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Highlights of experimental thermodynamics in the field of nuclear fuel development

Heiko Kleykamp *

Forschungszentrum Karlsruhe, Institut für Materialforschung I, Postfach 3640, 76021 Karlsruhe, Germany

Abstract

Results of basic thermodynamic studies are presented in the fields of oxide fuel pins and their alloys with fission products and of the neutron multiplier beryllium. Gibbs energy of formation measurements of solid phases using galvanic cells with CaF_2 electrolyte are exemplarily described for chromium carbides, URu_3 and URh_3. The calculation of the corresponding value of UPd_3 is demonstrated using the phase diagram of the U–Pd–Sn system. The phase behaviour of $(U,Pu)O_2$ in a steady-state temperature gradient between the solidus and the liquidus is explained. The $O/(U+Pu)$ redistribution in a temperature gradient is measured which allows the calculation of the heat of transport of the oxygen vacancies. The obstacles for measurements of the enthalpies of transformation and melting of beryllium are commented, the temperatures are only 14 degrees apart from each other below melting at 1283 °C. The high enthalpy of transformation is interpreted by the compressed c/a-axis ratio of the hcp modification.

1. Introduction

Thermodynamic studies on nuclear materials are presented which were conducted within the fast breeder, nuclear safety and nuclear fusion programs of Forschungszentrum Karlsruhe and were published earlier in the open literature stating full particulars. The highlights are recapitulated on the occasion of this conference which include more recent investigations of oxide fuels and alloys with fission products and of the neutron multiplier beryllium.

2. Gibbs energies of formation

Gibbs energies of formation of intermetallic compounds, alloys with broad homogeneity ranges and ceramic phases can be easily obtained by emf measurements with galvanic cells of the second type using solid electrolytes, e.g., $Zr(Y)O_2$, ThO_2, CaF_2, etc. The design of a cell is presented in Fig. 1. The quartz holding devices shield the thermocouple and confine the cell: the light electrolyte pellet is surrounded with the dark electrodes on both sides; the bright rhenium pellets protect the electrodes from incompatibilities of the platiunum–rhodium leads. An example is given by the measurement of the Gibbs energy of formation $\Delta_f G^\circ$ of Cr_3C_2 [1]:

$$(-)\mathrm{Cr}, \mathrm{CrF_2}|\mathrm{CaF_2}|\mathrm{CrF_2}, \mathrm{Cr_3C_2}, \mathrm{C}(+) \qquad (1)$$

The positive electrode on the right-hand side is the working electrode representing a coupled equilibrium with the auxiliary electrolyte CrF_2. As Cr forms fluorides with several Cr valencies, the ternary Cr–C–F system has to be worked out first in order to establish the fluoride in equilibrium with the Cr_3C_2–C couple.

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[*] Tel.: +49 7247 822888; fax: +49 7247 824567.
E-mail address: heiko.kleykamp@imf.fzk.de

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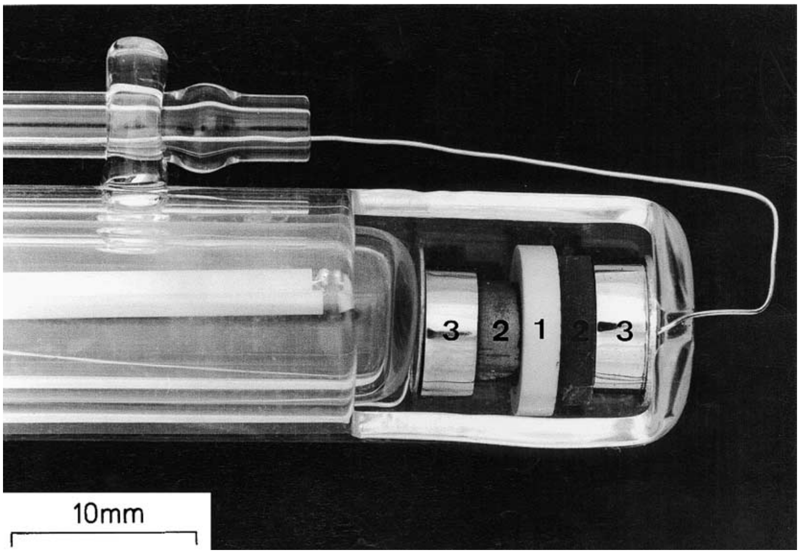

Fig. 1. Design of a galvanic cell arranged between two quartz tubes. The solid electrolyte (1) is located in the centre of the pellet stack, surrounded by the electrodes (2) and the rhenium buffers (3). The platinum–rhodium disks and leads are connected with an electrometer. The thermocouple tip is located within the inner quartz tube.

This necessary action is sometimes disregarded in the literature. The virtual left-hand and right-hand electrode reactions are

$$\text{left:}\ \ 3\mathrm{Cr} + 6\mathrm{F}^- = 3\mathrm{CrF}_2 + 6\mathrm{e}^- \tag{2a}$$

$$\text{right:}\ \ 6\mathrm{e}^- + 3\mathrm{CrF}_2 + 2\mathrm{C} = \mathrm{Cr}_3\mathrm{C}_2 + 6\mathrm{F}^- \tag{2b}$$

which result in the gross reaction and the corresponding thermochemical equation for the Gibbs energy of reaction $\Delta_r G^\circ$, resp.,

$$3\mathrm{Cr} + 2\mathrm{C} = \mathrm{Cr}_3\mathrm{C}_2 \tag{3}$$

$$\Delta_r G^\circ = 6\mathbf{F}E = \Delta_f G^\circ < \mathrm{Cr}_3\mathrm{C}_2 > \tag{4}$$

The constant **F** is the Faraday number. The measured emf E is essentially the difference of the logarithms of the fluorine partial pressures on both sides of the galvanic cell. The quantity $\Delta_f G^\circ$ of $\mathrm{Cr_3C_2}$ is obtained without any further thermodynamic data. Similarly, the Gibbs energies of formation of $\mathrm{Cr_7C_3}$ and $\mathrm{Cr_{23}C_6}$ have been obtained by this method. These results are important for rating the formation of chromium carbides in the steel claddings [1].

The fission platinum metals Ru, Rh and Pd, together with the fission products Mo and Tc, form quinary hexagonal phases [2] which appear as metallic inclusions in irradiated $\mathrm{(U,Pu)O_2}$ fuels. If a fast breeder pin becomes defected during irradiation the entering sodium coolant reduces the fuel into its hypostoichiometric state. The consequences are a strong decrease of the oxygen partial pressure as well as the formation of $\mathrm{Na_3(U,Pu)O_4}$ and intermetallic fcc $\mathrm{(U_xPu_{1-x})Rh_3}$ and $\mathrm{(U_{1-x}Pu_x)Pd_4}$ compounds and Sn rich Pu–Pd–Rh phases. This occurs by a coupled reduction of the fuel according to the simplified reaction scheme

$$\begin{aligned}&\mathrm{(U,Pu)O_2 + Mo,Tc,Ru,Rh,Pd + Na}\\ &\quad\rightarrow \mathrm{(U,Pu)O_{2-x} + Mo,Tc,Ru + (U,Pu)\cdot(Rh,Pd)_{3+x}}\\ &\qquad + \mathrm{Na_3(U,Pu)O_4}\end{aligned} \tag{5}$$

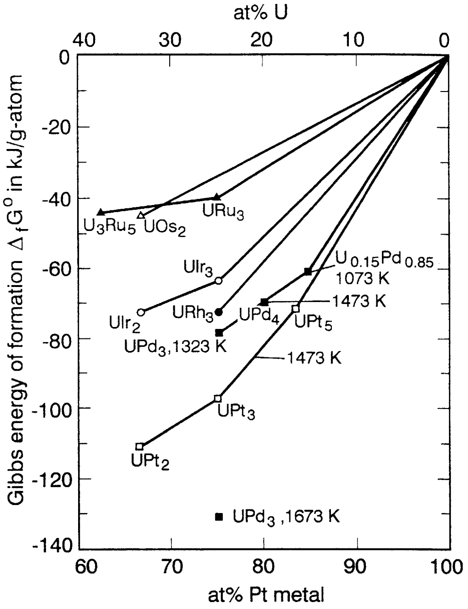

Fig. 2. Gibbs energies of formation of uranium–platinum metal phases at 1100 K unless otherwise stated.