Effect of Austenitizing Conditions on Hardenability of Boron-Added Microalloyed Steel

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ABSTRACT

The effects of austenitizing conditions on hardenability of a boron containing niobium microalloyed plate steel, ASTM A514, are investigated. Special attention is focused on prior austenite grain size, solute, and precipitation effects and interactions. Jominy end quench tests are used to characterize hardenability. Higher austenitizing temperature resulted in decreased hardenability, attributed to boron segregation to austenite grain boundaries at lower austenitizing temperatures. Processing variations were created to isolate the austenite grain size variable from niobium and boron effects. Samples were austenitized at various temperatures and held at lower austenitizing temperatures to equilibrate the samples with respect to Nb(C,N) and $Fe_{23}(C,B)_6$ precipitation. A significant increase in hardenability is obtained for samples equilibrated at a low austenitizing temperature ($850^{\circ}C$) in the presence of a prior austenite microstructure refined via Nb(C,N) pinning. The increased hardenability is hypothesized to involve a mechanism whereby solute is able to segregate to pinned austenite grain boundaries with very long austenitization associated with the equilibration process.

INTRODUCTION

The effects of austenitizing conditions on hardenability of modern high-performance plate steels can be complex, as competition between hardenability mechanisms may exist and their behavior is likely dependent on austenitizing temperature. Modern steels often have grain refiners, such as niobium, affecting prior austenite grain size, or alloying elements that change transformation kinetics such as boron, which can prevent ferrite nucleation.[1-7] It is important to understand the role of individual variables affecting hardenability in a complex steel, as well as interactive effects of different alloying additions, austenite grain size, and associated thermal processing influences.

Austenitizing conditions affect several variables which may influence hardenability, such as austenite grain size, precipitation, and segregation. It is well known that austenite grain size has an important effect on hardenability.[8-10] Austenite grain size effects may also be influenced by other hardenability mechanisms. For example, precipitation may cause austenite grain and sub-grain boundary pinning leading to finer grain size or abnormal grain growth. Some precipitates (i.e., VN) may act as nucleation sites for a second phase (i.e. ferrite).[11] Solute effects include the poisoning of grain boundary nucleation sites and solute drag effects.[12]

It is well known that increased prior austenite grain size (PAGS) retards ferrite and pearlite nucleation by decreasing grain boundary nucleation sites. The effects on bainitic transformations are smaller and perhaps negligible according to previous studies.[10,12-14] Matsuzaki and Bhadeshia have suggested that when the growth rate is rapid, reduced austenite grain size will retard the bainitic reaction, and when the growth rate is more limited, reduced grain size will accelerate the reaction but the changes in the kinetics of the reactions are small.[14]

Many modern plate steels contain microalloying additions and their effects on hardenability are not well established. The industrial steels in the present study contain Nb as a grain refiner. Although Nb decreases the average austenite grain size, it can increase hardenability by suppressing the austenite to ferrite or bainite transformation.[12,15,16] In the absence of deformation, an increase in austenitizing temperature for a Nb microalloyed steel decreases the Ar_3 temperature for air cooling and also increases the average austenite grain size.[12] Jian-Chun *et al.* determined that solute Nb retards the ferrite reaction and attributed a decrease in the initial transformation rate to Nb(C,N) particles pinning transformation interfaces.[16] The authors stated that particles were observed by TEM at the interfaces coupled with an increase in transformation time; however as Nb(C,N) particles coarsen, they were suggested possibly to act as ferrite nucleation sites.[16]

Boron can have a pronounced effect on hardenability. Solute boron is well established as the effective form of boron for contributing to hardenability by means of segregation to grain boundaries which decreases the number of grain boundary nucleation sites for ferrite.[1-7] Precipitation of boron is frequently found in the form of $Fe_{23}(C,B)_6$ or BN. BN can be prevented by addition of nitride forming elements such as Ti or Al.[1,7,17] If $Fe_{23}(C,B)_6$ is present in a fine enough array on a grain boundary, it may prevent nucleation of a ferrite at one side of the austenite boundary where the borocarbides have a semicoherent interface with one austenite grain.[2,18]

Interactions between Nb and B, and also between Mo and B, may retard the formation of $M_{23}(C,B)_6$ by means of decreasing the rate of C diffusion, allowing more solute B to be present at grain boundaries to contribute to hardenability by means of solute segregation.[19-21] Much of the research showing such effects has involved studies using ultralow-carbon steels and less research has been done with respect to interactions in medium- and low-carbon steels. It has been reported that the presence of B accelerates Nb precipitation by increasing diffusion of Nb at high temperatures.[22-23] The Nb diffusion coefficient is the limiting factor for formation of Nb(C,N), and the presence of B reportedly causes the diffusion of Nb to increase and the interfacial energy to decrease, according to results from a series of stress relaxation techniques.[23] It has been reported that adding B and Nb increases hardenability more than the sum of the two individual effects.[2,24] Maitrepierre *et al.* found that this synergism only exists when Nb is also in solution.[2] One hypothesis is that solute complexes may form at grain boundaries inhibiting back diffusion (solute at grain boundaries diffusing back to the matrix during non-equilibrium segregation), allowing solute to occupy grain boundaries for longer times.[24]

This paper examines the effects of austenitizing conditions on austenite grain size, Nb and B precipitation and segregation effects in microalloyed ASTM A514 plate steel, and interactive effects among such variables. An understanding of the effects of austenitizing conditions on the hardenability of steels containing Nb and B will aid in further understanding transformation kinetics in plate steels.

EXPERIMENTAL PROCEDURE

Materials

In order to evaluate the effects of austenitizing conditions on hardenability in modern high-performance plate steels, two industrially processed structural type ASTM A514 steels were investigated. The steels were boron-treated steels, one microalloyed with Nb. One steel is referred to as "No Nb" with 0.003 wt pct residual Nb and the other is referred to as "Hi Nb" with 0.021 wt pct addition of Nb. Ti was added to protect the boron, by preventing BN formation which is detrimental to hardenability.[7,1,17] Ti:N ratios ≥ 2.9 which are below the stoichiometric ratio of 3.4, have been found to be sufficient to protect boron in steels with similar carbon and boron levels.[25] The steels in this study have Ti:N ratios greater than 2.9. The steel compositions are presented in Table I.

Table I. ASTM A514 Steel Compositions in wt pct, B in ppm

	C	Mn	Si	Ni	Cr	Mo	Ti	Nb	V	Al	N	S	P	Cu	Ca	B
No Nb	0.20	1.26	0.23	0.08	0.12	0.12	0.033	0.003	0.006	0.035	0.008	0.004	0.010	0.20	0.001	13
Hi Nb	0.20	1.27	0.25	0.13	0.13	0.12	0.029	0.021	0.006	0.029	0.009	0.003	0.009	0.20	0.001	14

Hardenability Characterization

Jominy end quench (JEQ) tests were conducted to characterize hardenability. A Jominy end quench apparatus was constructed according to the ASTM standard.[26] Cylindrical specimens, 10.16cm long and 2.54cm diameter, were machined from each material with a small nub at the end in order to secure a washer for holding in the quenching apparatus. Samples were held for 35 minutes in a furnace preheated to the appropriate austenitizing temperature. Austenitizing temperatures were 900 and 1,200°C, selected to obtain differences in prior austenite grain size. Samples were placed in a steel cylinder and surrounded by crushed charcoal during heat treatment to avoid oxidation and decarburization. Samples were held in the quenching apparatus for 10 minutes and then submerged in room-temperature water. After quenching each bar, two parallel "flats" were ground to a depth of 0.762mm, and oriented 180° apart. Hardness measurements were taken every 1.6mm from the quenched end using a Rockwell hardness tester. Each hardness position is referred as an increment from the quenched end; e.g., J1 is 1.6mm from the quenched end and J2 is 3.2mm from the quenched end. Hardness values from the two parallel sides were averaged and the values were plotted as a function of distance from the quenched end.

Prior Austenite Grain Size Measurement

Prior austenite grain sizes were measured for each austenitizing condition. Etching was performed using a boiling solution of 100mL water, 6-7 grams wet (aqueous) picric acid, 4 mL Teepol, and 3-5 drops hydrochloric acid. A three-hour tempering treatment at 350°C prior to etching was required to enhance the etching response. It was necessary to back-polish with colloidal silica gel and repeat the etching procedure to reveal prior austenite grain boundaries on some samples. Photomicrographs of 5-10 fields of each sample were used to measure the ASTM grain size according to the ASTM standard, E112-96.[27] A statistical analysis was performed and relative accuracy for the measurements for each alloy and condition was better than 10%, which is suggested to be acceptable.[27]

Isolating the PAGS Variable

It is challenging to dissociate effects due to PAGS and competitive or synergistic alloying effects. By altering processing conditions it may be possible, however, to obtain similar PAGS with different solid solution and precipitate conditions. Special processing was designed in an effort to decouple the Nb solid solution and austenite grain size effects, starting with isolating the grain size variable by austenitizing at a higher initial temperature to establish a constant austenite grain size, and then holding at lower temperatures in an attempt to vary the amount of Nb and B in solution (following kinetic data in literature[1,5,28]), while still in the austenite regime. The first austenitizing temperature is referred to as the "initial austenitizing" treatment (IA) and the second treatment is referred to as the "holding" treatment (HT).

The initial austenitizing treatments were 900, 950, or 1,200°C for thirty-five minutes and the holding treatments were 950 or 850°C for 30 hours; assumed long enough to equilibrate the samples with respect to Nb(C,N), based on kinetic data from the literature.[28] Samples were Jominy end quenched from the holding temperatures. The purpose of holding at 950°C was to prevent borocarbide precipitation, but to completely precipitate the Nb present prior to Jominy end quenching based on $Fe_{23}(C,B)_6$ and Nb(C,N) precipitation kinetics reported in literature.[5,28] The purpose of holding at 850°C was to fully precipitate both the boron and the niobium prior to Jominy end quenching.[5,28] Based on predominant trends found in the literature, the boron hardenability mechanism involves boron segregation to grain boundaries as being a potent mechanism to increase hardenability. If held long enough to fully precipitate and coarsen the boron precipitates by holding at 850°C, the boron hardenability effect should no longer operate, while holding at 950°C may result in higher levels of solute boron, available to contribute to hardenability. These heat treatments should result in different PAGS due to the initial austenitizing treatment and minimal solute niobium and depending on the holding temperature, either *solute* boron (950°C) or *precipitated* boron (850°C). The heat treatment schedules used are shown schematically in Figure 1 for the two holding temperatures.

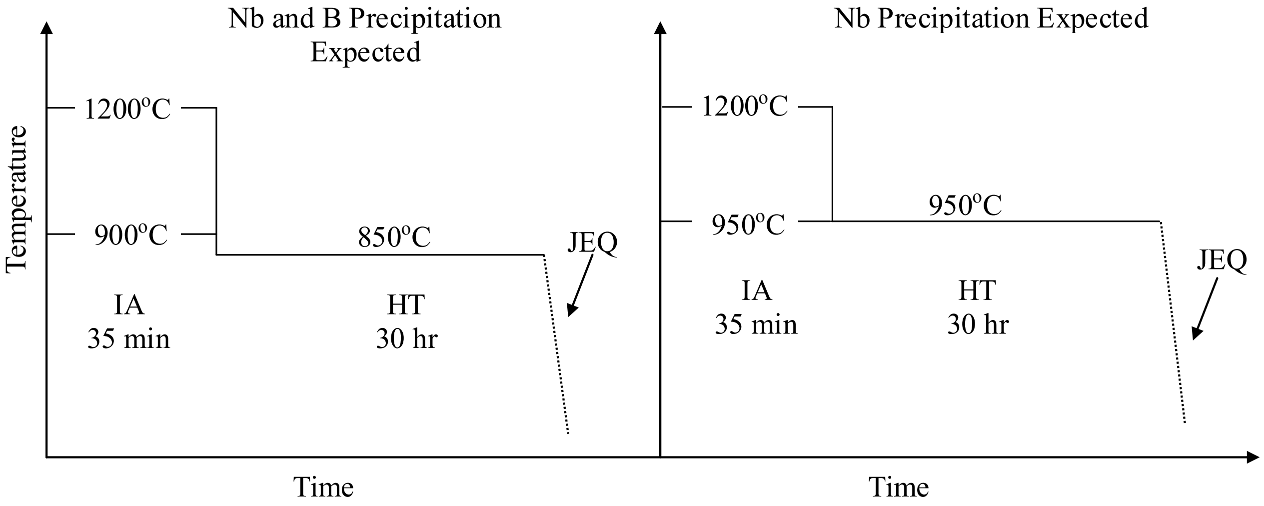


Figure 1. Heat treatment schedules for A514 steels are shown. The austenite grain size was expected to be controlled by the initial austenitizing temperature, while the two Nb(C,N) precipitation temperatures[28], 850°C (left) and 950°C (right) were expected to be associated with different $Fe_{23}(B,C)_6$ behaviors.[1,5]

Due to extended holding times, a different sample environment was required for heat treatment to prevent decarburization and oxidation of the specimens. The modified heat treatment method included a Jominy bar held in a stainless steel bag with titanium additions to prevent oxidation during the initial austenitizing treatment. A furnace was preheated to the holding temperature and purged with argon gas to prevent further oxidation. After the initial austenitizing treatment, the sample was removed from the stainless steel bag and transferred into another furnace preheated to the appropriate holding temperature for thirty hours. After holding at the lower temperature, the sample was removed and Jominy end quenched for ten minutes before quenching in water. Two test specimens for each condition were heat treated and analyzed. Jominy bars were analyzed by three hardness traverses along the length of each bar after four flats (instead of two as described earlier for tests without a holding treatment), 90° apart, were ground to a depth of 5.08cm.

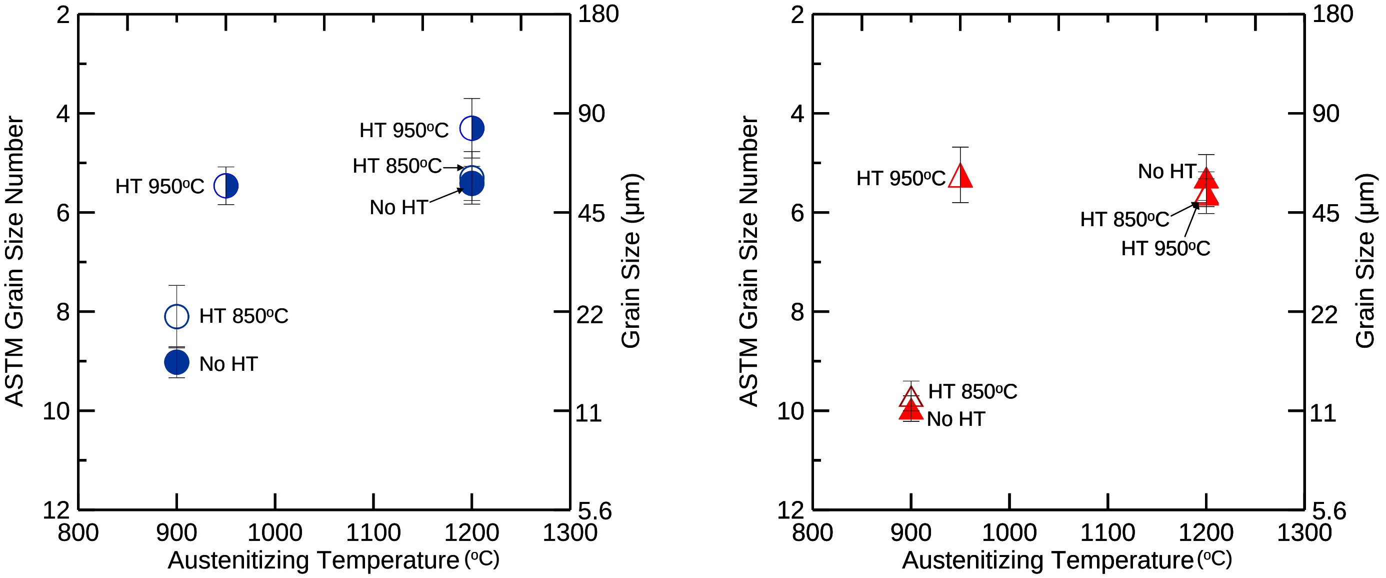
Microstructural Analysis

Microstructural analysis was conducted along the length of the bar on the flat which was not used for hardness testing. The Jominy end quench flats, from the quenched end to J28, were subsequently etched in 2 pct nital, and repolished and etched with LePera's etchant[29] to aid microstructural interpretation since it was difficult to differentiate martensite and bainite using a nital etch.

RESULTS

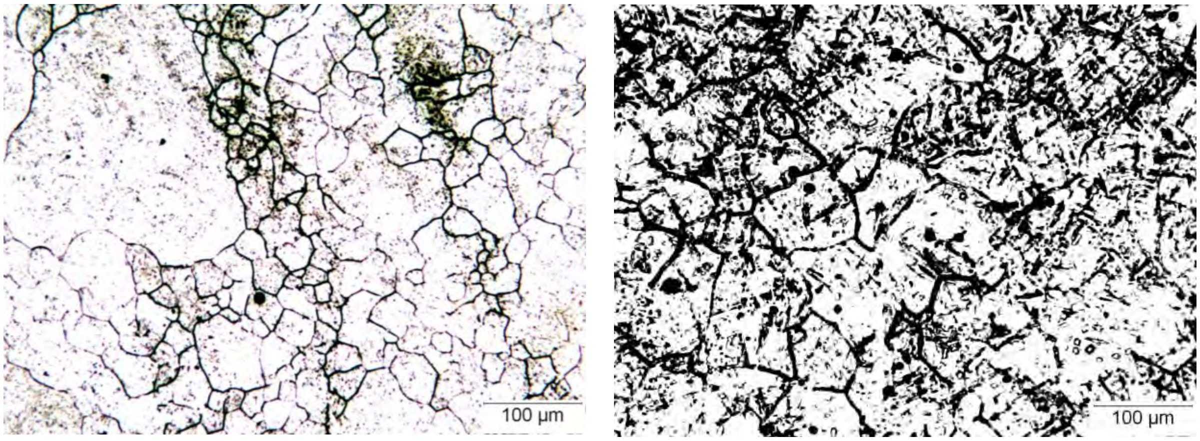
Prior Austenite Grain Size

The average prior austenite grain sizes for each Jominy condition are presented in Figure 2 as a function of austenitizing temperature. After IA at 1,200°C the PAGS did not vary significantly for most of the conditions as the average PAGS ranged from ASTM 5.3-5.6 (55-60μm), with the exception of the No Nb alloy after 1,200°C and HT at 950°C which had a PAGS as large as ASTM 4.3 (80μm). An IA of 950°C resulted in PAGS ranging between ASTM 5.3-5.5 (55-60μm) and abnormal grain growth while the IA of 1,200°C involved normal grain growth conditions, as shown in Figure 3.



(a) (b)

Figure 2. Prior austenite grain size as a function of austenitizing temperature for (a) No Nb (b) Hi Nb steels. Error bars are the standard deviation of the measurements.



(a) (b)

Figure 3. Light optical micrographs of Hi Nb steel exhibiting (a) abnormal grain growth after initial austenitization of 950°C and (b) normal grain growth after initial austenitization of 1,200°C. Holding temperature for (a) and (b) was 950°C. Boiling picral etch, tempered 350°C for three hours.

Abnormal grain growth results in very large grains which grow rapidly at the expense of arrays of fine grains resulting in an overall larger average grain diameter.[30] It is possible to have larger average grain diameters with abnormal grain growth at lower austenitizing temperatures than with normal grain coarsening at higher austenitizing temperatures.[30] At higher austenitizing temperatures where normal grain growth occurs due to lack of inhibition of growth when grain refining elements are dissolved, the average PAGS are similar to non-microalloyed steels.[30]

With IA at 900°C the PAGS ranged from ASTM 8.7-9.9 (10-18μm). After holding at 850°C for thirty hours the average PAGS was particularly refined following IA 900°C and grain growth was accelerated above 900°C, presumably associated with the dissolution of grain refining elements. The Hi Nb steel resulted in smaller PAGS, indicating that increased additions of Nb contributed to grain refinement.

Effect of Austenitizing Treatment on Hardenability

Results of Jominy end quench tests after austenitizing at 900 and 1,200°C are shown in Figure 4 by hardness variations along the Jominy end quench bar as a function of distance from the quenched end. Austenitization for 35 minutes at 900°C resulted in greater hardenability than austenitization at 1,200°C for both steels. This is likely attributed to greater amounts of boron segregation at lower austenitizing temperatures, consistent with some other reports in literature.[1-7] A Nb addition of 0.021 wt pct appears to have a beneficial effect on hardenability. At 900°C, with likely boron segregation to grain boundaries, the 0.021 wt pct Nb addition increased hardenability only slightly according to the results. At 1,200°C, there was a substantial increase in hardenability with the 0.021 wt pct Nb addition. The higher austenitizing temperature may result in less boron segregated to grain boundaries, but possibly more Nb in solution contributing to hardenability in relation to the lower austenitizing temperature.[12,16]

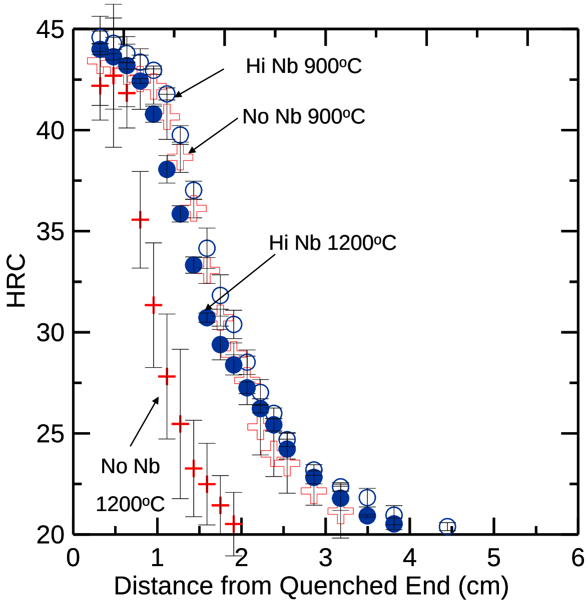


Figure 4. Hardness versus distance from quenched end of Jominy bar plotted for austenitization (35 min) at 900 and 1,200°C. Error bars are the standard deviation of the measurements.

The effects of initial austenitizing and holding temperature (IA and HT) on hardenability following two-step austenitizing, are presented in Figure 5 for both alloys. Figure 5a shows the effect of IA after HT 950°C. The curves overlay each other indicating that with a subsequent holding treatment at 950°C for thirty hours there is no effect of initial austenitizing temperature. The effects of IA after HT 850°C were very significant, as shown in Figure 5b. IA 1,200°C and HT 850°C resulted in hardenability similar to the HT 950°C condition for both steels. However, IA 900°C resulted in a marked increase in hardenability with HT 850°C. In fact, the increase in hardenability for both alloys with IA 900°C and HT 850°C was even greater than hardenability when austenitizing at 900°C without a holding treatment. The hardenability comparison with and without HT 850°C is shown in Figure 6 for the Hi Nb alloy. The plot clearly shows that an IA 900°C and HT of 850°C exhibits the greatest hardenability of all of the heat treatment conditions in this study, *despite* the associated finest PAGS at IA 900°C. Dotted lines at the J4 and J8 positions indicate the locations on the Jominy bar where microstructural analysis was focused.

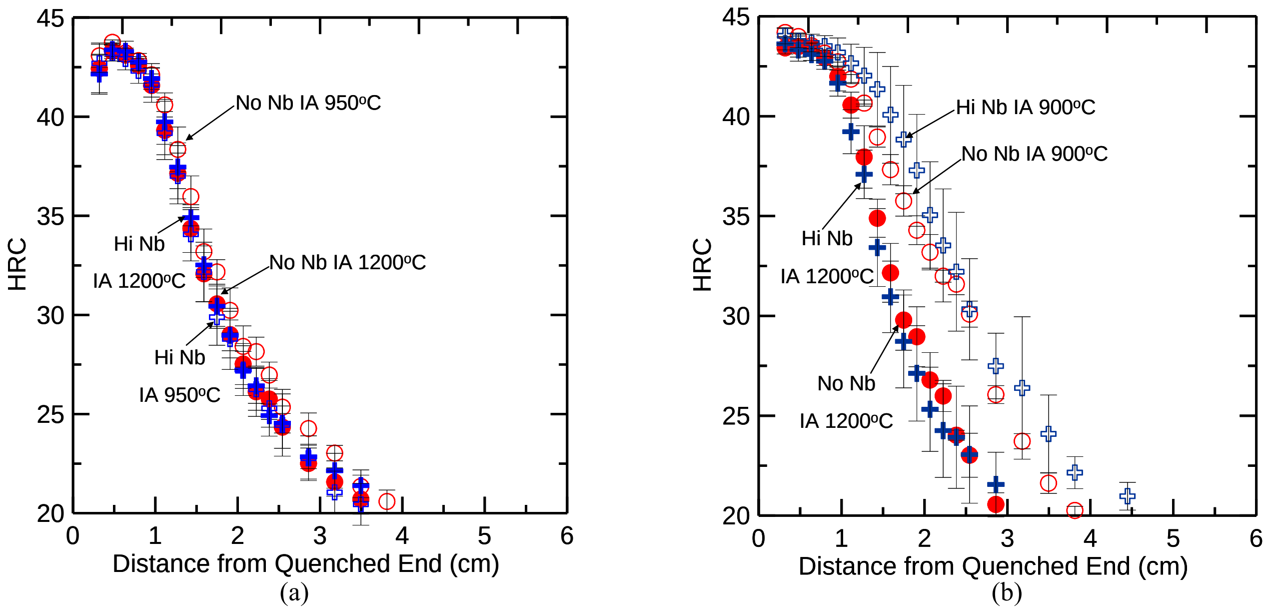


Figure 5. Hardness versus distance from quenched end of Jominy bar plotted for different IA conditions with holding treatments (a) 950°C and (b) 850°C. Error bars are the standard deviation of the measurements.

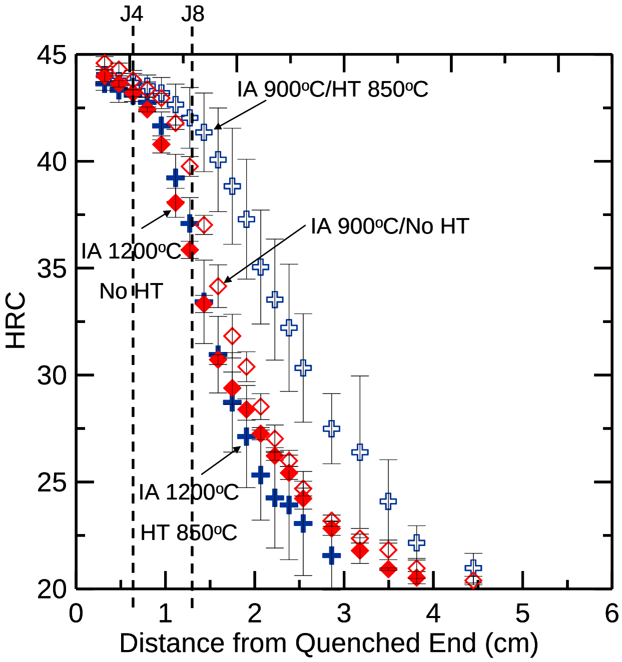


Figure 6. Hardness versus distance from quenched end of Jominy bar is plotted for the Hi Nb steel showing a marked increase in hardenability with IA 900°C and HT 850°C. Error bars are the standard deviation of the measurements. Dotted lines indicate the positions, J4 and J8, for the micrographs of the Hi Nb alloy shown in Figures 7 and 8.

Microstructure Evolution

Since the increase in hardenability with and without HT 850°C was slightly more pronounced for the Hi Nb alloy, attention was focused on this alloy for microstructural analysis. Micrographs of each JEQ specimen were taken at the J4 and J8 positions as indicated by the dashed reference lines in Figure 6. The J4 position was expected to be fully martensitic for both samples, based on carbon content and hardness (43-44 HRC),[27] while at the J8 position hardenability microstructural differences were expected based on JEQ results. Figure 7 shows microstructures after IA 900°C, with and without HT 850°C, after etching with 2 pct nital or with LePera's etchant. The microstructural observations suggest that a slightly finer martensitic microstructure was present without the holding treatment, observable both at the J4 and J8 positions in Figure 7. This may be attributed to slightly larger PAGS in the specimen which underwent the holding treatment. However, PAGS effects do not account for the overall increase in hardenability, as hardenability was much greater in samples with refined grain sizes (IA 900°C) versus unpinned austenite grains (IA 1,200°C). LePera's etch shows bainite in the darkest shade of gray (or black) on the micrographs shown, especially apparent at the J8 position. It is observed that there was a larger fraction of bainite without the holding treatment, indicating that with a 30 hour holding treatment at 850°C, there was a suppression of bainite transformation (consistent with hardness differences). Figure 8 shows the microstructures of the specimens after IA 1,200°C, with and without HT 850°C using a nital or LePera etch. The microstructures consisted of a much coarser martensitic structure at the J4 position and a greater presence of bainite at the J8 condition than the specimens with IA 900°C. The much coarser martensitic and bainitic structures shown in Figure 8 for IA 1,200°C are attributed to the larger PAGS. The microstructures after IA 1,200°C with HT 850°C were similar to those after IA 1,200°C with no hold, in agreement with similar PAGS (Fig. 2), and hardenability curves from JEQ tests.

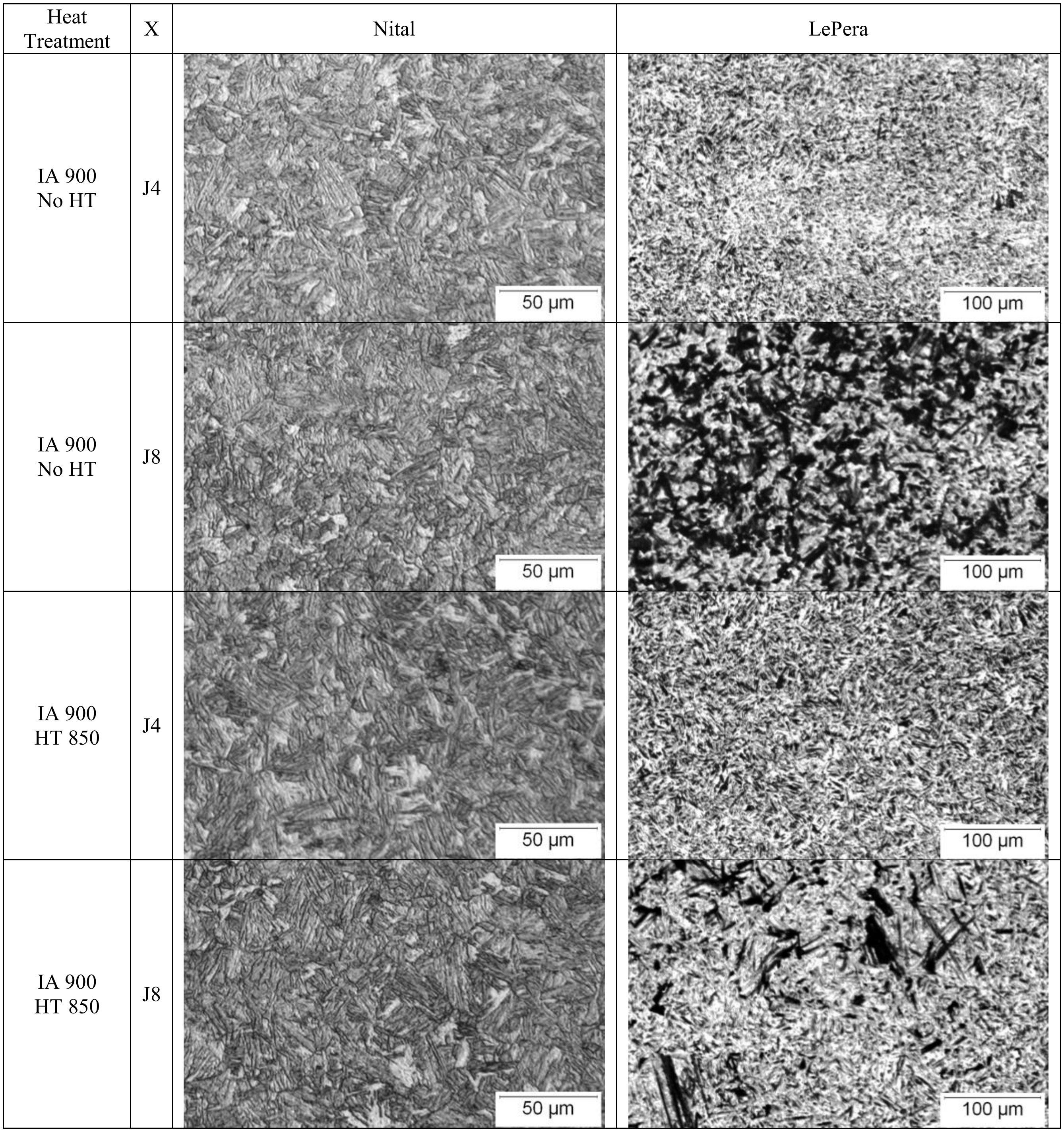


Figure 7. Microstructures for two locations on Hi Nb alloy Jominy bars are shown after IA 900°C with and without a hold at 850°C. 2 pct nital or LePera etch. Light optical micrographs.

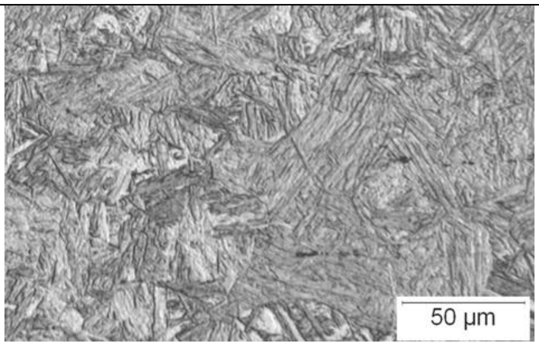
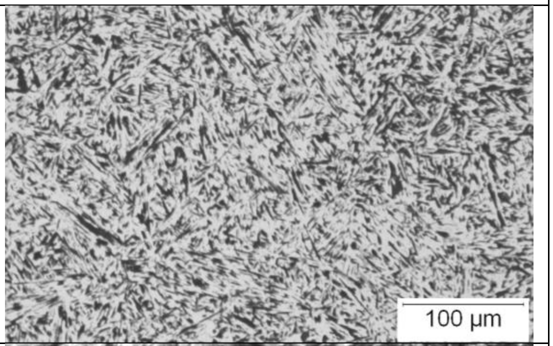
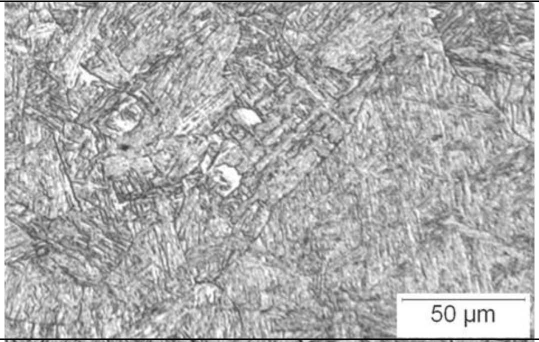
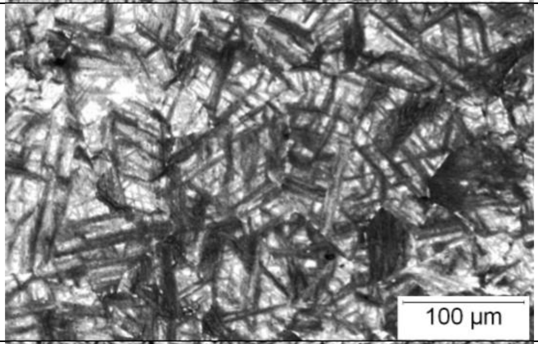
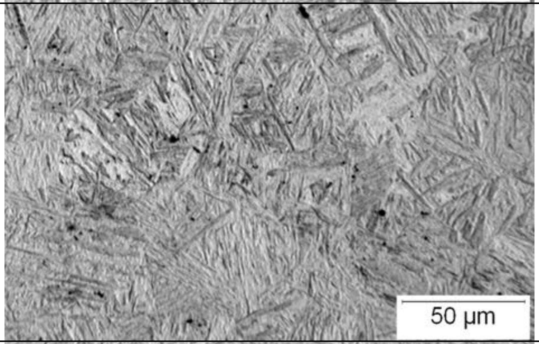
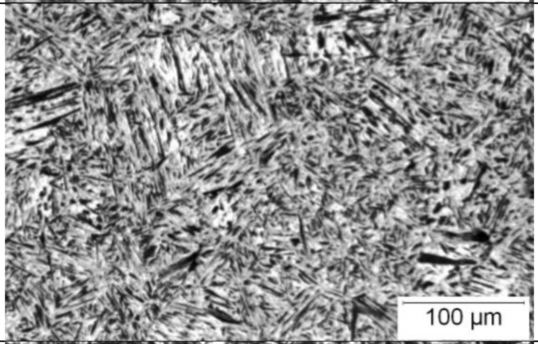
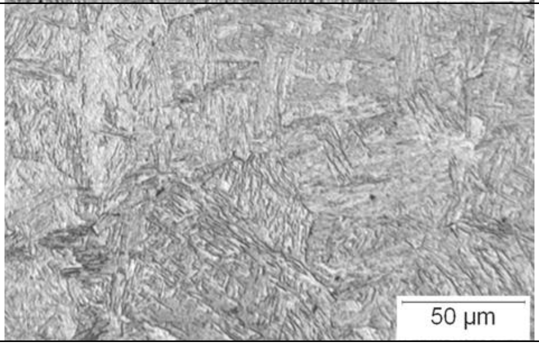
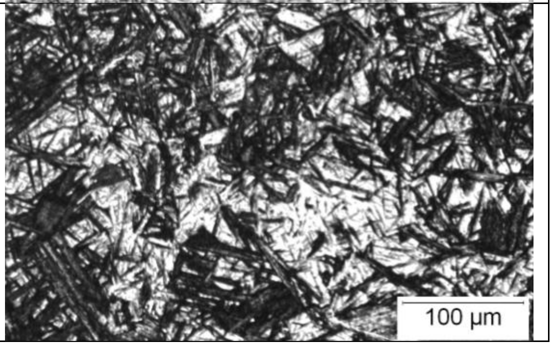
Heat Treatment	X	Nital	LePera
IA 1200 No HT	J4		
IA 1200 No HT	J8		
IA 1200 HT 850	J4		
IA 1200 HT 850	J8		

Figure 8. Microstructures for two locations on Hi Nb alloy Jominy bars are shown after IA 900°C with and without a hold at 850°C. 2 pct nital or LePera etch. Light optical micrographs.

DISCUSSION

The average prior austenite grain size and expected precipitation conditions with regard to Nb and B, all of which have been reported above, are summarized for each austenitizing condition for the two alloys in Table II, providing the reader with reference information for the discussion. The "free B" available refers to solute boron which is available to contribute to hardenability by potentially segregating to grain boundaries. The assumptions regarding B and Nb precipitation kinetics are based on previous studies,[1,5,28] as discussed earlier with respect to processing design.

Table II. Test matrix with resulting average PAGS and expected Nb and B precipitation behaviors.

Nb Level	IA	HT	PAGS (ASTM#)	Assumed Nb(C,N) Precipitation[28]	Assumed Free B[1,5]
No	1200	-	5.4	No	Yes
No	1200	950	4.3	Complete	Yes
No	1200	850	5.3	Complete	No
No	900	-	9.0	Some	Yes
No	950	950	5.5	Complete	Yes
No	900	850	8.1	Complete	No
Hi	1200	-	5.3	No	Yes
Hi	1200	950	5.6	Complete	Yes
Hi	1200	850	5.6	Complete	No
Hi	900	-	9.9	Some	Yes
Hi	950	950	5.3	Complete	Yes
Hi	900	850	9.7	Complete	No

It is generally assumed that in most steels that a larger PAGS results in greater hardenability due to a decrease in the number of grain boundary nucleation sites.[8-10] However, in the present study, larger PAGS were associated with lower hardenability, as is evident in the JEQ results presented in Figures 4 and 5, where samples with IA at 900°C resulted in *smaller* PAGS than after IA at 1,200°C, but *greater* hardenability, both without a HT and after HT at 850°C. This phenomenon may be attributed to beneficial boron segregation to grain boundaries at lower temperatures during austenitization without a holding treatment. The boron segregation mechanism has been shown to overcome the traditional PAGS effect.[1-6] When a HT of 30 hours at 950°C was employed it was expected that the boron hardenability effect, whereby solute boron is available to segregate to austenite grain boundaries, was active, although it is possible that with a 30 hour heat treatment the boron may have precipitated, as previous studies did not investigate such long holding times. No changes in hardenability with varying IA were observed with HT at 950°C. The significant difference in hardenability with varying IA with HT at 850°C is likely attributed to the variation in PAGS.

When a HT of 30 hours at 850°C was employed it was expected that boron would have precipitated and coarsened according to earlier boron precipitation studies.[1,5] If boron precipitated, a reduction in hardenability would be expected to occur. With IA 1,200°C and HT 850°C the hardenability was similar to simply austenitizing at 1,200°C without a HT, with similar PAGS for the two conditions. It would not have been surprising had the precipitated and coarsened B and Nb led to a decrease in hardenability, but such an effect was not observed. However, with IA 900°C and HT 850°C, results indicated an unexpected increase in hardenability, greater than with any other condition, *despite* the fine austenite grain size (when compared to IA 1,200°C). Considering that Nb and B were both expected to fully precipitate and coarsen, and the PAGS were refined, another mechanism causing the increase in hardenability must have been operating. Due to pinning of grain boundaries (predominantly by Nb(C,N) precipitates), key solutes (e.g., Mo, Mn, Cr, Nb) may have been able to more easily segregate to grain boundaries. Segregation is likely enhanced by ease of transport to a pinned grain boundary versus an unpinned moving grain boundary in combination with the decrease in austenite grain area that an atom needs to move across to reach a grain boundary. The proposed mechanism is in agreement with a study by Garbarz and Pickering where they hypothesized that in order for effective vanadium segregation to occur during austenitization, the grain boundaries must be sufficiently pinned.[31,32] If in fact this hardenability mechanism was operating, there may be greater effects of slower diffusing alloying elements that, without the holding treatment, would not have sufficient migration time to reach an austenite grain boundary.

It is also possible that grain boundary Nb or B precipitates may have an inhibiting effect on nucleation of a second phase (i.e., bainite).[2,18] With refined PAGS (IA 900°C), there is a greater likelihood of a very fine distribution of iron borocarbide precipitation along grain boundaries, which could act to inhibit bainite nucleation in the steels studied, as compared with IA 1,200°C, which has a greater propensity to result in fewer, but coarser precipitates. Coarse borocarbide nucleation has been previously shown to decrease hardenability.[1-6] However, it would also be expected that there would be a fine array of borocarbide precipitates with IA 900°C without HT which would result in similar hardenability as the sample austenitized at 900°C with HT 850°C, but the hardenability behavior of the two conditions was not the same.

SUMMARY

Jominy end quench tests were conducted to characterize hardenability with varying austenitizing conditions. Results indicate a decrease in hardenability with an increase in austenitizing temperature. The increase in hardenability after austenitizing at 900°C versus 1,200°C is likely attributed to boron segregation to prior austenite grain boundaries at the lower temperature. Processing variations were created to isolate the PAGS variable from niobium and boron precipitation effects. After specially designed austenitizing conditions, smaller grain size was unexpectedly associated with greater hardenability. It is hypothesized that austenite grains refined by Nb(C,N) precipitation may facilitate segregation of key solutes to austenite grain boundaries which may also contribute to hardenability.
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REFERENCES

1. M. Ueno and T. Inoue, “Distribution of Boron at Austenite Grain Boundaries and Bainitic Transformation in Low-Carbon Steels,” *Transactions of the Iron Steel Institute of Japan*, vol. 13, 1973, pp. 210-217.
2. Ph. Maitrepierre, D. Thivellier, and R. Tricot, “Influence of Boron on the Decomposition of Austenite in Low-Carbon Alloyed Steels,” *Metallurgical Transactions A*, vol. 6A, 1975, pp. 287-301.
3. D.T. Llwellyn and W.T. Cook, *Metals Technology*, vol. 1, no. 12, 1974, pp. 517-529.
4. R. Habu, M. Miyata, S. Sekino, and S. Goda, “ Effect of Boron on Hardenability of Al-B-N Low-Alloy Steels,” *Transactions of the Iron Steel Institute of Japan*, Vol. 18, 1978, pp. 492-500.
5. R.A. Grange and J.B. Mitchell, “On the Hardenability Effect of Boron in Steel,” *Transactions of the ASM*, Vol. 53, 1961, pp. 157-185.
6. R.A. Grange and T.M. Garvey, “Factors Affecting the Hardenability of Boron-Treated Steels,” *Transactions of the ASM*, 1946, pp. 136-191.
7. B.C. De Cooman, J.G. Speer, IY. Pyshmintsev, and N. Yoshinaga, *Materials Design: The Key to Modern Steel Products*, GRIPS media, Germany, 2007, pp. 440-452.
8. E.C. Bain, *Alloying Elements in Steel*, ASM, Cleveland, 1939.
9. D.A. Porter and K.E. Easterling, *Phase Transformations in Metals and Alloys*, 2nd Ed., Taylor & Francis Group, Boca, Raton, FL, 1992.
10. R.V. Fostini and F.J. Schoen, “Effects of Carbon and Austenitic Grain Size on the Hardenability of Molybdenum Steels”, *Symposium: Transformation and Hardenability in Steels*, Climax Molybdenum Company, 1967, pp. 195-210.
11. T. Furuhara, J. Yamaguchi, N. Sugita, G. Miyamoto, and T. Maki, “Nucleation of Proeutectoid Ferrite on Complex Precipitates in Austenite,” *ISIJ International*, Vol. 43, No. 10, 2003, pp. 1630-1639.
12. G.I. Rees, J. Perdrix, T. Maurickx and H.K.D.H. Bhadeshia, “The Effect of Niobium in Solid Solution on the Transformation Kinetics of Bainite,” *Materials Science and Engineering. A*, vol. 194A, 1995, p. 179-186.
13. H.K.D.H. Bhadeshia, *Bainite in Steel*, 2nd ed., Institute of Materials, Cambridge, 2001, pp. 129-189.
14. A. Matsuzaki and H.K.D.H. Bhadeshia, “Effect of Austenite Grain Size and Bainite Morphology on Overall Kinetics of Bainite Transformation in Steels,” *Materials Science and Technology*, vol. 15, 1999, pp. 518-522.
15. A.B. Cota, C.A.M. Lacerda, F.L.G. Oliveira, F.A. Machado, F.G. da Silva Araujo, “Effect of the Austenitizing Temperature on the Kinetics of Ferritic Grain Growth under Continuous Cooling of a Nb Microalloyed Steel,” *Scripta Materialia*, vol. 51, 2004, pp. 721-725.
16. C. Jian-chun, L. Qing-you, Y. Qi-long, and S. Xin-jun, “Effect of Niobium on Isothermal Transformation of Austenite to Ferrite in HSLA Low-Carbon Steel,” *Journal of Iron and Steel Research, International*, vol. 14, no. 3, 2007, pp. 51-55.
17. G. F. Melloy, P.R. Slimmon, and P.P. Podgursky, “Optimizing the Boron Effect,” *Metallurgical Transactions A*, Vol. 4A, 1973, pp. 2279-2289.
18. R.C. Sharma and G.R. Purdy, “Nucleation Limitation and Hardenability,” *Metallurgical Transactions*, Vol. 5, 1974, pp. 939-947.
19. H. Asahi, “Effects of Mo Addition and Austenitizing Temperature on Hardenability of Low Alloy B-added Steels,” *ISIJ International,* Vol. 42, No. 10, 2002, pp. 1150-1155.
20. T. Hara, H. Asahi, R. Uemori, and H. Tamehiro, “Role of Combined Addition of Niobium and Boron and of Molybdenum and Boron on Hardenability in Low Carbon Steels,” *ISIJ International*, Vol. 44, No. 8, 2004, pp. 1431-1440.
21. H. Tamehiro, M. Murata, R. Habu, M. Nagumo, *Trans. Iron Steel Inst. Jpn.*, Vol. 27, 1987, p. 120.
22. F. Zarandi and S. Yue, “Effect of Boron on the Hot Ductility of the Nb-Microalloyed Steel in Austenite Region,” *Metallurgical and Materials Transactions A*, Vol. 37A, 2006, pp. 2316-2320.

23. M. Djahazi, X.L. He, J.J. Jonas, and W.P. Sun, "Nb(C,N) Precipitation and Austenite Recrystallization in Boron-Containing High-Strength Low-Alloy Steels," *Metallurgical Transactions A*, Vol. 23A, 1992, pp. 2111-2120.
24. M. Jahazi and J.J. Jonas, "The Non-Equilibrium Segregation of Boron on Original and Moving Austenite Grain Boundaries," *Materials Science and Engineering*, Vol. A335, 2002, pp. 49-61.
25. Y. Shen and K.A. Taylor, "Boron Hardenability Effect in 0.2 Percent Carbon Steels," *40th MWSP Conference Proceedings*, ISS, 1998, pp. 837-838.
26. *ASTM A255*, "Standard Test Method for Determining the Hardenability of Steel," ASTM, 2007.
27. *ASTM Standard E112-96*, "Standard Test Methods for Determining Average Grain Size," ASTM, 2004.
28. A. LeBon, J. Rofes-Vernis, C. Rossard, "Recrystallization and Precipitation during Hot Working of an Nb-Bearing Steel," *Metal Science*, vol. 9, no. 1, 1975, pp. 36-40.
29. F.S. LePera, "Improved Etching Technique for the Determination of Percent Martensite in High-Strength Dual-Phase Steels," Metallography, vol. 12, 1979, pp. 263-268.
30. T. Gladman, *The Physical Metallurgy of Microalloyed Steels*, 1997, pp. 215-220, London.
31. B. Garbarz and F.B. Pickering, "Effect of Vanadium and Austenitizing Temperature on Hardenability of (0.2-0.3)C-1.6Mn Steels with and without Additions of Titanium, Aluminium, and Molybdenum," *Materials Science and Technology*, Vol. 4, 1988, pp. 117-126.
32. B. Garbarz and F.B. Pickering, "Effect of Austenite Grain Boundary Mobility on Hardenability of Steels Containing Vanadium," *Materials Science and Technology*, Vol. 4, 1988, pp.967-975.