MEASURING THE THERMODYNAMICS OF THE METAL / SCALE INTERFACE

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The oxidation behavior of an alloy in part depends on how close the metal/scale interface approaches a condition of thermodynamic equilibrium. Therefore, knowing the thermodynamic properties of the phases at an equilibrated metal/scale interface should add to our understanding of oxidation behavior. For example, β-NiAl alloys form a protective Al_2O_3-scale, therefore, it would be insightful to understand how the activities of Al, O, Al_2O_3 and Ni, at the metal/scale interface, change with alloy composition and temperature.

These thermodynamic properties can be studied directly with a Knudsen effusion-cell that is made from an oxide-compound. The 'closed' isothermal environment of the effusion-cell allows the vapor and condensed material to closely approach thermodynamic equilibrium. The condensed material includes, in addition to an alloy sample, any surface-layers on the alloy and the inner surface of the effusion-cell; and equilibrium means component activities are identical in all phases. Therefore an alloy/oxide equilibrium is actually considered and with a suitable choice of effusion-cell material this resembles the equilibrium metal/scale interface observed after extended oxidation. The thermodynamic properties of these phases are studied by measuring the relative pressure of characteristic vapor species. The only difficulty is how to define and measure $a(\mathrm{Al})$, $a(\mathrm{O})$, $a(\mathrm{Al_2O_3})$ and $a(\mathrm{Ni})$.

To this end a multiple Knudsen effusion-cell configured vapor source was developed for our mass spectrometer (*multi-cell KEMS*) to measure activities directly by comparing the pressure of characteristic vapor species in equilibrium with an alloy solution and reference state. A two phase mixture of $Al(l)+Al_2O_3(s)$ at the dissociation pressure of O(g) was developed as an experimental reference for Al, Al_2O, O, and Al_2O_3. For this mixture the equilibrium pressures: $p^o(\mathrm{Al})$, $p^o(\mathrm{Al_2O})$ and $p^*(\mathrm{O})$ are defined according the reactions 1-3.

$$\mathrm{Al(s,l) = Al(g)} \tag{1}$$

$$4/3\,\mathrm{Al(s,l)} + 1/3\,\mathrm{Al_2O_3(s) = Al_2O(g)} \tag{2}$$

$$2\mathrm{Al(s,l)} + 3\mathrm{O(g) = Al_2O_3(s)} \tag{3}$$

For alloys with significant aluminum concentrations in equilibrium with an oxide-compound, Al(g) and $Al_2O(g)$ dominate the vapor and $a(\mathrm{Al})$ and $a(\mathrm{Al_2O})$ can be measured directly according to: $a(\mathrm{Al}) = p(\mathrm{Al})/p^o(\mathrm{Al})$ and $a(\mathrm{Al_2O}) = p(\mathrm{Al_2O})/p^o(\mathrm{Al_2O})$. $a^*(\mathrm{O})$ and $a(\mathrm{Al_2O_3})$ are determined indirectly from measured $a(\mathrm{Al})$ and $a(\mathrm{Al_2O})$ values according to additional independent reactions in the Al-O system.

$$2\mathrm{Al(g)} + \mathrm{O(g) = Al_2O(g)} \tag{4}$$

$$a^*(\mathrm{O}) = \frac{a(\mathrm{Al_2O})}{a(\mathrm{Al})^2}$$

$$4\mathrm{Al(g)} + \mathrm{Al_2O_3(s) = 3Al_2O(g)} \tag{5}$$

$$a(\mathrm{Al_2O_3}) = \frac{a(\mathrm{Al_2O})^3}{a(\mathrm{Al})^4}$$

Where $a^*(\mathrm{O})$ is oxygen activity, $a^*(\mathrm{O}) = p(\mathrm{O})/p^*(\mathrm{O})$, relative to the dissociation pressure of O(g) in equilibrium with the $Al(l)+Al_2O_3(s)$, not $p^o(\mathrm{O}) = 1\mathrm{bar}$.

The use of $Al(l)+Al_2O_3(s)$ as a reference combined with the systematic measurement of the relative vapor pressures of Al and Al_2O allow the routine determination of $a(\mathrm{Al})$, $a(\mathrm{Al_2O})$, $a^*(\mathrm{O})$ and $a(\mathrm{Al_2O_3})$. This measurement procedure was developed for Ti-Al-O alloys in Y_2O_3 effusion-cells and was subsequently applied to a limited number of β-NiAl(Pt) alloys in ZrO_2, Al_2O_3 and Y_2O_3 effusion-cells. In addition to varying the cell material, alloy samples with different surface conditions ranging from, native oxide-layers to thermally grown oxide-scales were measured. This method of determining the thermodynamics of an equilibrated metal/oxide interface will be discussed in terms of the measurements made for the β-NiAl(Pt)/Al_2O_3 system.