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Solid state-reaction between Ir and Al_2O_3

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Thanks to its unique chemical stability and the high melting point of 2454°C the precious metal iridium is especially suitable for applications at the highest temperatures such as thermocouples and rocket parts [1]. It is considered that iridium should be protected by refractory metal oxides when used in severe erosion environment because precious metals and refractory metal oxides such as Pt–Al_2O_3 are classified as non-reactive, non-penetrative but bonded interface systems [2–4]. However, it has been reported that solid-state reaction between precious metals and refractory metal oxides occurred to yield intermetallics in the presence of H_2 or other reductive reactants at 1000 °C [5–7]. In fact, the chemical potential of the precious metals and refractory metal oxides involved drives charge transport and mostly also mass transport across the interface. The latter can lead to the formation of interfacial phases whose properties can markedly differ from the starting materials. Whether or not the reaction occurs depends on the nature of the materials and on the reaction conditions. In the precious metals-refractory metal oxide systems where the oxides contain a gaseous species, a reaction can be controlled by changing the activity of the ambient species.

In this work, the solid state reaction between Ir and Al_2O_3 powders in vacuum was studied. Moreover, the reaction thermodynamics were also calculated under nonstandard conditions.

Ir and Al_2O_3 powders were treated at temperatures of 1540°C and 1800°C in vacuum for 10 h. The evaluation of the reaction products was carried out by X-ray diffraction (XRD). The results revealed that some of the Ir and Al_2O_3 powders had reacted, yielding AlIr, and some unreacted Al_2O_3 and Ir remain in the mixture at 1540 °C in vacuum for 10 h from the XRD patterns shown in Fig. 1A. Fig. 1B shows the XRD patterns of Ir and Al_2O_3 powders after heating at 1800 °C in vacuum for 10 h. This shows that Ir and Al_2O_3 powders had reacted, yielding AlIr and unknown phases with no unreacted Al_2O_3 and Ir. The unknown phases are not Al_3Ir or Al_9Ir_2 but may be $Al_{13}Ir_4$ or $Al_{2.7}Ir$ or a new compound with a higher content of Ir than that of AlIr that has not been reported in the Ir–Al phase diagram [8]. The XRD peaks of unknown phases are broad.

The reaction yielding AlIr can be expressed as follows:

$$2Al_2O_3(s) + Ir(s) = 4AlIr(s) + 3O_2(g)$$

The experimental standard molar enthalpies of formation of AlIr is $-(185.5\pm3.5)$ kJ/mol [9]. For this type of intermetallics the effect of the change of entropy (ΔS) on the change of Gibbs free energy (ΔG) can be negligible [6], the ΔG of AlIr is constant, namely -185.5 kJ/mol at any temperature. The ΔG of Al_2O_3 is much higher than that of AlIr, so the ΔG of this reaction is positive under standard conditions in any given temperature range and will not proceed. Because of the vacuum atmosphere, the pressure of O_2 is very low and the activity of O_2 is much lower than unity. Under nonstandard conditions the reaction can proceed, and the total ΔG of this reaction can be expressed as follows:

$$\Delta G^1 = G(T) + RT\ \mathrm{In}\left(\frac{P_{O_2}}{P^{\theta}_{O_2}}\right)^3$$

The ratio $P_{O_2}/P^{\theta}_{O_2}$ can be calculated for equilibrium conditions, that is for $\Delta G^1 = 0$, according to

$$\frac{P_{O_2}}{P^{\theta}_{O_2}} = \exp - \left(\frac{G(T)}{3RT}\right)$$

In Fig. 2 the calculated ratio $P_{O_2}/P^{\theta}_{O_2}$, for $P^{\theta}_{O_2} = 1$ atm. is given with $1/T$ in the temperature range from 1527 °C to 2227 °C.

The pressure of O_2 is about 10^{-10} Pa and 10^{-7} Pa at 1540 °C and 1800 °C respectively, so the reaction proceeds only under extremely low O_2 pressure. The pressure of O_2 is about 10^{-3} Pa at 2227 °C, and the reaction will proceed easily in vacuum. The Ir–Al_2O_3 system should be considered as a reactive system in ultra-high vacuum at high temperature.

In reductive atmosphere the reaction can be expressed as follows:

$$2Al_2O_3(s) + Ir(s) + C(s) = 4\,AlIr(s) + 6CO(g)$$

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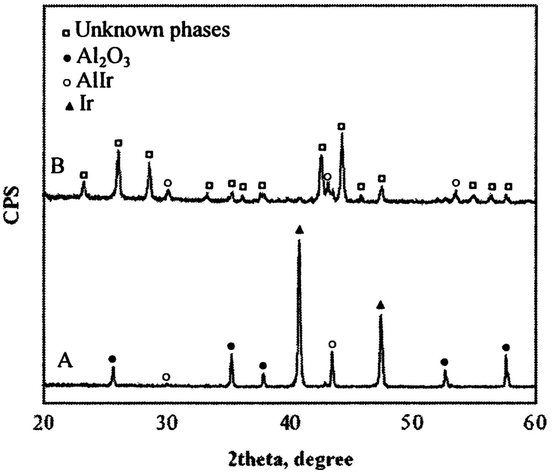

Figure 1 XRD spectra of the mixture of Ir with Al_2O_3 powders after heating at (A) 1540 °C in vacuum for 10 h; (B) 1800 °C in vacuum for 10 h.

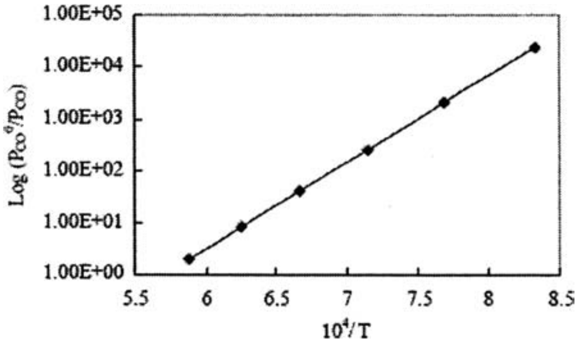

Figure 2 Reaction conditions of the Ir–Al_2O_3 system.

The ΔG of this reaction is negative and can proceed at 1527 °C under standard conditions, that is $P_{\mathrm{CO}}^{\theta} = 1$ atm. When the temperature is below 1527 °C the total ΔG of this reaction can be expressed as follows under nonstandard conditions:

$$\Delta G^1 = G(T) + RT\ \ln\left(\frac{P_{\mathrm{CO}}}{P_{\mathrm{CO}}^{\theta}}\right)^6$$

The ratio $P_{\mathrm{CO}}/P_{\mathrm{CO}}^{\theta}$ can be calculated for equilibrium conditions, that is for $\Delta G^1 = 0$, according to:

$$\frac{P_{\mathrm{CO}}}{P_{\mathrm{CO}}^{\theta}} = \exp - \left(\frac{G(T)}{6RT}\right)$$

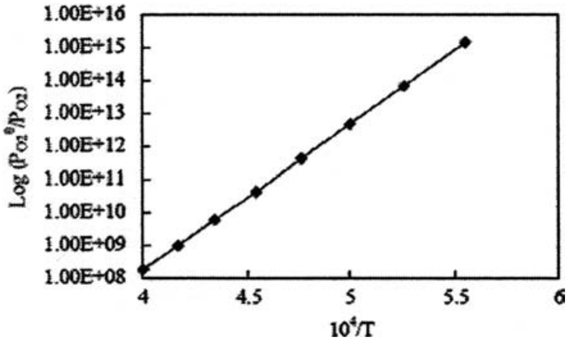

Figure 3 Reaction conditions of the Ir–Al_2O_3–C system.

In Fig. 3 the calculated ratio $P_{\mathrm{CO}}/P_{\mathrm{CO}}^{\theta}$, for $P_{\mathrm{CO}}^{\theta} = 1$ atm. is given with 1/*T* in the temperature range from 927 °C to 1427 °C.

The pressure of CO is about 4 Pa and 5×10^4 Pa at 927°C and 1427°C respectively, which is much higher than the pressure of O_2 in vacuum. The reaction between Ir and Al_2O_3 can proceed easily at low temperature in the presence of a reductive atmosphere such as C, and the same conclusion can be drawn for Ir–Al_2O_3-H_2 system.

Acknowledgments

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