal and water quench process, leading to roughly 40% vol. of martensite. There are no significant differences in the microstructures of steels B and C. Compared to the reference microstructures (Figs. 4(b) and 4(c)), there was a change in ferrite morphology in steels B and C; the ferrite grains became polygonal. This was attributed to the recrystallization of ferrite during the intercritical anneal. The main differences between steel A and steels B and C are that steel A has a smaller grain size, and the martensite phase is present in less distinct islands.

The ferrite peak broadening trends for the steels are illustrated in Figs. 5–7. The ferrite peak broadening results, Figs. 5–7, clearly indicate that ferrite peak breadth increases with increasing martensite volume fraction. There are several factors that influence the breadth or shape of a diffraction peak, as are discussed below.

(i) Particle Size Broadening

Broadening due to particle size occurs when a crystal or grain is so small that it no longer contains an infinite number of planes to cancel all rays scattering from planes slightly out of phase.5) The critical grain size at which peak broadening becomes resolvable is estimated by the Scherrer formula,6) which, according to the experimental setup, is roughly 30 nm. The microstructural analysis clearly demonstrates that the ferrite grain size is well above this critical size. Similarly, lath martensite would not have particle size broadening due to grain size as typical lath dimensions are 200×4×0.3 μm,7) however its substructure would cause some size broadening to occur.5)

(ii) Strain Broadening

The most obvious strain broadening effect is associated with the martensitic structure. Martensite is characterized by a heavily dislocated substructure and contains residual stresses from the quench process, which would cause the martensite peaks to be broadened. As previously mentioned, there is an additional increase in breadth due to particle size broadening of the dislocation substructure.

The final consideration lies in the volume change that occurs during the martensitic transformation. This would in-
variably cause the ferrite matrix to be locally strained around the martensite grains and cause the ferrite diffraction peak to be broadened.

(iii) Peak Overlap

The principal difficulty with martensite lies in the fact that there are two peaks, both inherently broad due to particle size and strain broadening effects, which overlap the ferrite diffraction pattern (refer to Fig. 1). Researchers have shown that the degree of tetragonality in the martensite crystal structure is carbon dependent.\(^6\)-\(^{10}\) This is schematically illustrated in Fig. 8 that summarizes X-ray diffraction studies on martensite lattice parameters for fully martensitic structures with varying carbon levels. However, in a dual-phase or multiphase system, the carbon content of the martensite will vary with the martensite volume fraction, as

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**Fig. 4.** Microstructure of (a) reference steel A, (b) reference steel B, (c) reference Steel C, (d) dual-phase steel A, (e) dual-phase steel B, and (f) dual-phase steel C.

**Fig. 5.** Ferrite peak broadening trend for steel A.

**Fig. 6.** Ferrite peak broadening trend for steel B.

**Fig. 7.** Ferrite peak broadening trend for steel C.

**Fig. 8.** Schematic diagram showing the variation of martensite lattice parameters with carbon content.
indicated in the Fe–C equilibrium diagram. Consequently, there exists a relationship between martensite peak position and martensite volume fraction; increasing fractions of martensite reduce the degree of tetragonality, and therefore shifts the peaks positions closer together (i.e., approaches a BCC diffraction pattern).

Texture analysis showed that the microstructures are highly random (never exceeding about 1.3×random) throughout the whole range of martensite volume fractions. This indicates that texture is not a significant factor in the analysis of the diffraction data.

(iv) Influence of Broadening Effects on Results
The ferrite peak-broadening trend for steel A is shown in Fig. 5. An initially steep rise in peak broadening at martensite fractions below 20% is evident. At martensite volume fractions greater than 20% there is a leveling off in the broadening behavior to a slightly increasing, near-linear trend. There are no results for steels B and C at martensite volume fractions below 20%, so there is no sign of the initial rapid increase in line broadening. As well, no evidence of leveling off exists in the broadening behavior for steel B (Fig. 6) or C (Fig. 7). Rather, steels B and C show a continuously increasing trend in peak broadening at martensite fractions greater than 20%.

The sharp initial rise seen in Fig. 5 is a result of ferrite straining from the volumetric expansion that occurs in the martensitic transformation. A model developed by Bourell and Rizk11) clearly indicate that the degree of ferrite straining by martensite is extensive even at low volume fractions. The influence of martensite overlap would be secondary at lower volume fractions since the peaks intensities would be minimal and the peaks positions would be furthest from the ferrite peak. This is related to the carbon dependency of the martensite crystal structure. As shown in Fig. 8, the degree of tetragonality of the martensite structure increases with increasing carbon content. Thus, assuming complete austenite decomposition into martensite upon quenching, and phase fractions based on the Fe–C equilibrium phase diagram, then decreasing amounts of martensite would contain larger amounts of carbon and therefore have a larger degree of tetragonality causing the martensite peaks to be shifted away from the ferrite peak.

With increasing martensite volume fractions, ferrite straining becomes a secondary effect. This is partly because the tetragonality of the martensite falls and partly because the amount of ferrite decreases. These two factors, in addition to the inherent broadness of martensite (even though the tetragonality is decreasing with increasing martensite volume fraction), become the dominant effect on the overall broadness results at higher volume fractions. Consequently, as martensite volume fraction increases, the degree of peak broadening decreases. This is evident for steel A (Fig. 5), which demonstrates a leveling off behavior in the broadening. However, no leveling off is observed in steels B (Fig. 6) and C (Fig. 7). This is explained by the higher carbon contents of these steels, which, according to the equilibrium Fe–C phase diagram, leads to a more gradual change in the carbon levels of the martensite as the martensite volume fraction (i.e., the prior austenite volume fraction) changes (Fig. 9).

3.2. Effect of Composition
Figure 10 includes the broadening results from all the steels. The results indicate that the broadening behavior of steel is carbon dependent. Clearly the maximum broadening observed is larger for the higher carbon steels. This is attributable to the increased tetragonality of the martensite and greater straining of the ferrite matrix due to an increased volume expansion during the martensitic transformation. Comparing Fig. 6 and Fig. 7, there is no obvious alloying effect since the ferrite peak broadening behavior does not change. The difference between steels B and C lies in their manganese content (refer to Table 1 for exact chemistries). Excluding carbon, manganese has the greatest effect on hardenability.12) As expected, the additional manganese in steel C produced higher fractions of martensite in the dual-phase specimens. The lack of change in the broadening of steels B and C indicate that manganese content, and most likely alloying in general, has no direct influence on ferrite peak broadening.

Below about 50% martensite volume fraction, the higher carbon steels exhibit lower peak broadening than the lower carbon steel. Above this martensite volume fraction, the higher carbon steels have higher broadening levels than the
lower carbon steel. This is attributable to the tetragonality of the steels. For a given martensite volume fraction, the higher carbon steels contain more carbon and therefore have a larger degree of tetragonality. While at larger volume fractions this causes an increase in broadening, at low volume fractions the split is too large to directly influence the ferrite peak breadth. Therefore, below 50% martensite volume fractions, the lower carbon steels produce more line broadening for a given martensite volume fraction.

3.3. Mechanical Properties

Tensile testing was used to evaluate the yield strength, ultimate tensile strength, and total elongation to failure of the three steels. Table 2 contains the results of the mechanical properties and outlines the intercritical anneal and water.

| Steel | Heat Treatment | Martensite Volume Fraction (%) | Yield Strength (MPa) | Ultimate Tensile Strength (MPa) | Total Elongation (%) |
|-------|----------------|--------------------------------|---------------------|-------------------------------|---------------------|
| A     | Reference      | 0                              | 210                 | 370                           | 21.3                |
|       | 775 ºC 20 min  | 22.62 ± 3.29                   | 380                 | 456                           | 10.0                |
|       | 825 ºC 20 min  | 28.68 ± 3.30                   | 380                 | 585                           | 5.8                 |
|       | 825 ºC 40 min  | 47.35 ± 6.54                   | 400                 | 625                           | 3.7                 |
|       | 850 ºC 20 min  | 72.38 ± 8.02                   | 450                 | 710                           | 6.6                 |
| B     | Reference      | 0                              | 190                 | 390                           | 35.5                |
|       | 750 ºC 5 min   | 17.02 ± 2.38                   | 450                 | 650                           | 13.0                |
|       | 750 ºC 10 min  | 16.63 ± 2.56                   | 440                 | 600                           | 2.5                 |
|       | 750 ºC 15 min  | 28.73 ± 4.65                   | 470                 | 670                           | 1.0                 |
|       | 750 ºC 20 min  | 26.39 ± 3.38                   | 485                 | 680                           | 1.7                 |
| C     | Reference      | 0                              | 225                 | 435                           | 34.5                |
|       | 750 ºC 5 min   | 22.09 ± 3.56                   | 410                 | 630                           | 18.4                |
|       | 750 ºC 10 min  | 23.99 ± 3.65                   | 410                 | 615                           | 16.4                |
|       | 750 ºC 15 min  | 24.89 ± 3.28                   | 490                 | 720                           | 1.7                 |
|       | 750 ºC 20 min  | 30.68 ± 4.10                   | 470                 | 700                           | 1.5                 |

Table 2. Mechanical properties summary of tensile tests.

Fig. 11. Yield strength as a function of (a) martensite volume fraction, and (b) ferrite peak broadening.

Fig. 12. Ultimate tensile strength as a function of (a) martensite volume fraction, and (b) ferrite peak broadening.

Fig. 13. Total elongation to fracture as a function of (a) martensite volume fraction, and (b) ferrite peak broadening.
quench heat treatments used for the various specimens.

The peak broadening versus martensite volume fraction trends observed in Figs. 5–7 were used to estimate the broadening for the mechanical properties specimens. The results are graphically illustrated in Figs. 11–13.

Lines have been included in the figures in order to help illustrate the trends of the three steels. These lines have no numerical significance to the mechanical properties. The results clearly follow the expected course for dual-phase microstructures in that there is an increase in strength (Figs. 11 and 12) with the associated decrease in ductility (Fig. 13). It is immediately obvious that line broadening illustrates a correlation with mechanical properties. In fact, the correlation is quite different compared to the correlation with martensite volume fraction. For example, if a linear correlation is performed between martensite volume fraction and strength in steel A, the r-value (sample correlation coefficient) is roughly 0.4. The same correlation with line broadening leads to an r-value of 0.8. This hints that line broadening, could be an additional way to characterize the microstructure, with a view to indicating mechanical properties. Whilst it is very desirable to fully characterize the microstructure by image analysis, line broadening certainly has the advantage of being a bulk measuring technique that is much less subjective than image analysis, especially when analyzing more complex multi-phase structures, containing bainite and retained austenite in addition to ferrite and martensite.

4. Conclusions

The use of neutron diffraction to determine the correlations between martensite volume fraction, ferrite peak broadening, and mechanical properties was investigated. The main conclusions are:

(1) Peak broadening of the (110) ferrite diffraction peak increases with increasing martensite volume fraction. For the simple dual-phase microstructures examined, it was theorized that ferrite peak broadening is a function of ferrite straining and martensite peak overlap.

* A sharp increase in peak broadening was observed in steel A for martensite volume fractions below 20%. It is believed that this initial stage of peak broadening is mainly attributable to the straining of ferrite by the volume expansion incurred by martensite during transformation from austenite. At martensite volume fractions greater than 20%, martensite overlap becomes the dominant factor.

* It was proposed that the martensite tetragonality is a function of the parent austenite carbon content prior to quenching, thus yielding a dynamic relationship between martensite peak positions and martensite volume fraction.

(2) Correlations between ferrite peak broadening and martensite volume fraction exists for the three steels examined. The trends indicate that the relationship is carbon dependent. No effect of alloying, specifically manganese, was observed.

(3) Mechanical properties were strongly dependant on both the peak broadening and the martensite volume fraction.

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