Solubility of Titanium Carbosulfide in Austenite

Luana E. IORIO and Warren M. GARRISON, Jr.1)

GE Corporate Research and Development, P. O. Box 8, Schenectady, NY 12309 USA.
1) Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA 15213 USA.

(Received on November 26, 2001; accepted in final form on January 25, 2002)

A titanium carbosulfide solubility product of log \([\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5} = -14.646/7 + 5.51\) and a Gibbs free energy of formation for titanium carbosulfide of \(\Delta^\circ G_{\text{Ti}_2\text{CS}} = -1121.9 + 0.1967 \text{ kJ/mol}\) were calculated from dissolution temperature experiments using a series of titanium-modified secondary hardening ultra-high strength steels.

The presence of other precipitates such as TiN, TiC and TiS could be neglected for this class of steels. The effect of the alloying additions on the activity of carbon and hence on the dissolution temperature of titanium carbosulfide was also found to not be significant for these steels. The experimentally determined solubility product and Gibbs free energy of formation are compared with previously published data for titanium carbosulfide.

KEY WORDS: titanium carbosulfide; solubility product; Gibbs free energy of formation; secondary hardening; ultra-high strength steels.

1. Introduction and Background

In recent years there has been significant interest in the effects of titanium carbosulfides on the mechanical properties of various steels. In ultra-low carbon and interstitial-free steels, titanium carbosulfide plays an important role in the stabilization of carbon and the presence of titanium carbosulfide has been shown to lead to lower recrystallization temperatures, improved texture and \(r\)-values.\(^1\)–\(^3\) Garrison and coworkers\(^4\)–\(^5\) have found that in ultra-high strength secondary hardening steels such as HY180 and AF1410, replacing MnS particles with Ti\(_2\)CS particles resulted in marked improvements in the fracture toughnesses of these steels.

Optimizing steel properties through the use of titanium carbosulfides requires an understanding of the factors controlling the formation of this phase and hence solubility data for titanium carbosulfide in austenite is essential.

In an effort to understand and predict titanium carbosulfide precipitation, several researchers\(^2\)–\(^6\)–\(^11\) have studied and estimated the solubility product and Gibbs free energy of formation of this phase.

The first estimation of the Gibbs free energy of formation for Ti\(_2\)CS was made by Liu and Jonas\(^8\) and was calculated by assuming that Ti\(_2\)CS is an ideal solution of TiC and TiS in order to calculate the temperature dependent entropy term and by using the sulfur partition coefficients calculated by Liu \textit{et al.}\(^6\) From these coefficients, the Gibbs free energy at a particular temperature can be estimated, assuming a limited mutual solubility between MnS and Ti\(_2\)CS, \(\Delta^\circ G_{\text{Ti}_2\text{CS}} = -1194.5 + 0.2317 \text{ kJ/mol}\).

Liu \textit{et al.}\(^6\) calculated the solubility product of Ti\(_2\)CS to be log \([\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5} = -15.600/7 + 6.50\). Liu \textit{et al.}\(^8\) followed up this work with new estimates for the Gibbs free energies of formation for TiS and Ti\(_2\)CS, made using the thermodynamic equilibrium data of a Fe–C–Ti–S system studied by Swisher\(^12\) and by assuming that TiS and Ti\(_2\)CS form an ideal solution. Their reevaluated free energy is \(\Delta^\circ G_{\text{Ti}_2\text{CS}} = -1171 + 0.2307 \text{ kJ/mol}\). Using this new Gibbs free energy of formation, the solubility product was calculated to be log \([\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5} = -15.310/7 + 6.03\). The solubility product calculation was made ignoring interaction parameters, as the steels under consideration were very low alloy steels.

Liu \textit{et al.}\(^11\) built on this work by developing a model capable of predicting the mole fractions of five precipitates; AlN, MnS, (Nb,Ti,V)(C,N), Ti\(_2\)CS and TiS taking into account the effects of thirteen alloying elements. The Gibbs free energy of formation of Ti\(_2\)CS used in this case was \(-1187 + 0.2307 \text{ kJ/mol}\).

Subramanian \textit{et al.}\(^2\) performed diffusion stack experiments as well as dissolution experiments on two IF steels to determine the solubility product of TiS. These workers considered the TiS solubility product obtained from the dissolution experiments to be a more realistic and reliable value compared to that obtained from the dissolution experiments. Using this solubility product and a regular solution model, it was possible to calculate dissolution temperatures for Ti\(_2\)CS and these were found to be in good agreement with those experimentally observed.

Yoshinaga \textit{et al.}\(^7\) studied a series of titanium-modified ultra-low carbon steels in order to determine the effects of

\[^{*1}\] The reference state for all the Gibbs free energies of formation reported is infinite dilute solution in austenite.
varying titanium and sulfur levels on the precipitation of sulfides in these steels. Solubility products for TiS and Ti₂CS in austenite were calculated using data obtained from precipitate residues extracted from the steels. The solubility products obtained are log [Ti][C]₀.₅[S]₀.₅ = −5208/T − 0.78 and log [Ti][S] = −3.252/T − 2.01. These products differ significantly from those previously obtained by other researchers.

In response to this large discrepancy in solubility products, Liu and Jonas⁷) reevaluated their data and Gibbs free energies of formation and were able to reconcile their treatment of the data of Swisher⁷) with that of Yoshinaga et al.⁷) by assuming that TiS and Ti₂CS precipitate as mutually insoluble particles, whereas previously an ideal solution of the two phases was assumed. Using the solubility products of Yoshinaga et al.,⁷) Liu and Jonas⁷) calculated the following Gibbs free energy values for titanium carbosulfide; ΔG_{T_i,C,S}^{\delta} = −398.4 − 0.310T kJ/mol.

More recent solubility product data for Ti₂CS was published by Yang et al.⁸) log [Ti][C]₀.₅[S]₀.₅ = −7.945/T + 7.9. This value was calculated from dissolution experiments done on ultra-low carbon steels of varying titanium and sulfur levels. These results agree more closely with those obtained prior to the work of Yoshinaga et al.⁷) than with Yoshinaga’s work. The Gibbs free energy of formation calculated from this solubility product is ΔG_{T_i,C,S}^{\delta} = −304.3 + 0.338T kJ/mol.

Yang et al.⁸) compared the experimental results of several research groups⁶,⁷,⁸) with the mole fraction of precipitates predicted using their solubility products and those of Yoshinaga et al.⁷) Both sets of solubility products produced results which did not always agree with the experimental results and thus at this point it is difficult to access which solubility products should be preferred. The spread in solubility products calculated thus far can be seen in Fig. 1.

The thermodynamic properties reviewed above were all determined from data obtained using very low alloy steels. In the low alloy steels previously studied, the interaction parameters of the various alloying elements and impurities can be fairly safely neglected when calculating the Gibbs free energy of formation from the solubility product of titanium carbosulfide. The objectives of this work are to determine a solubility product and a Gibbs free energy of formation of titanium carbosulfide. However, the class of steels considered in this work is highly alloyed and the effects of these alloying additions, particularly on the activity of carbon should be determined and the importance of these effects assessed. The need to consider the possibility of formation of TiN, TiC and TiS is also discussed.

2. Experimental Procedure

Six heats of titanium-modified ultra-high strength steels were used in this study. Five heats with the nominal AF1410 composition of 14 wt% cobalt, 10 wt% nickel, 2 wt% chromium and 1 wt% molybdenum were made and examined along with a commercially-produced heat of HY180. HY180 has a nominal composition of 8 wt% cobalt, 10 wt% nickel, 2 wt% chromium and 1 wt% molybdenum. The compositions of the heats studied are given in Table 1. The heats were made by VIM-VAR processing and all have 0.01 wt% manganese and 0.01 wt% silicon except for the HY180 steel which has 0.04 wt% manganese and 0.05 wt% silicon.

Heats 811, 812 and 813 were given solutionizing treatments at 1300, 1345 and 1390°C for one hour followed by water quenching. G618 and G784-1 heats were given solutionizing treatments at two temperatures; 1250 and 1300°C for one hour followed by water quenching. The HY180 steel was solutionized at 1350°C for one hour followed by water quenching. Polished cross-sections from these specimens were examined by scanning electron microscopy to determine the extent of sulfide dissolution. Carbon extraction replicas were also made from lightly etched polished cross-sections of the steels for transmission electron microscope examination to further assess the extent of sulfide dissolution.

3. Experimental Results

3.1. Examination of Precipitates in the Steels

SEM and TEM examination of polished cross-sections of 811, 812 and 813 solutionized at 1300, 1345 and 1390°C revealed that a temperature of 1300°C was insufficient to dissolve all of the titanium carbosulfides in all three of the heats examined, while no sulfur-rich particles were observed in any of the heats after solutionizing at a temperature of 1390°C. No titanium carbosulfides were observed in any of the heats after solutionizing at 1300, 1345 and 1390°C for one hour followed by water quenching. The HY180 steel was solutionized at 1350°C for one hour followed by water quenching. Polished cross-sections from these specimens were examined by scanning electron microscopy to determine the extent of sulfide dissolution. Carbon extraction replicas were also made from lightly etched polished cross-sections of the steels for transmission electron microscope examination to further assess the extent of sulfide dissolution.
temperature for heat 813 is slightly higher than 1345°C, but less than 1390°C.

After a heat treatment of 1250°C for an hour, examination of polished cross-sections of heats G618 and G784-1 by SEM revealed that titanium carbosulfide particles remained in both steels. A solutionizing treatment of 1300°C for an hour was sufficient to completely dissolve all sulfur-rich particles in G618 and G784-1 as extensive examination of polished cross-sections by SEM and TEM failed to reveal any sulfur-rich particles. The dissolution temperature of titanium carbosulfide for both G618 and G784-1 can hence be estimated to lie between 1250 and 1300°C.

SEM examination of the HY180 specimen revealed that the dissolution temperature for this heat was greater than 1350°C.

3.2. Determination of Titanium Carbosulfide Solubility Product

The experimentally observed dissolution temperatures were used to estimate a solubility product of Ti2CS, which in turn can be used to estimate a Gibbs free energy of formation.

Table 2 shows the temperature ranges over which titanium carbosulfide dissolved in the steels studied in this work. Also listed in Table 2 are the sulfur, carbon and titanium contents of these heats. These contents were used to calculate the given \( \log([\text{Ti}]_0[\text{C}]^{0.5}[\text{S}]^{0.5}) \) values. This information is shown graphically in Fig. 2 along with a solubility curve, which represents a linear best fit curve calculated using the average temperature values of \( T_{\text{low}} \) and \( T_{\text{high}} \). This gives the following solubility product for titanium carbosulfide;

\[
\log ([\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5}) = -14.65 + 5.51.
\]

The calculated solubility product can be used to estimate the Gibbs free energy of titanium carbosulfide, which is calculated to be \( 
\Delta^0 G_{\text{Ti}_2\text{CS}} = -1121.9 + 0.1967 \text{ kJ/mol.}
\)

4. Discussion

Before the calculated solubility product can be compared with the solubility products in the literature, several factors need to be considered. Firstly, it is necessary to determine the extent to which the presence of other precipitates containing titanium, carbon or sulfur, such as TiN, TiC and TiS may effect the solubility products calculated from dissolution temperatures. Secondly, the previously determined thermodynamic properties were all established from data obtained using very low alloy steels. In these steels the interaction parameters of the various alloying elements and impurities can be safely neglected when calculating the solubility product and the Gibbs free energy of formation of titanium carbosulfide. However, the class of steels considered in this work is highly alloyed and the effects of these alloying additions, particularly on the activity of carbon should be determined.

4.1. Influence of Other Precipitates

Three phases, other than Ti2CS, are considered; TiN, TiC and TiS, since these phases will alter the amounts of titanium, carbon and sulfur found in solution in the steel.

The solubility of TiN, \( \log [\text{Ti}][\text{N}] = -14.400/T + 4.96 \), is taken from the work of Wada and Pehlke.16) This solubility product is valid over the temperature range 1000 to 1290°C. The dissolution temperature of TiN in an Fe–0.02Ti–0.0003N alloy is calculated to be 1140°C. To getter 3 wt ppm nitrogen as TiN will require 0.001 wt% titanium which is approximately 5% of the titanium typically found in the steels being studied.

Given the low nitrogen levels in the steels used in this work, less than 5 wt ppm, the relatively low dissolution temperature of TiN at these nitrogen levels, compared to the observed dissolution temperatures for titanium carbosulfide and the possibility of TiN altering the titanium level by a maximum of 5%, it seems appropriate to ignore the presence of TiN.

The titanium carbide solubility products given by Narita17) and Irvine et al.18) both predict a dissolution temperature of less than 1000°C for a Fe–0.01Ti–0.16C alloy. For a Fe–0.02Ti–0.25C alloy the dissolution temperature rises to 1110°C. Thus it is assumed that the extent of precipitation of titanium carbosulfide is unaffected by formation of titanium carbide since the carbide precipitates at lower temperatures.

Most of the reported work on Ti2CS has been done in steels with carbon levels of less than 0.02 wt%. Carbon level is a critical factor in determining the equilibrium between titanium carbosulfide and titanium sulfide. Yoshinaga et al.7) observed that an increase in carbon level from 0.00025 to 0.0036 wt% is sufficient to significantly alter the proportions of TiS and Ti2CS in an interstitial-free steel. The Ti2CS phase becomes more predominant as the carbon level increases. Hua et al.19) observe that the change in carbon level from high strength low alloy steels (~0.04 to 0.10 wt% C) to ultra-low carbon steels (~0.003 wt% C) is sufficiently large to have a substantial effect on the precipi-

| Heat     | \( T_{\text{low}} \) (°C) | \( T_{\text{high}} \) (°C) | \( \log([\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5}) \) | Ti | C | S |
|----------|--------------------------|--------------------------|---------------------------------|----|---|---|
| B11      | 1300                     | 1345                     | -3.60                           | 0.020 | 0.16 | 0.0010 |
| B12      | 1300                     | 1345                     | -3.60                           | 0.020 | 0.20 | 0.0008 |
| B13      | 1345                     | 1390                     | -3.50                           | 0.020 | 0.25 | 0.0010 |
| G618     | 1250                     | 1300                     | -3.94                           | 0.018 | 0.16 | 0.0005 |
| G784-1   | 1250                     | 1300                     | -4.05                           | 0.009 | 0.20 | 0.0005 |
| HY180    | 1350                     | NA                       | -3.33                           | 0.020 | 0.11 | 0.005  |

Fig. 2. Solubility curve from dissolution data.
tation sequence of titanium sulfides and titanium carbosulfides in these steels. To determine the compositional and temperature ranges where TiS and Ti₂CS are simultaneously present, the following calculations were performed. Using the solubility product equations of TiS and Ti₂CS found by Yang et al.⁹¹ and mass balance equations for carbon, sulfur and titanium shown below, the temperature range over which TiS and Ti₂CS coexist in steels of various compositions was determined.

\[
\log [Ti][C]^{0.5}[S]^{0.5} = -17,045/T + 7.9
\]
\[
\log [Ti][S] = -13,975/T + 5.43
\]
\[
[Ti] = \%Ti - M_{Ti} \left( \frac{f_{TiS}}{M_{TiS}} + \frac{2f_{Ti₂CS}}{M_{Ti₂CS}} \right)
\]
\[
[S] = \%S - M_{S} \left( \frac{f_{TiS}}{M_{TiS}} + \frac{f_{Ti₂CS}}{M_{Ti₂CS}} \right)
\]
\[
[C] = \%C - M_{C} \left( \frac{f_{Ti₂CS}}{M_{Ti₂CS}} \right)
\]

Where \(\%X\) is the weight percent of X in the steel, \(M_X\) is the atomic weight of element X and \(M_{AB}\) and \(f_{AB}\) are the molecular weight of compound AB and the mass of AB precipitated in the steel respectively.

The temperature range over which both phases coexisted was determined by calculating the temperatures for which both \(f_{TiS}\) and \(f_{Ti₂CS}\) were non-zero for given \(\%Ti\), \(\%S\) and \(\%C\) levels. For a steel with 0.01 wt% titanium and a sulfur level of 50 ppm, the carbon should not exceed 0.02 wt% if TiS and Ti₂CS will exist if the carbon level exceeds 0.02 wt%. For the same titanium level and a sulfur level of 10 wtppm, only Ti₂CS will exist if the carbon level exceeds 0.003 wt%. For the same titanium level and a sulfur level of 5 wtppm, TiS and Ti₂CS are only present simultaneously if the carbon content is less than 10 wtppm. Thus, it can be concluded that at the carbon levels of interest in this work, 0.11 to 0.25 wt%, TiS will not form.

Since TiS will not form in the steels studied, only a negligible amount of TiN will form due to the low nitrogen levels and TiC is not expected to precipitate above 1100°C, these phases can safely be ignored in the calculation of a solubility product of titanium carbosulfide. These thermodynamic predictions are consistent with microstructural observations of these steels.

4.2. Effect of Alloying Additions on Carbon Activity and Gibbs Free Energy

The activity of carbon in austenite for Fe–C binary alloys is represented by the following equation²⁰:

\[
a_{C} = \frac{X_{C}}{1 - 5X_{C}} \quad \text{(1)*²}
\]

\(X_{C}\) is the atomic fraction of carbon. The effect of nickel, cobalt, chromium and molybdenum on the activity of carbon can be determined by adding several terms to the Eq. (1).

From the work of Greenbank²¹ the effect of nickel on the activity of carbon is given by adding the following expression to Eq. (1):

\[
0.914 + \left( \frac{1006}{T} \right) X_{Ni} + \left( \frac{2831}{T} \right) X_{Ni}^2
\]

This expression was obtained for data taken at temperatures between 750 to 1120°C and for nickel contents ranging from 0 to 40 wt%.

Several papers²²–²⁷ discuss the influence of cobalt on the carbon activity. In this work, the interaction expression suggested by Williams and Bodsworth²² is used;

\[
0.92X_{Co} \quad \text{(3)}
\]

This factor was obtained from studies of Fe–Co–C alloys with cobalt levels ranging from 2.7 to 10.4 wt% and carbon levels of up to 1.6 wt% at 850, 925 and 1050°C.

From the work of Greenbank,²⁸ the following interaction expression is used to include the influence of chromium on the activity of carbon;

\[
\left( 9.88 - \frac{18150}{T} \right) X_{Cr} \quad \text{(4)}
\]

This expression was obtained from studies of Fe–Cr–C alloys with 4.35 to 14.3 wt% chromium at temperatures between 900 and 1125°C.

Finally the effect of molybdenum is considered using the expression taken from the work of Greenbank²⁸ on a series of alloys containing 0 to 6.7 wt% molybdenum at temperatures ranging from 975 to 1125°C.

\[
7.83 - \frac{15930}{T} X_{Mo} \quad \text{(5)}
\]

Greenbank²⁹ found that for (at%Ni+at%Cr)<35%, the individual nickel and chromium factors could be used and that no cross-products were necessary in determining the carbon activity in the system. Since the total alloying element content in the steels of interest in this study is less than 35 at%, it is presumed that the four interaction expressions chosen above can simply be added to Eq. (1), producing the following equation for the activity of carbon in an Fe–Ni–Co–Cr–Mo–C alloy;

\[
a_{C}= \frac{X_{C}}{1 - 5X_{C}} \left[ 0.914 + \left( \frac{1006}{T} \right) X_{Ni} + \left( \frac{2831}{T} \right) X_{Ni}^2 + \left( 9.88 - \frac{18150}{T} \right) X_{Cr} \right] + 0.92X_{Co} + \left( 7.83 - \frac{15930}{T} \right) X_{Mo} \quad \text{(6)}
\]

\(X_i\) is the atomic fraction of element \(i\) and \(T\) is the tempera-

*² Unless specifically stated, all the activity data presented is with respect to the Henrian or infinitely dilute standard state.
ture in Kelvin.

The solubility product and Gibbs free energy of formation of titanium carbosulfide can be related to each other using the following formula:

$$\Delta^\circ G_{Ti,C,S} = -RT \ln \left( \frac{a_{Ti,C,S}}{a_i^{\circ} a_j^{\circ} a_k^{\circ}} \right)$$

In order to convert Eq. (7) into a solubility product equation two assumptions are initially made. Firstly the titanium carbosulfide is assumed to precipitate as a pure phase and hence its activity will be regarded as one. Secondly the activity coefficients for carbon, sulfur and titanium are taken to be one, i.e. the self-interaction parameters as well as the interaction parameters with alloying elements are ignored.

Since it is standard to present solubility products in terms of wt%, the activities need to be converted to the 1 wt% standard state by the conversion formula, $a_i^{\circ} = M_i/\{100M_i\}$, where $M_i$ is the molar mass of element $i$ and $[i]$ is the wt% of element $i$ in solution. This leads to the following equation for the solubility product;

$$\log [Ti][C]^{0.5}[S]^{0.5} = \frac{1}{2.3} \left( \frac{-\Delta^\circ G}{4RT} - \ln \left( \frac{M_i^{1.5}}{100^2 M_{Ti} M_C M_S^{0.5}} \right) \right)$$

The assumption that the activity coefficients for carbon, sulfur and titanium can be taken to be one is no longer possible to directly quote a solubility product since Eq. (6) is used for the carbon activity term in Eq. (9), terms of wt%, the activities need to be converted to the standard state by the conversion formula, $a_i^{\circ} = M_i/\{100M_i\}$. Hence its activity will be regarded as one. Secondly the activities will still be taken to be one as the required interaction parameters are not available in the literature. The assumption appears reasonable in view of the low levels of both of these elements in the steels considered. When this is done, the following equation is obtained:

$$\log [Ti][C]^{0.5}[S]^{0.5} = \frac{1}{2.3} \left( \frac{-\Delta^\circ G}{4RT} - \ln \left( \frac{M_i^{1.5}}{100^2 M_{Ti} M_C M_S^{0.5}} \right) \right)$$

The term [C] in Eq. (8) has been replaced with the term $a_i([C], T)$ in Eq. (9), $a_i([C], T)$ is calculated using Eq. (6). Since Eq. (6) is used for the activity term in Eq. (9), it is no longer possible to directly quote a solubility product as [C] cannot be isolated. Instead solubility limit plots of temperature versus carbon content at fixed titanium and sulfur levels are used. These plots are similar to those of manganese sulfide published by O’Brien et al. using the equations developed by Turkdogan et al.

A titanium carbosulfide solubility limit plot is given in Fig. 3, which shows the solubility limit of titanium carbosulfide in an AF1410 steel with 0.01 wt% titanium and a sulfur level of 5 ppm for the case where the interaction effects of the alloying elements are considered, (a), and for the case where they are neglected, (b).

Including the effects of the cobalt, nickel, chromium and molybdenum additions increases the dissolution tempera-

![Fig. 3. Calculated solubility limits for Ti2CS in austenite. a) Limit using carbon activity given by Eq. (6), b) limit using Eq. (8).](image)

![Fig. 4. Comparison of solubility products.](image)
5. Conclusions

Dissolution temperature experiments were used to calculate a solubility product of titanium carbosulfide of log [Ti][C]^{0.5}[S]^{0.5} = −14646/T + 5.51 and a Gibbs free energy of formation for titanium carbosulfide of \( \Delta^o G_{Ti4C2S2} = -1219.9 + 0.1967 \) kJ/mol.

It was determined that, for the class of steels investigated, the presence of other precipitates such as TiN, TiC and TiS could be neglected. The effect of the alloying additions, nickel, cobalt, chromium and molybdenum on the activity of carbon and hence on the dissolution temperature of titanium carbosulfide was found not to be significant in this class of steels.

The results of this work agree most closely with the data of Liu et al., however, the reason for this agreement is not clear.

Acknowledgements

This work was funded by the National Science Foundation of the United States of America under DMR-9712620.

REFERENCES

1) K. Kawasaki, S. Sanagi, T. Semuma, S. Akamatsu, N. Yosihaga and O. Akisue: *Tetsu-to-Hagané*, 79 (1993), 76.
2) S. V. Subramanian, M. Prikey, A. Ulhabaj and K. Balasubramanian: Interstitial Free Steel Sheet: Processing, Fabrication and Properties, ed. by L. E. Collins and D. L. Baragar, Canadian Institute of Mining, Metallurgy and Petroleum, Ottawa, Canada, (1991), 15.
3) M. Morita, K. Sat0 and Y. Hosoya: *ISIJ Int.*, 34 (1994), 92.
4) J. W. Bray, J. L. Maloney, K. S. Raghavan and W. M. Garrison, Jr.: *Metall. Trans. A*, 22 (1991), 2277.
5) J. L. Maloney and W. M. Garrison, Jr.: *Scr. Metall.*, 23 (1990), 2097.
6) W. J. Liu, S. Yue and J. J. Jonas: *Metall. Trans. A*, 20 (1989), 1907.
7) N. Yoshinaga, K. Ushioda, S. Akamatsu and O. Akisue: *ISIJ Int.*, 34 (1994), 24.
8) X. Yang, D. Vanderschuenen, J. Dilewijns, C. Standaert and Y. Houbaert: *ISIJ Int.*, 36 (1996), 1286.
9) W. J. Liu and J. J. Jonas: *Metall. Trans. A*, 20 (1989), 1361.
10) W. J. Liu, J. J. Jonas, D. Bouchard and C. W. Bale: *ISIJ Int.*, 30 (1990), 985.
11) W. J. Liu, J. J. Jonas and E. B. Hawbolt: Mathematical Modeling of Hot Rolling of Steel, Canadian Institute of Mining and Metallurgy, Hamilton, Canada, (1990), 457.
12) J. H. Swisher: *Trans. Metall. Soc. AIME*, 242 (1968), 2433.
13) W. J. Liu and J. J. Jonas: *ISIJ Int.*, 34 (1994), 761.
14) S. Sanagi, K. Kawasaki and T. Kawano: *CAMP-ISIJ*, 2 (1989), 2015.
15) A. Okamoto and N. Mizui: Metallurgy of Vacuum-Degassed Steel Products, ed. by R. Pradhan, TMS, Warrendale, PA, (1990), 161.
16) H. Wada and R. D. Pehlke: *Metall. Trans. B*, 16 (1985), 815.
17) K. Narita: *J. Chem. Soc. Jpn.*, 80 (1959), 266.
18) K. J. Irvine, F. B. Pickering and T. Gladman: *J. Iron Steel Inst.*, 205 (1967), 161.
19) M. Hua, C. I. Garcia and A. J. DeArdo: *Metall. Trans. A*, 28 (1997), 1769.
20) T. Ellis, I. M. Davidson and C. Bodsworth: *J. Iron Steel Inst.*, 201 (1963), 582.
21) J. C. Greenbank: *J. Iron Steel Inst.*, 209 (1971), 819.
22) R. Williams and C. Bodsworth: *J. Iron Steel Inst.*, 210 (1972), 106.
23) R. P. Smith: *Trans. Metall. Soc. AIME*, 233 (1965), 397.
24) V. K. Chandhok, J. P. Hirth and E. J. Duls: *Trans. Metall. Soc. AIME*, 224 (1962), 858.
25) B. Uhrenius: *Scand. J. Metall.*, 6 (1977), 83.
26) J. Chipman and E. F. Brush: *Trans. Metall. Soc. AIME*, 242 (1968), 35.
27) C. H. P. Lupis: Chemical Thermodynamics of Materials, Prentice-Hall, Upper Saddle River, NJ, (1983).
28) J. C. Greenbank: *J. Iron Steel Inst.*, 209 (1971), 986.
29) J. C. Greenbank: *J. Iron Steel Inst.*, 210 (1972), 111.
30) R. N. O’Brien, D. H. Jack and J. Nutting: *Proc. of 16th Int. Heat Treatment Conf.*, The Metals Society, London, (1977), 161.
31) E. T. Turkdogan, S. Ignatowicz and J. Pearson: *J. Iron Steel Inst.*, (1955), 349.