Analysis of the Effect of Mn on the Recrystallization Kinetics of High Nb Steel: An Example of Physically-based Alloy Design

H. S. ZUROB, G. ZHU, S. V. SUBRAMANIAN, G. R. PURDY, C. R. HUTCHINSON and Y. BRECHET

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, Domaine Universitaire, BP 75, 38402, St. Martin d'Hères, Cedex, France. E-mail: hatem@zurob.com 1) Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, L8S 4L7, Hamilton, ON, Canada. 2) School of Physics and Materials Engineering, Monash University, Clayton, 3168, Victoria, Australia.

(Received on November 1, 2004; accepted on January 28, 2005)

Strip casting and thin slab casting are new near net-shape technologies, which have successfully emerged in steels because of significant energy savings, substantial reduction in green house gas emissions and cost benefits. Extensive research was undertaken aimed at integrating microalloying technology with near net-shape casting technology, using a base chemistry of low carbon (0.03 wt%) and high niobium (up to 0.1%wt), which is a well established chemistry for higher grade pipeline steels.

In the present contribution, physically-based modelling is used to optimize the Mn content and the processing conditions for the application of strain-accumulation in the new steels. The results of the modelling confirm the distinct advantage of the low Mn chemistry for the application of plate rolling which is carried out in the high temperature window using small to medium deformation passes. The high Mn chemistry is found to be more advantageous when the rolling is carried out in the low temperature window and using large pass reductions. This result is in agreement with recent rolling simulations and mill trials which show that the high Mn chemistry is superior to the low Mn chemistry for the application of near net-shape strip-rolling.

KEY WORDS: strip-rolling; effect of Mn; recrystallization; recovery; precipitation; solute-drag; process optimization.

1. Introduction

The first detailed investigations of the effect of microalloying on the solidification and mechanical behaviour of C-Mn steels date back to the 1950’s. It was quickly apparent that the addition of small amounts of Nb, Ti and/or V has the effect of reducing the final ferrite grain-size and, consequently, increasing the strength and toughness of the steel. In the decades that followed, the response of microalloyed steels to thermo-mechanical processing became the subject of a great deal of experimental work. Advanced databases and powerful empirical relations were developed to relate the extent of recrystallization to the deformation temperature, the amount of deformation and the chemistry of the material. Today, the chemistries and processing conditions of microalloyed steels are carefully optimized to produce steels with a grain-size of less than 5 μm and a yield-strength in excess of 650 MPa.

The next major step in the evolution of microalloyed steels would most likely involve the introduction of thin-slab (15–35 mm) and thick-strip (12–15 mm) casting. These processes are based on the concept of near net-shape casting which has the potential for reducing the energy consumption and the environmental emissions associated with the hot-rolling of steel. The advent of these casting techniques has necessitated some changes in the chemistry of microalloyed steels. The most important of these is the adoption of a low carbon design in order to achieve a very homogenous solid-state microstructure and avoid microsegregation. Solidification models show that the large temperature window in the δ-phase field, which is associated with low carbon design, allows adequate post-solidification homogenisation of the substitutional solutes. It is thus possible to design new microalloyed steels with as much as 0.1 wt% Nb and 1.8 wt% Mn. In addition to this new opportunity, there are new challenges associated with the new casting processes. The small initial thickness of the new products requires the elimination of the thermomechanical roughing step, which is traditionally used to refine the grain-size before finish rolling. As such a new approach is needed to produce fine grain-size in the new steel grades. Subramanian et al. demonstrated that strain-accumulation by multi-pass rolling can lead to grain-refinement in austenite by dynamic recrystallization. The above authors established the possibility of achieving a final grain-size of less than 3 μm in a low-carbon, high-Nb steel. More recent work has clearly demonstrated that the success of strain accumulation and hence of grain refinement, is strongly affected by the Mn content. It is thus clear that the successful application of thin-slab and thick-strip casting to microalloyed steels requires the re-optimization of the steel chemistry (Mn content) and of the hot-rolling process-parameters (temperature and strain).

In the present contribution we develop a physically-based model to rationalize existing laboratory and mill data on the effect of Mn on static recrystallization in high-Nb steels.
The predictive capability of the physically-based approach makes it possible to explore material behaviour over short interpass times which are difficult to access experimentally. We are thus able to optimize, to a first order, the steel chemistry and processing conditions for the strip-rolling of high Nb steels. Further optimization of the chemistry and processing conditions requires experimental inputs that would allow for the verification and improvement of the model. Thus, an important theme of the present contribution is the need to use physically-based modelling in parallel with carefully designed experiments.

We start by reviewing the existing experimental observations on the effect of Mn on precipitation and recrystallization (Sec. 2). We then present a physically-based model for the microstructural evolution of hot-rolled austenite during the interpass time (Sec. 3). In Sec. 4, the model is used to analyze the effect of Mn content on the softening kinetics for various processing conditions (i.e. various combinations of temperature and strain). The industrial implications of the model are considered in Sec. 5.

2. Recapitulation of Experimental Observations

Table 1 identifies the base chemistry of the steels being investigated for the application of strain-accumulation in the low temperature window. As mentioned earlier, the low carbon design is based on the need to achieve a very homogeneous solid-state microstructure even with high alloying addition of substitutional solutes like Mn and Nb. The contents of N and Ti are based on quantitative modelling of the thermodynamic potential for the precipitation of Ti–Nb carbo-nitrides. These models show a distinct advantage of low nitrogen (0.003 wt%) design. The titanium content (0.015 wt%) is that required to tie up all the nitrogen as Ti-rich nitrides in the high temperature range. These nitrides are thermodynamically stable at high-temperatures and are therefore used to advantage to minimize grain growth during slab-reheating and in the heat affected zone of plates during high heat-input welding. The elevated Nb content of the present steels is based on the need to retard static softening between passes during strain accumulation. It is worth pointing out that high Nb steels are already being used to advantage for some plate rolling applications. The retardation of recrystallization by high solute niobium makes it possible to roll plates in the high temperature window using a rolling mill, which is of insufficient power to impart heavy reduction in the low temperature window. This design of chemistry for high temperature processing (known as HTP) is well established for many plate-rolling products as well as several higher grade pipeline steels.

The purpose of the present contribution is to identify the Mn content which is most suitable for the application of strain-accumulation. In general, there is a tendency to use a high Mn design because the base chemistries of higher grade steels invariably contain high Mn content, Mn being the cheapest alloying addition. In addition to enhancing the strength of the steel, increasing the Mn content lowers the austenite to ferrite transformation temperature, which allows a large temperature window for finish rolling. This also allows rolling at low temperatures which is more favourable for strain-energy accumulation. Earlier work on the high Mn design has shown, however, that Mn delays the onset of strain induced precipitation of NbC. The effect of this delay on the effectiveness of NbC at retaining recovery and recrystallization is one of the issues considered in this contribution. In what follows, we summarize the existing literature on the effect of Mn on precipitation and recrystallization. The experimental facts established here will serve as a guide for the physically-based modelling which is aimed at optimizing the Mn content.

Table 1. Typical compositions of the steels being studied for strain-accumulation applications.

| C         | N    | Nb   | Ti | Mn     | Si    |
|-----------|------|------|----|--------|-------|
| 0.03-0.04 | 0.003-0.004 | 0.06-0.09 | 0.015-0.030 | 0.3-1.8 | 0.2-0.4 |

2.1. Effect of Mn Content on Precipitation

The thermodynamic potential for the precipitation of NbC is a function of the base chemistry of the steel. Koyama et al. measured the solubility product of NbC as a function of the Mn content:

\[
\log([\text{Nb}][\text{C}]) = -7.970/T + 3.31 + (1.371/T - 0.9)[\text{Mn}] - (75/T - 0.0504)[\text{Mn}]^2
\]

In the above equation, the concentrations are in wt% and the temperature is in K. The results indicate that Mn has the effect of increasing the solubility of niobium carbide in austenite. Accordingly, the effect of Mn addition is to decrease the rate of precipitation and the equilibrium precipitation fraction at a given temperature.

Akben et al. investigated the effect of Mn on the kinetics of strain induced precipitation of NbC by increasing the Mn content from 0.42 to 1.9 wt% on a steel containing 0.05wt% C and 0.035 wt% Nb. The time for the start of strain-induced precipitation of NbC was shown to increase with Mn content. Zhu et al. arrived at a similar conclusion on analysis of the extensive softening database of Lutz–Meyer. It appears from this last investigation that the addition of about 1.5% Mn delays the onset of strain induced precipitation by 2–4 s. While the delayed precipitation kinetics in high Mn steels is consistent with the increase in the equilibrium solubility of NbC with Mn content, the magnitude of the effect is difficult to reconcile without consideration of kinetic factors contributing to the delayed precipitation of NbC in high Mn steels. For example, Kurokawa speculated that the decrease in the Nb diffusion coefficient with increasing Mn content in austenite would contribute to the aforementioned delay in precipitation. Another possibility is that Mn segregates to dislocations in austenite (as it does in ferrite) and in so doing interferes with the precipitation of NbC on dislocations.

For the purposes of the present investigation, we are only interested in the results that: (i) there is less precipitation in the high Mn steel because of the increased solubility of NbC, and (ii) precipitation occurs more slowly in the high Mn steel. The details of the mechanism causing the delay in precipitation are beyond the scope of this work.

2.2. Effect of Mn Content on Recrystallization

The effect of Mn on the softening kinetics during short
interpass times was investigated by Zhu et al.\(^7\) The experiments were carried out on the WUMSI hot-rolling simulator at the Max-Plank-Institute für Eisenforschung, Düsseldorf, Germany. The compositions of the steels used are listed in Table 2. The two alloys received four reductions of 28\% at 830°C. The interpass times were 4, 3 and 2 s, respectively. The flow stress and temperature were monitored during loading and the results are shown in Fig. 1. Very little softening took place during the interpass time in the case of the low Mn steel. By contrast, extensive softening is observed in the case of the low Mn steel. Examination of the microstructure after the four passes showed a bimodal grain-size distribution in the low Mn steel as a result of static recrystallization. Mixed grain size was not observed in the high Mn steel indicating that static recrystallization was successfully prevented.

In principle, the observed effect of Mn on the softening kinetics could be either a “direct” effect which is due to Mn itself or an “indirect” effect which is due to the effect of Mn on the precipitation of NbC. The first possibility is ruled out because experimental observations indicate that in Nb-free steels, the low Mn chemistry offers greater resistance to softening than the high Mn one.\(^{12,13}\) The reversal of this trend for the high-Nb steels used in the WUMSI simulations must then be related to the effect of Mn on strain-induced precipitation.

Two arguments could explain the WUMSI observations. It could be argued that the delayed precipitation in the high Mn steel allows significant recovery to take place, resulting in the depletion of the net driving force available for recrystallization nucleation. This in turn will increase the incubation time for recrystallization nucleation beyond the short interpass time. The second argument is based on the solute drag effect of Nb in solid solution. It may be that Nb in solid solution is more effective than precipitation at retarding recrystallization in the low temperature window considered here. If this is the case, then this result would be contrary to the widely held view that NbC precipitates are more effective than solute Nb at retarding recrystallization. In the well-cited review by Jonas et al.,\(^{16}\) it was convincingly shown that Nb in solute delays recrystallization by an order of magnitude compared to Nb-free steel. When precipitation takes place an additional delay of another order of magnitude is observed. This clearly showed that precipitation is the more effective means of retarding recrystallization. The same conclusion was reached based on the physically-based model of Zurob et al.\(^4,17,18\) Thus the phenomenological observations in the present work on high Nb steel with different Mn levels warrant more in-depth analysis to sort out the relative contributions of solute and strain-induced precipitation to the retardation of recovery and recrystallization kinetics.

### Table 2. Compositions of the “low” and “high” Mn steels used in the WUMSI simulations and mill trials.

|          | C      | N      | Nb     | Ti     | Mn |
|----------|--------|--------|--------|--------|----|
| Low Mn (Laboratory heat) | 0.035  | 0.006  | 0.082  | 0.021  | 0.3 |
| High Mn (Laboratory heat) | 0.034  | 0.006  | 0.082  | 0.022  | 1.1 |
| HTP (Industrial Heat)     | 0.03   | 0.005  | 0.086  | 0.011  | 1.49|

3. Development of a Physically-based Model

The time evolution of strain-induced precipitation and its interaction with recovery and recrystallization are the basic building blocks of any physically-based model for evaluating the static softening kinetics and hence strain accumulation behaviour in multi-pass rolling. In recent work, Zurob et al.\(^{17,18}\) have explicitly considered the time evolution of strain-induced precipitation and its interaction with recovery and recrystallization. The model assumes that precipitation takes place heterogeneously on the dislocations created by deformation. The precipitates pin the dislocation segments on which they form and this significantly retards the rate of recovery. Once the precipitates start to coarsen, some dislocations will be unpinned, and recovery resumes at a rate controlled by the coarsening kinetics of the precipitate. Additional details of the precipitation model and of the interaction between precipitation and recovery are available elsewhere.\(^{17,19}\) In what follows we focus on the effect of the Mn content on the relative contributions of solute Nb and strain induced precipitation to the retardation of static recovery and recrystallization. The analysis is carried out for a range of rolling conditions, covering small and large strain passes as well as high and low temperature window of rolling.

3.1. Effect of Solute on Recrystallization

The recrystallization kinetics of single phase materials is often described by the Johnson–Mehl–Avrami model.\(^20\) In the case of site-saturation the model is expressed as:

![Fig. 1. Temperature corrected strengthening-deformation strain curves plotted from WUMSI measurements, showing more static softening of low Mn–high Nb steel (a) compared to high Mn–high Nb steel (b). Four rolling passes of ~28% were applied to each steel. The interpass times were 4, 3 and 2 s, respectively.](image-url)
According to Cahn’s theory of solute drag, the grain crystallization nuclei, $\alpha CV$, is the grain boundary mobility. Equation (3) is essentially an energy balance; the driving force ($V/M_f$) and the solute-drag pressure ($\alpha CV(1+\beta V^2)$). The constants $\alpha$ and $\beta$ in the solute drag term are defined as:

$$\alpha = \frac{N_i k T^2}{\delta E_d D_x} \left( \sinh \left( \frac{E_0}{kT} \right) - \frac{E_0}{kT} \right), \quad \beta = \frac{\alpha k T \delta}{2N_i E_d^2 D_x}$$

where $k$ is Boltzmann’s constant, $T$ is the absolute temperature, $N_i$ is the number of particles per unit volume and $\delta$ is the grain boundary thickness. The other quantities appearing in Eq. (4) are the cross-boundary diffusion coefficient of the solute, $D_x$, and the segregation energy of the solute to the grain boundary $E_o$. Elements that exhibit a strong solute-drag effect do so by virtue of the fact that they bind strongly to the boundary (large $E_o$).

The correlation between the driving force and the velocity is illustrated in Fig. 2 for increasing levels of solute concentration. When the solute concentration is very small, we approach the behaviour of the pure material; the driving force and the velocity are linearly related with the proportionality constant being the intrinsic mobility (curve a). As the solute content increases, the force–velocity curve gradually develops two branches. Strong solute-drag is observed on the “low velocity branch” of the force–velocity curve. Under these conditions the speed of the boundary is controlled by the rate of diffusion of the solute. A large increase in $F$ is needed to bring about a small increase in $V$. By contrast, the high velocity branch corresponds to conditions under which the boundary breaks away from the solute atmosphere and is able to move at speeds approaching those expected in the pure material. The transition form one branch to the other can be smooth as in curve (b) or abrupt as in curve (c). “The nature of the transition is determined by the concentration of the solute and the magnitude of the driving force”.

In our previous analysis, we assumed that the low-velocity conditions were applicable at all times. This is a good assumption given the fact that the driving force associated with recrystallization after hot-deformation is usually small. However, when deformation is carried out at lower temperatures, the above assumption becomes increasingly less appropriate because the stored energy becomes increasingly larger. In Sec. 4, we demonstrate that under some circumstances it is possible to arrive at driving forces that would lead to a transition to the fast branch of the solute-drag curve.

### 3.2. Effect of Precipitation on Recrystallization

The effect of precipitation on recrystallization is often discussed in terms of the effect of the Zener pinning force on boundary motion. In addition, one needs to discuss the effect of the precipitates on the dislocation rearrangements which are necessary for the nucleation step of recrystallization. As such, this section is divided into two subsections, which deal with the effect of precipitation on the nucleation and growth of recrystallization.

#### 3.2.1. Nucleation Stage of Recrystallization

At the earliest stages of recrystallization, precipitation may retard recrystallization by hampering the rearrangement of dislocations which is essential for the formation of the recrystallization nuclei. Inspired by the classical observations of Bailey and Hirsh, we argue that the nucleation of recrystallization requires the movement/rearrangement of dislocations on a scale of $D_c$, where $D_c$ is the diameter of the critical recrystallization nucleus. Precipitation will restrict dislocation movement to a scale of $l$, where $l$ is the spacing of the precipitate particles on the dislocation network. Thus, if $l$ is smaller than $D_c$, the ability of a nucleus to develop is reduced by a factor of $\psi = l/D_c$. Equation (1) is then rewritten as:

$$X = 1 - \exp \left( \frac{v(t) d t}{N} \right) \quad \text{......(5a)}$$

where,

$$\psi(t) = \min (l/D_c, 1) \quad \text{......(5b)}$$

In the above equations, the inter-particle spacing is estimated as $\rho/n$, where $\rho$ is the dislocation density and $n$ is the number of precipitate particles per unit volume. The function, $f_3$, is an efficiency factor which captures the fact that the particle’s ability to pin a dislocation depends on the size of the particle. We assumed that the value of $f_3$ increases linearly from 0 to 1 as the particle radius increases from 0.
to 1 nm. For particles larger than 1 nm radius, the value of $f_s$ is assumed equal to 1.

One of the distinguishing features of the present treatment is that the nucleation-probability term, $\psi$, depends on the number density of the precipitate particles and not on their volume fraction. This is critical because, in most cases, precipitate nucleation is complete within a second or a fraction of a second. Therefore, the probability term can lead to strong retardation of recrystallization even at the shortest interpass times. Figure 3 illustrates the time evolution of the nucleation-probability term. In the example shown, it takes 2 s for precipitate particles to nucleate and grow to a size of 2 nm, which is the size at which they become completely effective at pinning dislocation-segments. Thus, there is a dramatic drop in the probability of recrystallization once the dislocations are pinned. The probability continues to be very low, until the onset of precipitate coarsening. The dissolution of the smallest precipitate particles during coarsening will increase the average value of $f$ and the probability of nucleation will increase as a result. Thus the strong retarding effect of the microalloying elements on the onset of recrystallization is due to the role of fine precipitate particles in delaying the nucleation of recrystallization.

### 3.2.2. Growth Stage of Recrystallization

Precipitate particles retard the growth of the recrystallizing grains by exerting a pinning pressure on the advancing grain-boundaries. The effect of boundary pinning (Zener pinning) is conveniently incorporated into the JMAK framework by reducing the driving force for recrystallization by an amount equal to the Zener pressure, $Z(t)$. Thus the net driving force in Eq. (3) is written as:

$$F(t) = G(t) - Z(t) = \frac{1}{2} \rho v b^3 - \frac{3 f_s \gamma}{2 r}$$

In this equation, the stored energy of deformation, $G(t)$, was estimated as $\rho v b^3/2$, where $\rho$ is the dislocation density, $v$ is shear modulus and $b$ is the Burger vector. The pinning pressure, $Z(t)$ is expressed as $3 f_s \gamma/2 r$, where $\rho$ and $f_s$ are the precipitate radius and volume fraction, respectively, and $\gamma$ is the grain-boundary energy.\(^{(1,23)}\) The evolution of the Zener pressure is shown schematically in Fig. 4. The initial increase in Zener drag is due to the nucleation and growth of the precipitate particles. The peak pressure corresponds to the precipitation of a large fraction of fine precipitate particles. When these begin to coarsen, the Zener pressure starts to decrease gradually.

It is important to note that the build up of the Zener force is very slow compared to the inter-pass times of strip rolling. This is due to the fact that the build up is controlled by the evolution of the precipitate volume fraction which is, in turn, controlled by the growth kinetics of the precipitate. As a result of this slow build up, the newly formed precipitates will exert very little pinning pressure on the recrystallization boundaries at the earliest annealing times. The Zener pressure becomes increasingly important at long times for two reasons: The first is the increase in the precipitate volume fraction, which leads to a larger pinning pressure. The second reason is the decay of the stored-energy of deformation as a result of recovery. Eventually, the Zener force may exceed the stored-energy of deformation and this would bring recrystallization to a complete halt. This, however, is unlikely to happen during short-interpass times.

### 3.3. Competition between Solute Drag and Precipitation

The results of Zhu et al.\(^{(7)}\) clearly show that for low $T$ and large deformation, static recrystallization is more strongly retarded in the high Mn steel compared to the low Mn steel. At the same time, the existing literature indicates that increasing the Mn content slows down the precipitation kinetics of NbC and lowers the equilibrium precipitate fraction. When the above facts are considered together, one is led to conclude that it is essential to retain Nb in solution above a threshold to prevent the boundary from breaking away from its solute atmosphere. This threshold is dependent on the magnitude of the driving force as shown by Cahn.\(^{(21)}\) For the remainder of this section, we will discuss, qualitatively, the effect of the Mn content on the competition between precipitation and solute drag. A quantitative discussion follows in Sec. 4, where we examine the above competition under various processing conditions (small and large strains as well as high and low rolling temperatures).

Building on the discussion in Secs. 3.1 and 3.2, the evolution of recrystallization in the presence of solute-drag and precipitation can be expressed in terms of the modified JMAK equation:
where we expressed the velocity as \( V(t) = M(t)F(t) \); \( M(t) \) being the effective mobility of the grain-boundary and \( F(t) \) being the net driving force. In order to understand the competition between solute drag and precipitation we need to explore the time evolution of the triple product, \( \psi(t)M(t)[G(t) - Z(t)] \).

3.3.1. Evolution of Nucleation-probability (\( \psi \))

In general, the value of the probability term decreases from 1, prior to precipitation, to 0.005–0.05 when the precipitate particles are most closely spaced on the dislocations. The fact that the nucleation-probability term changes by about two orders of magnitude due to precipitation means that under most conditions it is the probability of nucleation that dominates the evolution of the triple product (\( \psi M [G-Z] \)) and hence the evolution of recrystallization.

The delayed precipitation kinetics in the high Mn steel means that the probability term will start to decrease only after several seconds of holding. By contrast, the value of \( \psi \) will decrease immediately in the low Mn steel. We therefore expect that low Mn steel would generally offer greater resistance to static recrystallization than the high Mn steel.

3.3.2. Evolution of the Boundary Mobility

The mobility will gradually increase as the amount of Nb in solution decreases due to precipitation. Given that precipitation is faster in the low Mn steel, it follows that the mobility will increase more quickly in this steel than in the high Mn steel. The increased grain boundary mobility makes the low Mn steel more susceptible to recrystallization. One should keep in mind, however, that the mobility would typically increase by a factor of 2 to 5 times, which is still small in comparison to the large changes in the value of \( \psi \). Thus it is the evolution of \( \psi \) which is usually expected to dominate the value of the product and, hence, the recrystallized fraction.

Under special circumstances, however, it is possible for mobility to increase dramatically by a factor of 10 to 100 times. This could happen, for example, if the amount of Nb in solution drops below the minimum concentration needed to prevent the boundary from breaking away from it solute atmosphere. In other words, the decrease in Nb could result in a jump from the slow to the fast branch of the solute-dragn domain. Under these circumstances, solute drag would be more effective than precipitation at retarding recrystallization.

Figure 2 serves to illustrate the possibility of a transition from the slow to the fast branch of the solute drag domain. In this figure, the force–velocity relation is plotted for decreasing levels of solute. If the driving force for recrystallization is assumed to have a constant value of say \( \sigma \), and if the Nb content is assumed to decrease gradually due to precipitation, then a velocity-jump would be expected when the Nb concentration drops below that corresponding to curve (d). A first order estimate of the solute concentration below which the boundary is able to break away from its solute atmosphere was given by Cahn as\(^{21}\):

\[
C^* = \frac{4}{M \alpha} \left( \frac{B \beta M_*}{\sqrt{3}} + 1 \right) \tag{8}
\]

This expression is known to overestimate the value of \( C^* \). The important point to keep in mind, however, is that \( C^* \) increases linearly with the net driving force.

3.3.3. Evolution of the Driving Force

The driving force becomes the dominant factor controlling the evolution of recrystallization when the value \( G-Z \) approaches zero. In fact, recrystallization could come to a permanent stop if the value of the Zener drag exceeds that of the stored energy of deformation. Typically, the net driving force will approach zero only at very long times because of the slow build up of the Zener force and the slow decay of the stored energy. It is therefore very unlikely that the driving force would be the dominant factor in during strip rolling.

4. Quantitative Discussion of the Interplay between the Optimum Mn Content and Processing Conditions

We have so far established that the precipitation of Nb in the form of fine carbonitrides is generally more effective at retarding recrystallization nucleation than the presence of Nb in solution. This amounts to arguing that in general low Mn steels would be more resistant to softening than their high Mn counterparts. Under some special circumstances, however, this trend is reversed and one finds that the high Mn steel offers greater resistance to softening than the low Mn steel. According to the model developed in Sec. 3, this reversal of the general trend is likely to be due to the depletion of Nb from the matrix of the low Mn steel. When the Nb content drops below a critical value, \( C^* \), the boundary is able to break away from its solute atmosphere and the mobility is dramatically increased leading to rapid recrystallization.\(^1\)

In this section we quantitatively model three illustrative

\( ^1 \) It should also be pointed out that in the WUMSI trials on the low Mn steel,\(^7\) there is the possibility of forming strain-induced ferrite. This possibility exists because decreasing the Mn content can significantly increase the Ar3 temperature. Deformation dilatometry work would be required to rule out this possibility.
cases which are of industrial interest (Fig. 5). The first case corresponds to high temperature deformation. In this case, the driving force for recrystallization is relatively small and the equilibrium Nb content in the matrix is relatively high. Consequently, the Nb concentration in the matrix is always higher than the critical concentration for preventing the boundary from breaking away from its solute atmosphere, $C^*$. We show that in this case, the low Mn steel is more effective than the high Mn steel at preventing static softening. The second and third cases that we examine correspond to low temperature deformation such that the equilibrium Nb concentration is very low. Under these circumstances precipitation will eventually bring down the Nb concentration to a value below $C^*$. When the driving force is small, as in case II, the value of $C^*$ is low and it takes a long time ($\sim 75$ s) for precipitation to deplete the Nb content in the low Mn steel to below this level. Consequently, the low Mn steel is found to offer better resistance to recrystallization over short annealing times ($<50$ s). The trend is reversed for long annealing times ($t > 100$ s) as a result of boundary breakaway in the low Mn steel. The same trend is observed in case III, except that the driving force for recrystallization is large, leading to a large value of $C^*$. Consequently precipitation quickly ($t \sim 5$ s) brings down the Nb concentration in the low Mn steel below $C^*$ leading to boundary breakaway at very early times. Under these conditions the high Mn steel is better at retarding recrystallization as shown in the WUMSI simulations. 7)

4.1. Case I: Recrystallization after High Temperature Deformation

In the context of finish rolling, high temperatures would typically refer to temperatures in the range of 900 to 950°C. The equilibrium Nb concentration in this temperature range is typically 0.012–0.022% Nb for the low Mn steel and 0.020–0.040% Nb for the high Mn steel. The initial driving force for recrystallization would generally be of the order of 0.3 to 0.5 MPa. This force will decay relatively quickly because high temperature enhances the kinetics of recovery. Figure 6 shows the evolution of the nucleation probability term, the net-driving force and the mobility as a function of time for both the low and the high Mn steels. These quantities are calculated for an alloy containing 0.08% Nb and 0.04% C at a temperature of 900°C and using a deformation which results in a stored energy of 0.45 MPa. The Mn content of the high Mn alloy was set equal to 1.8% and that of the low Mn design was set equal to 0.3%. Additional details on the calculations are provided in Appendix 1. In Fig. 6(a) we observe that the precipitation kinetics in the high Mn steel is very sluggish and no significant precipitation is observed within the first 5 s or so. By contrast, significant precipitation takes place almost immediately in the low Mn steel. The value of $\psi$ is about 20 times smaller for the low Mn steel than for high Mn steel. By contrast the mobility of the low Mn steel is only slightly larger than that of the high Mn steel. This suggests that the amount of Nb left in solution in the low Mn steel is sufficient to prevent the boundary from breaking away from the solute atmosphere. We thus find that the low Mn steel is better at preventing static recrystallization than the high Mn steel. Thus low Mn steels are better for strain accumulation than high Mn steels for plate-rolling and traditional (high temperature) strip-rolling applications. Excellent strength and toughness properties are reported in pipeline steels (high-Nb and low-Mn) which are produced by plate rolling. 8,24,25) This process is typically carried out in the high temperature window, with small and medium pass reductions as discussed above.

4.2. Case II: Recrystallization after Small Deformation at Low Temperature

In the present example we are interested in low tempera-
tures of 850°C or less. Under these conditions, the equilibrium concentration of Nb in low Mn steel is very low. As such there is a serious risk of the Nb concentration dropping below the value of \( C^* \) in the course of precipitation.

To better analyze the problem we plotted, as before, \( \psi, M \) and \( G/Z \) as a function of time for both the high and low Mn steels (Fig. 7). The deformation temperature was assumed to be 830°C and the initial stored energy was taken to be 0.45 MPa. As expected, the probability term decreases very quickly in the case of the low Mn steel, while there is a delay of several seconds in the case of the high Mn steel. The evolution of the \( G \) and \( Z \) follows the expected trends; \( G \) decrease quickly in high Mn steel due to the lack of precipitate pinning of dislocations and \( Z \) increases slowly due to the lack of boundary pinning. Concerning the mobility, it is seen that the mobility of the low Mn steel increases more quickly than that of the high Mn steel. In Fig. 7(d) we see that the overall balance is in favour of the low Mn steel over short times of \(<70\) s. For longer times, the balance shifts in favour of the high Mn steel because boundary breakaway takes place in the low Mn steel. We thus find that for long annealing times \((t>70\) s\) the high Mn steel is better at retarding recrystallization than the low Mn steel. This is in agreement with industrial practice of using high Mn steels in Steckle mill rolling which involve long interpass times of up to 100 s.\(^{26}\)

### 4.3. Case III: Recrystallization after Large Deformation at Low Temperature

The processing conditions of Sec. 4.1 corresponded to those encountered during plate rolling and high-temperature strip-rolling. In this section, we consider the conditions associated with the WUMSI trials which correspond to near net-shape finish rolling of thin-slab and thick cast strip. We are thus dealing with low temperatures \((<850^\circ \text{C})\), large deformations \((G>0.6 \text{ MPa})\) and short interpass times.

The time evolution of \( \psi, G/Z \) and \( M \) for the present case are shown in Fig. 8. The temperature was assumed to be 830°C and the initial driving force was assumed to be 0.9 MPa. These values correspond approximately to the conditions used in the WUMSI trials. The evolution of the probability of nucleation and the net driving force resemble those shown in Fig. 7. The distinguishing feature of the present example is that the abrupt change in mobility as a result of the boundary breaking away from its solute atmosphere happens at relatively short times. In the case of the low Mn steel the breakaway happens at \( t=8 \) s which corresponds to a Nb content of 0.059%. By contrast, the breakaway in the high Mn steel happens much later at \( t=30 \) s. We thus find that the recrystallization kinetics of the low Mn steel is accelerated with the depletion of solute niobium below the critical level. The delayed precipitation kinetics of NbC precipitation in the high Mn steel ensures adequate solute niobium to retard recrystallization. Consequently, the high Mn steel is more suitable than the low Mn steel for the strip-rolling of thin-slab and thick-strip castings.

### 5. Industrial Implications for Strain-accumulation

The present work was motivated by the need to optimize the chemistry of the steels which are produced by thin-slab and thick-strip casting and used for the application of strain-accumulation. We have shown that under the extreme conditions of very low finishing temperature and large accumulated strains, solute Nb is more effective at retarding recrystallization than NbC precipitates. As such, the high Mn design is preferable to the low Mn design for the above application. An important consequence of this result is that the HTP steels (high Nb, high Mn), could be used to advantage in near net shape processing. In addition to being very effective at retarding static recrystallization, the high-Mn design of HTP steels offers a number of additional benefits:

1. The addition of Mn enhances the yield stress of the
steel. The yield-stress increment per wt% of Mn is estimated by $30 \text{ MPa.}$1) As such, the high Mn design is well suited for high strength applications.

(2) Mn depresses the Ar3 temperature of the steel. As a result, it is possible to roll the high Mn steel at temperatures that are much lower than those used in the case of the low Mn steel. For example, the lowest finishing temperature of the low Mn design is about 830°C. By contrast, the high Mn steel could be rolled at temperatures as low as 730°C. Rolling at low temperatures is advantageous for two reasons: The first is that static recovery and recrystallization are both temperature dependent and as such reducing the temperature retards both processes making it possible to accumulate strain energy more efficiently. Secondly, the final grain-size which is achieved by dynamic recrystallization decreases as the Zener–Hollomon parameter increases.27) Decreasing the rolling temperature increases the Zener–Hollomon parameter and consequently leads to a finer final grain size.

(3) The WUMSI results on the high Mn steel indicate very little softening during the interpass time. One is then lead to speculate the Mn has a retarding effect on the kinetics of recovery in austenite. This seems plausible given the fact that experimental and theoretical evidence exists for a strong dislocation pinning effect due to Mn–C clusters in ferrite.15)

In the case of plate rolling, the low Mn design offers a distinct advantage for strain accumulation. The industrial conditions used for plate rolling resemble those described in Sec. 4.1 (case I), namely, high finishing temperature window and small to medium deformations. In this case, precipitate interaction with recrystallization nucleation is identified as the dominant factor. While high Mn offers other advantages from solid solution hardening and low temperature transformation products, the retardation of strain induced precipitation and the low precipitation density does not weigh in its favour in strain accumulation compared to low Mn steel in plate rolling. Once again, the predictions of our model are in agreement with industrial practice.

6. Conclusions

Physically-based modeling was used to analyze the effect of Mn addition on the kinetics of static recrystallization in low-carbon, high Nb steels. It is found that the optimum Mn content for retarding static softening depends on the processing conditions. Three industrially important conditions were considered in detail:

I. High Temperature Deformation: The low Mn design was shown to have a distinct advantage under plate rolling and traditional strip-rolling conditions (high temperature window and small pass reduction). In the low Mn steel a high density of strain-induced precipitates quickly pins the dislocation structure and in so doing effective inhibits the nucleation of recrystallization. At the same time, there is an adequate amount of Nb in solution to prevent the boundary from breaking away from its solute atmosphere.

II. Low Temperature and Small Deformations: When the temperature window is lowered and the pass reduction is small, the term representing the probability of nucleation decreases more quickly in the case of the low Mn steel compared to the high Mn steel. This advantage in favor of the low Mn design is offset by the risk that the NbC precipitation may bring the concentration of Nb in solution below the critical level needed to prevent the boundary from breaking away from its solute atmosphere. We find that at short interpass times, the overall balance is in favor of low Mn design. The trend is reversed for long interpass times, for which the high Mn design is found to offer greater resistance to softening.

III. Low Temperature and Large Deformation: When the pass reduction is large, the amount of solute niobium
required to prevent the boundary from breaking away from solute atmosphere is increased. In multi-pass rolling aimed at large strain accumulation, the accelerated strain-induced precipitation kinetics in the low Mn steel depletes the amount of Nb in solution below the critical level needed for effective solute drag on the boundary. Further, the onset of recovery before the onset of strain induced precipitation in high Mn steel is an added benefit as it decreases the driving force for recrystallization. Thus for the application of rolling near net-shape thin-slab and thick-strip castings, the high Mn design is superior to the low Mn design. Consequently, HTP steels (high Nb, high Mn) could be used effectively for this application as demonstrated by the WUMSI simulations and mill trials.

Acknowledgements

Experimental results on HTP were provided by Dr. Thomas Heller, Thyssen Krupp AG, and Dr. R. Kaspar, Max Planck Institute, Düsseldorf, and Dr. C. Klinkenberg and Dipl. Ing. Klaus Hulka, Niobium Products Company, Germany. HSZ, SVS, GRP gratefully acknowledge the financial support of the NSERC of Canada and Niobium Product company GmbH, Düsseldorf.

REFERENCES

1) T. Gladman: The Physical Metallurgy of Microalloyed Steels, Institute of Metals, London, (1997), 1.
2) G. Li, T. M. Maccagno, D. Q. Bai and J. J. Jonas: ISIJ Int., 36 (1996), 1479.
3) C. Devadas, I. V. Samarasekera and E. B. Hawthold: Metall. Trans. A, 22A (1991), 335.
4) S. V. Subramanian, G. Zhu, H. S. Zurob, G. R. Purdy, G. C. Weatherly, J. Patcl, C. Klinkenberg and R. Kaspar: Proc. of Int. Conf. on Thermo-mechanical Processing: Mechanics, Microstructure and Control, ed. by J. H. Beynon, Institute of Metals, London, (2003), 148.
5) E. J. Palmiere, C. M. Sellars and S. V. Subramanian: Niobium Science and Technology, Proc. Int. Symp. Niobium 2001, Niobium 2001 Ltd., Bridgeville, PA, (2001), 501.
6) S. V. Subramanian, S. Shima, G. Ocampo, T. Castillo, J. D. Embury and G. R. Purdy: Proc. of Int. Conf. on HSLA Steels: Metallurgy and Applications, ed. by J. M. Gray et al., ASM International, Materials Park, OH, (1985), 151.
7) G. G. Zhu, S. V. Subramanian, C. Klinkenberg and K. Hulka: Proc. Int. Symp. on Ultra-fine Structured Steels, ed. by E. Essaidji and J. Thompson, METSOSC, Montreal, Canada, (2004), 71.
8) K. Hulka, P. Boudignon and J. M. Gray: Niobium Tech. Rep., No. 1, (2004), 18.
9) M. G. Akben, I. Weiss and J. J. Jonas: Acta Metall., 29 (1981), 111.
10) S. Koyama, T. Ishii and K. Narita: J. Jpn. Inst. Met., 35 (1971), 698.
11) S. Koyama, T. Ishii and K. Narita: J. Jpn. Inst. Met., 35 (1971), 1089.
12) G. Robilier and L. Meyer: Recrystallization and Grain Growth in Multi-Phase and Particle Containing Materials—First Riso Int. Symp, on Metallurgy and Materials Science, ed. by N. Hansen, A. R. Jones and T. Jeffers, Riso National Laboratory, Roskilde, (1980), 311.
13) G. Robilier, L. Meyer and S. R. Datta: Recrystallization behaviour of niobium alloyed steels at hot working temperatures, Thyssen Tech. Ber., 7/1 (1975), 14.
14) S. Kurokawa, J. E. Ruzzante, A. M. Hey and F. Dyment: Met. Sci., 17 (1983), 433.
15) K. Ushiohda, N. Yoshinaga and O. Aikisse: ISIJ Int., 34 (1994), 85.
16) J. J. Jonas and M. G. Akben: Met. Forum, 4 (1981), 92.
17) H. S. Zurob: Ph.D. Thesis, McMaster University, Hamilton, Canada, (2003).
18) H. S. Zurob, C. R. Hutchinson, Y. Brechet and G. R. Purdy: Mater. Sci. Eng. A, 382 (2004), 64.
19) H. S. Zurob, C. R. Hutchinson, Y. Brechet and G. R. Purdy: Acta Mater., 50 (2002), 3075.
20) F. J. Humphreys and M. Hatherly: Recrystallization and Related Annealing Phenomena, Pergamon Press, Oxford, (1996), 188.
21) J. W. Cahn: Acta Metall., 10 (1962), 789.
22) J. E. Bailey and P. B. Hirsch: Proc. R. Soc. A, 267 (1962), 11.
23) C. S. Smith, Trans. Am. Inst. Miner. Eng., 175/15 (1948), 15.
24) L. E. Collins, D. L. Baragar, J. T. Bowker, M. M. Kostic and S. V. Subramanian: Microalooying 95 Conf. Proc., ed. by M. Korchnisky et al., ISS-AIME, Warrendale, PA, (1995), 141.
25) L. E. Collins: Niobium Science and Technology, Proc. Int. Symp. Niobium 2001, Niobium 2001 Ltd., Bridgeville, PA, (2001), 527.
26) S. V. Subramanian, X. Zheng, L. E. Collins, M. Bucholtz and M. Kostic: Proc. Int. Symp. on Low Carbon Steels for the 90’s, ed. by R. Asfahani and G. Tither, TMS-AIME, Warrendale, PA, (1993), 313.
27) B. Derby and M. F. Ashby: Scr Metall., 21 (1987), 879.
28) J. Geise and C. Herzig: Z. Metallkd., 76 (1985), 622.
29) H. J. Frost and M. F. Ashby: Deformation Mechanism Maps, Pergamon Press, Oxford, (1982), 21.
30) A. Yoshie, T. Fujita, M. Fujikoa, K. Okamoto and H. Morikawa: ISIJ Int., 36 (1996), 467.

Appendix (1). Values of the Parameters Used in the Model

The physically based model, on which the present contribution is based, has been described in detail in earlier publications.17–19 This appendix summarizes the model parameters which are necessary to reproduce the results of Figs. 6, 7 and 8. This should allow the reader to explore, quantitatively, the process-interactions that are described in the model.

It should be emphasized that the model contains two adjustable parameters, one relating the number of precipitate nucleation sites and the other to the number of recrystal-

Table A1. Values of the parameters used to calculate Figs. 6, 7 and 8.

| Parameter | Ref. |
|-------------------------|-------------------------------|
| $D_{h}$: Bulk diffusion coefficient of Nb in austenite | $8.3 \times 10^{-10} \text{exp}^{-266500/RT}$ m$^2$/s | [28] |
| $D_{c}$: Diameter of a critical recrystallization nucleus at $4\gamma F_{0}$ | [20, 22] |
| $D_{c}$: Cross-boundary diffusion coefficient of Nb at $10 D_{h}$ | [17] |
| $E_{b}$: Binding energy of Nb to austenite grain boundaries at $0.2 eV$ | [17] |
| $M$: Intrinsic grain-boundary mobility: $(2.63/T) \exp(-20754/T) m^2/s$ | [17] |
| $N$: Number of recrystallization nuclei. The value of $N$ is calculated using the method described in [17, 19] with the precipitation adjustable parameter set to equal to 0.05 in case I and 0.25 in cases II and III. | [17, 19] |
| $n_{r}$: Number density and radius of NBC precipitates. These quantities are calculated using the model described in [19] with the precipitation adjustable parameter set to 0.0035 in all cases. | [17, 19] |
| $U$: Activation energy for recovery to $286000$ J/mole | [17, 19] |
| $V$: Activation volume for recovery to $356^3$ | [17] |
| $\gamma$: Grain-boundary energy to $13115 - 0.0005 T KJ/m^2$ | [17, 19] |
| $t$: Width of grain boundary segregation zone in Eq. (4) $1$ mm | [17, 19] |
| $\mu$: Shear modulus to $81 \times 10^{-10} \text{[1 - 0.91(T - 300)/1810]}$ Pa | [29] |
| $\rho(t)$: Flow stress to $22.7e^{1210} (0.89 - 0.037$t$/3000)^{-1}$, Pa$^{-1}$ | [30] |
| $\sigma$: Yield stress. Evaluated as $\rho(t)$ at a strain of 0.01. | [30] |