Intragranular Nucleation of Ferrite on Precipitates and Grain Refinement in a Hot Deformed V-microalloyed Steel

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The intragranular nucleation of ferrite has been studied in a V microalloyed steel (C=0.103; Mn=1.463; V=0.139; N=0.0100 % mass). Using torsion tests and applying the double deformation method known as “back extrapolation”, the recrystallised fraction of austenite has been determined for several deformation temperatures and two strain values (0.20 and 0.35) and has been plotted as a function of time. Recrystallisation-precipitation-time-temperature (RPTT) diagrams have then been drawn. The RPTT diagrams depict precipitation kinetics as a function of the temperature and time and this information has been used to study the intragranular nucleation of ferrite, cooling specimens from programmed temperatures and moments for which the precipitated volume and the average precipitate size (determined by TEM) are known. The results have allowed us to determine the contribution of intragranular nucleation to ferritic grain refinement, which was approximately 20%.

KEY WORDS: intragranular nucleation; ferrite; precipitates.

1. Introduction

In addition to the known classic sites for heterogeneous nucleation of ferrite, such as grain boundaries and dislocations, in recent years a third way is being studied which consists of the intragranular nucleation of ferrite on precipitates and inclusions. Some authors have studied the intragranular nucleation of acicular ferrite on MnS–CuS inclusions1) and also on Ti2O3 particles.2–5) Others have studied the intragranular nucleation of idiomorphic ferrite on complex precipitates formed by V(C, N) type inclusions and precipitates.6–8)

The mechanisms that promote intragranular nucleation vary according to the type of particle or inclusion. On the one hand, the presence of MnS type inclusions causes a local Mn depletion that increases the Ar3 value, favouring the nucleation of ferrite. On the other hand, VC or VN have a low interfacial energy in relation to ferrite but a relatively high interfacial energy in relation to austenite for the (001)V(C, N) boundary compared to MnS. These advantages of VC and VN over MnS in the interphase boundary energy balance presumably promote the intragranular ferrite transformation for complex precipitates.9)

However, the intragranular nucleation of ferrite has not yet been clearly demonstrated and its contribution to ferrite grain refinement is still to be quantified. The present work represents the continuation of previous work by the authors on induced precipitation and on the intragranular nucleation of ferrite in vanadium microalloyed steels, using an own methodology developed over recent years, which seeks to demonstrate and to quantify the contribution of intragranular nucleation of ferrite on V(CN) precipitates.10–13)

2. Materials and Experimental Procedure

The steel, whose chemical composition is shown in Table 1, was manufactured industrially and is a low carbon V-microalloyed structural steel. It has been denominated Y5 in order to distinguish it from other microalloyed steels manufactured by the same factory.

The specimens for torsion tests had a gauge length of 50 mm and a diameter of 6 mm. The austenitisation temperature was 1 200°C for 10 min. The recrystallised fraction was determined for several deformation temperatures and two strain values (0.20 and 0.35) and has been plotted as a function of time. Recrystallisation-precipitation-time-temperature (RPTT) diagrams have then been drawn. The RPTT diagrams depict precipitation kinetics as a function of the temperature and time and this information has been used to study the intragranular nucleation of ferrite, cooling specimens from programmed temperatures and moments for which the precipitated volume and the average precipitate size (determined by TEM) are known. The results have allowed us to determine the contribution of intragranular nucleation to ferritic grain refinement, which was approximately 20%.

KEY WORDS: intragranular nucleation; ferrite; precipitates.

3. Results and Discussion

3.1. Static Recrystallisation

First of all the solubility temperatures of vanadium carb...
bides and nitrides were calculated in accordance with Turkdogan’s solubility product and the precipitated volume fraction at 950°C according to procedure of Manohar et al., yielding the values shown in Table 2.

Austenitisation at 1200°C for 10 min was sufficient to completely dissolve the vanadium precipitates. With the aim of measuring the austenite grain size at the austenitisation temperature, one specimen was quenched in water. The grain size was measured applying ASTM standard E-112, obtaining a value of 127 μm.

The recrystallised fraction \( (X_a) \) determined by torsion tests at several temperatures was plotted against time, obtaining curves such as those included in Figs. 2 and 3, which correspond to strains of 0.20 and 0.35, respectively. The curves corresponding to temperatures equal to or below 1000°C present a plateau, or the inhibition of recrystallisation, due to strain-induced precipitation of V(C, N) particles.

The curve that does not present a plateau has the typical sigmoidal shape of Avrami’s law. The length of the plateau is not unlimited, and after a short inhibition time recrystallisation once again progresses until reaching completion. The recommencement of recrystallisation is due fundamentally to the reduction of pinning forces by the growth of particles during heterogeneous precipitation, versus the driving forces for recrystallisation. The start and end of the plateau are approximately identified with the start and end of precipitation. It is conventionally accepted to estimate a 5% recrystallised fraction for the start and a 95% fraction for the end.

It is known that once the plateau has ended, and recrystallisation is again progressing, the pinning forces exerted by the precipitates are now lower than the driving forces for recrystallisation.

However, while the start of the plateau seems to coincide with good exactness with the start of strain-induced precipitation, recent studies have demonstrated that at the end of the plateau a small fraction of precipitates conserve the same size as the precipitates formed at the start of precipitation. Therefore, this suggests that the end of the plateau, or the \( P_f \) curve, coincides approximately with the end of the precipitation.

On the other hand, once the plateau has started, the experimental points that define it are not exactly on it but are normally below it. This is due to the fact that the double deformation technique, and in particular back extrapolation, is a mechanical method and the start of precipitation increases the flow stress of the steel, which is translated into a pseudo-reduction in the recrystallised fraction. Obviously, as the holding time after deformation increases, so the recrystallised fraction cannot decrease.

### Table 2

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>( T_s, ^\circ C )</th>
<th>( X_p ) (950°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VN</td>
<td>1074</td>
<td>4.07x10^-3</td>
</tr>
<tr>
<td>VC(^{275})</td>
<td>812</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2. RPTT Diagrams

Recrystallised fraction versus time curves were used to plot recrystallisation-precipitation-time-temperature (RPTT) diagrams. The points defining the start and end of the plateau were taken to plot curves for the start \( (P_s) \) and end \( (P_f) \) of precipitation, respectively. On the other hand, the lines corresponding to different recrystallised fractions were determined by regression of the points resulting from the intersection of horizontal lines corresponding to different \( X_a \) values with the recrystallised fraction curves. In this way, RPTT diagrams were obtained for the two strains of 0.20 and 0.35, and are shown in Figs. 4 and 5, respectively.

The recrystallised fraction does not change between \( P_s \) and \( P_f \), and for times in excess of \( P_f \) the slope of the straight line for any \( X_a \) value is lower, which means that recrystallisation is more difficult after precipitation. Physically this means that the activation energy for the recrystallisation of austenite is higher when precipitation has taken place.

The RPTT diagrams provide ample information on the
recrystallisation–precipitation interaction, apart from showing the precipitation kinetics. It is seen that the nose of the \( P_s \) curve, or the minimum incubation time of strain-induced precipitation, interacts approximately with the 50% recrystallised fraction line. In other words, the optimum microstructure for precipitation to take place is that corresponding to the 50% recrystallised fraction, where saturation and diffusion reach a maximum. When \( X_a \) is equal to or less than 30%, precipitation is very difficult. On the other hand, the temperature of the nose of the \( P_s \) curve corresponded to a temperature close to 950°C for a strain of 0.20 and somewhat lower, approximately 940°C, for a strain of 0.35.

At the moment when precipitation starts, whatever the temperature (\( P_s \) curve), it is assumed that the precipitated fraction corresponds to a value of 5%. In the same way, the optimum microstructure for precipitation to take place is that corresponding to the 50% recrystallised fraction, where saturation and diffusion reach a maximum. When \( X_s \) is equal to or less than 30%, precipitation is very difficult. On the other hand, the temperature of the nose of the \( P_s \) curve corresponded to a temperature close to 950°C for a strain of 0.20 and somewhat lower, approximately 940°C, for a strain of 0.35.

\[
x_a = 0.20, 0.35, \text{ and } 3.63 \text{ s}^{-1}
\]

The RPTT diagrams, and especially the \( P_s \) and \( P_f \) curves, define a time interval, whatever the temperature, during which the precipitation state (size and precipitated volume) is changing. For times after \( P_f \), the recrystallised fraction does not vary but a coarsening of the precipitates occurs due to the effect of Ostwald ripening.\(^{20}\)

Finally, Figs. 4 and 5 show a series of arrows that indicate the holding times at 950°C, after deformation, in new tests performed with the aim of studying the influence of precipitation on intragranular nucleation, as will be seen in the following section.

According to the RPTT diagrams, the deformation conditions were selected to coincide approximately with times before the nose of the \( P_s \) curve, close to \( P_s \) and \( P_f \), and after \( P_f \), respectively. In this way it was possible to evaluate the effect of precipitation kinetics on the intragranular nucleation of ferrite.

The aim of these tests is to verify whether two austenitic microstructures subjected to the same deformation at a certain temperature, with holding times after deformation situated between the \( P_s \) and \( P_f \) curves, equivalent to a plateau, and cooled at the same cooling rate, would yield the same or a different ferrite grain size. It should be noted that two or more holding times corresponding to the \( P_f-P_s \) interval would have the same microstructure, \( i.e. \) the same recrystallised fraction, which means the same dislocation density and the same average austenite grain size, and the only difference would be the precipitated volume. In other words, both microstructures will be differentiated by the precipitated volume, conventionally from 5% corresponding to \( P_s \), which corresponds to the start of the plateau, and 95% corresponding to \( P_f \).

The deformation conditions are shown in Table 3. After the holding time at the deformation temperature, the specimens were cooled at a rate \( (dT/dt)_900-950°C \) of 3.5 K/s. Table 3 also reports the recrystallised fraction and the precipitated volume, calculated in accordance with the RPTT diagrams.

Metallographic preparation of the specimens allowed the measurement of the ferrite grain size, as is shown in the ferritic microstructures obtained in the conditions noted below the figure (Figs. 6(a)–6(g)). Ferrite grain sizes were measured applying the linear intersection method and the values obtained were graphically represented as a function of the austenite holding time after the deformation temperature (Fig. 7).

An increase in the holding time (\( \Delta t \)) after deformation reduces the ferrite grain size, but is insufficient to suggest that grain refinement has been due exclusively to VN precipitates acting as nucleation sites for ferrite during cooling. In this sense, Fig. 6 does not adequately clarify the contribution of intragranular nucleation of ferrite on precipitates, and thus it would be necessary to set out the results in another way.

As has been noted at the start of this work, when austenite is deformed at a given temperature and held for a certain time at that temperature, the resulting microstructure can recrystallise either partially or completely. A hardening of austenite, originated by incomplete recrystallisation, in-

<table>
<thead>
<tr>
<th>( T_d ), °C</th>
<th>( \varepsilon )</th>
<th>( X_a ), %</th>
<th>( X_p ), %</th>
<th>( D_{fa} ), μm</th>
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</thead>
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<tr>
<td>950</td>
<td>0.20</td>
<td>20</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>20</td>
<td>5</td>
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</tr>
<tr>
<td>700</td>
<td>20</td>
<td>90</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>10</td>
<td>48</td>
<td>0</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>55</td>
<td>5</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>55</td>
<td>75</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>73</td>
<td>100</td>
<td>12.5</td>
<td></td>
</tr>
</tbody>
</table>

\[(\frac{dT}{dt})_{900-950°C} = 3.5 \text{ K/s}\]
creases the density of dislocations and consequently the number of nucleation sites. Therefore, the contribution of intragranular nucleation on precipitates to ferrite grain refinement must be evaluated in conditions where both the austenite grain size and the dislocation density remain constant. In this sense, it is supposed that two austenitic microstructures would have the same dislocation density if the recrystallised fraction is the same.

The recrystallised fractions and precipitated fractions may be deduced from the RPTT diagrams (Figs. 4 and 5), making the opportune interpolations. Thus, for a strain of 0.20 the values of $X_a$ (Table 3) corresponding to holding times ($\Delta t$) of 50 and 700 s were 53%. The precipitated fractions for these times were 5%, coinciding with $P_s$ and 90%, slightly before $P_f$ (Fig. 4), and thus close to the start and the end of precipitation. Between these two conditions, both the average austenite grain size and the dislocation density are approximately the same and only the precipitated fraction varies. The latter has been calculated bearing in mind that the precipitation kinetics between $P_s$ and $P_f$ obey Avrami’s law. Nevertheless, a linear approximation between $P_s$ and $P_f$ would yield very similar results.

These results are shown in Fig. 8, where the ferrite grain size has now been represented as a function of the recrys-
tallised fraction, related with the dislocation density, noting on each point the corresponding precipitated fraction. The contribution of ferrite intragranular nucleation would be measured on the approximately vertical segment of each representation corresponding to the strains of 0.20 and 0.35, respectively, if necessary making extrapolations to the 0% and 100% precipitated fraction, respectively.

The reduction in the ferrite grain size \( (D_a) \) obtained between the two aforementioned conditions (holding times of 50 s and 700 s) was 3.5 \( \mu \text{m} \), which extrapolated to a 95% precipitated fraction would mean approximately 4 \( \mu \text{m} \), which compared to the grain size corresponding to a 5% precipitated fraction \( (D_a = 17 \mu \text{m}) \) implies a 24% reduction. In the same way, for a strain of 0.35 and holding times \( (\Delta t) \) of 50 and 700 s, the \( X_p \) values were 55%. In these conditions of the same average austenite grain size and the same dislocation density, the precipitated volume varies between 5% and 80%. Between these conditions the reduction obtained for \( D_a \) was 2 \( \mu \text{m} \), which extrapolated to a 95% precipitated fractions would mean 2.5 \( \mu \text{m} \), representing a reduction of approximately 16% from the size corresponding to a 5% precipitated fraction \( (D_a = 15.5 \mu \text{m}) \).

Comparing the above results it is seen that the recrystallised fraction between \( P_s \) and \( P_f \) is approximately 53% and 55% for strains of 0.20 and 0.35, respectively. This means that both the recrystallised and the non-recrystallised fractions are similar, and in particular that the austenite hardening reached in the latter case on the non-recrystallised fraction is obviously greater. On the other hand, the recrystallised grain size decreases as the strain increases. Thus it may be concluded that in the case of the strain of 0.35, the dislocation density was greater and the average austenite grain size was smaller than with the 0.20 strain. Both aspects favour the nucleation of ferrite, both at austenite grain boundaries and on subgrains formed by the stacking or cluster of dislocations. Therefore, it was expectable that the contribution of intragranular nucleation to ferrite grain refinement would be less in the case of the 0.35 strain than in the case of the 0.20 strain, as has indeed been the case.

Finally, it is not possible to measure the percentage contribution of each of the nucleation sites separately, since as the recrystallised fraction increases so the average grain size decreases, favouring nucleation at the grain boundaries, and at the same time the dislocation density decreases, reducing the capacity of dislocations to serve as nucleation sites for ferrite. This is observed very well when the holding time after the 0.20 strain increases from 10 to 50 s (Fig. 7), causing an increase in the recrystallised fraction from 20 to 53% (Fig. 8) and an undetermined reduction in the dislocation density.

Finally, in other work reported by the authors\(^{13,24}\) it was shown that in V-microalloyed steels with a greater precipitated volume fraction, which is obviously achieved with higher V and N contents, the percentage reduction in the ferrite grain size due to intragranular nucleation on VN precipitates rises notably, and in a steel with \( C = 0.100; V = 0.151 \) and \( N = 0.0227 \) (%) has achieved a 45% reduction. In this case\(^{24}\) the total precipitated fraction at the deformation temperature was \( 1.1 \times 10^{-3} \), more than one order of magnitude higher than in the present case (Table 2).

### 3.3. Precipitate Analysis

The precipitation states were characterised by studying the nature, size and distribution of vanadium nitrides-carbonitrides formed in hot-deformed specimens. Transmission Electron Microscopy (TEM) techniques on carbon extraction replicas have been used. The particle size distribution of second phase particles and determination of the average particle diameter have been obtained by measuring an average number of 200 particles on each specimen. **Figure 9(a)** shows a TEM micrograph in which the VN precipitates can be seen. The electron energy dispersive X-ray spectrum (Fig. 9(b)) shows the presence of V and N and the lattice parameter determined revealed a f.c.c. cubic lattice with a value of 0.414 nm (Fig. 9(c)), which corresponds to V(C, N) precipitates.

**Fig. 9.** TEM images of steel used. (a) Image showing precipitates for specimen tested at reh. temp. of 1 200°C; deformation temp. of 950°C, \( \varepsilon = 0.35; \Delta t = 20 \text{s} \); (b) EDAX spectrum of precipitate. (c) Electron diffraction pattern.

**Figures 10(a) and 10(b)** show the particle size distributions obtained for the steel used. The specimens were deformed \( (\varepsilon = 0.35) \) at 950°C and held for times of 20 s and 100 s, which coincide with the nose of the \( P_s \) curve and before \( P_f \) respectively, in the RPTT diagram. It can be seen that the average particle size was 6.4 nm at the start of precipitation and that after 100 s (end of plateau) the average particle size had reached 9.5 nm, which was still small. The average precipitate size is relatively small and a larger size
With the aim of revealing possible intragranular ferrite nucleation on V-precipitates, a further microscopy study was carried out using a scanning electron microscope (SEM-FEG). Figure 11 shows a small ferrite grain, well below the average size, in preference to subgrains, in the present study. It has been seen that the ferrite grain size was notably reduced by the intragranular nucleation of ferrite on precipitates. Intragranular nucleation led to a reduction of approximately 25% in the ferrite grain size with a strain of 0.20 and 16% with a strain of 0.35.

In accord with the above, the contribution of intragranular nucleation decreases as the applied strain increases. An increase in the strain favours nucleation of ferrite at austenite recrystallised grain boundaries, as the austenite grain is finer, and on subgrains, in preference to intragranular nucleation on VN-precipitates.

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REFERENCES