

# Carbonitride Precipitation in Niobium/Vanadium Microalloyed Steels

J. G. SPEER, J. R. MICHAEL, and S. S. HANSEN

A detailed study of carbonitride precipitation in niobium/vanadium microalloyed steels is presented. A thermodynamic model is developed to predict the austenite/carbonitride equilibrium in the Fe-Nb-V-C-N system, using published solubility data and the Hillert/Staffansson model for stoichiometric phases. The model can be used to estimate equilibrium austenite and carbonitride compositions, and the amounts of each phase, as a function of steel composition and temperature. The model also provides a method to estimate the carbonitride solution temperatures for different steel compositions. Actual carbonitride precipitation behavior in austenite is then examined in two experimental 0.03Nb steels containing 0.05V and 0.20V, respectively. Samples were solution treated, rolled at 954 °C (20 pct or 50 pct), held isothermally for times up to 10,000 seconds at 843 °C, 954 °C, or 1066 °C, and brine quenched. The process of carbonitride precipitation in deformed austenite is followed by analytical electron microscopy (AEM) of carbon extraction replicas. Precipitates are observed at prior-austenite grain boundaries, and also within the grains (presumably at substructure introduced by the rolling deformation). Analysis of the grain-boundary and matrix precipitate compositions by AEM indicates that the grain-boundary precipitates are consistently richer in vanadium than the matrix precipitates, although compositional trends with holding time and temperature are similar for the two types of precipitates. The compositions of both the grain-boundary and matrix precipitates are not significantly influenced by the rolling reduction or the holding time at temperature. As predicted by the thermodynamic model, the precipitates become more vanadium-rich as the vanadium level in the steel is increased and as the temperature is reduced. The agreement between the measured and predicted precipitate compositions is quite good for the grain-boundary precipitates, although the matrix precipitates are consistently more niobium-rich than predicted by the model.

## I. INTRODUCTION

THE role of microalloying elements in improving the strength and toughness of high-strength, low-alloy (HSLA) steels has been the subject of numerous investigations during the past 15 years (*e.g.*, References 1 through 3). The alloying elements of interest are typically niobium, vanadium, and titanium, either individually or in combination. These elements precipitate in austenite and ferrite as fine carbides, nitrides, or carbonitrides, and contribute to mechanical properties *via* grain refinement and precipitation hardening. Carbonitride precipitates can greatly improve the resistance of a steel to grain coarsening during high-temperature austenitizing treatments. In addition, carbonitride precipitation in austenite during controlled rolling is used to retard austenite recrystallization, which results in substantial flattening of the austenite grains in the later stages of commercial rolling. The resulting high ratio of grain boundary surface area to grain volume enhances the ferrite nucleation kinetics, and a fine ferrite grain size is obtained after completion of the  $\gamma \rightarrow \alpha$  transformation during cooling.

Previous research in the area of austenite recrystallization behavior suggests that the retardation of austenite recrystallization kinetics results from the pinning of austenite grain boundaries by either (1) alloy carbonitride precipitates, or (2) microalloying elements in solution in the austenite. Although the exact mechanism of recrystallization

retardation is controversial, most investigators agree that the dramatic retardation of austenite recrystallization which occurs during commercial thermomechanical processing results from the precipitation of alloy carbonitrides.<sup>4-8</sup> Obviously a thorough understanding of carbonitride precipitation behavior is necessary in order to control the response of microalloyed steels to thermomechanical processing.

The solubility of carbonitrides is fairly well understood in commercial steels containing a single microalloying addition. Experimental determinations of carbonitride compositions (*viz.*, the C/N ratio in the precipitates) are generally lacking, but theoretical models have been developed to describe these systems.<sup>9-13</sup> In systems containing mixed carbonitrides, very few observations have been made. Crooks *et al.* first showed that the carbonitrides which form in Nb/V steels contain both Nb and V.<sup>14</sup> Mehta *et al.* measured the Nb and V concentrations in HSLA steels containing relatively high aluminum levels, and found that the niobium concentration in the precipitates increased with time during isothermal annealing.<sup>15</sup> Michael has suggested recently that the vanadium level in these precipitates decreased as nitrogen was tied up with aluminum during the (relatively sluggish) precipitation of AlN.<sup>16</sup> Modeling of the thermodynamics of precipitation has been performed for systems containing two<sup>17,18</sup> or more<sup>19</sup> microalloying elements. Gruzic *et al.* developed the first model relating to carbide precipitation in steels containing Nb + V,<sup>20</sup> and developed a later model to account rigorously for nitrogen effects,<sup>21</sup> concurrently with the present work.<sup>22</sup> Considerable activity remains in the area of precipitate composition modeling.<sup>23</sup> The purposes of this paper are (1) to present a thermodynamic model that can be used to predict the solubility and composition of carbonitrides in this alloy system, and (2) to

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define the carbonitride precipitation behavior in austenite microalloyed with niobium and vanadium, using transmission electron microscopy and X-ray microanalysis.

## II. EXPERIMENTAL PROCEDURES

The thermodynamic model which will be presented is capable of predicting the amount and composition of precipitates in a given Nb/V steel, which is at equilibrium at any particular temperature within the austenite (plus carbonitride) phase field. The experimental portion of this investigation was undertaken in order to provide quantitative data on the compositions of carbonitrides in Nb/V steels, and thus to provide a means to begin to verify the validity of the thermodynamic model. This work was part of a larger program which also examined isothermal austenite recrystallization behavior, the results of which will be reported separately.

### A. Materials and Processing

Two Nb/V steels were produced, having the compositions given in Table I. The steels were vacuum induction melted as 136 kg ingots, and hot-rolled to a thickness of 1.0 cm. Specimens 2.5 cm wide by 7.6 cm long were cut from the plates, retaining the original rolling direction. Thermocouple holes were drilled into the longitudinal faces of these specimens at mid-thickness. The specimens were austenitized for 1 hour in an endothermic atmosphere (40 pct H<sub>2</sub>, 40 pct N<sub>2</sub>, 20 pct CO) at 1288 °C. This treatment resulted in an average grain size of 430 μm for the 0.03Nb, 0.05V steel and 485 μm for the 0.03Nb, 0.20V steel. Upon removal of the specimens from the reheating furnace, a sheathed thermocouple was immediately inserted into the drilled hole. The temperature of the specimens was then monitored during air cooling until the desired rolling temperature of 954 °C was reached, at which time the specimens were deformed 20 pct or 50 pct in a two-high rolling mill at a constant roll-speed, which resulted in an average strain rate<sup>24</sup> of 6.1 s<sup>-1</sup> (20 pct reduction) or 10.2 s<sup>-1</sup> (50 pct reduction). A standard rolling temperature of 954 °C was used in order to maintain a constant starting microstructure before further processing. After rolling, the specimens were either quenched immediately into a 10 pct brine solution, or transferred immediately to a molten chloride salt bath, and held for 10, 100, 1000, or 10,000 seconds at various temperatures, followed by brine quenching.

### B. Analytical Electron Microscopy

Analytical electron microscopy (AEM) was used for measuring the composition of individual carbonitride precipitates, since the precipitates were usually very small

(~5 to 100 nm).<sup>16</sup> In order to measure the composition of individual particles, they were separated from the iron-rich matrix using extraction techniques. In this investigation, direct carbon extraction replicas were prepared by metallographically polishing the specimens down to 1 μm using diamond paste, followed by ultrasonic cleaning. The specimens were then etched for 15 seconds in 2 pct nital. A thin carbon film (~20 nm) was evaporated onto the etched specimens. The carbon film with attached carbonitrides was released from the specimen surface by etching in 10 pct nital (methanol based). The samples were immersed into distilled water, where the replicas floated to the surface and were collected on copper support grids. Fresh solutions were used at each step in the replicating process, in order to eliminate the possibility of cross-contamination.

The extraction replicas were examined with a Philips EM 400T AEM, equipped with an EDAX energy dispersive X-ray spectrometer (EDS), operating at 120 kV. Microanalysis was performed in STEM mode using an electron beam diameter of approximately 10 nm. The X-ray data were quantified using the Cliff-Lorimer *k*-factor approach in which

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \quad [1]$$

where *C<sub>A</sub>* and *C<sub>B</sub>* are the weight percentages of elements *A* and *B*, *k<sub>AB</sub>* is a sensitivity factor (*k*-factor), and *I<sub>A</sub>* and *I<sub>B</sub>* are the intensities of the characteristic X-ray peaks from elements *A* and *B*.<sup>25</sup> The major difficulty with this technique is that the *k<sub>AB</sub>* factor must be measured experimentally using a standard having a known composition. The *k*-factor can be calculated theoretically,<sup>26,27</sup> but Michael has recently shown that the use of predicted *k*-factors does not provide sufficient accuracy of quantification for the present application. Michael has reported the *k<sub>V<sub>Kα</sub>Nb<sub>L</sub></sub>* appropriate to the operating conditions used in this investigation as *k<sub>VNb</sub>* = 0.93 ± 0.02.<sup>16</sup> It was not possible to measure carbon and nitrogen compositions during the present investigation, since the characteristic X-rays for C and N have low energies and were absorbed in the Be window of the EDS detector. Calculations showed that the Nb and V X-ray data do not need to be corrected for absorption or fluorescence effects for the particle sizes observed in this study.<sup>28</sup> At least 20 matrix precipitates and eight grain boundary precipitates were analyzed in each sample. Fewer grain boundary precipitates were analyzed since their greater mass resulted in less uncertainty in the microanalysis, because of the better X-ray counting statistics. Convergent-beam electron diffraction patterns were obtained from a number of precipitates. The patterns were obtained at ambient temperature using a 10 nm diameter incident probe having a convergence angle of 2α = 1.6 × 10<sup>-3</sup> radians.

Table I. Compositions of Experimental Nb/V Steels (Wt Pct)

	C	Mn	P	Si	S	Al	N	Nb	V	Ti
0.03Nb, 0.05V steel (Heat 704A036)	0.094	2.02	0.003	0.014	0.004	0.027	0.015	0.030	0.051	<0.002
0.03Nb, 0.20V steel (Heat 704A039)	0.110	2.03	0.003	0.013	0.003	0.026	0.016	0.032	0.200	<0.002

### C. Thermodynamic Modeling of Nb<sub>x</sub>V<sub>1-x</sub>C<sub>y</sub>N<sub>1-y</sub> Precipitation

The intention here was to develop a model to calculate the austenite/carbonitride equilibrium at any temperature for iron containing low levels of Nb, V, C, and N. That is, given a steel composition and temperature, we would like to estimate the precipitate composition, the amount of precipitate which is formed, and the composition of the austenite which is in equilibrium with the precipitate. It was desired to base the model on published solubility data for the binary carbides and nitrides, assuming dilute solution behavior, *i.e.* that the activities of the solute species in austenite may be represented by Henry's law. Interactions with additional solute species such as manganese are expected to be small in these steels, and are not accounted for at this time. It is also assumed that the carbonitrides are perfectly stoichiometric and do not contain iron; therefore that they may be represented by the chemical formula

$$\text{Nb}_x\text{V}_{1-x}\text{C}_y\text{N}_{1-y}, \quad \text{where } 0 \leq x \leq 1 \quad \text{and} \quad 0 \leq y \leq 1.$$

It is useful to consider the merits of the assumptions which have been made. The question of iron solubility in the carbonitrides is somewhat controversial, and iron has occasionally been reported during chemical analysis of extracted particles.<sup>29</sup> However, iron has not been detected in the investigations which have been performed at this laboratory.<sup>15,16</sup> With regard to stoichiometry, it is widely recognized that the MX-type carbides and nitrides have defect lattices in which some of the sites for carbon and nitrogen may be unfilled.<sup>30</sup> Therefore, the assumption of perfect stoichiometry is not strictly valid. However, sufficient data do not exist to predict the stoichiometry of the precipitates as a result of the model, and it is common to assume a fixed stoichiometry for this kind of calculation. For example, the common practice of presenting solubility data in terms of a solubility product also involves the implicit assumption of a fixed stoichiometry. For the sake of simplicity, perfect stoichiometry is assumed (*i.e.*, the total number of Nb + V atoms in the precipitate phase is equal to the total number of C + N atoms in the precipitates). The choice of a different fixed stoichiometry would not alter the trends predicted by the model.

In order to express the free energy of the Nb<sub>x</sub>V<sub>1-x</sub>C<sub>y</sub>N<sub>1-y</sub> phase in terms of the free energies of the binary compounds, it is necessary to define the amount of each individual binary compound in the precipitate. A difficulty arises in modeling because it is not straightforward to define the mole fraction of each binary compound in the four-component precipitate phase. Consider, for example, one mole of the precipitate Nb<sub>0.5</sub>V<sub>0.5</sub>C<sub>0.5</sub>N<sub>0.5</sub>. It is tempting to claim that ¼ mole each of NbC, NbN, VC, and VN must have been mixed together, but there is no *a priori* reason that this must be so. This mixture could be described as a combination of ½ mole of NbC and ½ mole of VN, with *no* moles of NbN or VC, and an infinite number of similar descriptions is possible. Thus it is clear that caution must be used when referring to Nb<sub>x</sub>V<sub>1-x</sub>C<sub>y</sub>N<sub>1-y</sub> in terms of its pure binary carbides and nitrides, rather than in terms of the pure elements themselves. The model and assumptions proposed by Hillert and Staffansson to describe the thermodynamics of stoichiometric phases shall be adopted here.<sup>31</sup> Hillert and Staffansson do not specify explicitly the amount of each binary compound in the precipitate, but they propose that

the molar free energy of the precipitate may be written as

$$G_{\text{Nb}_x\text{V}_{1-x}\text{C}_y\text{N}_{1-y}} = xyG_{\text{NbC}}^\circ + x(1-y)G_{\text{NbN}}^\circ + (1-x)yG_{\text{VC}}^\circ + (1-x)(1-y)G_{\text{VN}}^\circ - T^{\prime}S^m + {}^E G^m \quad [2]$$

where  $G_{\text{NbC}}^\circ$ ,  $G_{\text{NbN}}^\circ$ ,  $G_{\text{VC}}^\circ$ , and  $G_{\text{VN}}^\circ$  are the molar free energies of the pure binary compounds at the temperature of interest,  ${}^{\prime}S^m$  is the integral ideal molar entropy of mixing,  ${}^E G^m$  is the integral excess molar free energy of mixing, and  $T$  is the absolute temperature. Hillert and Staffansson therefore imply that the free energy of the precipitate may be represented as though the precipitate is a mixture of

$$xy = \text{mole fraction of NbC}$$

$$x(1-y) = \text{mole fraction of NbN}$$

$$y(1-x) = \text{mole fraction of VC}$$

$$(1-x)(1-y) = \text{mole fraction of VN}$$

Turning back to the example of Nb<sub>0.5</sub>V<sub>0.5</sub>C<sub>0.5</sub>N<sub>0.5</sub>, the model allows this precipitate to be thought of as a mixture of equal parts of NbC, NbN, VC, and VN, which is intuitively satisfying. Hillert and Staffansson calculate the ideal entropy of mixing according to Temkin,<sup>32</sup> assuming that Nb and V, and C and N mix independently on two different sublattices in the interstitial compound; thus

$$-\frac{{}^{\prime}S^m}{R} = x \ln x + (1-x) \ln(1-x) + y \ln y + (1-y) \ln(1-y) \quad [3]$$

where  $R$  is the universal gas constant.

The integral excess molar free energy of mixing is expressed using a regular solution model, allowing for C-N and Nb-V interactions. The expression is

$${}^E G^m = x(1-x)yL_{\text{NbV}}^{\text{C}} + x(1-x)(1-y)L_{\text{NbV}}^{\text{N}} + xy(1-y)L_{\text{CN}}^{\text{Nb}} + (1-x)y(1-y)L_{\text{CN}}^{\text{V}} \quad [4]$$

where  $L_{\text{NbV}}^{\text{C}}$ ,  $L_{\text{NbV}}^{\text{N}}$ ,  $L_{\text{CN}}^{\text{Nb}}$ , and  $L_{\text{CN}}^{\text{V}}$  are the four regular solution parameters.<sup>31</sup> The partial molar free energies of the individual compounds in solution in the precipitate are given by

$$\bar{G}_{\text{NbC}} = G_{\text{NbC}}^\circ + (1-x)(1-y)\Delta G + RT \ln x + RT \ln y + {}^E \bar{G}_{\text{NbC}} \quad [5]$$

$$\bar{G}_{\text{NbN}} = G_{\text{NbN}}^\circ - (1-x)(y)\Delta G + RT \ln x + RT \ln(1-y) + {}^E \bar{G}_{\text{NbN}} \quad [6]$$

$$\bar{G}_{\text{VC}} = G_{\text{VC}}^\circ - x(1-y)\Delta G + RT \ln(1-x) + RT \ln y + {}^E \bar{G}_{\text{VC}} \quad [7]$$

$$\bar{G}_{\text{VN}} = G_{\text{VN}}^\circ + xy\Delta G + RT \ln(1-x) + RT \ln(1-y) + {}^E \bar{G}_{\text{VN}} \quad [8]$$

where  $\Delta G$  is defined by  $\Delta G = G_{\text{NbN}}^\circ + G_{\text{VC}}^\circ - G_{\text{NbC}}^\circ - G_{\text{VN}}^\circ$ , and the partial excess molar free energies may be written in terms of the regular solution parameters. The complete expressions for the partial excess molar free energies are given by Hillert and Staffansson, but some simplifications are possible here, since the regular solution

parameters are not well known for this system. No data are available for the mixing of Nb and V in the carbonitrides, and thus the parameters  $L_{\text{NbV}}^{\text{C}}$  and  $L_{\text{NbV}}^{\text{N}}$  will be taken to be zero (*i.e.*, ideality assumed). A regular solution parameter has been determined for C-N mixing in the Ti-C-N system,<sup>33,34</sup> and previous investigations have used this parameter to describe C-N mixing in the V-C-N system.<sup>9,12,34</sup> The assumption made is that C-N mixing should be approximately the same in the different microalloy carbonitrides, in view of the general similarity of the systems. The observed deviation from ideal solution behavior was not large, and thus it shall be assumed that  $L_{\text{CN}}^{\text{Nb}} = L_{\text{CN}}^{\text{V}} = L_{\text{CN}}^{\text{Ti}}$  since no other data are available. The partial excess molar free energies are then given by

$${}^E\bar{G}_{\text{NbC}} = {}^E\bar{G}_{\text{VC}} = L_{\text{CN}}(1 - y)^2 \quad [9]$$

$${}^E\bar{G}_{\text{NbN}} = {}^E\bar{G}_{\text{VN}} = L_{\text{CN}}(y)^2 \quad [10]$$

The austenite/carbonitride equilibrium condition is identified by requiring the partial molar free energies of each atomic species to be identical in both phases. Equilibrium is satisfied when

$$\Delta G_{\text{NbC}} = \bar{G}_{\text{NbC}} - \bar{G}_{\text{Nb}}^{\gamma} - \bar{G}_{\text{C}}^{\gamma} = 0 \quad [11]$$

$$\Delta G_{\text{NbN}} = \bar{G}_{\text{NbN}} - \bar{G}_{\text{Nb}}^{\gamma} - \bar{G}_{\text{N}}^{\gamma} = 0 \quad [12]$$

$$\Delta G_{\text{VC}} = \bar{G}_{\text{VC}} - \bar{G}_{\text{V}}^{\gamma} - \bar{G}_{\text{C}}^{\gamma} = 0 \quad [13]$$

$$\Delta G_{\text{VN}} = \bar{G}_{\text{VN}} - \bar{G}_{\text{V}}^{\gamma} - \bar{G}_{\text{N}}^{\gamma} = 0 \quad [14]$$

where  $\bar{G}_{\text{Nb}}^{\gamma}$ ,  $\bar{G}_{\text{V}}^{\gamma}$ ,  $\bar{G}_{\text{C}}^{\gamma}$ , and  $\bar{G}_{\text{N}}^{\gamma}$  are the partial molar free energies of each of the elemental species in austenite, and  $\bar{G}_{\text{NbC}}$ ,  $\bar{G}_{\text{NbN}}$ ,  $\bar{G}_{\text{VC}}$ , and  $\bar{G}_{\text{VN}}$  are given by Eqs. [5] through [8]. It can be shown that only three of the equilibrium equations ([11] through [14]) are independent.<sup>22</sup> Equilibrium may be represented by any three independent combinations of these equations, and it is convenient to write the conditions for equilibrium as

$$y \Delta G_{\text{NbC}} + (1 - y) \Delta G_{\text{NbN}} = 0 \quad [15]$$

$$x \Delta G_{\text{NbC}} + (1 - x) \Delta G_{\text{VC}} = 0 \quad [16]$$

$$x \Delta G_{\text{NbN}} + (1 - x) \Delta G_{\text{VN}} = 0 \quad [17]$$

since all of the terms containing  $\Delta G$  are then eliminated. If the activities of Nb, V, C, and N in austenite are represented using Henry's law, and the solubility products which apply to the formation of the pure carbides and nitrides are given by  $K_{\text{NbC}}$ ,  $K_{\text{NbN}}$ ,  $K_{\text{VC}}$ , and  $K_{\text{VN}}$ , the equilibrium equations become

$$y \ln \frac{xyK_{\text{NbC}}}{[\text{Nb}_e][\text{C}_e]} + (1 - y) \ln \frac{x(1 - y)K_{\text{NbN}}}{[\text{Nb}_e][\text{N}_e]} + \frac{L_{\text{CN}}}{RT} [y(1 - y)] = 0 \quad [18]$$

$$x \ln \frac{xyK_{\text{NbC}}}{[\text{Nb}_e][\text{C}_e]} + (1 - x) \ln \frac{y(1 - x)K_{\text{VC}}}{[\text{V}_e][\text{C}_e]} + \frac{L_{\text{CN}}}{RT} [(1 - y)^2] = 0 \quad [19]$$

$$x \ln \frac{x(1 - y)K_{\text{NbN}}}{[\text{Nb}_e][\text{N}_e]} + (1 - x) \ln \frac{(1 - x)(1 - y)K_{\text{VN}}}{[\text{V}_e][\text{N}_e]} + \frac{L_{\text{CN}}}{RT} y^2 = 0 \quad [20]$$

where  $[\text{Nb}_e]$ ,  $[\text{V}_e]$ ,  $[\text{C}_e]$ , and  $[\text{N}_e]$  represent the mole fractions of each species in solution in the austenite at equilibrium. In addition, the total number of atoms of each species must remain unchanged during the reaction. The necessary mass-balance expressions may be written as

$$[\text{Nb}_s] = f\left(\frac{x}{2}\right) + (1 - f)[\text{Nb}_e] \quad [21]$$

$$[\text{V}_s] = f\left(\frac{1 - x}{2}\right) + (1 - f)[\text{V}_e] \quad [22]$$

$$[\text{C}_s] = f\left(\frac{y}{2}\right) + (1 - f)[\text{C}_e] \quad [23]$$

$$[\text{N}_s] = f\left(\frac{1 - y}{2}\right) + (1 - f)[\text{N}_e] \quad [24]$$

where  $[\text{Nb}_s]$ ,  $[\text{V}_s]$ ,  $[\text{C}_s]$ , and  $[\text{N}_s]$  are the mole fractions of these elements in the steel before any precipitation occurs, and  $f$  is the mole fraction of precipitates at equilibrium.

Equations [18] through [24] are seven equations in seven unknowns which are solved numerically to determine the austenite/carbonitride equilibrium. For a given steel at any appropriate temperature, the equilibrium matrix composition, precipitate composition, and precipitate volume fraction can be determined (*i.e.*,  $[\text{Nb}_e]$ ,  $[\text{V}_e]$ ,  $[\text{C}_e]$ ,  $[\text{N}_e]$ ,  $x$ ,  $y$ , and  $f$ ). The necessary input data are the solubility products applicable to the formation of the pure carbides and nitrides in austenite, and the regular solution parameter. The accuracy of the model, of course, is limited by the quality of the input data. Various experimentally determined solubility products are available (*e.g.*, References 11, 13, 18, 34-40), and the following data have been adopted here:

$$\log_{10} K_{\text{NbC}} = -6,770/T + 2.26 \quad [25]$$

$$\log_{10} K_{\text{NbN}} = -10,230/T + 4.04 \quad [26]$$

$$\log_{10} K_{\text{VC}} = -9,500/T + 6.72 \quad [27]$$

$$\log_{10} K_{\text{VN}} = -7,840/T + 3.02 \quad [28]$$

where  $T$  is in degrees Kelvin and the solubility data apply to concentrations in weight percent (conversion to atom fraction is required). The solubility product for NbC precipitation is taken from the classic paper by Irvine *et al.*<sup>35</sup> The data for NbN are taken from R. P. Smith,<sup>38</sup> and were determined between 1191 °C and 1336 °C, although the data are extrapolated below 1191 °C in this investigation. The solubility products for pure VC and VN precipitation are taken from the work of Roberts and Sandberg,<sup>34</sup> who obtained "best fit" relationships using the data of several investigators. As mentioned previously, the appropriate regular solution parameters have not been determined, and the value  $L_{\text{CN}} = -4260$  J/mole is used, following Roberts and Sandberg.<sup>34</sup>

### III. RESULTS AND DISCUSSION

#### A. Thermodynamic Modeling

The thermodynamic model predicts the austenite/carbonitride equilibrium at any temperature. For a "typical" HSLA steel containing 0.1C, 0.01N, 0.03Nb, and 0.07V, for example, the model predicts the following equilibrium condition at 950 °C:

austenite composition—0.098C, 0.004N, 0.002Nb, 0.053V, balance Fe/Mn

chemical formula of carbonitride— $\text{Nb}_{0.47}\text{V}_{0.53}\text{C}_{0.34}\text{N}_{0.66}$

mole fraction of carbonitrides— $0.71 \times 10^{-3}$

In addition, the carbonitride solution temperature is estimated to be 1195 °C for this steel. The solution temperature is defined as the temperature where all of the Nb and V goes into solution in the austenite, *i.e.*, the temperature at which the calculated mole fraction of precipitates goes to zero.

It is of interest to evaluate the effects of different alloying variations on the precipitation reaction, using the "typical" steel as a basis for comparison. Specific alloying variations to be considered here are (1) a change in the carbon level in the steel to 0.02C, (2) a change in the nitrogen level to 0.02N, and (3) substitution of niobium and vanadium for one another. The calculated precipitate compositions for these conditions are presented in Figures 1(a) and 1(b). The precipitate compositions were calculated at 950 °C and 1050 °C for the base steel, in order to examine the effect of a temperature variation. The weight ratios of Nb/(Nb + V) in the precipitates are shown in Figure 1(a), and the ratios of C/(C + N) in the precipitates are given in Figure 1(b). Both Nb/(Nb + V) and C/(C + N) are plotted against the weight ratio of Nb/(Nb + V) in the steels, since the substitution of Nb and V for one another was accomplished at a constant level of Nb + V = 0.1 pct.

The results in Figure 1(a) demonstrate several important effects. The Nb/(Nb + V) ratio in each case is greater in the precipitate than in the steel. This is not surprising, since

niobium is generally considered to be less soluble than vanadium in HSLA steels. The precipitates are also found to become richer in Nb as (1) the temperature is increased, (2) the Nb concentration in the steel is increased, and (3) the C and/or N level in the steel is reduced. The first two effects will be examined in the experimental portion of this work. The effects of carbon and nitrogen variations have never been investigated, and it should be interesting in the future to ascertain whether or not the predictions are correct. The effects of C and N are of more than academic interest, since a continuing trend in the design of HSLA steels is toward substantially reduced carbon levels. Figure 1(b) demonstrates the predicted variations of the carbon and nitrogen concentrations in the precipitate phase. In each case, the precipitates become richer in carbon as niobium is substituted for vanadium in the steels. This effect is due to differences in the relative solubilities of carbides and nitrides between the Nb-rich and the V-rich ends of the diagram. That is, VN is extremely insoluble in austenite compared to VC, whereas the solubilities of NbC and NbN are more similar to one another. Therefore, as the steels become richer in vanadium, it is not surprising that the precipitates become more nitrogen-rich. Increases in the nitrogen content of the steel result in higher nitrogen levels in the carbonitride, as expected. Similarly, the carbon level in the precipitate increases as the carbon concentration in the steel is increased. The effect of temperature is more complex. Figure 1(b) shows that the carbon level in the precipitate is higher at 950 °C than at 1050 °C for the steels which are highest in vanadium, and the opposite result is obtained on the niobium-rich side of the diagram. This effect is due to the differences in the temperature dependencies of the solubility products of the pure binary compounds. That is, the temperature dependence of the solubility product for NbN is greater than that for NbC, whereas the solubility product changes more with temperature for VC than it does for VN (see Eqs. [25] through [28]).

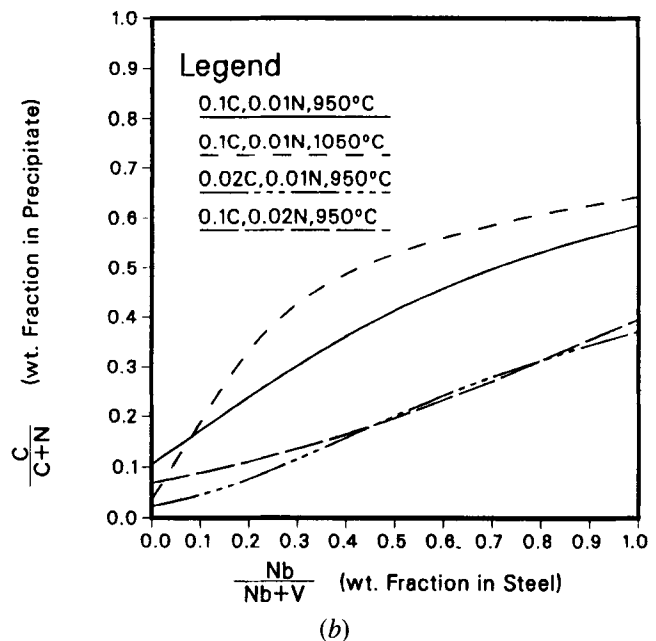
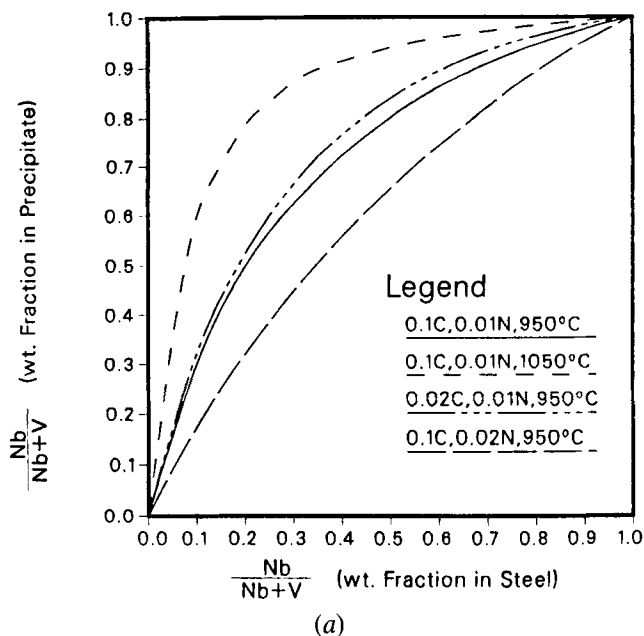


Fig. 1—Predicted effects of steel composition and temperature on carbonitride precipitate compositions. (a) Nb/(Nb + V) and (b) C/(C + N) weight fractions in the carbonitride are given for steels having a total Nb + V = 0.1 pct.

The effects of alloying on the carbonitride solution temperature are also important. The carbonitride solution temperatures are given in Figure 2 for steels containing Nb + V = 0.1 pct. The calculations are presented for steels containing the base levels of 0.1C and 0.01N, and for steels in which the carbon and nitrogen levels are adjusted to 0.02C, 0.01N; 0.1C, 0.02N; and 0.02C, 0.02N, respectively. The curves demonstrate some very important effects. As expected, the solution temperature increases as niobium is substituted for vanadium in the steel. Also, the solution temperature increases as the nitrogen level or the carbon level is increased in the steel. However, the effect of carbon is much different in the steels containing higher levels of vanadium than it is for steels containing higher levels of niobium. For example, an increase in the carbon level from 0.02 to 0.1 pct raises the solution temperature by only a few degrees for the steels containing 0.1V, whereas an identical increase in the carbon level in the 0.1Nb steels results in an increase in the solution temperature of more than 100 °C.

The results in Figure 2 demonstrate that the solution temperature is more strongly affected by changes in the nitrogen level at the lower carbon concentration (0.02C) than at the higher carbon concentration (0.1C) in the steel. For the sake of simplicity, a common assumption in the past has been that the precipitates which form in niobium-containing steels do not contain much nitrogen, and therefore that nitrogen effects need not be accounted for rigorously. The predictions show, however, that the precipitates may generally be expected to contain substantial amounts of nitrogen. In addition, nitrogen is predicted to have a strong influence on the carbonitride solution temperature, and thus on the precipitate undercooling. Clearly, the model presented here suggests strongly that nitrogen effects must not be ignored.

The austenite/carbonitride equilibrium was calculated for the two experimental steels, using the thermodynamic model. The predicted precipitate compositions, matrix compositions, and mole fractions of precipitation are presented in Table II, for the appropriate holding temperatures of 843 °C, 954 °C, and 1066 °C. The predictions again indicate that (1) increasing the temperature should reduce the vanadium concentration in the carbonitride, and (2) adding more vanadium to the steel should increase the vanadium concentration in the carbonitride.

### B. Carbonitride Precipitation in the Experimental Steels

The important variables which were expected to affect the precipitate compositions are the temperature and the steel composition, as discussed in the preceding section (see Table II). In addition, it was of interest to examine whether

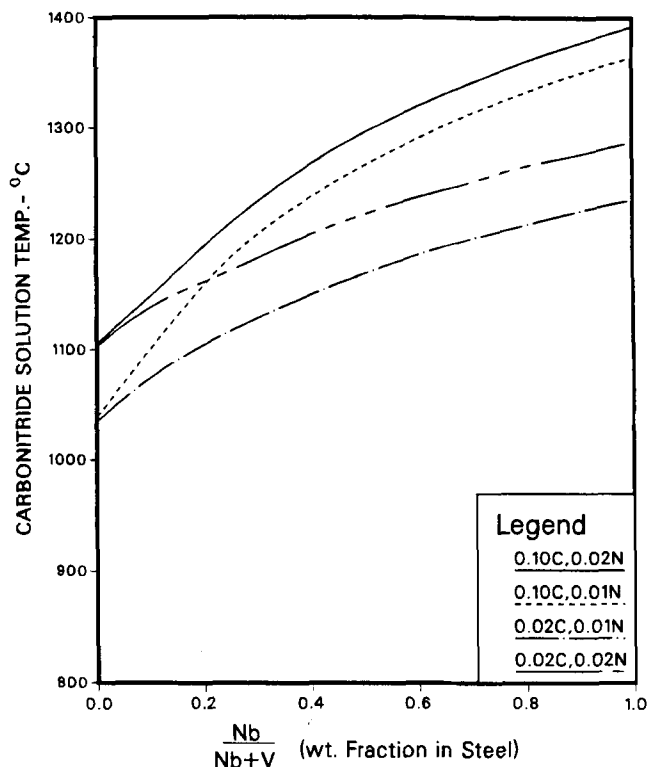


Fig. 2—Effects of carbon and nitrogen on the carbonitride solution temperature for steels having Nb + V = 0.1 pct.

other factors were also significant, such as the rolling reduction and the isothermal holding time after deformation. It is important to recognize that, for the thermomechanical treatments used in this study, the austenite recrystallization kinetics of these steels are relatively slow. In fact, only in the samples rolled 50 pct and held for 10,000 seconds at 1066 °C did the volume fraction of recrystallized austenite exceed 0.5. Consequently, the carbonitride precipitation reaction being examined here occurs predominantly in unrecrystallized austenite.

The precipitation reactions were followed in these steels using transmission electron microscopy. All of the specimens examined during this investigation contained both matrix precipitates and grain-boundary precipitates. The matrix precipitation was always much finer than the grain-boundary precipitation. This is clearly demonstrated in the micrograph in Figure 3, which shows a typical grain-boundary and the surrounding matrix in the 0.05V steel after reheating, rolling 50 pct at 954 °C, and holding for 1000 seconds at 1066 °C.

Table II. Predicted Austenite/Carbonitride Equilibrium for Experimental Steels at 843 °C, 954 °C, and 1066 °C

Steel Composition	Temperature °C	Precipitate Composition (Chemical Formula)	Mole Fraction of Precipitates	Equilibrium Austenite Composition (Wt Pct)			
				Nb	V	C	N
0.03Nb, 0.05V	843 °C	Nb <sub>0.31</sub> V <sub>0.69</sub> C <sub>0.25</sub> N <sub>0.75</sub>	0.12 × 10 <sup>-2</sup>	<0.001	0.014	0.091	0.004
	954 °C	Nb <sub>0.45</sub> V <sub>0.55</sub> C <sub>0.21</sub> N <sub>0.79</sub>	0.76 × 10 <sup>-3</sup>	0.002	0.032	0.092	0.008
	1066 °C	Nb <sub>0.78</sub> V <sub>0.22</sub> C <sub>0.36</sub> N <sub>0.64</sub>	0.35 × 10 <sup>-3</sup>	0.007	0.047	0.093	0.012
0.03Nb, 0.20V	843 °C	Nb <sub>0.12</sub> V <sub>0.88</sub> C <sub>0.60</sub> N <sub>0.40</sub>	0.31 × 10 <sup>-2</sup>	<0.001	0.078	0.091	<0.001
	954 °C	Nb <sub>0.21</sub> V <sub>0.79</sub> C <sub>0.35</sub> N <sub>0.65</sub>	0.17 × 10 <sup>-2</sup>	0.002	0.14	0.10	0.002
	1066 °C	Nb <sub>0.31</sub> V <sub>0.69</sub> C <sub>0.20</sub> N <sub>0.80</sub>	0.10 × 10 <sup>-2</sup>	0.006	0.17	0.11	0.006

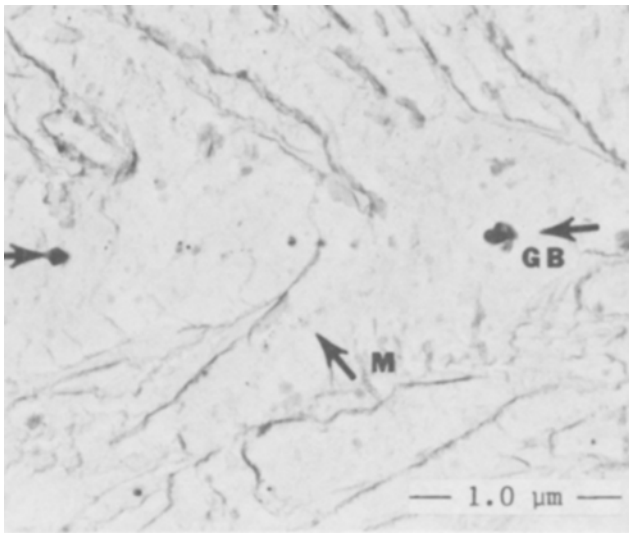


Fig. 3—Electron micrograph of extraction replica from 0.03Nb, 0.05V steel, showing carbonitride precipitates along a prior-austenite grain boundary (GB), and within the austenite matrix (M). Specimen was solution treated at 1288 °C, rolled 50 pct at 954 °C, and held for 1000 sec at 1066 °C.

Fine carbonitrides are visible in each steel immediately after rolling, as shown in Figure 4 for the 0.05V steel. The specimen was reheated at 1288 °C, rolled 50 pct at 954 °C, and immediately quenched. After this treatment the matrix precipitates are observed to be very fine (approximately 2 to 4 nm in diameter). The progress of the matrix precipitation reaction in this steel is shown in Figures 5(a) through 5(d). The specimens were rolled 50 pct at 954 °C and held for times up to 10,000 seconds at 954 °C. The precipitates clearly increase in size as the time at temperature increases, with many particles approaching sizes of several tens of nanometers after 10,000 seconds. Similar matrix precipitation behavior is observed in the 0.20V steel, as shown in

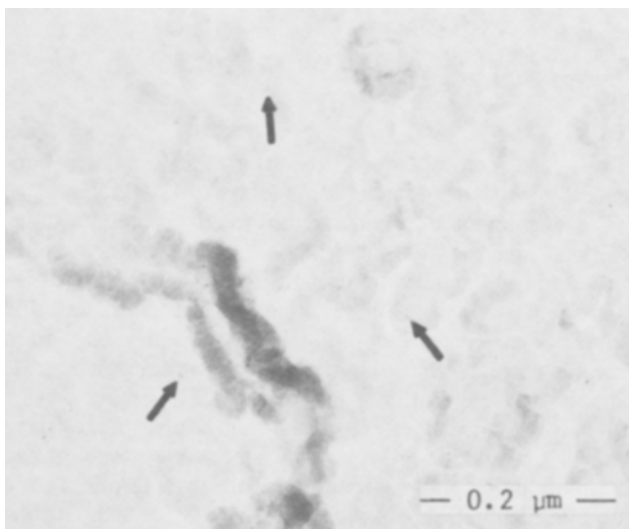


Fig. 4—Electron micrograph of extraction replica from 0.03Nb, 0.05V steel, which shows the fine matrix precipitation (see arrows) which is present immediately after rolling. The steel was solution treated at 1288 °C, rolled 50 pct at 954 °C, and immediately quenched to room temperature.

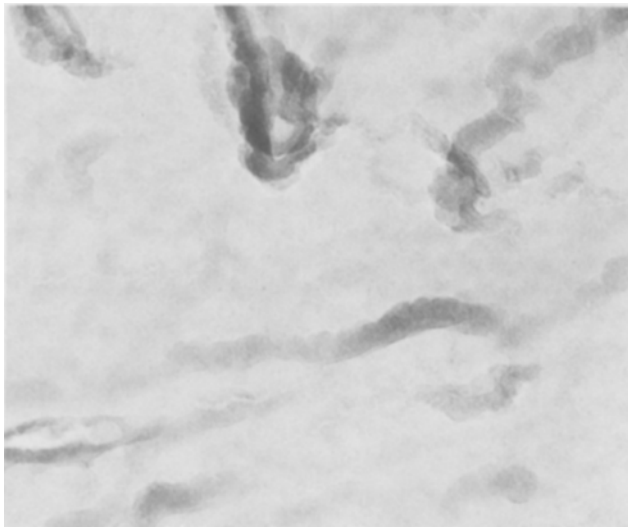
Figures 6(a) through 6(d), although there appears to be a greater amount of precipitation in the 0.20V steel than in the 0.05V steel. At the longer holding times, it is clear that the number density of precipitates decreases as the particle sizes increase, indicating that coarsening of the matrix precipitates is underway. Similar coarsening behavior has been reported previously by Hansen *et al.* in niobium steels.<sup>4</sup>

The carbonitrides were also examined in steels which received a 20 pct rolling reduction. The micrograph in Figure 7 shows the matrix precipitates which are found in the 0.05 V steel after a 20 pct reduction plus a 100 second hold at 954 °C. Fewer precipitates are visible after the 20 pct rolling reduction than after a 50 pct reduction, although the particle size appears to be somewhat larger (compare Figure 7 with Figure 5(b)). Similar behavior has been reported previously by le Bon *et al.* in Nb-steels.<sup>41</sup> These effects of deformation on the carbonitride precipitation behavior are thought to result from differences in the heterogeneous nucleation kinetics, which are due to the differences in dislocation density and deformation substructure.

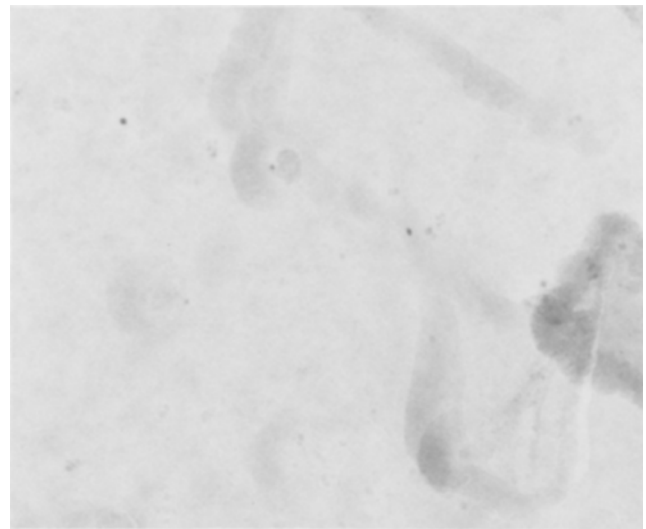
The carbonitride compositions were measured for both matrix and grain-boundary precipitates, at holding temperatures of 843 °C, 954 °C, and 1066 °C, and are presented in Tables III and IV for the 0.05V and 0.20V steels, respectively. The data are reported as weight ratios of Nb/(Nb + V), in percent. Data are included only for holding times of 100, 1000, and 10,000 seconds, as the precipitates at shorter times were not large enough to be analyzed with statistical certainty using the AEM available for this study. The error estimates represent a 95 pct confidence interval about the mean composition.

Comparison of the precipitate compositions in Tables III and IV shows that the amount of deformation (rolling reduction) does not have a significant effect on the precipitate chemistry. Similarly, there are no consistent variations in the precipitate compositions after different annealing times. Although the data indicate that the precipitate composition does not change with time during the isothermal holding treatment, it must be noted that measurements were not made at holding times shorter than 100 seconds, and the possibility remains that compositional changes may occur during the early stages of precipitation. The behavior observed here is different from that which was reported by Mehta *et al.*, where the precipitates in similar steels containing much higher levels of aluminum became more Nb-rich with time.<sup>15</sup> As mentioned previously, the observed behavior has been postulated to result from aluminum nitride precipitation in the high-Al steels, which reduces the amount of nitrogen available to be combined with Nb and V in the form of carbonitrides.<sup>16</sup> Calculations made using the thermodynamic model presented here indicate that the precipitate composition would be expected to become more Nb-rich if the amount of available nitrogen is reduced (see Figure 1).

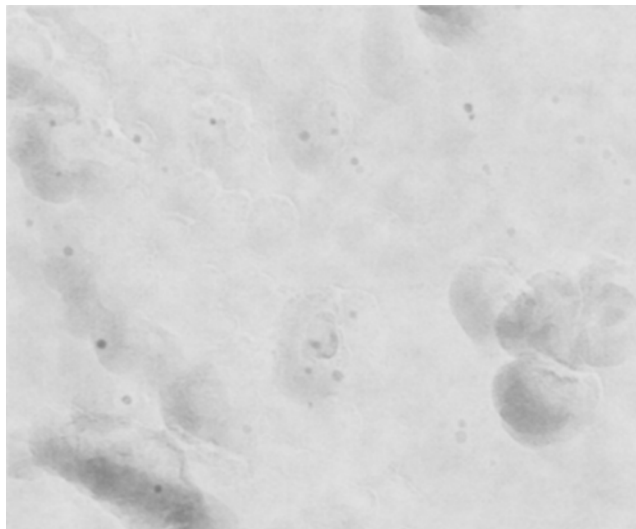
The results presented in Tables III and IV clearly demonstrate that the precipitate composition is dependent on the steel composition and on temperature, as predicted. Also, the grain boundary precipitates appear to be consistently richer in vanadium than the matrix precipitates, as reported previously by Crooks *et al.*<sup>14</sup> The effects of temperature and steel composition are shown in Figures 8 and 9, where the precipitate compositions are shown for all of the specimens



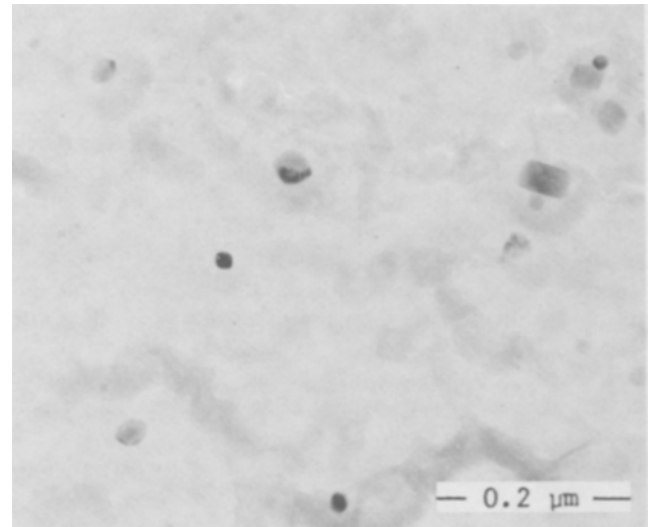
(a)



(b)



(c)



(d)

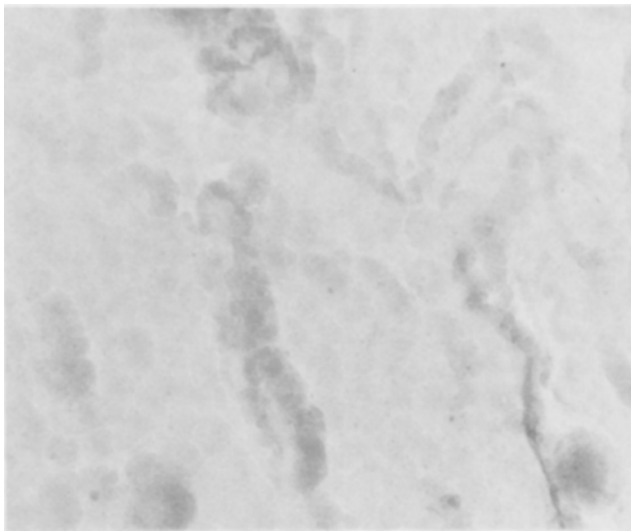
Fig. 5—Electron micrographs of extraction replicas illustrating the effect of holding time on the carbonitride precipitation behavior in the 0.03Nb, 0.05V steel. Specimens were solution treated at 1288 °C, rolled 50 pct, and held at 954 °C for (a) 10 sec, (b) 100 sec, (c) 1000 sec, and (d) 10,000 sec before quenching.

which were held for 10,000 seconds after rolling. The compositions of the matrix precipitates are shown in Figure 8, and the compositions of the grain-boundary precipitates are given in Figure 9. The 10,000 second samples were chosen for this comparison because they are probably the best representation of the equilibrium condition, particularly since the particles were largest, and thus resulted in the best X-ray counting statistics. Although the matrix precipitates are systematically richer in niobium, the effects of temperature and steel composition are similar for both the matrix and grain-boundary precipitates. Also shown in Figures 8 and 9 are the precipitate compositions which were predicted using the thermodynamic model (results taken from Table II). The precipitates in the 0.20V steel contained higher levels of vanadium than the carbonitrides in the 0.05V steel. In addition, the precipitates in both steels became more niobium-rich as the temperature increased from 843 °C to

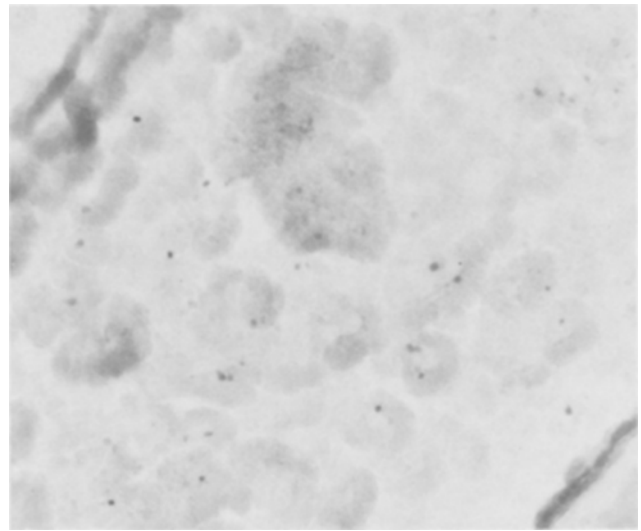
954 °C, and then to 1066 °C. Both of these trends are predicted by the thermodynamic model.

The agreement between the observed precipitate compositions and the thermodynamic model is much better for the grain-boundary precipitates than for the matrix precipitates, as shown in Figures 8 and 9. The consistent discrepancy between the compositions of matrix and grain boundary precipitates is difficult to understand. It is unlikely that capillarity effects (due to the particle size difference) are involved, since the matrix precipitates have attained sizes which are relatively large for surface energy contributions to play a significant role in determining the austenite/carbonitride equilibrium. Clearly, then, the differences must result from kinetic (*i.e.*, nonequilibrium) effects, which could be related to nonequilibrium differences in the environments at the different precipitation sites, composition gradients which are established during the reaction,

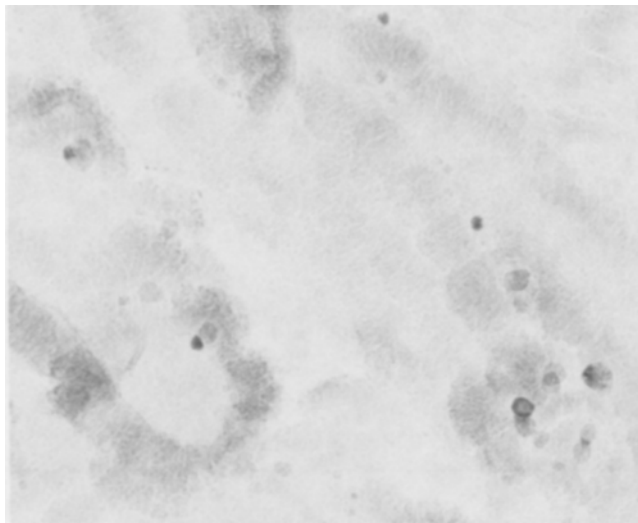




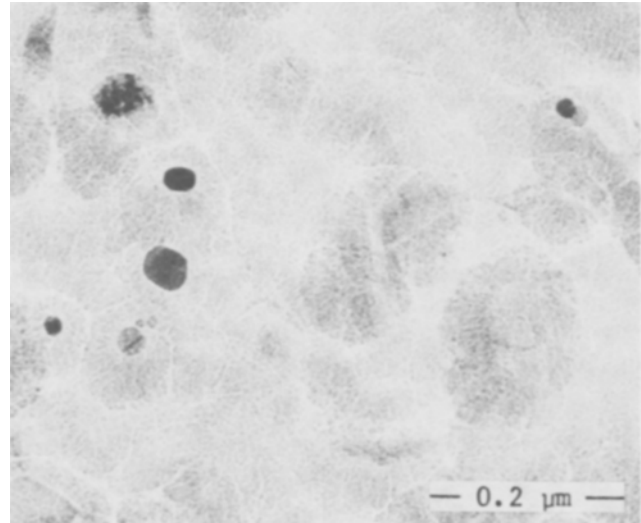
(a)



(b)



(c)



(d)

Fig. 6—Electron micrographs of extraction replicas illustrating the effect of holding time on the carbonitride precipitation behavior in the 0.03Nb, 0.20V steel. Specimens were solution treated at 1288 °C, rolled 50 pct, and held at 954 °C for (a) 10 sec, (b) 100 sec, (c) 1000 sec, and (d) 10,000 sec before quenching.

or differences in the nature of the two precipitates. For example, it is possible that the matrix and grain-boundary precipitate phases are different, one of them being metastable and the other being an equilibrium phase. Such behavior is often observed in aluminum alloy systems, for example, where the equilibrium precipitate phase forms at the grain boundaries.<sup>42,43</sup> In order to investigate this possibility, convergent beam electron diffraction patterns were obtained from grain-boundary and matrix precipitates in the 0.20V steel which had been rolled 20 pct and annealed for 10,000 seconds at 954 °C. Several patterns were obtained, and in all cases the reflections could be indexed in terms of the face-centered cubic NaCl type structure which is common for the MX-type carbonitrides.<sup>30</sup> It is possible that a

more detailed study using convergent beam diffraction would yield observable structural differences between the two precipitates, although in view of the small size of the precipitates, considerable difficulty may be involved in obtaining the dynamical diffracting conditions which are required to image the necessary fine structure in the convergent beam patterns.<sup>28</sup> Clearly, further work is required to understand the differences between the matrix and grain-boundary particles, but it is important to recognize that the compositional trends are the same for the two precipitates, and therefore that the trends are predicted correctly by the thermodynamic model for the matrix precipitates as well as for those on the grain boundaries.

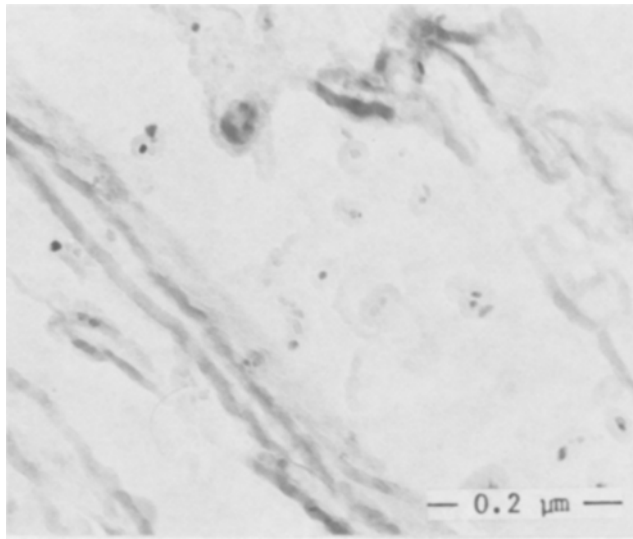


Fig. 7—Electron micrograph of extraction replica from 0.03Nb, 0.20V steel which was rolled 20 pct and held for 100 sec at 954 °C.

#### IV. GENERAL DISCUSSION

This investigation has shown that the carbonitride solubility in Nb/V microalloyed steels is strongly affected by the vanadium addition, at temperatures which are appropriate to commercial hot-rolling practices. A thermodynamic model has been developed, and its validity is supported by the good agreement between the predicted and observed precipitate compositions. Further experimental verification would be helpful, however. For example, quantitative measurements of carbon and nitrogen levels in the precipitates are necessary. Such data should be forthcoming with the recent improvements in the ability to perform quantitative light-element analysis in the analytical electron microscope.

Some additional comments are necessary for the reader who wishes to apply the thermodynamic model to other types of alloy steels. First, the model assumes that the activities of the solute species in austenite may be represented by Henry's law; *i.e.*, that the solutions are dilute. Therefore, if higher solute concentrations are to be considered, it may be necessary to include corrections for non-Henrian behavior and for interactions among the solute species. Also, the presence of competing reactions must be considered. For example, depending upon the temperature and steel composition,<sup>44</sup> aluminum nitride precipitation may be expected to take place concurrently with the Nb, V(C, N) precipitation. The two reactions compete for the available nitrogen, and the progress of one reaction is therefore dependent on the progress of the other. In the case of microalloyed HSLA steels, the kinetics of AlN precipitation are too slow to compete with Nb, V(C, N) precipitation during normal hot-rolling, and thus it is not usually necessary to account for AlN precipitation. In instances where substantial AlN precipitation occurs, however, it should be possible to predict an austenite/carbonitride/aluminum nitride three-phase equilibrium, but substantial compositional variations might be expected as equilibrium is approached.

#### V. SUMMARY

A thermodynamic model has been developed to predict the austenite/carbonitride equilibrium in the Fe-Nb-V-C-N alloy system. The model may be used to estimate the equilibrium compositions of the austenite and carbonitride phases in microalloyed steels, as well as the mole fraction of each phase, at any particular temperature. Caution must be used if additional (competing) reactions are possible, such as the formation of AlN in aluminum-killed steels. A number of general trends are predicted by the model, including:

Table III. Precipitate Compositions as Wt Pct Nb/(Nb + V) in the 0.03Nb, 0.05V Steel, Determined Using AEM

Temperature (°C)		Holding Time (sec.) after 20 Pct Rolling Reduction			Holding Time (sec.) after 50 Pct Rolling Reduction		
		100	1000	10,000	100	1000	10,000
843	matrix	77.6 ± 2.2	68.5 ± 3.3	64.4 ± 3.7	53.1 ± 5.1	61.1 ± 4.7	48.7 ± 4.7
	grain boundary	51.1 ± 9.1	46.3 ± 7.6	56.3 ± 7.8	49.2 ± 5.8	41.9 ± 6.0	38.2 ± 8.5
954	matrix	86.4 ± 0.8	88.3 ± 0.8	85.5 ± 0.7	86.4 ± 2.2	85.3 ± 2.4	82.4 ± 2.7
	grain boundary	64.4 ± 6.9	74.0 ± 4.5	53.5 ± 10.0	69.7 ± 4.8	63.8 ± 7.6	55.0 ± 8.2
1066	matrix	94.2 ± 0.9	95.1 ± 0.8	95.5 ± 0.7	95.2 ± 0.6	95.0 ± 0.9	91.7 ± 1.6
	grain boundary	93.0 ± 2.0	95.5 ± 0.9	96.5 ± 0.6	94.9 ± 1.6	95.8 ± 0.3	95.9 ± 0.3

Table IV. Precipitate Compositions as Wt Pct Nb/(Nb + V) in the 0.03Nb, 0.20V Steel, Determined Using AEM

Temperature (°C)		Holding Time (sec.) after 20 Pct Rolling Reduction			Holding Time (sec.) after 50 Pct Rolling Reduction		
		100	1000	10,000	100	1000	10,000
843	matrix	31.4 ± 3.9	31.9 ± 3.4	32.9 ± 3.1	32.6 ± 2.9	33.2 ± 4.8	28.9 ± 3.0
	grain boundary	21.0 ± 7.9	16.5 ± 3.3	23.5 ± 3.4	18.0 ± 5.9	16.3 ± 3.5	19.1 ± 2.2
954	matrix	41.0 ± 1.9	40.5 ± 2.0	40.6 ± 3.5	38.4 ± 3.3	39.1 ± 4.8	38.9 ± 3.3
	grain boundary	25.1 ± 4.1	25.0 ± 1.1	26.3 ± 2.8	20.2 ± 3.9	25.9 ± 3.5	31.6 ± 3.3
1066	matrix	59.0 ± 2.3	65.0 ± 3.5	53.6 ± 2.9	73.3 ± 2.8	65.6 ± 4.5	60.1 ± 3.9
	grain boundary	37.6 ± 6.3	55.8 ± 7.0	65.2 ± 6.0	50.4 ± 8.8	61.6 ± 5.5	46.9 ± 9.0

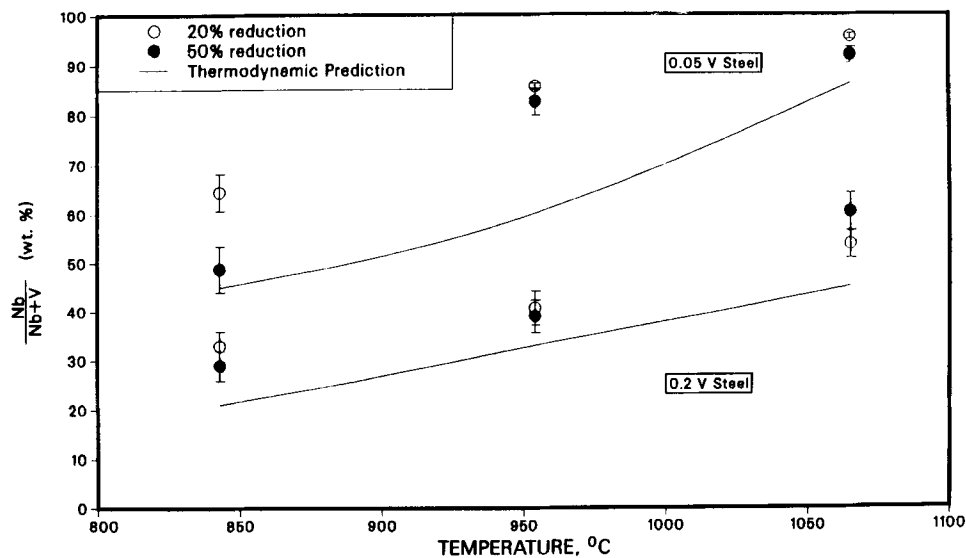


Fig. 8—Comparison of experimental results with predicted carbonitride compositions (for matrix precipitates after 10,000 sec holding time following a 20 pct or 50 pct rolling reduction).

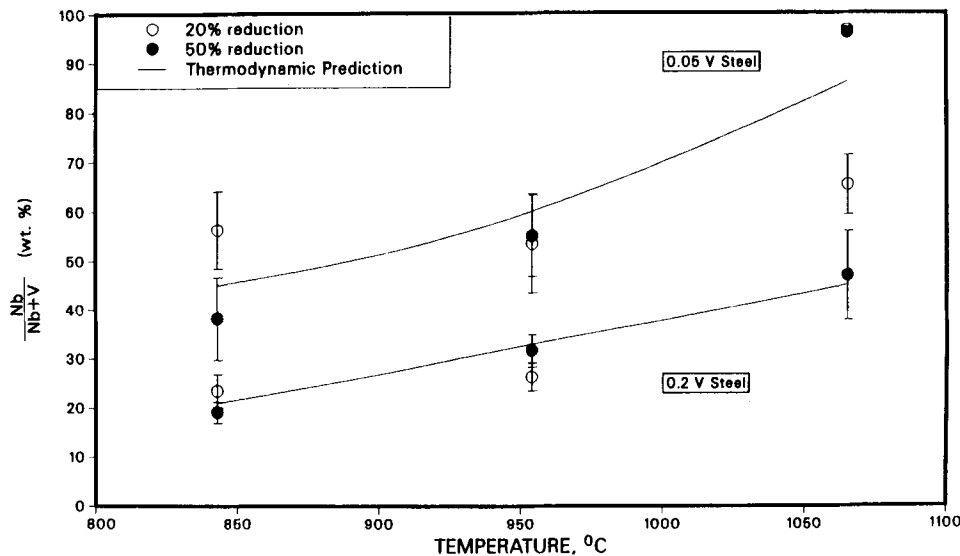


Fig. 9—Comparison of experimental results with predicted carbonitride compositions (for grain-boundary precipitates after 10,000 sec holding time following a 20 pct or 50 pct rolling reduction).

1. The Nb/(Nb + V) ratio is greater in the precipitate than in the steel.
2. The carbonitrides become more niobium-rich as the temperature is increased, the niobium concentration in the steel is increased, or the carbon and/or nitrogen levels in the steel are reduced.
3. The carbonitrides become richer in carbon as niobium is substituted for vanadium in the steel, as the carbon level in the steel is increased, or as the nitrogen level in the steel is reduced.
4. The carbonitride solution temperature increases with increasing levels of either Nb, V, C, or N in the steel. The solution temperature increases as niobium is substituted for vanadium in the steel. The effect of carbon additions on the solution temperature is expected to be greater for steels containing higher levels of niobium than for steels containing higher levels of vanadium.

The carbonitride precipitation behavior was investigated in two experimental 0.03Nb steels containing 0.05V and 0.20V, respectively. The steels were reheated to 1288 °C, rolled at 954 °C, and held for times up to 10,000 seconds at temperatures of 843 °C, 954 °C, and 1066 °C. Precipitate compositions were determined using analytical electron microscopy. The experimental portion of this work may be summarized as follows:

1. Carbonitride precipitates are found in the matrix and on prior-austenite grain boundaries in each steel. The grain-boundary precipitates are larger than the matrix precipitates, and are consistently more vanadium-rich, although the compositional trends are similar in the two precipitates.
2. The precipitate compositions are not found to vary significantly with the rolling reduction or the holding time after deformation.

3. The observed effects of steel composition and temperature are successfully predicted by the thermodynamic model. The agreement between the measured and the predicted precipitate compositions is quite good for the grain-boundary precipitates.

### ACKNOWLEDGMENTS

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