

**Component Activity Measurements in the Ti-Al-O System by Knudsen Cell Mass Spectrometry**

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Titanium-aluminides (containing  $\alpha_2$ -Ti<sub>3</sub>Al and  $\gamma$ -TiAl intermetallic phases) have received continued research focus due to their potential as low-density materials for structural applications at intermediate temperatures. However their application above about 850°C is hindered by poor oxidation resistance, characterized by the formation of a non-protective TiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> scale and an oxygen-enriched subsurface zone<sup>1,2,3</sup>. Consistent with this are measured titanium and aluminum activities in "oxygen-free" titanium-aluminides, which indicate Al<sub>2</sub>O<sub>3</sub> is only stable for aluminum concentrations greater than 54 atom percent at 1373 K<sup>4</sup>. However, the inability to form a protective Al<sub>2</sub>O<sub>3</sub> scale is in apparent conflict with phase diagram studies, as experimental isothermal sections of the Ti-Al-O system show  $\gamma$ -TiAl +  $\alpha_2$ -Ti<sub>3</sub>Al structures are in equilibrium only with Al<sub>2</sub>O<sub>3</sub>.

The apparent resolution to this conflict lies in the inclusion of oxygen effects in the thermodynamic measurements. The phase diagram studies do indicate that a substantial amount of dissolved oxygen in  $\alpha_2$ -Ti<sub>3</sub>Al is necessary for equilibrium with Al<sub>2</sub>O<sub>3</sub>. Thus a series of Ti-Al-O compositions in and around the  $\alpha_2$ -Ti<sub>3</sub>Al phase were prepared. The Knudsen cell mass spectrometric method was utilized to measure component activities of Ti, Al, and O in these alloys.

The pressure of the vapor species,  $P_i$ , effusing from the Knudsen cell is given by:

$$P_i = \frac{k I_i T}{\sigma_i} \quad (1)$$

where  $I_i$  is the measured ion intensity,  $T$  is the temperature,  $k$  is the machine constant and  $\sigma_i$  is the ionization cross section. The component activity is given by:

$$\ln a_i = \ln \frac{P_i}{P_i^0} = \ln I_i T - \ln P_i^0 + \ln \frac{k}{\sigma_i} \quad (2)$$

where,  $P_i^0$  is the vapor pressure over pure  $i$  and is taken from the tabulated values<sup>5</sup>. A major issue in determining absolute pressures and/or activities is knowledge of  $k/\sigma$ . An elegant solution is the use of an *in situ* standard with a multiple Knudsen cell configuration<sup>6,7</sup>. Ideally the pure component is used as the standard but this is not usually possible due to mixing of the molecular beams emerging from adjacent cells. In the current measurements copper (in Al<sub>2</sub>O<sub>3</sub> cell) was used as an *in situ* standard for aluminum and oxygen, while nickel (in Y<sub>2</sub>O<sub>3</sub> cell) was used for titanium.  $k/\sigma_i$  was determined in each activity measurement from the measured  $k/\sigma_{insitu}$  for the *in situ* standard together with the ionization cross-section ratios,  $\sigma_{Cu}/\sigma_{Al}$ ,  $\sigma_{Ni}/\sigma_{Ti}$ , and  $\sigma_{Cu}/\sigma_{Al2O}$  from separate calibration runs, according to:

$$\ln k/\sigma_i = \ln k/\sigma_{insitu} + \ln \sigma_{insitu}/\sigma_i \quad (3)$$

This method removes the need to rely on absolute values of the ionization cross sections<sup>7</sup>. The ionization cross-section ratios and  $k/\sigma_{insitu}$  for the *in situ* standard were

determined by comparing the measured vapor pressures to the tabulated vapor pressures<sup>5</sup> over of pure copper, nickel, titanium and a mixture of pure aluminum and Al<sub>2</sub>O<sub>3</sub>.

The component activities for aluminum and titanium were calculated from the ratio of the measured component intensity over the alloy and the *in situ* standard in addition to the measured ionization cross-section ratios according to equations (2) and (3).  $P(O_2)$ , was determined from the measured intensities of Al(g) and Al<sub>2</sub>O(g) by a third law calculation with the tabulated  $K$  values for the reaction:  $2Al + \frac{1}{2}O_2 = Al_2O(g)$ <sup>5,8</sup>. Values of titanium, aluminum, and oxygen activities are reported for selected alloys in and around the  $\alpha_2$ -Ti<sub>3</sub>Al phase. These data are compared to the recent assessment of the Ti-Al-O system by Lee and Saunders<sup>9</sup>.

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