THE THERMODYNAMICS OF LIQUID TITANIUM ALLOYS

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Abstract

The chemical activity of titanium in the tin-rich side of the Ti-Sn alloy has been calculated for the temperature range of 1200 - 1400° C from measurements of the nitrogen-nitride equilibria of the alloy. The temperature dependency of the nitride forming reaction follows the Arrhenius relationship. Isoactivity line representing the solvent corner of the nitrogen-titanium-tin solvent metal ternary diagram are used to determine the stoichiometry of the titanium nitride phase formed.

Introduction

Knowledge of the chemical activity of titanium in various titanium alloys at elevated temperatures can be used to better correlate their chemical behavior and to develop the thermodynamic understanding necessary to design new titanium systems. Experimental measurements have been made of the chemical activity of titanium in the 0 - 5 weight percent range in the Ti-Sn binary alloy for the temperature range of 1200 - 1400° C using a simple volumetric technique. This method appears to be ideally suited for titanium alloys and compares very favorable with the techniques described below.

A common method for determining the chemical activity of a component in solution is to measure its specific vapor pressure and compare that value with the value for the pure substance. Various arrangements of Knudsen cells and mass-spectrographic techniques are used in this approach. There can be difficulty with this method when one component has a very high vapor pressure.

A second method for measuring chemical activity is to measure the electromotive force of a cell in which the two electrodes are composed respectively of the pure metal and the alloy. For elevated temperatures the electrolyte used is generally a molten salt. The difficulty with this method is that there is an upper temperature limit at which this technique can be used and for many purposes this limit may be too low to be useful.

If the effect on the melting point of adding a component of a second substance is known precisely, the activities of both components may be determined. This method has the potential of approximating activity data from phase diagrams. However, in practice it has been little used for metals since their phase diagrams, in most cases, affords only the roughest kinds of estimates of activities.

The distribution ratio can be used to calculate the activity of a substance that is soluble in each of two immiscible liquids. The ratio of the equilibrium concentration in one phase to that in the second is called...
the distribution ratio. Solution thermodynamics requires that the activity of the substance be the same in both phases. Therefore, if the activity coefficient in one phase is known, the distribution ratio allows the activity in the other phase to be calculated. This technique has limited use for metal systems because of the immiscibility requirement which few systems of interest can fulfill.

The experimental technique used in this study to measure the chemical activity of one species in a binary alloy utilizes the Sieverts volumetric apparatus to measure the amount of nitrogen absorbed into the alloy at a given temperature and pressure. These measurements establish the chemical equilibrium for the reacting species in the alloy. This nitrogen-nitride equilibrium data can then be used to establish the solution thermodynamics for the system. This technique uses uncomplicated experimental apparatus and yet is capable of producing very accurate thermodynamic information over a range of temperatures and alloy compositions.

Experimental Procedures

The reactions of nitrogen with titanium-tin alloys were studied by volumetric measurements using a modified Sieverts type of apparatus that has been previously described in the literature. This apparatus is particularly well suited to gas-metal reactions involving relatively large volumes of gas (10 cc or more). This apparatus consists essentially of a vertically mounted, induction-heated, quartz reaction tube connected by means of a ground-glass ball joint to a glass manometer system. The manometer, in turn, is connected through stopcocks to a vacuum system and a 100 ml water jacketed gas burette. The alloy is contained in a graphite crucible located in the quartz reaction tube. The temperature of the melt is optically measured through an optical flat on the top of the quartz reaction tube.

Appropriate amounts of titanium and tin metal are weighted out and placed in the graphite crucible. The graphite crucible is placed inside a second alumina crucible which serves as a heat shield and this assembly was placed vertically in the quartz reaction tube. Following hookup to the Sieverts apparatus, a hard vacuum is pulled on the cold system for several hours to degas the crucible and to conduct preliminary checks for leaks. The cold leak test is necessary to lessen the chance of a leak being masked by the gettering properties of titanium at elevated temperatures.

The evacuated system is heated to 1200 - 1400°C for several hours to dissolve the titanium in the tin and further degas the system. The dead volume of the system is determined at the experimental temperature by using argon gas which is not absorbed by the alloy. The volume of argon in the system is measured by the gas burette.

The system is again evacuated after the dead volume determination with argon is complete. Argon is replaced by nitrogen in the burette, and small amounts of nitrogen are admitted into the reaction tube and allowed to come to equilibrium. The volume of nitrogen added is measured by the difference in burette readings and corrected to standard temperature and pressure. This procedure produces one point on a graph showing the volume of nitrogen
absorbed per 100 grams of alloy versus the square root of the nitrogen pressure in the system at equilibrium. To accumulate data points at higher pressures, additional additions of nitrogen are admitted to the system and allowed to come to equilibrium. The temperature is held constant during the course of nitriding each alloy.

At the conclusion of the experiments the induction furnace is turned off and, after cooling, the alloy is removed. In a number of cases the alloy was examined by x-ray diffraction to confirm the presence of the nitride phase.

Discussion

The Stability of the Titanium Carbide Phase

The titanium-tin alloy is held in a graphite crucible and inductively heated. The presence of the graphite crucible insures that the chemical activity of the carbon in the liquid alloy is unity. Therefore, the determination of titanium activity using the nitrogen-nitride equilibrium must be carried out under conditions where the nitride compound of titanium is more stable than the carbide. This requires that the temperature of the alloy be less than 1600°C. At higher temperatures, the carbide will be more stable and the nitride reaction cannot be used unless a different crucible material is chosen.

The Titanium-Tin Alloy

The tendency of titanium to form strong intermetallic compounds with tin indicates the presence of considerable negative deviation from ideal solution behavior. The result of this effect is that the chemical activity of titanium is depressed below that of its mole fraction concentration. This relationship holds for other alloys that exhibit strong intermetallic behavior such as titanium-copper.

Tin is an excellent solvent metal for thermodynamic measurements because of its wide experimental temperature range with a melting point of 232°C and a boiling point over 2000°C. Tin also has very low solubility for nitrogen and carbon which is desirable for volumetric type experiments. The solubility of nitrogen in liquid tin is well below the detection limit of the Sieverts apparatus. The low solubility of carbon in tin makes it essentially inert to the graphite crucible.

For the reasons listed above, the titanium-tin alloy was chosen for initial study. It is expected that other titanium alloys, both binary and more complex ternary, will be examined later.

Experimental Results and Calculations

Stoichiometry of the Titanium Nitride Precipitate

The stoichiometry of the solid nitride phase formed by the titanium in the liquid alloy is unpredictable and must be determined experimentally. Perhaps the easiest approach is to use the isoactivity analysis technique described below. Changes in temperature of the liquid alloy or nitrogen pressure can greatly affect the Ti/N ratio and extrapolation of stoichiometry to conditions beyond those experimentally investigated is not reliable.
For the experimental conditions used in this study of the Ti-Sn alloy, the stoichiometry was calculated to be Ti$_x$N, where $x$ equals approximately 2.6 at the low temperature range of 1200°C and approximately 2.7 at the high temperature range of 1400°C. This Ti/N ratio appears to follow the titanium side of the delta TiN phase region of the binary Ti-N diagram.

The isoactivity method of analysis of the stoichiometry of the nitride phase is based on the examination of the tin-rich corner of the Ti-N-Sn ternary diagram. The point of intersection on the Ti-N axis of the ternary diagram by the isoactivity tie lines extending from the liquid-gas-solid phase boundary of the tin-rich corner determines the stoichiometry of the solid nitride phase. This point (or region) of interception is calculated from the slope of the isoactivity lines on a plot of atomic percent titanium versus atomic percent nitrogen. The data used in constructing the isoactivity plot is taken from the experimentally determined solubility curves. These curves show the amount of nitrogen absorbed at a given pressure by specific titanium alloys. By selecting a single nitrogen pressure and measuring the volume of nitrogen absorbed at this pressure and at constant temperature, a series of data points can be generated. These data are converted to atomic percents, and the sequence can be repeated for other nitrogen pressures to produce a series of isoactivity (constant nitrogen pressure) lines on a plot of atomic percent titanium versus atomic percent nitrogen. The slope of these lines then are directly related to the Ti/N ratio of the nitride precipitate.

Examination of the precipitate by x-ray diffraction shows that coring (composition variance between the center and the surface of the nitride crystal) is not present and that the Ti/N stoichiometry is uniform throughout the nitride phase. This lack of coring may be due to the very slow precipitation rate of the nitride which is on the order of days in these experiments. This slow rate of nitriding tends to insure that equilibrium conditions are maintained with the gas-liquid-solid phases throughout the system, and this in turn serves to keep the stoichiometry of the nitride constant.

**Equilibrium Calculations**

The data from these experiments consists of the equilibrium volume of nitrogen gas absorbed at a given pressure by the alloy. The experimental data is plotted as volume of nitrogen in cc absorbed per 100 gram tin versus the square root of the nitrogen pressure in atmospheres. The square root of the pressure is used because by the Sieverts Law, the solubility of a gas in a liquid metal is directly proportional to the square root of the pressure of the gas and hence the solubility portion of the experiment should plot in a straight line. Because the solubility of nitrogen in liquid tin is very low, there is no measurable uptake of nitrogen until the nitride first starts to form. Beyond the point where titanium nitride starts to form there is a large uptake of gas. Hence, the data can be extrapolated back to zero nitrogen absorbed to determine the pressure required for a given alloy concentration to start to form the nitride.

At the pressure where the nitride first begins to form, the titanium, nitrogen and nitride are all in equilibrium. The equilibrium constant, $K$, for the high temperature reaction

$$x\text{Ti} + \frac{1}{2}N_2(g) = \text{Ti}_xN(\text{precipitate})$$

(1)
is given by

\[ K = \frac{a_{TiXN}}{a_{TiX^2PN_2^{\frac{1}{2}}}} \]  

(2)

where \( a \) refers to the activity of the component. The \( p_{N_2^{\frac{1}{2}}} \) term in the equation is the square root of the partial pressure of nitrogen at the break point where the nitride firsts start to form. The line under Ti indicates that this element is in solution. The activity of the solid titanium nitride phase can be taken as one since the compositional change over the experimental conditions is small. Therefore, the equilibrium constant may be rewritten as:

\[ K = \frac{1}{a_{TiX^2PN_2^{\frac{1}{2}}}} \]  

(3)

The standard state of the titanium in the alloy is chosen for convenience such that the activity coefficient, \( f_{Ti} \), goes to one as \( %Ti \) goes to zero. At low nitrogen pressures, where the nitride precipitation points first occur, the concentration of nitrogen in solution is extremely small. For this reason, the activity coefficient factor to correct for the effect of \( N \) on \( f_{Ti} \) can be taken as equal to one. Hence, the activity of titanium on this scale is given by the equation:

\[ a_{Ti}(%) = f_{Ti} \cdot %Ti \]  

(4)

where \( %Ti \) is the weight percent of titanium dissolved in tin.

A pseudo equilibrium constant, \( K' \), similar to equation (3) but lacking the activity coefficient can be defined as:

\[ K' = \frac{1}{%Ti^X \cdot p_{N_2^{\frac{1}{2}}}} \]  

(5)

where the quantity \( %Ti \cdot p_{N_2^{\frac{1}{2}}} \) is commonly referred to as the mass-action product.

The equilibrium constant, \( K \), can be evaluated for a given temperature by calculating values for the pseudo equilibrium constant, \( K' \), and plotting these values on a log \( K' \) versus weight % titanium graph. Extrapolating the data to zero percent titanium provides the point where \( K = K' \) since, by definition, the activity coefficient, \( f_{Ti} \), is zero at zero percent titanium. Table 1, below, tabulates the values of log \( K \) determined at zero percent titanium, and the free energy of formation of the nitride in question calculated using the equation

\[ \Delta G = -RT\ln K. \]  

(6)

The \( R \) in equation (6) is the ideal gas constant which may be taken as 1.98. \( T \) is temperature in degrees Kelvin, and \( K \) is defined by equation (3).
Table 1

Equilibrium constants and free energies calculated at three temperatures from plots of Log K' versus percent titanium

<table>
<thead>
<tr>
<th>Temperature</th>
<th>log K (intercept at 0% Ti)</th>
<th>ΔG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1473</td>
<td>6.79x10^{-4}</td>
<td>1.69</td>
</tr>
<tr>
<td>1573</td>
<td>6.36x10^{-4}</td>
<td>1.38</td>
</tr>
<tr>
<td>1673</td>
<td>5.98x10^{-4}</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Log K for the nitride forming reaction was found to be linear when plotted against 1/temperature in °K in the Arrhenius manner. The slope of this Arrhenius plot is equal to the negative quantity of the enthalpy of the nitride forming reaction divided by 4.575. Measurement of the slope of the straight line plotted with the data in table 1 provided a value of approximately -33,000 calories for the enthalpy of nitriding.

The entropy of the reaction is determined by calculating the free energy values and plotting the data against temperature. The slope of the line is equal to the entropy which is calculated to be -17 eu using the data in table 1. This negative value for entropy is consistent with reactions that form solids from gas since the amount of disorder is decreased in going from a gas to a solid.

The thermodynamic expression for the free energy of the reaction given by equation (1) is:

\[
\Delta G = -33,000 + 17T
\]

This equation is only reliable for the conditions of temperature and composition previously stated.

Solving equation (7) for the temperature that makes the free energy zero establishes this temperature to be 1941°K or 1668°C. At this temperature the nitride should not form at 1 atmosphere nitrogen pressure. This calculated value for the temperature is consistent with experimental observations.

The standard reference base for the chemical activity of titanium used here is based on the activity coefficient, fTi, going to one as the % titanium goes to zero. As stated before, this reference state has been used as a convenience in the analysis. The Raoultian activity, based on the activity of the pure titanium being taken as one is more common and decidedly more easily applied. The conversion from one reference state to the other is carried out in the manner described below.

The equilibrium constant for the reaction

\[
\%_{Ti} = Ti_{mf}
\]
where the subscript \( \text{mf} \) refers to the mole fraction activity scale, is given by the equation

\[
K = \frac{a_{\text{Ti, mf}}}{a_{\text{Ti}}^0} = \frac{N_{\text{Ti, \text{mf}}}}{a_{\text{Ti}}^0} \quad (9)
\]

where \( a^0 \) is the point of interception of Henry's law line extrapolated to intercept titanium at mole fraction equal to one. \( a^0 \) is also the activity coefficient on the mole fraction scale where \( a = N \) at \( N \) goes to one for titanium at very low concentration. Evaluation of \( a^0 \) is required inorder to compare titanium activity in tin with pure titanium.

The ratio of \( N_{\text{Ti}}/a_{\text{Ti}}^0 \) at low concentrations of titanium in an alloy is approximated by

\[
\frac{N_{\text{Ti}}}{a_{\text{Ti}}^0} = \frac{\text{mole weight solvent}}{(\text{mole weight of solute})100} = \frac{118.7}{47.9\times100} = 0.02 \quad (10)
\]

Since the free energy for equation (8) is related to the equilibrium constant by the equation

\[
\Delta G = -RT\ln K \quad (11)
\]

the free energy can be evaluated and used in equations (11) and (9) inorder to determine \( a^0 \). The free energy for equation (8) is calculated from the difference in thermodynamic values for the following two equations:

\[
\text{T}_{\text{mf}} + \frac{1}{2}N_2(\text{gas}) = \text{TiN (solid)} \quad \text{(pure Titanium)} \quad (12)
\]

and

\[
x_{\text{Ti}}(\%) + \frac{1}{2}N_2 = \text{Ti}_xN \quad \text{(Ti-Sn alloy)} \quad (13)
\]

The free energy for the first equation for pure titanium (12) is available from the literature. Using the thermodynamic data of Wicks and Block for the temperature range in question, the following expression is obtained:

\[
\Delta G = -80,700 + 22T \quad (14)
\]

The experimental value for the alloy on the weight percent bases is given by equation (7). If the stoichiometric factor for \( x \) is taken as 2.65 (the average value for the temperature range studied), the free energy equation for the reaction

\[
\frac{2.65}{\text{Ti}} = \text{Ti}_{\text{mf}} \quad (15)
\]

is given by the difference between equation (7) and equation (14) which is

\[
\Delta G = +47,700 - 5T \quad (16)
\]
Equation (16) is the free energy for the equilibrium constant

\[ K = \frac{a_{Ti}^{mf} \cdot a_{TiN}^{2.65}}{a_{\%Ti}^{2.65} \cdot a_{Nitrogen}} \]  

(17).

Since both nitrides are solid phases, their chemical activity may be taken as one and equation (17) can be rewritten to reflect this simplification:

\[ K = \frac{a_{Ti}^{mf}}{a_{\%Ti}^{2.65}} = \frac{N_{Ti}^{\circ}}{a_{Ti}^{2.65}} \]  

(18).

Taking the log of equation (18) we can write:

\[ \log K = \log N_{Ti}^{\circ} + \log a_{\%Ti}^{2.65} - 2.65 \log a_{\%Ti} \]  

(19).

Equation (19) can be further rewritten as:

\[ \log K = 1.65 \log N_{Ti}^{\circ} + \log a_{\%Ti}^{2.65} - 2.65 \log (N_{Ti}/a_{\%Ti}) \]  

(20).

Using equations (20), (16), (11) and (10), \( \log a_{\%Ti}^{2.65} \) at \( N_{Ti} = 1 \) is found to be given by the expression

\[ \log a_{\%Ti}^{2.65} = -10.426/T + 5.3 \]  

(21).

Assuming a temperature of 1400 °C (1673 °K), equation (21) gives a value for \( \log a_{\%Ti}^{2.65} \) of -0.93 or a value for \( a_{\%Ti}^{2.65} \) of 0.12.

The activity of titanium in liquid tin alloy can now be expressed on the mole fraction reference basis as follow:

\[ a_{Ti}^{mf} = N_{Ti}^{\circ} \]  

(22)

and

\[ \frac{a_{Ti}^{mf}}{a_{\%Ti}^{2.65}} = \frac{N_{Ti}^{\circ}}{a_{\%Ti}^{2.65}} \times \frac{1}{a_{\%Ti}^{1.65}} = 0.0029 \]  

(23)

Multiplying equation (23) by \( a_{\%Ti}^{2.65} \) gives the following expression

\[ a_{Ti}^{mf} = 0.0029 \cdot a_{\%Ti} = 0.0029 \cdot \%Ti \cdot f_{Ti} \]  

(24)

for a temperature of 1400 °C.
If the activity coefficient is known for a given titanium composition, equation (24) can be used to calculate the activity on the mole fraction scale. For example, a 5% titanium alloy at 1400°C has an activity coefficient of 0.060. Values of $f_{Ti}$ at titanium concentrations greater than 0% are calculated from the equation

$$K'/K = (f_{Ti} \cdot \%Ti)^{2.65} \cdot \frac{P_{N_2}}{1.0} \cdot f_{Ti} \cdot \%Ti$$

Equation (26)

Table 2 lists mole fraction activities for different concentrations of titanium in tin at 1400°C.

Table 2

<table>
<thead>
<tr>
<th>%Ti (wgt.)</th>
<th>Mole fraction Ti</th>
<th>$f_{Ti}$</th>
<th>$a_{%Ti}$</th>
<th>$a_{Ti_{mf}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.22</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.024</td>
<td>0.22</td>
<td>0.22</td>
<td>6.38x10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>0.048</td>
<td>0.12</td>
<td>0.24</td>
<td>6.96x10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.077</td>
<td>0.08</td>
<td>0.26</td>
<td>7.54x10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>0.094</td>
<td>0.07</td>
<td>0.28</td>
<td>8.12x10^{-4}</td>
</tr>
<tr>
<td>5</td>
<td>0.115</td>
<td>0.06</td>
<td>0.30</td>
<td>8.70x10^{-4}</td>
</tr>
</tbody>
</table>

The mole fraction activities shown in Table 2 illustrate the effect of negative deviation from ideality for this alloy. The 5% (by weight) alloy has titanium present at a mole fraction of 0.115. In an ideal solution the mole fraction concentration of titanium would correspond with the activity so that the activity would be 0.115. However, in the case of tin, the activity is 132 times less than the mole fraction concentration.

The deviation from ideal solution is less at higher temperatures and increases as the temperature is lowered. For example, the 5% alloy at 1200°C has a weight percent activity of 0.08 and a mole fraction activity of 0.00023 which is 348 times less than the mole fraction activity of an ideal solution.

Conclusions

This work has demonstrated the successful application of the Sieverts method to measuring the high temperature properties of titanium in alloys. The Ti-Sn binary alloy used in these experiments was expected to have considerable negative deviation from ideality because of the strong intermetallic compounds shown in the phase diagram. These experiments confirmed the low activity of titanium in the tin.

This technique has applications to other alloys of titanium where titanium is one of the principal reactive metals present. For example, an alloy containing both titanium and aluminum in equal amounts would provide thermodynamic data for both titanium and aluminum. The method will work for a wide range of titanium activities. However, if the titanium activity is very high, the nitrogen-nitride equilibrium point will occur at such low nitrogen pressure that it becomes difficult to distinguish the break point for
different alloy compositions. For this reason, the method does not appear applicable for alloys with over 20% titanium present.

References