Effect of Silicon on the Kinetics of Nb(C, N) Precipitation during the Hot Working of Nb-bearing Steels

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The effect of Si on the rate of Nb(C, N) precipitation was investigated by using fractional softening measurements. Compression specimens, with diameters of 7.6 mm and lengths of 11.4 mm, were prepared from four Nb microalloyed steels containing a range of Si concentrations from 0.01 mass% to 0.41 mass%. Double-hit compression tests, with a strain of 0.3 for each pass and a strain rate of 0.1/sec., were employed. A solution heat treatment was applied immediately prior to each test. It was found that the rate of Nb(C, N) precipitation in hot deformed austenite increases with Si concentration. This phenomenon is attributed to the increases in the activities of C and N that result from Si addition.

KEY WORDS: Nb microalloyed steels; Nb(C, N) precipitation; Si additions; PTT curves; solubility product.

1. Introduction

It is well known that carbonitride precipitation influences microstructural evolution during the hot rolling of microalloyed steels. It therefore plays a key role in determining the final mechanical properties of a wide range of steel products. Despite extensive studies carried out during the past decades, many details regarding the precipitation behavior remain unclear. One such example is how the addition of a third element, such as Si, influences the precipitation kinetics of Nb(C, N) in austenite during hot working.

The effect of Si on the thermodynamics of precipitation was taken into account as early as 1972,¹⁾ but it has attracted more attention recently. It has been suggested that Si addition should increase the precipitation rate, but there has been no direct experimental confirmation of this effect to date. Recent investigations,^{2–4)} indicate that the addition of Si may be responsible for accelerating Nb(C, N) precipitation in Nb-bearing microalloyed steels and therefore for preventing the occurrence of softening during hot strip rolling. These *indirect* observations indicate that there is a clear need for fundamental information regarding the effect of Si on the thermodynamics and kinetics of Nb(C, N) precipitation.

The present research was aimed at: 1) measuring the effect of Si level on the solubility product of Nb(C, N) in austenite; 2) measuring the Nb carbonitride precipitation kinetics in steels containing different Si levels; and 3) carrying out a thermodynamic analysis of Nb(C, N) precipitation using Wagner interaction parameters derived from the literature.

2. Experimental Materials and Procedures

2.1. Experimental Materials

Six Nb microalloyed steels containing Si concentrations from 0.012 mass% to 0.48 mass% were prepared at the Materials Technology Laboratory, CANMET in Ottawa, Canada. The chemical compositions of the steels are listed in **Table 1**. It can be seen that the base composition was approximately constant in these steels.

2.2. Experimental Procedure

2.2.1. Solubility Product Measurement

Samples of the six steels were reheated at 1 200, 1 150, 1 100, and 1 050°C for 2 hr and then water quenched. Carbon replicas were prepared from each sample; these were systematically studied and analyzed using TEM. It was found that, at and below 1 150°C, Nb(C, N) particles were present in all six steels. However, at 1 200°C, particles were only observed clearly in steels F712 (0.48% Si) and slightly in F752 (0.41% Si). With the aid of the Nb(C, N) solubility product⁵⁾ and a variety of Wagner parameters^{6,7)} reported in the literature, and using the present experimen-

Table 1. Chemical composition of the steels. (mass%)

Steel	C	Si	Mn	Al	Nb	P	S	O	N
F751	0.08	0.01	0.9	0.03	0.035	<.004	0.0024	0.007	0.0048
F715	0.09	0.02	1.3	0.07	0.036	<.004	0.0028	--	-
F717	0.11	0.11	1.0	0.03	0.034	<.004	0.0029	0.005	0.0038
F716	0.11	0.26	1.1	0.03	0.038	<.004	0.0028	0.004	0.0034
F752	0.09	0.41	1.0	0.04	0.040	<.004	0.0021	0.006	0.0050
F712	0.09	0.48	1.2	0.02	0.038	<.004	0.0027	0.004	0.0047

tal results as a guideline, the following solubility product formula, which includes the effects of both Mn and Si, was derived from a basic thermodynamic model:

$$\log[\text{Nb}] \left[\text{C} + \frac{12}{14} \text{N} \right] = 3.14 - 8049/T - [\text{Mn}](0.91 - 1371/T) + [\text{Si}](0.35 - 923/T) \dots\dots\dots(1)$$

The solution temperatures specified by the above formula are plotted against silicon level for the present steel compositions in **Fig. 1**. It can be seen that the agreement between the formula and the TEM observations is reasonably good.

2.2.2. Measurement of the Precipitation Kinetics

A. Compression Specimen Preparation

Only four of the steels were chosen for the compression tests: F751, F717, F716 and F752. Compression specimens, with diameters of 7.6 mm and lengths of 11.4 mm, were machined from the as-received 12 mm thick plate with their longitudinal axes along the rolling direction. Boron nitride (BN) powder was used as a lubricant between the tooling and the specimen and was applied as a slurry made up with alcohol on a Pelco mica sheet.

Fig. 1. Comparison between the experimental TEM data and the newly derived solubility product.

B. Solution Heat Treatment

• Calculated Solution Temperature

A solution treatment was carried out immediately prior to the testing of each sample. This operation has two functions: 1) to dissolve all the carbonitride particles present; and 2) to produce approximately the same austenite grain size in all the steels tested. For the first purpose, the equilibrium solution temperatures of Nb(C, N) in austenite were evaluated using Eq. (1); these are shown in **Table 2**. The reheat temperatures selected (see below) were nevertheless higher than any of the calculated temperatures.

• Reheat Temperature-Austenite Grain Size Relation

To achieve the second purpose, *i.e.* to produce the same initial austenite grain size in the four Nb-bearing steels, individual samples were reheated to different temperatures and held at these temperatures for ten minutes, then water quenched. The reheated austenite structures were examined by means of optical microscopy. A typical set of micrographs showing the austenite structures at 1 225°C is given in **Fig. 2**. The mean grain size was measured by the linear intercept method applied to five micrographs of each sample. The relationship between mean austenite grain size and reheat temperature is presented in **Fig. 3a**. The grain size vs. Si concentration relationships are plotted in **Fig. 3b**. It can be seen that, at a given temperature, the effect of Si content on austenite grain size is small.

From the equilibrium solution temperatures of Nb(C, N) in austenite and the relation between mean austenite grain size and reheat temperature, a reheat temperature of 1 225°C was chosen for all four Nb-bearing steels (F751,

Table 2. Calculated solution temperatures of the tested steels.

Steel	Solution Temperature, °C
F751	1132
F717	1175
F716	1202
F752	1204

Fig. 2. Typical austenite microstructures of steels F751 0.01% Si (left) and F752 0.41% Si (right) at 1 225°C.

Fig. 3a. Relation between mean austenite grain size and reheat temperature.

Fig. 3b. Relation between grain size and Si concentration.

F717, F716 and F752).

C. Compression Testing Equipment and Softening Measurements

The experiments were carried out on a computerized materials testing system. The upper and lower anvils, made of the molybdenum alloy TZM, were fixed to the actuator and load cell, respectively, by means of internally water-cooled stainless steel extension rods. A Research Inc. model E4-10 radiant furnace, which was mounted on the column of the MTS load frame, was employed to produce the required high temperatures. To minimize oxidation, the specimen and anvils were enclosed in a quartz tube in which a high purity argon atmosphere was maintained. After solution treatment, each specimen was immediately cooled to the test temperature at a cooling rate of 1.5°C/sec. On attaining this temperature, each sample was held for 1 min to promote temperature uniformity before the deformation was applied. During each test, the temperature was controlled to within $\pm 0.5^\circ\text{C}$ using a K-type thermocouple linked to a Micristar digital controller/programmer.

The fractional softening method was used to follow the progress of precipitation. A strain of 0.3 and strain rate of 0.1/sec were used for all four steels during these tests. Details of the testing procedure are described elsewhere.⁸⁻¹¹⁾

Fig. 4. True stress-true strain curve of the 0.01 mass% Si steel deformed at 850°C with an interpass interval of 0.5 s.

Fig. 5. A group of interrupted stress-strain curves of the 0.26 mass% Si steel deformed at 850°C. The effect of increasing the length of the interval between the first and second deformations is shown.

3. Results and Discussion

3.1. True Stress-True Strain Curves

A true stress-true strain curve for the 0.01 mass% Si steel deformed at 850°C, with an interpass interval of 0.5 s, is displayed in Fig. 4. The fractional softening (X) was calculated by using the following Eq. (2), with a strain offset of 2%.

$$X = (\sigma_m - \sigma_2) / (\sigma_m - \sigma_1) \quad \dots\dots\dots(2)$$

where σ_m is the flow stress at the end of the first strain, and σ_1 and σ_2 are the stresses at an offset strain of 2% in the first and second deformations, respectively.

Note that Li *et al.*⁹⁾ found that the fractional softening calculated using an offset of 0.2% is approximately the same as that determined from the mean flow stress method. By contrast, the softening measured using the present 2% offset approach is consistently lower than that calculated using either the 0.2% offset or the mean flow stress technique. Thus they concluded that the 2% offset method is particularly well suited for following the progress of recrystallization alone (while neglecting the softening attributable to recovery). In practice, the 2% offset method avoids the “noise” that sometimes appears in the early part of experimental high temperature flow curves. In this way it makes the calculation of fractional softening more reliable.

A group of stress-strain curves for the 0.26 mass% Si steel deformed at 850°C is presented in Fig. 5. It can be

Fig. 6a. A group of fractional softening vs. interpass interval curves for the 0.01 mass% Si steel.

Fig. 6b. A group of fractional softening vs. interpass interval curves for the 0.26 mass% Si steel.

seen that, given the same heat treatment history and deformation schedule, the flow stress in the second deformation decreases as the interpass interval is increased from 1, to 50, 100, 200 and then 500 sec. This indicates that the fractional softening increases with the length of the interpass interval.

It is worth noting that, during the interpass interval from 200 to 500 sec, there is little further decrease in flow stress. This can be explained in terms of the strong interaction between recrystallization and precipitation at such a low temperature *i.e.* 850°C. This phenomenon can be seen more clearly in Figs. 6a and 6b.

3.2. Fractional Softening–Interpass Time Curves

A group of fractional softening vs. interpass interval curves is presented in Fig. 6a for the 0.01 mass% Si steel. It is evident that, at 1000°C, the softening curve follows the Avrami equation; *i.e.* it has a conventional “S” shape. This is because recrystallization is complete before precipitation can begin at this relatively high temperature. This result indicates that there is no interaction between these two processes at this temperature.

By contrast, at 925 and 900°C, the “S” shaped softening curves are interrupted. This phenomenon can be attributed to the initiation of precipitation, which retards the recrystallization process. The point of the “break” can be associated with the precipitation start time. As identified in the figure,

Fig. 7. Relationship between precipitation start time and temperature for the four steels tested.

the start times determined in this way are about 150 sec at 900°C and 200 sec at 925°C. Compared with the 900 and 925°C curves, the 850°C curve is again different. It can be seen that, after 200 sec, the recrystallization process is completely arrested by precipitation. This is consistent with the curves illustrated in Fig. 5.

Some fractional softening vs. interpass interval curves are illustrated in Fig. 6b for the 0.26 mass% Si steel. The same three kinds of curve can be seen. Nevertheless, the higher Si content is responsible for decreases in the retardation start times. It should be noted that the softening plateau becomes less marked as the test temperature is increased. This change can be ascribed to the decrease in the volume fraction of precipitate formed during the delay time as well as to the increased rate of coarsening of the precipitates.¹²⁾

3.3. PTT Curves

The relationship between precipitation start time and temperature determined in the present four steels is shown in Fig. 7 in the form of a PTT diagram. It can be seen that the addition of Si decreases the precipitation start time, *i.e.* it shifts the C curve to the left. The results clearly indicate that the addition of Si increases the rate of precipitation. Over the present range of Si concentration, the rate increases by a factor of about 2.5.

3.4. Application of the Present Work to the Understanding of Rolling Behavior

The Dutta and Sellars model¹³⁾ for the precipitation start time is given below:

$$t_{ps} = 3 \times 10^{-6} [\text{Nb}]^{-1} \varepsilon^{-1} Z^{-0.5} \exp \frac{Q_d}{RT} \exp \frac{2.5 \times 10^{10}}{T^3 [\ln(K_s)]^2} \quad \dots \dots \dots (3)$$

where [Nb] is the Nb content in mass%, ε is the strain, and Z is the Zener–Hollomon parameter given by $\dot{\varepsilon} \exp(350\,000/RT)$. The diffusion activation energy (Q_d) of Nb in austenite is 270 000 cal/mol, and the supersaturation ratio (K_s) that applies to Nb(C, N) in austenite is specified by the relation below:

$$K_s = \frac{10^{-6} 770/T_{RH} + 2.26}}{10^{-6} 770/T_{PASS} + 2.26}} \quad \dots \dots \dots (4)$$

where T_{RH} and T_{PASS} are the reheat and deformation temperatures, respectively.

Fig. 8. Effect of increasing the strain rate from 0.1 to 200/sec on the precipitation kinetics; calculated using the present modified Dutta and Sellars equation.

The above model can now be modified to take into account the effect of Mn and Si level on the precipitation-start time during hot strip rolling.^{3,4,14} As indicated above, the addition of Si decreases the solubility of Nb(C, N), see Eq. (1). Because of the resulting additional supersaturation, Si increases the driving force and therefore the kinetics of precipitation. Koyama *et al.*¹ pointed out that such an effect is due to the increased activities of C and N that result from Si addition. In addition, Kurokawa *et al.*¹⁵ showed that Si addition increases the diffusivity of Nb (a kinetic effect) in austenite over a wide temperature range. Their observations also support the view that Si has an accelerating effect on precipitation, as proposed here. The latter researchers also demonstrated that Mn has the opposite effect (deceleration) on Nb diffusivity¹⁵.

Han came to somewhat similar conclusions in his investigation of V steels in 1993.¹⁶ He introduced the following model to correct for the effect of Si addition on the solubility of vanadium carbide:

$$K_{X_1} / K_{X_2} = \exp \left[- \sum_{i=1} \varepsilon_{ci} (K_i - K_{i_2}) \right] \dots \dots \dots (5)$$

where K_{X_1} and K_{X_2} represent the solubility products associated with Si contents of X_1 and X_2 , respectively. ε_{ci} is the interaction parameter between carbon and the element of interest. If the Si content is increased by about 1 mass%, the solubility product ratio (K_{X_1}/K_{X_2}) is expected to decrease to approximately 0.86. He concluded that the addition of Si decreases the solubility of the precipitate in his system.

3.5. Effect of Strain Rate on Precipitation Start Time

The present experiments were necessarily carried out under laboratory conditions, using a strain rate of 0.1/sec. By contrast, under industrial conditions, the strain rate falls in the range 10–200/sec. In order to extend the present experimental results to mill conditions, it is important to take the effect of strain rate into account. It is well established that increasing the strain rate increases the dislocation density, and thus decreases the start time for strain-induced precipitation. The Dutta and Sellars model calls for the precipitation start time (t_{ps}) and the strain rate to be related (through the Z term in Eq. (3)) as follows:

$$t_{ps} \propto \dot{\varepsilon}^{-0.5} \dots \dots \dots (6)$$

The result of increasing the strain rate from 0.1 to 200/sec is presented schematically in Fig. 8. It can be seen that the precipitation start time is advanced from about one hundred seconds to the range one to ten seconds. These results are in reasonably good agreement with the indirect evidence obtained from industrial rolling mill logs by Siciliano *et al.*^{2-4,14} Of particular interest here is that the precipitation start times fall in the range of the times that elapse during passage of a strip through a finishing mill. Furthermore, depending on the exact Si level, such precipitation can either occur during rolling, or else after the steel has left the finishing train.

4. Conclusions

The effect of Si addition on the kinetics of Nb(C, N) precipitation was investigated during the hot working of steels. For this purpose, four steels containing different levels of Si were tested using the double-hit method. Three main conclusions can be drawn:

- (1) The double-hit method can be used successfully to follow the kinetics of strain-induced precipitation during hot deformation.
- (2) The addition of Si increases the rate of Nb(C, N) precipitation in hot deformed austenite in Nb-bearing steels. This phenomenon can be attributed to the increases in the activities of C and N associated with Si addition.
- (3) Using a precipitation model, laboratory results obtained at low strain rates can be extrapolated to the industrial rolling range, which involves much higher strain rates.

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REFERENCES

- 1) S. Koyama, T. Ishii and K. Narita: *Japan Inst. Met. J.*, **35** (1971), 1089.
- 2) K. Minami, F. Siciliano Jr., T. M. Maccagno and J. J. Jonas: *ISIJ Int.*, **36** (1996), No. 12, 1507.
- 3) F. Siciliano, Jr., T. M. Maccagno, Brian D. Nelson and J. J. Jonas: THERMEC '97-Int. Conf. on Thermomechanical Processing of Steels & Other Materials, Wollongong, Australia, ed. by T. Chandra and T. Sakai, The Minerals, Metals & Materials Society, Warrendale, PA, (1997), 347.
- 4) F. Siciliano Jr. and J. J. Jonas: *Metall. Mater. Trans. A.*, **31** (2000), 511.
- 5) K. J. Irvine, F. B. Pickering and T. Gladman: *J. Iron Steel Inst.*, **205**

- (1967), 161.
- 6) R. C. Sharma, V. K. Lakshmanan and J. S. Kirkaldy: *Metall. Trans. A.*, **15A** (1984), 545.
- 7) K. Hashiguchi, J. S. Kirkalady, T. Fukuzumi and V. Pavaskar: *Calphad*, **8** (1984), 173.
- 8) D. Q. Bai: Ph. D. thesis, McGill University, (1995).
- 9) G. Li, T. M. Maccagno, D. Q. Bai and J. J. Jonas: *ISIJ Int.*, **36** (1996), No. 12, 1479.
- 10) K. B. Kang, O. Kwon, W. B. Lee and C. G. Park: 37th MWSP Conf. Proc., ISS, Vol. XXXIII, (1996), 695.
- 11) S. F. Medina: *J. Mater. Sci.*, **32**, (1997), No. 6, 1487.
- 12) W. J. Liu and J. J. Jonas: *Metall. Trans.*, **A19** (1988), 1403.
- 13) B. Dutta and C. M. Sellars: *Mater. Sci. Technol.*, **3** (1987), 197.
- 14) F. Siciliano Jr.: Ph. D. Thesis, McGill University, (1999).
- 15) S. Kurokawa, J. E. Ruzzante, A. M. Hey and F. Dymont: *Met. Sci.*, **17** (1983), 433.
- 16) K. Han: *Scr. Metall. Mater.*, **28** (1993), 699.