Congruent Kinetic Steady-State Vaporisation Of Al₂O₃ Surfaces In Presence Of Graphite By High Temperature Mass Spectrometry

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Determinations of thermodynamic data for the Al-C-O system from vaporization experiments and particularly for the Al_2O_3-C cross section are known to be difficult owing to kinetic problems. Thermodynamic equilibrium calculations [1] show that the pseudo binary Al_2O_3-C system should loose an excess of $CO(g)$ and the condensed phases should turn into triphasic mixtures including oxycarbides, first Al_4CO_4 and for higher losses of CO, Al_2CO.

Alumina and graphite samples of known area are loaded without contact altogether in an effusion cell, and mass spectrometric detection shows that the only three gaseous species are $Al(g)$, $Al_2O(g)$ and $CO(g)$. Retarded (or hindered) vaporization is studied using the multiple Knudsen cell mass spectrometric method [2] in order to compare partial pressures of each gaseous species for the same sample disposed in four cells with different orifice sizes. Marked differences are observed, the more "reversible" the cell is (smallest orifice) higher is the partial pressure as shown in figures 1 and 2.

The vaporization process was observed to be stable. In order to characterize it, we analyzed both of alumina and graphite surfaces by XPS after heat treatments performed at different temperatures (4h at 1700°C and 1800°C). The alumina and graphite surfaces appeared purified (fig. 3 for alumina XPS O1s photopeak) and we never observed any shifts that could indicate the formation of a carbide or oxycarbide layer. We conclude that the vaporization of {C + alumina} samples occurs with a pseudo congruent behaviour and according to a kinetic steady-state regime for the total reaction:

$$Al_2O_3(s) + C(s) + 2 Al(g) = 2 Al_2O(g) + CO(g)$$
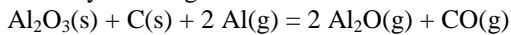
Implications about the gas phase composition are also discussed. More extended mass spectrometric measurements show that this steady-state depends on the surface ratios. Condensation and evaporation coefficients are determined.

[1] M. Heyrman, C. Chatillon, C . Barat, S . Fargeas, *Thermodynamique des phénomènes de vaporisation et de condensation dans les fours de coulée de superalliages sous vide,* La Revue de Métallurgie – CIT/Science et Génie des Matériaux, N°2, 141-156 (Février. 2003).

[2] M. Heyrman, C. Chatillon, H. Collas, J-L. Chemin, *Improvements and new capabilities for the multiple Knudsen cell device used in high temperature mass spectrometry*, Rap. Comm. Mass Spectrom., 18, 163-174 (2004)
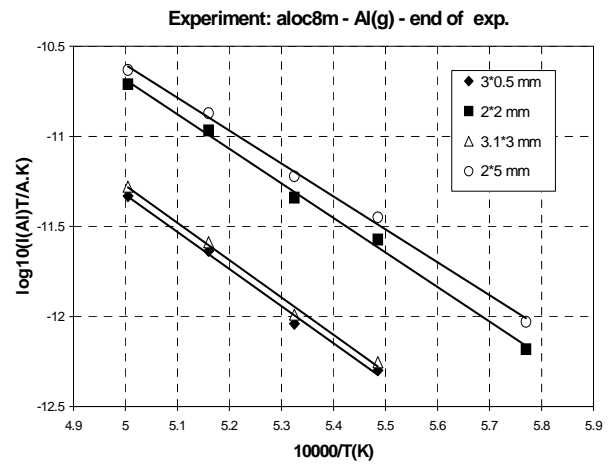
Fig.1: Evolution of decimal logarithm of products (ionic intensity times temperature) proportional to pressure for Al(g) as a function of the inverse of temperature for four different cells with different orifice size (numbers are diameters*lengths of orifices in mm).
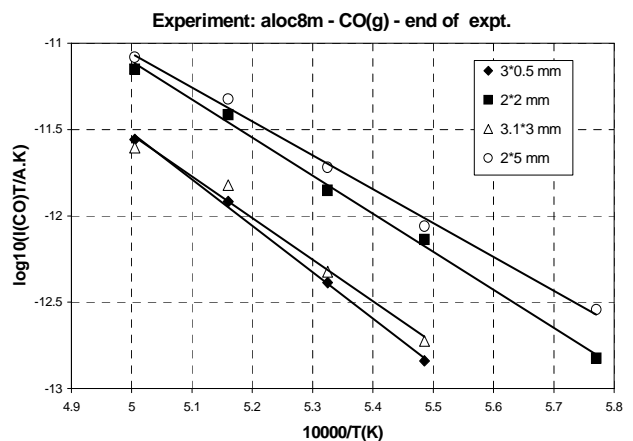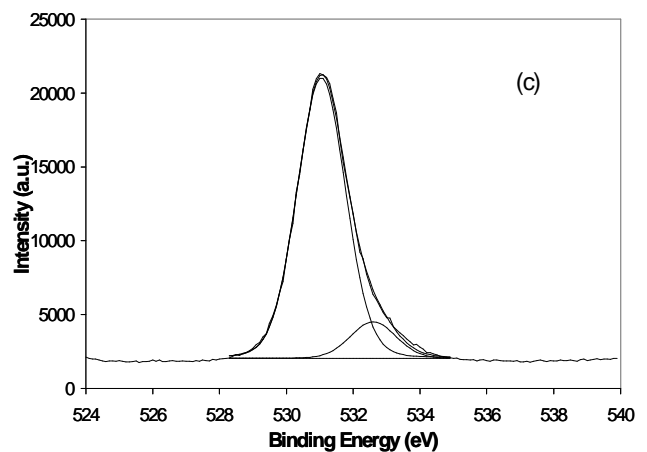

Fig. 2. Same as fig. for CO(g).

Fig. 3(c). The XPS O1s photopeak for the alumina surface after vaporization experiment.