

Prediction of Solubility of Carbonitrides in High Strength Low Alloy Steel

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ABSTRACT : High Strength Low Alloy steels are of particular interest for large submarines, offshore structures, line-pipes and other structural applications that require a combination of strength and toughness. To achieve these properties, the addition of microalloying elements such as Nb, Ti and V is well established. These elements form carbides, nitrides and carbonitrides, which effectively refine the austenitic grain size and improve the properties of the final products.

In the present work, a simple analytical approach has been presented to predict the equilibrium solubility of carbonitrides in steel and the prediction of solubility has been made in Nb-bearing HSLA steels. Solubility product relationships and mass balance equations have been formulated for estimating the solubility of carbonitrides. The solubility of niobium carbonitride predicted by the present analysis is in agreement with that reported in the literature. Formation of AlN precipitates has also been considered to examine the extent of its influence on the solubility of carbonitrides. The presence of AlN precipitates is observed to have an appreciable influence on the solubility of niobium, nitrogen and carbon, and consequently on the solubility of carbonitrides. The effect of stoichiometry of the precipitates on the solubility behaviour has also been studied. The solubility of Nb and nitrogen in the case of non-stoichiometric precipitates is predicted to be higher than that of stoichiometric precipitates; but the solubility of carbon does not appear to depend on the stoichiometry of the precipitate.

KEY WORDS: High Strength Low Alloy steel, Solubility of Microalloying Elements, Niobium Carbonitride, Aluminium Nitride

1. Introduction

The use of micro-alloying elements in high strength low alloy (HSLA) steels for a wide variety of engineering structural applications is well known [1-3]. It increases the strength and toughness of the steel by the mechanism of grain refinement and precipitation strengthening [1-2]. Initially, grain refinement was achieved by aluminium and nitrogen addition [3], but, later, in the sixties, the necessity of adding microalloying elements such as niobium, vanadium and titanium to steel was recognised. The role of these elements in imparting finer grain size and precipitation strengthening has been elaborately documented in the literature [4,5]. Knowledge of the solubility of their carbides, nitrides and carbonitrides in austenite is important in order to control the precipitation behaviour during hot working, welding and further heat-treatment processes. Nb is preferred as an alloying element by most of the alloy designers due to its lower affinity for oxygen compared to titanium and favourable solubility relation compared to vanadium [6,9]. Solubility product relationships for their carbides and nitrides have been reported by various authors [9-14] and these are useful in assessing the solubility of individual carbide or nitride in steel. Due to the mutual solubility of the carbides and nitrides, they are

expected to form carbonitrides. Hence it is necessary to evaluate the solubility of carbonitrides rather than individual carbide or nitride. Nordberg and Aronsson^[10] assessed the solubility of niobium carbonitrides in steel, followed by Hudd *et al.*^[11]

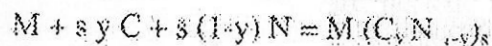
Some studies also report the composition of the carbides, nitrides and carbonitride in steel to be non-stoichiometric. Mori *et al.*^[15] found an average compositions of the precipitates to be $NbC_{0.87}$ and $NbC_{0.08}Nb_{0.88}$, while Mayer^[16] found the precipitates to be stoichiometric corresponding to $NbC_{0.9}Nb_{0.1}$ and the $NbC_{0.5}Nb_{0.95}$. Some investigations have been carried out to understand the solubility of non-stoichiometric carbonitrides in steel. However, more work is required to understand the influence of various process parameters on the composition and solubility of these precipitates. For example, the co-precipitation of AlN along with the carbonitrides of micro-alloying elements has not been investigated sufficiently. Generally, steel melt is killed with Al before the addition of microalloying elements. During subsequent processing and heat treatment of these steels, the precipitation of AlN is expected to occur simultaneously along with the carbonitrides of the micro-alloying elements. Experimental studies show the presence of AlN along with the Nb carbonitride in HSLA steel^[17]. Most of the earlier studies have ignored this aspect while evaluating the solubility of carbonitrides.

The present study focuses its attention on the solubility predictions in three HSLA steels supplied by the Naval Research Laboratory of USA. Niobium is the primary micro-alloying element present in these steels. In the present work, the influence of the precipitation of aluminium nitride on the precipitation and stoichiometry of the carbonitride of niobium is considered.

2. Prediction of Solubility

Due to significant levels of carbon and nitrogen in many HSLA steels, both carbides and nitrides can form in these alloys. Since the lattice parameter and crystal structure of the carbides and nitrides of individual microalloying element are similar^[18], it is assumed that they usually form solid solutions resulting in the precipitation of carbonitrides. On the other hand AlN will precipitate independent of the carbonitride because of its different crystal structure^[13]. A general method for the prediction of solubility of non-stoichiometric carbonitrides for a micro alloying element is presented below. This method can also be used for the stoichiometric carbonitrides as well.

It is assumed that a non-stoichiometric carbonitride of a composition $M(C_yN_{1-y})_s$ forms in the steel through a reaction:



where, M denotes microalloying element, i.e., Nb, Ti or V; $y = C / (C+N)$ ratio in the carbonitride. The free energy of formation of carbonitride can be expressed as:

$$\Delta G_{M(C_yN_{1-y})_s} = -RT \ln \{ [M(C_yN_{1-y})_s] / ([M].[C]^y.[N]^{s(1-y)}) \}$$

Where, [M], [C] and [N] are the activity of the metal, carbon and nitrogen, respectively, and can be represented in terms of weight percent in case of HSLA steels. R is the gas constant and T is temperature in K. $[M(C_yN_{1-y})_s]$ is the activity of the carbonitride, and is taken as unity.

$$\text{Hence, } \Delta G_{M(C_yN_{1-y})_s} = RT \ln \{ [M].[C]^y.[N]^{s(1-y)} \}$$

Assuming the compound $M(C_yN_{1-y})_s$ to be an ideal solution of MC_s and MN_s , the free energy of formation of the carbonitride can be written as^[12]:

$$\Delta G_{M(C,N)(1-y)s} = y \Delta G_{MCs}^0 + (1-y) \Delta G_{MNs}^0 + sRT [y \ln y + (1-y) \ln (1-y)] \quad \dots (2)$$

Combining equations (1) and (2), we get,

$$RT \ln \{ [M] \cdot [C]^{sy} \cdot [N]^{s(1-y)} \} = RT \{ y \ln K_{MCs} + (1-y) \ln K_{MNs} + s[y \ln y + (1-y) \ln (1-y)] \} \quad \dots (3)$$

$$[M] \cdot [C]^{sy} \cdot [N]^{s(1-y)} = (K_{MCs})^y \cdot (K_{MNs})^{(1-y)} \cdot y^{ys} \cdot (1-y)^{(1-y)s} \quad \dots (4)$$

where, K_{MCs} and K_{MNs} are the solubility products in austenite for carbides and nitrides, respectively. The equation (4) can be assumed to be a combination of two different equations for carbides and nitrides separately as follows:

$$y^{ys} \cdot (K_{MCs})^y = [M]^y \cdot [C]^{ys} \quad \dots (5)$$

$$(1-y)^{(1-y)s} \cdot (K_{MNs})^{(1-y)} = [M]^{(1-y)} \cdot [N]^{(1-y)s} \quad \dots (6)$$

It may be noted that the product of above two equations results in equation (4). After simplification of equations (5) and (6), respectively, we get,

$$K_{MCs} = [M] \cdot [C]^s / y^s \quad \dots (7)$$

$$K_{MNs} = [M] \cdot [N]^s / (1-y)^s \quad \dots (8)$$

Solubility product relationship for AlN in austenite can be expressed as,

$$K_{AlN} = [Al] \cdot [N] \quad \dots (9)$$

>From the mass balance of carbon and nitrogen, following equations can be derived:

$$[C] = C_T - [(M_T - [M]) \cdot y \cdot s \cdot A_C / A_M] \quad \dots (10)$$

$$[N] = N_T - [(M_T - [M]) \cdot (1-y) \cdot s \cdot [A_N / A_M]] - [(Al_T - [Al]) \cdot A_N / A_{Al}] \quad \dots (11)$$

where, A_M , A_C and A_N are the atomic weight of M, C and N, respectively. Al_T , $[Al]$ and A_{Al} denote the total amount (in wt. %) of Al in steel, Al in solid solution and atomic weight of Al, respectively. C_T , N_T and M_T are total amount of C, N and microalloying element M in steel, respectively. Now the equations (7) to (11) can be solved and the solubility of M, C, N and Al and the value of y can be evaluated.

3. Results and Discussions

Comparison of the Present Results with Literature Data

The solubility product relationships used in the present calculations were taken from literature [10,12,13,19] and the predictions of solubility of Nb(C,N) were made for some steels reported by Hudd *et al.* [11]; the compositions of these steels are given in Table 1. The predicted solubility of non-stoichiometric precipitates ($s = 0.87$) at various temperatures is shown in Table 1. In the present calculation, the solubility of stoichiometric precipitates was estimated by putting the value of non-stoichiometric factor ' s ' = 1 and using solubility product relationships for stoichiometric carbide and nitride from literature [11]. The solubility predicted by the present analysis is shown in Table 1 and it has been compared with those from Hudd *et al.* [11]. It may be seen that the present results match well with that of the Hudd *et al.* and with the experimental values reported in literature [11]. In the case of non-stoichiometric precipitates, it is observed that the solubilities of niobium and nitrogen are higher than that for the stoichiometric compounds. The solubility of carbon is relatively insensitive to the stoichiometry of carbonitride. Eckstein *et al.* [20] have predicted the solubility of niobium carbonitride in an Al

killed steel. The solubility of niobium predicted in the present work is in good agreement with the earlier predictions.

Predictions for HSLA-100 Steels

The chemistry of the HSLA steels under present investigation is given in Table 2, which contain a significant amount of Al along with the Nb. It is expected that the precipitation of AlN will occur simultaneously along with the niobium carbonitrides in these steels. The solubility in these steels was first calculated ignoring the precipitation of AlN. Subsequently, the precipitation of AlN was factored into the calculation. The predicted results of the solubilities of niobium, nitrogen, carbon and the C/N ratio "y" for S1 steel are plotted as a function of temperature in Fig. 1(a)-(d). In all the cases, curve-I (factoring AlN precipitation) and curve-II (ignoring AlN precipitation) intersect at one or more points. Similar results were observed for all the three steels. The solution temperatures of AlN were computed by the method mentioned above as 1149, 1127 and 1070°C in S1, S2 and S3 steels, respectively. These values are found to be quite close to the intersection point, in the case of the solubility of nitrogen and niobium and "y". A similar result is noticed for the second intersection of the solubility curves of carbon. This is because, after the complete dissolution of AlN in the steel, the precipitation of niobium carbonitride is independent of the aluminium-content of the steel, if the interaction between aluminium and the alloying elements is ignored. The solution temperature of AlN, thus predicted was found to depend on the chemistry of steel.

When the precipitation of AlN is considered along with the carbonitrides, the solubility of niobium increases (Fig. 1(a)) whereas the solubility of nitrogen decreases (Fig. 1(b)). The decrease in the solubility of nitrogen is as expected since some nitrogen is removed from the solution by the concurrent precipitation of AlN and further due to this, lower amount of niobium is combining as carbonitride, resulting into more of Nb in solution. In the case of carbon, the curves I and II meet at two points which have designated as point "Y" and point "X" (Fig. 1(c)). The significance of point X is described above as the solution temperature of AlN. The first intersection point Y appears to be also related with the precipitation of aluminium nitride. When the temperature is low, more nitrogen is consumed for the formation of aluminium nitride and leaving less nitrogen for carbonitride precipitation and hence more of carbon is consumed for carbonitride precipitation as indicated by the lower solubility of carbon (curve II) than that of without considering the AlN precipitation (Fig. 1(c)). It means when nitrogen is fixed as AlN, the niobium carbonitride contains more of carbon.

As the temperature increases, the AlN dissolves in the steel resulting into more of nitrogen available for the formation of niobium carbonitride. Hence less of carbon combines with the niobium showing an increase in the solubility of carbon in Fig. 1 (c), curve I and the carbon/nitrogen ratio (y) in the carbonitride decreases as the temperature increases. This also indicates that the AlN dissolves faster than niobium carbonitride with increase in temperature. When the precipitation of AlN is not considered, the carbon/nitrogen ratio of the niobium carbonitride increases with temperature, initially. Later, it almost becomes constant and hence, the trend in the solubility of carbon is somewhat different (Fig. 1 (c), curve II). The change in the slope of this curve causes this to intersect the curve I at two points since the curve I is monotonous in nature.

The precipitation of AlN therefore, influences the solubility of niobium, carbon and nitrogen as discussed above. The temperature of dissolution of niobium carbonitride is also influenced by the presence of aluminium in the steel. This would significantly influence the optimum alloying

When the formation of non-stoichiometric carbonitrides was considered, the solution temperatures were found to be significantly lower i.e. 1100, 1096 and 1120 °C for these steels, respectively. The change in the temperature was not significant when the precipitation of AlN was taken into consideration. For a similar steel, the solubility has been predicted elsewhere on the basis of successive partial equilibration^[2]. It is observed that the predicted solubilities by both the methods are comparable; further the solution temperature of niobium carbonitrides predicted by the present method is in good agreement with that computed by the method of successive partial equilibration.

4. Conclusions

A simple analytical approach has been presented to predict the equilibrium solubility of stoichiometric as well as non-stoichiometric carbonitrides in steels using solubility product data and formulating the mass balance equations. The solubility predicted by the present method agrees well with that reported in the literature. The solubilities of Nb, C, nitrogen and niobium carbonitride in HSLA steels are remarkably influenced by the presence of AlN. The solution temperatures of AlN and Nb(C,N) in the HSLA steels were found to be a function of alloy chemistry.

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Table 2 Chemical Compositions of HSLA Steels (in wt.%)

Steel	C	Mo	Cr	Mn	Cu	Ni	Nb	Al	Ti	N	Si
S1	0.038	0.57	0.54	0.87	1.98	3.39	0.032	0.038	0.003	0.0145	0.23
S2	0.04	0.60	0.57	0.86	1.58	3.55	0.03	0.032	0.003	0.0145	0.27
S3	0.044	0.60	0.58	0.95	1.23	1.65	0.037	0.023	0.003	0.0142	0.34

Table 1 A Comparison of the Present Results of Solubility Predictions in Austenite with the Values Reported by Hudd et al. [11]

Temp. °C	Composition, wt %			Predicted wt.%[10] Nb	Value of γ and solubility (in wt. %) predicted by present model (Stoichiometric)			Value of γ and solubility (in wt. %) predicted by present model (Non-stoichiometric)			Expt. Data [after 10:1] Nb
	C	N	Nb		C	N	Nb	C	N	Nb	
900	0.22	0.005	0.035	0.001	0.216	0.00378	0.00127	0.216	0.0045	0.00225	0.005
900	0.20	0.0039	0.11	0.002	0.187	0.00169	0.00170	0.187	0.0027	0.00331	0.010
900	0.026	0.0065	0.105	0.012	0.0188	0.00075	0.0113	0.0191	0.0020	0.022	0.015
1000	0.026	0.0065	0.105	0.032	0.0206	0.00147	0.0306	0.022	0.0033	0.053	—
1200	0.074	0.036	0.329	0.055	0.0584	0.0128	0.0546	0.059	0.0173	0.09	0.109
1000	0.004	0.0170	0.094	0.016	0.0035	0.00587	0.0162	0.0035	0.0096	0.041	—

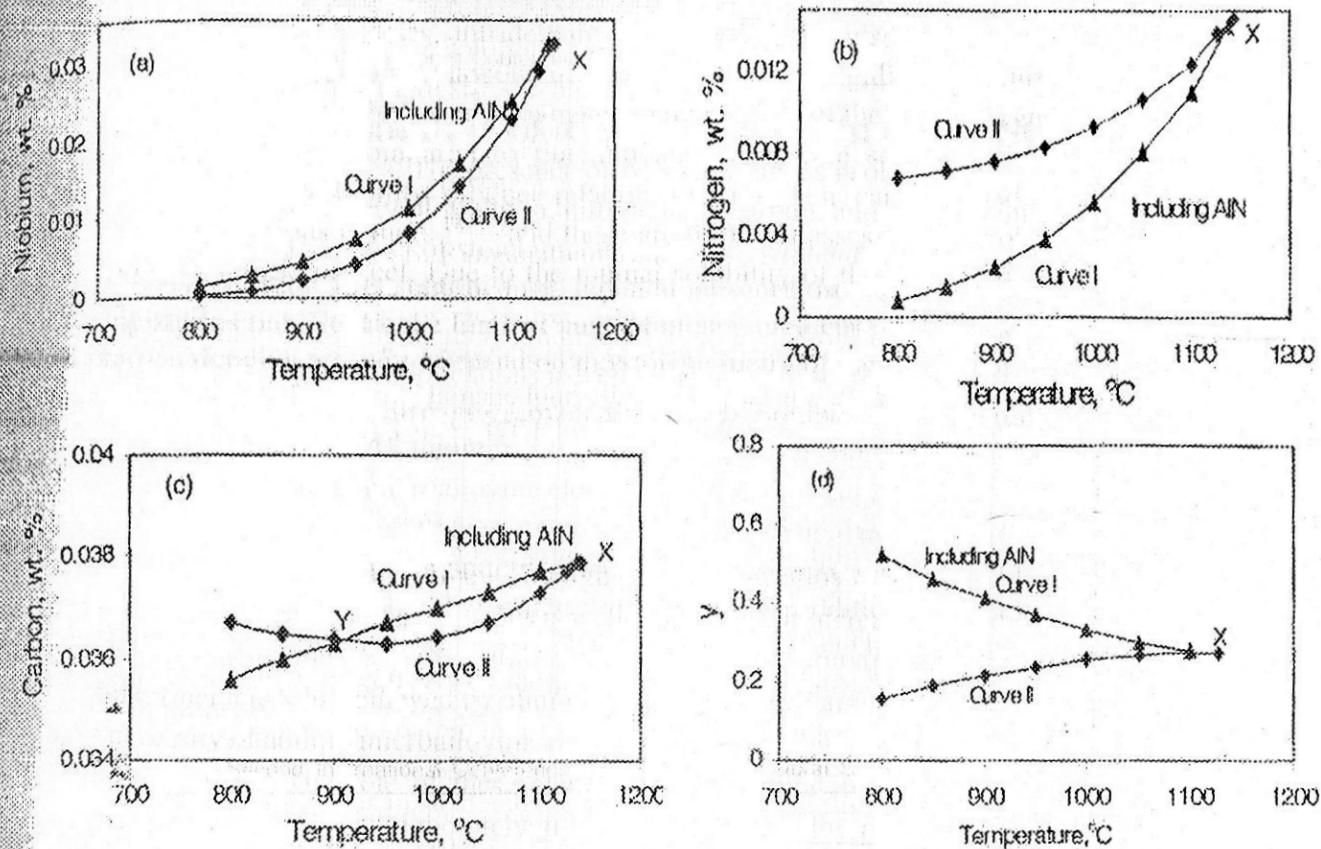


Fig. 1 Predicted Solubility of (a) Nb (b) Nitrogen (c) Carbon and Value of "y" as Function of Temperature with and without Consideration of AlN Precipitation in S1 Steel