Original Article

The constitution of martensite volume fraction in Fe-31wt%Ni-0.02wt%C

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ABSTRACT

This paper analyzes the constitution of martensite volume fraction, that is, the size-distribution of martensite units in quenched-transformed austenite in the microstructure. We correlate this distribution to the martensite shape-strain relaxation. The modes of relaxation athermal/auto-accommodation or thermal-activated dislocation mobility and the sequential formation of the martensite units control the variation of the mean martensite unit volume as well as the uniformity of the transformation.

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1. Introduction

Practical applications of martensitic transformation demand knowledge of the transformation curve, which expresses the fraction transformed as a function of the external variable e.g. temperature, time, or stress/strain. The transformation curve reflects the autocatalytic nucleation-controlled kinetics that speedup the reaction otherwise limited by the scarcity of heterogeneous nucleation loci [1]. Early papers [2–6] acknowledged the importance of the steel chemistry on the martensite transformation temperature, on the specific crystallography and on the typical morphologies. However, the description of the transformation curve is still a topic of discussion/research [7–12].

In this context, characteristics of martensite transformation such as the coordinated atomic motion, lattice correspondence and its diffusionless nature prevent the incorporation of high-angle boundaries by the transformation. Therefore, the units do not grow or coalesce after they form. Moreover, the austenite volumes within which they form restrain them. Consequently, the microstructure has a hierarchical organization of units which make up the volume fraction transformed. In low-medium carbon steels the martensite transforms above room temperature, exhibiting a lath morphology and the different textures described in Ref. [13]. The laths are much smaller than the austenite mean intercept distance. They group into blocks that form the packets that subdivide the austenite grains, contributing to relax the transformation strains. On the other hand, in high-carbon as well as in high-nickel steels that transform about or below room temperature, the martensite units with plate morphology tend to run across the austenite grains. The mutual impingements of units as well as between the units and the austenite grain boundaries are frequent. These events concentrate stress that promotes mechanical autocatalytic-chains that yield the sequential martensite propagation comprising

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martensite zigzags. These may as well induce the transformation into a next grain. The variant-selection associated with the sequential martensite propagations causes the relaxation of the shear-component of the martensitic shape-change: this is the so called autocatalytic feedback [14].

In this work, we “disassemble” the martensite microstructure to characterize the fraction transformed by the different generations of martensite units, bearing the size-distribution function typical of the martensite transformation in Fe-31wt%Ni-0.02wt%C.

2. Experimental aspects

The database [15] is typical of the reference alloy (Fe-31wt%Ni-0.02wt%C) with austenite grain sizes 0.0142 mm and 0.048 mm (mean grain intercepts) prepared as described in Ref. [16]. Briefly, fully austenitic annealed specimens were transformed by direct quenching into a volume of refrigerated ethanol 1000 X larger. The lenticular martensite morphology with a conspicuous midrib is seen down to 77 K, see Fig. 3 of Ref. [17]. The Fe-30wt%Ni-0.02wt%C transforms at sub-zero temperatures that allows characterization at room-temperature. There is a one to one correspondence between midrib and martensite unit. Tantamount, the martensite midrbs seen in a random polished section are chords of intercepted martensite midplanes. Thence, assuming circular midplanes, we obtained the size-distribution using DeHoff’s [18] approach to characterize circles of different diameters based on their intersections with random planes. For this, the transformed specimens were systematically observed and photographed (10 areas) under an optical microscope at 400× magnification. The midrbs were measured on enlarged prints. Considering that the martensite units cannot cross grain boundaries, the class-sizes were scaled with respect to the austenite grain mean intercept, d, to compare materials with different grain-sizes. In the following, the class-sizes are G1(3.0 > 2r/d > 1.2), G2(1.2 > 2r/d > 0.6), and G3 (0.6 > 2r/d > 0), where r is the midplane radius. However, the data used in the present work were compiled by scanning/digitizing the graphs shown in Figs. 2 and 4 of the original paper [15]. The volume and the number of martensite units per unit volume of material, $V_{VM}$ and $N_{VM}$ (sub-v marked) were obtained on the same areas used to measure the midrbs. The values of $V_{VM}$ were determined by systematic point-counting; those of $N_{VM}$ were determined using Fullman’s equations [19] and checked against DeHoff’s method in [15]. The original data admittedly did not display error-bars. However, our experience with these determinations permits ascribing an upper value of 20%, including the influence of operator harshness. Tables 1 and 2 show the overall microstructure descriptors and the correspondent size-distributions.

3. Numerical procedure

The relationship between the volume fraction, $V_{VM}$, and the number of martensite units per unit of volume, $N_{VM}$, is

$$V_{VM} = \bar{v}_M \cdot N_{VM}$$

where $\bar{v}_M$ is the mean unit volume. The mean unit volume is a result of their size and arrangement within the austenite matrix. The $\bar{v}_M$ values shown in Tables 1 and 2, were calculated with Eq. [1]. However, to relate the transformation curve to the size distribution of the martensite unit it is necessary to delve into $\bar{v}_M$.

### Table 1 - Microstructure descriptors and martensite diameter-distribution for coarse grain size.

<table>
<thead>
<tr>
<th>T, K</th>
<th>Overall microstructure descriptors</th>
<th>Martensite units per unit volume of material in bins, mm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d = 0.142$ mm</td>
<td>$V_{VM}$, $N_{VM}$, mm⁻³</td>
</tr>
<tr>
<td>220</td>
<td>0.230</td>
<td>2.658E+03</td>
</tr>
<tr>
<td>213</td>
<td>0.390</td>
<td>1.148E+04</td>
</tr>
<tr>
<td>203</td>
<td>0.543</td>
<td>1.740E+04</td>
</tr>
<tr>
<td>188</td>
<td>0.681</td>
<td>2.967E+04</td>
</tr>
<tr>
<td>171</td>
<td>0.753</td>
<td>6.679E+04</td>
</tr>
<tr>
<td></td>
<td>Ref. [16]</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2 - Microstructure descriptors and martensite diameter-distribution for fine grain size.

<table>
<thead>
<tr>
<th>T, K</th>
<th>Overall microstructure descriptors</th>
<th>Martensite units per unit volume of material in bins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d = 0.048$ mm</td>
<td>$V_{VM}$, $N_{VM}$, mm⁻³</td>
</tr>
<tr>
<td>215</td>
<td>0.21</td>
<td>6.847E+04</td>
</tr>
<tr>
<td>205</td>
<td>0.37</td>
<td>9.114E+04</td>
</tr>
<tr>
<td>188</td>
<td>0.47</td>
<td>9.546E+04</td>
</tr>
<tr>
<td>173</td>
<td>0.65</td>
<td>1.922E+05</td>
</tr>
<tr>
<td></td>
<td>Ref. [16]</td>
<td></td>
</tr>
</tbody>
</table>

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In the following we assumed time-independent (“athermal”) transformation of our reference alloy by direct-quenching. Henceforth, recasting Eq. [1],

\[ V_{VM}(T) = \sum_i N_{VM}(T, i) \cdot \tilde{v}(T, i) \]

where \( N_{VM}(T, i) \) and \( \tilde{v}(T, i) \) stand for the number density and the mean volume of the martensite units in the \( i \)th class-size of the material transformed at temperature \( T \). \( T \) is the transformation temperature, and \( i \) indicates the size-class bin (G1–G3).

The choice of notation: “G1”, “G2” and “G3” meant to stress that not all martensite plates were “generated” at the same time. The first generation, G1, are large plates that partition the grains as will be shown below.

For completeness, the overall mean martensite unit volume is

\[ \bar{v}(T) = \frac{\sum_i N_{VM}(T, i)}{N_{VM}(T)} \cdot \tilde{v}(T, i) \]

and the total number density of martensite transformed is

\[ N_{VM}(T) = \sum_i N_{VM}(T, i) \]

The present analysis is based on a three – bin distribution \( i \leq 3 \). Hence, the martensite fraction transformed at quenching temperature \( T_i \) is given by

\[ V_{VM}(T_i) = \sum_{i=1}^{3} N_{VM}(T_i, i) \cdot \tilde{v}(T_i, i) \]

Then, we consider the distribution bins fixed, that is, they are temperature independent. Moreover, the martensite units in the present Fe-31wt%Ni-0.02wt%C alloy partition the austenite grains. The plate size in each bin describes the transformation sequence set by the autocaltectic chains that mechancially optimize the accommodation of the shape-change in a grain [14]. Therefore, the martensite units collected in a bin characterize a temperature-independent generation of martensite units. Henceforth, we substitute the mean martensite unit volume in a bin, \( \bar{v}(G_i) \), for \( \tilde{v}(T_i, i) \) in Eq. [5], and relate \( \bar{v}(G_i) \) to a specific \( 2r^* / d \) ratio in the ith bin. For oblate-spheroid (lenticular) martensite, a morphology compatible with the Fe-31wt%Ni-0.02wt%C transformation, we have

\[ \bar{v}(G_i) = \frac{\pi}{6} \bar{a} \cdot d^3 \left( \frac{2r^*}{d} \right)^3 \]

where the parameter \( \bar{a} \) is the spheroid thickness to radius ratio, and \( d \) is the austenite mean intercept. Eq. [6] gives a link between the martensite unit volume and the radial size-distribution taken from [15]. The thickness to radius ratio of Fe-Ni martensite varies with the temperature of transformation [20]. A reasonable approximation is to use the mean thickness to radius ratio, \( \bar{a} \), in Eq. [6].

The martensite population in the three class-sizes \( i \leq 3 \) are characterized by the values of \( N_{VM}(T_i, i) \) in Tables 1 and 2. The values of \( V_{VM}(T_i) \) are the martensite volume fractions transformed at quenching temperatures \( T_i \) \( i > 3 \). Thus, substituting Eq. [6] into Eq. [5] yields a system of \( i \) equations and 3 unknowns,

\[ \begin{bmatrix} N_{VM}(1, 1) & \cdots & N_{VM}(1, 3) \\ \vdots & \ddots & \vdots \\ N_{VM}(T_i, 1) & \cdots & N_{VM}(T_i, 3) \end{bmatrix} \times \begin{bmatrix} \frac{\pi}{6} \bar{a} \cdot d^3 \left( \frac{2r^*}{d} \right)^3 \end{bmatrix} = \begin{bmatrix} V_{VM}(T_i) \end{bmatrix} \]

The solution of this system gives the values of \( \bar{v}(G_i) \). Since Eq. [7] are overdetermined, we sought a parametric least-squares solution by fitting \( 2r^* / d \) to describe the experimental values of \( V_{VM}(T) \). Fig. 1 shows the quality of fitting. Table 3 gives the values of \( \bar{a} \), a coefficient of determination \( R^2 \geq 0.85 \), and the mean martensite unit volumes, \( \bar{v}(G_i) \) calculated with Eq. [6].

Note that the values of \( \bar{v}(G_i) \) are naturally less in the finer grained material, as expected. On the other hand, the values of \( \bar{a} \) that are compatible with the semi-thickness to radius ratios reported in Ref. [20], do not evidence grain size dependence.

4. Contributed volume fractions transformed

Bearing the temperature independence of the mean martensite unit volume in the bins, \( \bar{v}(G_i) \), the martensite volume

\[ \begin{array}{c}
\text{Table 3 – Mean martensite unit volumes} \quad \bar{v}(G_i), \text{ mm}^3 \\
\text{for coarse and fine grain sizes.}
\end{array} \]

<table>
<thead>
<tr>
<th>d (mm)</th>
<th>0.142</th>
<th>0.048</th>
</tr>
</thead>
<tbody>
<tr>
<td>v</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>R^2</td>
<td>0.85</td>
<td>0.92</td>
</tr>
<tr>
<td>G1 (1.2 &lt; 2r/d &lt; 3.0)</td>
<td>9.59E–04</td>
<td>3.41E–05</td>
</tr>
<tr>
<td>G2 (0.6 &lt; 2r/d &lt; 1.2)</td>
<td>1.90E–04</td>
<td>1.10E–05</td>
</tr>
<tr>
<td>G3 (2r/d &lt; 0.6)</td>
<td>1.20E–07</td>
<td>6.37E–09</td>
</tr>
</tbody>
</table>

Fig. 1 – Martensite volume fractions calculated with Eq. (1) compared with the experimental values. Coefficients of determination are \( R^2 = 0.85 \) and \( R^2 = 0.92 \) for the coarse and the fine-grained conditions, respectively.
fractions contributed by the units collected in the different bins as function of the quenching temperature is

\[ V_{VM}(T, \dot{\gamma}) = N_{VM}(T, \dot{\gamma}) \cdot \bar{v}(G) \]  

(8)

Using the values of \( N_{VM}(T, \dot{\gamma}) \) from Tables 1 and 2, and those of \( \bar{v}(G) \) from Table 3, it is possible to calculated the values of \( V_{VM}(T, \dot{\gamma}) \) depicted in Fig. 2.

Fig. 2a shows that in the coarser-grained material, the G1 units contribute with a flat fraction transformed of \( \sim 0.30 \) that compares with the \( \sim 0.23 \) transformed in the initial transformation burst. On the contrary, the contributions of the G1 units in the finer grained material, continuously increase as the quenching temperature is lowered. Similar contributions by the G2 units are observed in either grain size condition – see Fig. 2b. The effect of grain size on the G3 transformation is notable – see Fig. 2c. Although the transformation increases with lowering the quench-temperature the contributions by G3 units are barely discernible in the fine-grained condition.

These different behaviors reflect the limitation imposed by the grain boundaries to the propagation of the martensite units. Indeed, it is accepted that the initial martensite unit formed in a grain stimulates the coupled transformation of another unit with nearly parallel (primary) or perpendicular (secondary) habit planes. These autocatalytic chains are segmented by impingements evident by the characteristic zigzags in the microstructure. In the Fe-31wt%Ni-0.02wt%C, the martensite units run-across the austenite. Thus, the first formed autocatalytic chain subdivides the austenite grain into wedge-shaped partitions that are naturally longer in a coarse-grained material. As seen in Fig. 3, these partitions tend to be filled by secondary autocatalytic chains made of G2-G3 units with variants nearly perpendicular to the components of the initial chain. This “grouping” optimizes the overall accommodation
of the shear component of the shape-change [14]. Note also that it is the hierarchy resultant from this “mechanical” autocatalysis that backs the utilization of a limited number of size-classes to describe the martensite microstructure, as well as the substitution of $\tilde{u}(G_i)$ for $u(T_i, i)$ in Eq. [5].

Consider the area of martensite midplane per unit volume of material contributed by the bins

$$S_{VM}(T_i, G_i) = \frac{\pi}{4} d^2 \cdot N_{VM}(T_i, G_i) \cdot \left(\frac{2r^*}{d}\right)^2$$ (9)

where the variable and the parameters have been previously introduced. Taking the values of $2r^*/d$ used to obtain $u(Gi)$ in Table 3, we calculated the values of the mean area of mid planes in each size-class, $\tilde{u}(G_i) = \pi \cdot r^*_i \cdot d^4$ and, in the sequence, the values of $S_{VM}(T_i, G_i)$, at the different quench temperatures. The contributed mean area of martensite midplanes reproduce the trends shown in Fig. 2. The charts in Fig. 4 show the results typical of the coarse-grained material ($d = 0.142$ mm). See that the G1 units contribute with a flat $\sim 0.01$ mm$^{-1}$ mean midplane area from $M_0$ down to $\sim 170$ K, while the contributions from G2 and G3 units increase by 1–2 orders of magnitude. These charts corroborate that the austenite grain boundaries set limits for the segments of the internal autocatalytic chain that delimit the next generation of autocatalytic chains.

Moreover, the dilatational component of the shape change is not auto-accommodated and the austenite partitions are constrained by the earlier formed martensite units. Thus, the local transformation needs a higher driving force than available at the quench-temperature to continue. This favors the spread of the transformation in a neighboring grain under the influence of stress concentration by martensite-grain boundary impingements, yielding clusters of transformed grains [16].

In this context, the determinant of the size of the clusters needs consideration. The stress concentration on martensite-grain boundary impingements is larger when grain-partitioning is effective. Normally, Fe-31wt%Ni-0.02wt%C in fine-grained condition favors spread and therefore makes the clustering conspicuous. Nonetheless, it is not easy to explain exhaustion of clusters in fine-grained materials. We analyze the latter by considering the ultimate size of the clusters in extended space avoiding the complications of impingement. Therefore, the mean intercept of an extended cluster, $\lambda_{CE}$, is given by the well-known relationship $\lambda_{CE} = 4V_{VCE}/S_{VCE}$, where $V_{VCE}$ and $S_{VCE}$ are the volume fraction of material in the extended clusters, and the surface area of such clusters per unit volume of material. Recalling that the clusters inherit the randomicity of the grains where the initial nucleation events occur [1], as a first approximation, we relate $V_{VCE}$ and $S_{VCE}$ to their real counterparts observed in the microstructure, using the relationships [21–24].

$$V_{VC} = 1 - \exp(-V_{VCE})$$ (10)

and

$$S_{VC} = S_{VCE} \cdot (1 - V_{VC})$$ (11)

where the subscripts “C” and “E” refer to cluster and to extended space, respectively. The volume and mean intercept of an isolated cluster relate as $Q_{CE} = \beta \cdot \lambda_{CE}^3$ where $\beta$ is a geometric factor ($\approx 5.31$ for tetrahedron). Hence, we estimate the ultimate cluster size (free from impingement) at the different quenching temperatures by calculating

$$Q_{CE}(T_i) = \beta^3 \left(\frac{1 - V_{VC}(T_i) \ln(1 - V_{VC}(T_i)^{-1})}{S_{VCE}(T_i)}\right)^3$$ (12)

The values of $Q_{CE}(T_i)$ related to the data described in Ref. [16] decreases with lowering the quenching temperature or increasing the chemical driving force. Remarkably, these values of $Q_{CE}(T_i)$ may be described in an Arrhenius plot as shown in Fig. 5. Although the coefficients of determination were impaired by the experimental difficulty to delineate the clusters in a finer grained material, an Arrhenius dependence is clear in both charts. Moreover, the apparent activation energies obtained therefrom, $E_{AQCE} = 2.4 \times 10^{-20}$ J/event, $d = 0.048$ mm, $R^2 = 0.79$, and $E_{AQCE} = 2.1 \times 10^{-20}$ J/event, $d = 0.026$ mm, $R^2 = 0.36$, suggest that a thermally activated process balances the post-impingement

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**Figure 4** – Area of martensite midplane per unit volume of material, $d = 0.142$ mm.
stress-assisted martensite transformation. This stress can be relieved by further martensite transformation or by dislocation processes in the austenite on either side of the boundary. Noteworthy, on the impingement side further transformation can be readily helped by mutual accommodation while across the grain boundary that depend on the possible variant selection. Moreover, it is apparent that the initial transformation in a grain heavily depends on the accommodation of the shape strain in the austenite and/or the incorporation by dislocations from the adjacent plastic zone into the martensite [25,26]. Thence there is also a probabilistic aspect in the spread as suggested by recent computer simulation studies [27]. Finally, it should be clear that the possibility of martensite impingement on grain boundaries depends on austenite plasticity [28], so that beyond a certain grain size the inter-grain process becomes irrelevant.

5. Summary and conclusions

In this work, we analyzed the constitution of volume fraction of martensite based on the size distribution of martensite units in quench-transformed Fe-31wt%Ni-0.02wt%C. The contributions by the martensite units of different sizes were obtained by “disassembling” the microstructure. This approach allowed discussing the intragrain as well as the inter-grain aspects of the autocatalysis associated with the partitioning of the austenite grains by the martensite units. The size distribution of martensite units in quench-transformed Fe-31wt%Ni-0.02wt%C shows that the austenite grains are partitioned by a small fraction of the average number of units per grain. As consequence, the volume fraction transformed results from the fill-in of the austenite partitions created by the autocatalytic chains initiating the transformation. The containment of the fill-in transformation favors the inter-grain spread of the transformation promoted by the athermal (Patel-Cohen) stimulus from the stress build-up at martensite-grain boundary impingement; this renders martensite nucleation accessory to strain relaxation. However, the accommodation of the transformation strains inherent to the growth of a unit is accomplished by dislocation processes in the austenite. Thus, the inter-grain spread of the transformation refers to the relaxation of transformation strains in specific manner that contributes with athermal and thermal-activated components to the martensite transformation curve. Furthermore, we propose the idea that the inhibition of the clustering process by an overwhelming austenite plasticity tends to promote a microstructure comprised by martensite packets.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


