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A study of the characteristics of Ti(CN) solid solutions

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The activities of TiC and TiN in Ti(CN) solid solutions can be calculated by means of an integration method. In order to obtain accurate activities for a given set of data, two approaches were evaluated. A linear regression with one curve was found to be more proper than a two-curve approach. The activity exhibited a strong negative deviation from ideal solution behavior. The free energy of formation was obtained at given temperatures using the activity values. Isothermal curves of the free energy of formation with respect to composition had a minimum value near $\mathrm{Ti(C_{0.3}N_{0.7})}$ and $\mathrm{Ti(C_{0.6}N_{0.4})}$ at 1700 and 2100 K, respectively. The investigation shows that the Ti(CN) solid solution cannot be treated as a regular solution. Thus, a subregular solution model was introduced to describe the temperature dependence of free energy.

1. Introduction

Ti(CN)-based cermets have gained great attention from researchers as a potential replacement for WC in the cutting tool field. The positive effects of nitrogen in TiC systems have given rise to considerable research in the area of cermet design for purposes of improved performance. To date, only a few studies have reported on the behavior of Ti(CN) solid solutions, which have great potential in this area. Since the use of Ti(CN) have become common in cermet applications, the phase stability of Ti(CN) based on its nitrogen content during high temperature processing is clearly an important issue.

The activity coefficients of TiC and TiN in Ti(CN) solid solutions were calculated based on the equilibrium nitrogen pressures in forming Ti(CN). In this paper two approaches for obtaining accurate values for the activities of TiC and TiN in the Ti(CN) solid solutions were evaluated. The obtained activity values were used to calculate the free energy of formation of Ti(CN) and the behavior of the solution was tested via a regular solution model. In addition a subregular solution model was applied to this system, in order to predict the variation of the formation free energy with temperature.

2. Computations method

In the framework of a solid solution, composed of TiC and TiN, the activities of TiC and TiN can be expressed as the following equations through the Belton and Fruehan integration method [1]. The activity coefficients were calculated using the equilibrium nitrogen pressures at 1400–1500 and 1800 °C [2, 3]. A detailed procedure for calculation has been reported in other sources [4–6].

$$\begin{aligned}\log \gamma_{\mathrm{TiC}}|_{X_{\mathrm{TiC}}} &= \int_{X_{\mathrm{TiC}}=1}^{X_{\mathrm{TiC}}} X_{\mathrm{TiN}}\,\mathrm{d}\left[\log\left(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}}\right)\right]\\ \log \gamma_{\mathrm{TiN}}|_{X_{\mathrm{TiN}}} &= \int_{X_{\mathrm{TiN}}=1}^{X_{\mathrm{TiN}}} X_{\mathrm{TiC}}\,\mathrm{d}\left[\log\left(\frac{\gamma_{\mathrm{TiN}}}{\gamma_{\mathrm{TiC}}}\right)\right]\end{aligned} \tag{1}$$

For the integration of Equation 1, the value of $\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}}|_{X_{\mathrm{TiC}}=1}$ and $\frac{\gamma_{\mathrm{TiN}}}{\gamma_{\mathrm{TiC}}}|_{X_{\mathrm{TiN}}=1}$ is required as limits for the integration. Because no information for these values exists, it is necessary to estimate them from a plot of X_{TiC} versus $\log(\frac{\gamma_{\mathrm{TiN}}}{\gamma_{\mathrm{TiC}}})$.

3. Results and discussion

3.1. Approach using a single linear line

In this case a single linear curve was employed in order to determine $\log(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}})|_{\mathrm{at}\,X_{\mathrm{TiC}}=1,0}$. The curves for TiC and TiN are shown as linear, single curves in Figs 1 and 2. Using the data points, integrations, based on the regressed line and a pathwise integration from $\log(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}})|_{\mathrm{at}\,X_{\mathrm{TiC}}=1}$, were carried out to provide values for a_{TiC}. The same method was used for TiN and the final results are plotted in Fig. 3. Closed and dotted triangles and circles show the activities of TiC and TiN at 1700 and 2100 K, respectively. Solid and dotted curves correspond to the closed and dotted symbols.

It was apparent that all the results exhibit negative deviations from Raoultian. The activity coefficient of TiC observing the Henrian law, $\gamma^{\mathrm{o}}_{\mathrm{TiC}}$, is less than 0.2 at 1700 K and slightly larger at 2100 K. The curve for 2100 K is located above that for 1700 K for every composition. This trend is consistent with the fact that the solution behaves more like a Raoultian solution as temperature increases. The activity (coefficients)

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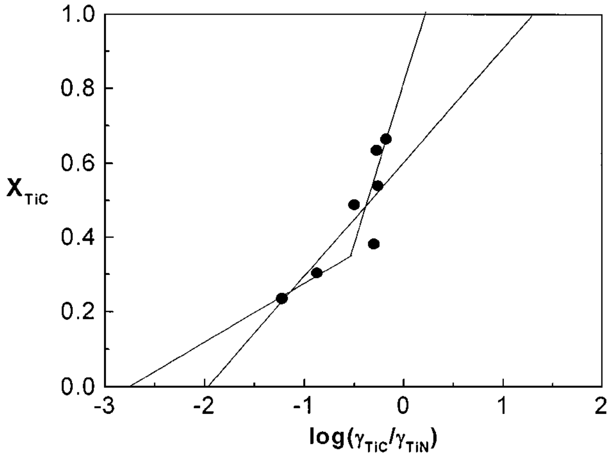

Figure 1 X_{TiC} Plotted as a function of $\log(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}})$ at 1700 K to obtain limits.

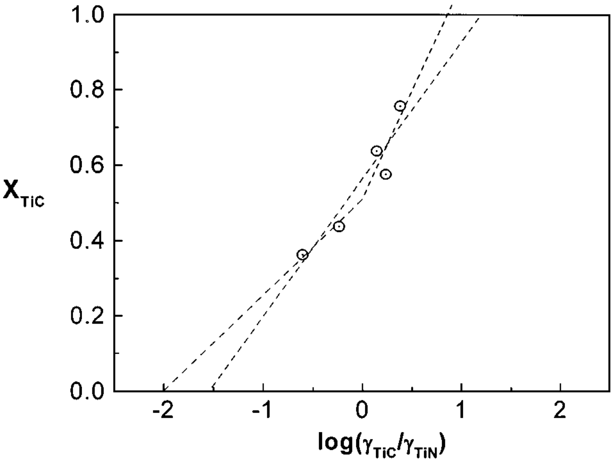

Figure 2 X_{TiC} Plotted as a function of $\log(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}})$ at 2100 K to obtain limits.

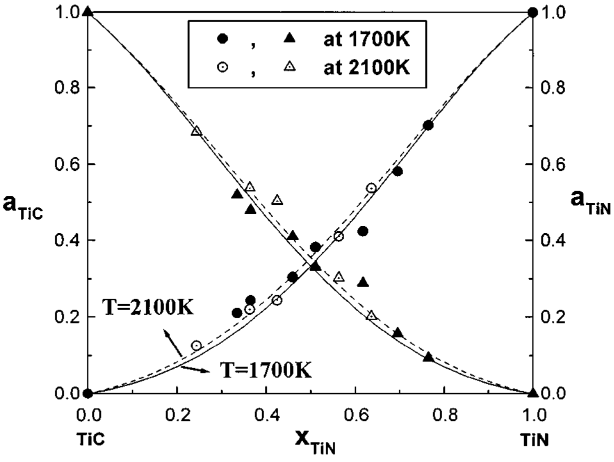

Figure 3 The activities of TiC and TiN in Ti(CN) at 1700 K and 2100 K.

approaches unity as the mole fraction of its component increases to unity.

3.2. Approach using double linear lines

In the previous approach, the calculation of activities relies on the assumption that X_{TiC} is a straight line with respect to $\log(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}})$. Darken [7] and Belton and Fruehan [1] suggested the existence of three regions in most A-B metallic solutions, i.e., two terminal regions having different slopes and one intermediate region, for a plot of X_{A} vs. $\log(\frac{\gamma_{\mathrm{A}}}{\gamma_{\mathrm{B}}})$. Therefore, an approach with two or three straight lines of different slopes was evaluated, in order to achieve more accurate activity values, which would be expected to provide a more precise initiation point for the integration.

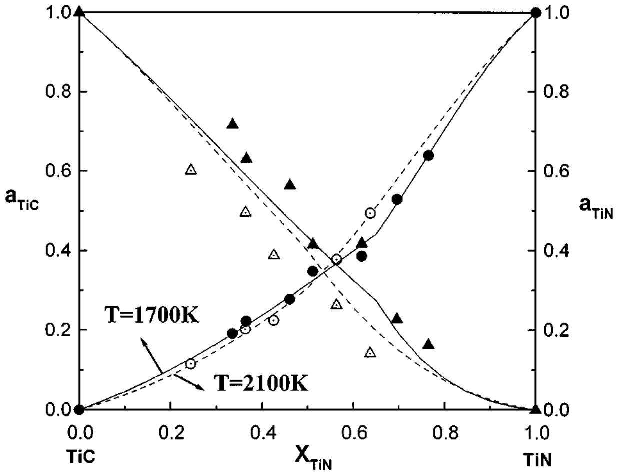

Figure 4 Activity curves plotted using double linear lines.

The composition range was divided into two regions in this study and a different linear curve was applied to each region. This was carried out using a small number of data points as shown in Figs 1 and 2 and thus, the applicability of this approach might be limited. Three-region approximations were performed. Two terminal regions of dilute solutions were approximated using straight lines and the intermediate region was estimated at the junction of the straight lines. The approximation using two straight lines was merged, as shown in Figs 1 and 2. In each figure, two lines were employed for the data of X_{TiC} vs. $\log(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}})$ to obtain a value for $\log(\frac{\gamma_{\mathrm{TiC}}}{\gamma_{\mathrm{TiN}}})$ at $X_{\mathrm{TiC}}=0$ and 1. The activity coefficients were obtained using the same procedure as was used in the single line approach. It was found, however, as can be seen in Fig. 4 that each curve not only has an abrupt point but also a cross-over between the curves for the two different temperatures. The abrupt points can be attributed to improper treatment of the transition regions, i.e., bridging one region with the other. Thus, a more sophisticated treatment will be required for the case of the abrupt point to provide a continuous smooth curve.

Based on the values in Figs 3 and 4, the approach involving a single line appears to be an acceptable method to calculate the free energy for the formation of Ti(CN) solid solutions in the present system.

3.3. Characterization of Ti(CN) solutions

Based on the TiC-TiN solution model, a value for the free energy of formation of Ti(CN) was obtained [8] using the following equations and the data from JANAF tables.

$$G^{\mathrm{M}} = X_{\mathrm{TiC}}\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{TiC}} + X_{\mathrm{TiN}}\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{TiN}} + \Delta G^{\mathrm{M}} \qquad (2)$$

where ΔG^{M}, the change in the free energy of mixing, is equal to $\mathrm{RT}\{X_{\mathrm{TiC}}\ln a_{\mathrm{TiC}} + X_{\mathrm{TiN}}\ln a_{\mathrm{TiN}}\}$. In Fig. 5,

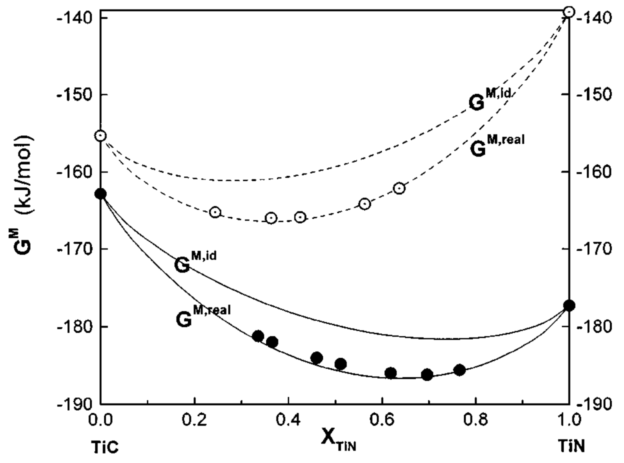

Figure 5 The Gibbs free energy of formation of Ti(CN) (kJ/mol); the minimum points of $G^{M,real}$ are at X_{TiN} ~0.7 and 0.4 for the temperature of 1700 and 2100 K, respectively.

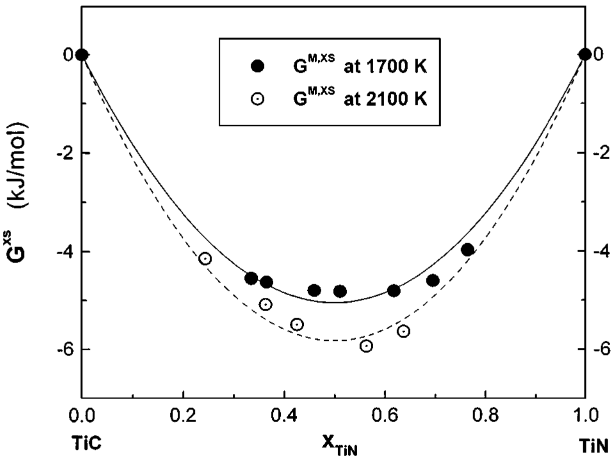

Figure 6 A plot for G^{xs} vs. X_{TiN}.

$G^{M,id}$ and $G^{M,real}$ represent the absolute free energy of formation based on ideal mixing of TiC with TiN, and by using the above derived activity coefficients. The G^M graphs of 1700 and 2100 K were drawn as a solid and dashed curve, respectively. The data in the figures are those calculated by means of pathwise integration.

Each curve for $G^{M,real}$ has a unique minima at certain compositions. At 1700 K this minimum is located in the nitrogen-rich composition ($X_{TiN} = 0.6$–0.7). However, the minimum point swings to carbon-rich composition ($X_{TiN} = 0.3$–0.4) at 2100 K. From this plot it demonstrates that a stable composition exists for the various temperatures, since G^M is an indicator of the phase stability of a material. The solid solution with a high-nitrogen content would be expected to be more stable at 1700 K, while that with a high-carbon content to be more stable at 2100 K. The behavior of the solid solution at 1700 K is a little surprising since the nitrogen in Ti(CN)-based cermets is known to have a destabilizing effect by dissociating in sintering at 1400–1500 °C. However, the more negative is G^M, the less a substance evaporates or reacts. Thus, the composition with a minimum G^M value would be expected to be the most stable, even if the stability region were to be extended further to the compositions in the vicinity of the minimum point.

The variation of free energy with temperature can be visualized when the excess Gibbs free energy, G^{xs}, is obtained. In order to obtain G^M as a function of temperature, G^{xs} was calculated by means of some solution models [9, 10]. A regular solution model was tested for its applicability to Ti(CN) solid solutions. The heat of mixing for a regular solution can be expressed by the equation below;

$$\Delta H^M = G^{xs} = \alpha' X_{TiC} X_{TiN} \tag{3}$$

α' has to be a constant which is independent of temperature. However, the data shown in Fig. 6 cannot be represented by a single α' value as in the case of a regular solution. It shows the temperature dependence. The strong deviation from ideal solution behavior in Fig. 3 is evidence for this.

Therefore, it is necessary to treat the G^{xs} of the solution as a temperature function. By the addition of a temperature function, G^{xs} can be represented as Equation 4. The coefficient, a, is related to the extent of deviation from ideal behavior. The value of τ indicates the degree of sensitivity of G^{xs} to temperature dependence. The larger the absolute value of τ, the weaker is its dependence with temperature. As τ increases, G^{xs} in Equation 4 becomes close to that of a regular solution. In fitting the data using Equation 4, the values of a and τ were calculated to be -6.94 and 889.9 K, respectively.

$$G^{xs} = a X_{TiC} X_{TiN} \left(1 + \frac{T}{\tau}\right) \tag{4}$$

A general function of G^M can be obtained from the incorporation of G^{xs} into Equation 5 and the relative stability can be estimated as a function of temperature. The G^M curves at some temperatures are shown in Fig. 7.

$$G^M = X_{TiC} \Delta_f G^o_{TiC} + X_{TiN} \Delta_f G^o_{TiN} + (\Delta G^{M,id} + G^{xs}) \tag{5}$$

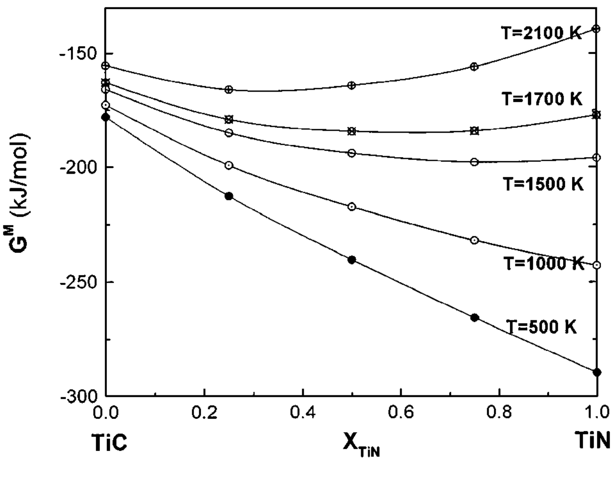

Figure 7 Curves of the free energy of a solid solution of Ti(CN) using G^{xs} calculated from a subregular solution model.

As is seen in Fig. 7, $\Delta_f G^o_{TiN}$ is far more negative than $\Delta_f G^o_{TiC}$ at lower temperatures. The value near TiN increases rapidly compared with TiC. The free energy near the TiN composition is lower than that of TiC at low temperatures (below 1500 K), whereas TiC tends to have lower values at higher temperatures (above 2500 K). It means that the relative stability among Ti(CN) solid solutions is strongly dependent on the temperature.

4. Summary and conclusions

An analysis was carried out for obtaining the activity and free energy for the formation of Ti(CN). They were calculated using a TiC-TiN solution model and the Belton and Fruehan integration method. It was found that a linear regression with a single curve was a more proper approach than a two-curve approach in calculating the activity values. Activity curves are observed to exhibit strong negative deviations from ideal solution behavior. The free energy for the formation of Ti(CN) was also obtained at 1700 and 2100 K by calculating mixing energy terms using activities. Each curve of the formation energy of Ti(CN) had a minimum point close to $Ti(C_{0.3}N_{0.7})$ and $Ti(C_{0.6}N_{0.4})$ at 1700 and 2100 K, respectively. This indicates that the stability of the solid solution is a moderate temperature function. For an extension of the free energy of formation to other temperatures a regular solution and a subregular solution model were employed. The solution behavior is found to be beyond a regular solution range and it appears to show ordering tendency. However, based on the subregular solution model, the sensitive dependence of relative stability on temperature could be described.

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