JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 399–401

On the determination of oxygen potentials and O/M ratios in mixed U–Pu oxides by means of solid state galvanic cells

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Received 5 June 1977

Measurements of oxygen potential on uranium–plutonium mixed oxides by means of solid state galvanic cells are discussed and compared with precedent data. Discrepancies in the $\Delta\bar{G}_{O_2}$ values at low temperature (1000 K) as well as in the $\Delta\bar{G}_{O_2}$ versus T slopes are found, which disappear when the samples are thermally cycled. An analysis is performed of this effect, showing that the absence of a good homogeneization of the sample in oxygen and/or in plutonium content can give rise to mixed potentials and hence to erroneous results.

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1. Introduction

The oxygen potential over hypostoichiometric uranium–plutonium oxides has been determined in the temperature region 800–1100 K by solid state galvanic cell measurements and in the temperature region 1800–2500 K by thermogravimetric methods [1–3]. Until recently the principal data for the lower temperature region has been that of Markin and McIver [1]; the poor correlation between the two sets of data when extrapolated to the technically important region around 1600 K has given rise to some concern. This is the temperature region of uranium–plutonium mixed oxides fuel element production and it covers an important part of the temperature range to which these elements are submitted when employed in a fast reactor. In this range, the knowledge of important parameters, as oxygen activity and the related oxygen concentration, are essential both for the assessment of specifications for the fuel elements and for predicting their behaviour and their lifetime during the reactor operation.

Recently, more data have become available for the region 800–1100 K, derived from various types of galvanic cells [4, 5]. These data have not in all cases agreed with those of Markin and McIver. Some anomalous results of this work may account for the discrepancies in the sets of published results.

2. Experimental

Using a miniature high temperature solid state galvanic cell, we have measured oxygen potentials on powder samples as small as 0·5 mg of irradiated and unirradiated uranium–plutonium mixed oxides fuel elements [4, 6].

The cell is designed to work as the solid state electrochemical chain

$$\mathrm{Pt}/(\mu'_{\mathrm{O}_2})\mathrm{Fe},\ \mathrm{FeO}/\mathrm{ThO}_2,$$
$$\mathrm{Y}_2\mathrm{O}_3(t_{\mathrm{O}^{2-}} = 1)/(\mathrm{U},\mathrm{Pu})\mathrm{O}_{2-x}(\mu''_{\mathrm{O}_2})/\mathrm{Pt}$$

and it consists of an alumina crucible which is supported by a wire acting also as a thermocouple and

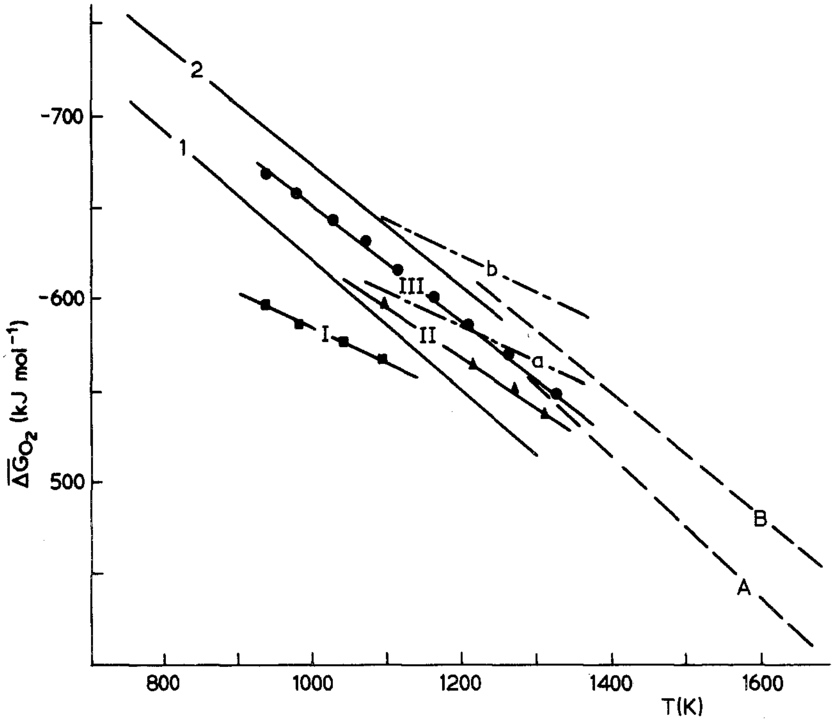

Fig. 1. Comparison of measured $\Delta\bar{G}_{O_2}$ versus T on anomalous samples of $(U_{0\cdot8}Pu_{0\cdot2})O_{2-x}$ with results for regular samples and with literature data. Curve A, O/M = 1·99; curve B, O/M = 1·98 Woodley [2]; curve a, O/M = 1·99; curve b, O/M = 1·98 Markin and McIver [1]; curve 1, O/M = 1·995; curve 2, O/M = 1·980 Mari *et al.* [3]. Curve I first result, uncycled; curve II after first cycle; curve III after second and third cycle (O/M = 1·985, present work).

electrical conductor for the cell. The reference electrode and the YST (yttria stabilized thoria) electrolyte pellet are assembled inside the crucible. The specimen for analysis is placed in a small cavity (ϕ = 2 mm) bored in the YST pellet, and the electrical contact to the specimen is made by another thermocouple which is spring-loaded in order to maintain contact during the experiment. The complete assembly is fitted inside an alumina tube which is connected to an ultra high vacuum system.

3. Results and discussion

During the development and testing procedure leading to additional thermodynamic data on the uranium–plutonium–oxygen system we have observed that certain samples departed from the behaviour already reported in [4].

These samples show that the gradients of the $\Delta\bar{G}_{O_2}$ versus temperature curves ($\Delta\bar{S}_{O_2}$) are smaller and that the O/M ratios, deduced from the measured oxygen potentials, correspond to a more oxidized state than the determinations by gravimetric analysis would suggest. Normally we obtain values of $\Delta\bar{S}_{O_2}$ approaching those of Woodley, whereas samples showing anomalous behaviour approach the $\Delta\bar{S}_{O_2}$ found by Markin and McIver (Fig. 1).

The X-ray analysis of an anomalously behaving sample showed the presence of two phases indicating either different oxygen or different plutonium content, possibly of the type observed as surface gradients on similar specimens [7].

The coexistence of two or more compositions, not in thermodynamic equilibrium and in contact with the electrolyte, produces two or several electrode systems giving rise to a mixed potential as a consequence of local conditions of short circuiting between the different electrodes. The mixed potential will approach one of the reversible potentials according to the kinetics of the electrochemical process occurring in each electrode and at their interfaces, i.e. their characteristic polarization potentials. Electrode polarization may also arise in the case of an oxygen potential gradient across the sample (as would be the case for a superficial oxidation) because the chemical diffusion process, which takes place towards the bulk, interferes with the electrochemical process. In such a situation oxygen ions move from the oxidized surface layer, in contact with the electrolyte, to the more reduced bulk. In order to maintain electroneutrality conditions, a contrary electronic flow arises, producing an electronic polarization which influences the measurements. As diffusion processes are temperature activated, it is clear that by increasing the temperature the homogenization process becomes faster, so that by waiting for a sufficient time it is possible to obtain a homogeneous oxygen activity that produces no polarization phenomena.

To confirm our hypothesis, we have thermally cycled one of the anomalously behaving samples up to 1350 K. A set of measurements was carried out after each cycle; on each occasion a potential consistent with a more reduced composition and a higher gradient of $\Delta\bar{G}_{O_2}$ versus T were obtained. This suggests that a more reduced phase was in contact with the electrolyte. When the last cycle produced no further changes, the slope and the oxygen potential corresponded well with those of regular samples (Fig. 1).

On the basis of these admittedly limited observations, we would postulate that the discrepancies between the data of Markin and McIver, and more recent data, [4, 5], can be attributed to inhomogeneity of the samples of the former study.

Many causes for this behaviour can be surmized. If solid state diffusion of oxygen is slow because of poor contact between the oxide particles, and/or the gas–solid exchange is unappreciable because of the absence of suitable oxygen carriers, as is the case when operating in a rather good and clean vacuum, multi-electrode systems can be formed. This is particularly true when the oxide consists of particles which are inhomogeneous either in O/M or in plutonium content. On the other hand, the presence of even a few ppm of oxygen in the gaseous atmosphere, as is normally the case when operating in inert gas flow systems, may induce, by solid–gas exchange, oxygen gradients between the surface and the bulk of the oxide particles, and hence cause polarization effects.

Acknowledgments

The authors wish to thank Dr Hj. Matzke for helpful suggestions and discussion of the manuscript.

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