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LETTER TO THE EDITORS

ON THE EXISTENCE OF A TWO-PHASE FIELD IN THE URANIUM–OXYGEN SYSTEM WITHIN THE COMPOSITION RANGE 2.65 < O/U < 2.67 BELOW 1273 K

1. Introduction

There are different propositions regarding the nature of the phase diagram of the uranium–oxygen system in the composition range $2.65 < O/U < 2.67$, below 1273 K. In this region some authors [1–6] observed only an homogeneous solid solution, other authors [7,8] suggest the existence of more than one phase separated by second (or higher) order phase transitions without the presence of two-phase fields, and a third group of authors [9,10] showed evidence indicative of the coexistence of two phases of different crystal structure.

Recently, using *dynamic* thermogravimetry (heating and cooling runs at constant oxygen partial pressure), Dharwadkar et al. [11] concluded that a two-phase field exists between $UO_{2.65}$ and $UO_{2.67}$ at least for temperatures ranging from 1023 K to 1243 K. These authors support their conclusion by means of X-rays and electrical conductivity measurements. The coexisting phases, designated [10,11] U_3O_{8-z} and U_8O_{21+x}, have respectively hexagonal and monoclinic crystal structures [11,12].

The conclusions of Dharwadkar et al. [11] do not agree with previous work due to Ackermann and Chang [6] and Matsui et al. [7]. Using *equilibrium* thermogravimetry, the latter authors [6,7] determined the partial pressure of oxygen, P_{O_2}, in composition and temperature ranges including those of interest here and, although their results are not in good mutual agreement, neither [6,7] shows any evidence of the presence of a two-phase field, as suggested by Dharwadkar et al. [11].

The purpose of this work was to further investigate the existence, or not, of a two-phase field between $UO_{2.65}$ and $UO_{2.67}$ below 1273 K. It was carried out making use of equipment recently developed in our laboratory [13] useful for *equilibrium* thermogravimetric measurements of P_{O_2} as a function of composition and temperature. A convenient fixed temperature was chosen for our measurements, namely 998 K.

2. Experimental

The construction details and performance of the experimental equipment used in our thermogravimetric measurements have been described in detail elsewhere [13]. In essence, this equipment consists of a symmetrical Cahn 1000 electrobalance coupled to an electrochemical system (pump and oxygen gauge) [14,15] for the measurement and regulation of P_{O_2}. Weight changes can be measured within $\pm 10\ \mu g$, so, for our samples of about 1 g of U_3O_8, it was possible to determine changes in O/U ratio within $\pm 2 \times 10^{-4}$. The appropriate oxygen atmosphere is obtained by a mixture of argon–oxygen supplied by the electrochemical system, with P_{O_2} values ranging between 10^{-4} and 10^2 kPa. Errors in P_{O_2} [13] are $\pm 2\%$, including systematic errors.

Equilibration times at the working temperature (998 K) varied significantly with P_{O_2}, ranging from 2 h at 10^2 kPa to 5 days at 9.2×10^{-4} kPa.

The quilibrium criterion used in this work was "constant sample weight with time, within $\pm 10 \mu g$". In the range $P_{O_2} \lesssim 10^{-2}$ kPa this equilibrium criterion was always verified over periods of 24 h at least, in some cases up to 3 days.

The original material for our uranium–oxygen sample was powdered UO_2 provided by Koch–Light Laboratories (England), with a total impurity content of less than 300 ppm in weight (Ca, Si and Fe are the main impurities). The sample had a specific surface area of about 2.4 m^2/g. The absolute oxygen content was determined by the usual procedure of reducing to UO_2 in dry hydrogen, at 1173 K [7,16].

3. Results and discussion

The results of our thermogravimetric measurements of P_{O_2} at 998 K are shown in fig. 1, where all the indicated data points represent equilibrium states in the sense explained above.

Three different isotherms of P_{O_2} can be observed in fig. 1, namely isotherms AB, CD and DE.

In order to obtain isotherm AB, the sample was previously prepared by slowly oxidizing UO_2 at 773 K in argon–oxygen mixtures of increasing oxygen content; then, and under 10^2 kPa of pure oxygen, the sample was kept 24 h at 773 K and finally heated to the working temperature (998 K) thus obtaining the starting point A

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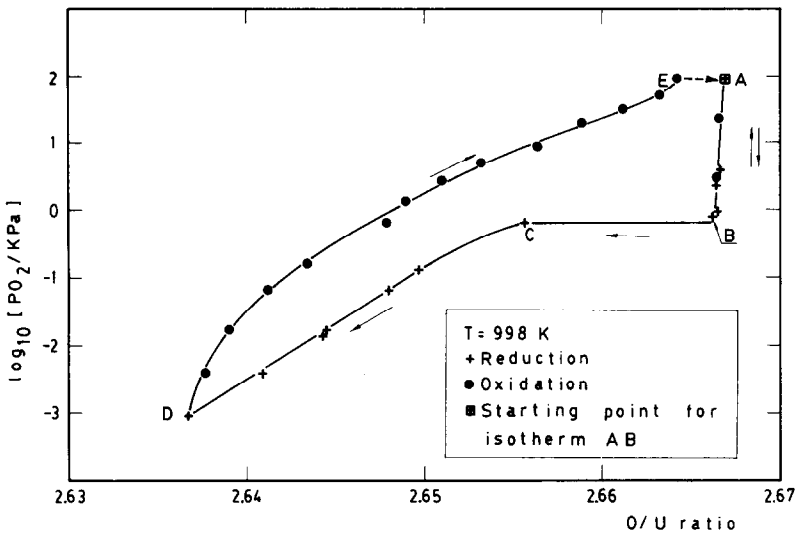

Fig. 1. Plot of $\log_{10} P_{O_2}$ as a function of O/U ratio in the uranium–oxygen system, for $2.63 < O/U < 2.67$, at 998 K.

on isotherm AB (see fig. 1). Isotherm AB, which is found in the range $2.666_8 \leqslant O/U \leqslant 2.667_1$, 8.0×10^{-1} kPa $\leqslant P_{O_2} \leqslant 10^2$ kPa, is perfectly reproducible upon oxidation (reduction) and subsequent reduction (oxidation) of the sample, and therefore we consider it to be constituted by stable equilibrium states of the uranium–oxygen system. Isotherm AB becomes suddenly unstable when P_{O_2} is lowered however slightly below the value corresponding to point B ($P_{O_2} = 8.0 \times 10^{-1}$ kPa, $O/U = 2.666_8$), and for $P_{O_2} = 6.6 \times 10^{-1}$ kPa the uranium–oxygen sample was found to reduce slowly (in 2 days) from the initial composition equal to that of point B to the final equilibrium composition, thus determining point C ($P_{O_2} = 6.6 \times 10^{-1}$ kPa, $O/U = 2.655_6$) on isotherm CD (see fig. 1).

An experimental fact we found is that point B on isotherm AB cannot be reobtained directly from point C by simply reoxidizing the sample at constant temperature (998 K). What actually happens is that, upon isothermal oxidation under pressures up to $P_{O_2} = 10^2$ kPa, the sample evolves from the state represented by point C (see fig. 1) to point E on isotherm DE. This is a manifestation of the existence of well-defined metastable equilibrium states in this region of the uranium–oxygen system.

Isotherm CD, which is found in the range $2.636_7 \leqslant O/U \leqslant 2.655_6$, 9.2×10^{-4} kPa $\leqslant P_{O_2} \leqslant 6.6 \times 10^{-1}$ kPa, was obtained and can be reproduced upon systematic reduction of the sample starting from isotherm AB. None of the points on isotherm CD can be reobtained merely by reoxidation of the sample. This implies that isotherm CD corresponds to metastable equilibrium states of the uranium–oxygen system.

Isotherm DE, found in the range $2.636_7 \leqslant O/U \leqslant 2.664_2$, 9.2×10^{-4} kPa $\leqslant P_{O_2} \leqslant 10^2$ kPa, was obtained and can be reproduced only upon systematic oxidation of the sample starting from point D on isotherm CD. As in the case of isotherm CD, isotherm DE represents metastable equilibrium states of the uranium–oxygen system. To reobtain point A from point E it was necessary to cool the sample to 773 K or lower, keeping $P_{O_2} = 10^2$ kPa, and then heating it again up to 998 K.

The obtained isotherms clearly show that, in the composition range around $UO_{2.66}$ and at 998 K, there is a substantial hysteresis in the behaviour of P_{O_2} as a function of oxygen content. This isothermal hysteresis concurs with observations by other authors [6,11,17] to the effect that near $UO_{2.66}$ there occurs a marked compositional hysteresis upon heat-treatment (heating and cooling) at constant P_{O_2}. Strictly speaking, this hysteresis is undesiderable for our purposes here, but it strongly suggests the underlying presence of at least a two-phase field around $UO_{2.66}$ in the stable-equilibrium phase diagram of the uranium–oxygen system: the correlated existence of stable two-phage regions (first-order phase transformations) and hysteresis phenomena of the kind we discuss has been proved to be the case in other oxide systems such as Pr–O [18–20], Ti–O [21], Nb–O [22] and Tb–O [23].

Important for our purposes here is that, in spite of

the existence of hysteresis, we were able to observe at around $UO_{2.667}$ one stable phase of the uranium–oxygen system, that is, the phase to which isotherm AB belongs. For this stable phase P_{O_2} decreases extremely rapidly with decreasing oxygen content (see fig. 1) and, in view of its instability for P_{O_2} values lower than that of point B on isotherm AB, we can safely place the lower limit of its homogeneity range at $O/U = 2.667 \pm 0.001$, at 998 K. Thus, we are lead to conclude that there must necessarily exist a two-phase field in the range of $UO_{2.66}$ in the stable equilibrium phase diagram of the uranium–oxygen system.

The conclusion expounded above agrees with the results obtained by Dharwadkar et al. [11], and we are in a position to confirm the existence of a stable two-phase field in the range of $UO_{2.66}$. The stable phase that we observed correlates perfectly with the U_3O_{8-z} hexagonal phase proposed by Dharwadkal et al. [11], who give an almost vertical lower phase boundary for U_3O_{8-z} placed around $O/U = 2.666$ in the range 1023 to 1243 K.

It must be remarked that the ratio $O/U = 2.655_6$ corresponding to point C on isotherm CD is close to the value $O/U = 2.652$ suggested by Dharwadkar et al. [11] for the almost vertical oxygen-rich phase boundary of $U_8\ O_{21+x}$. However, our measurements show that, in principle, point C represents only a metastable equilibrium state of the uranium–oxygen system and therefore cannot be taken to define the width of the stable equilibrium two-phase field between U_8O_{21+x} and U_3O_{8-z}.

Finally, let us mention that upon reduction we observed a clear discontinuity in O/U ratio (transition from B to C in fig. 1) which is completely absent in the oxidation experiments; this suggests that the metastable states obtained upon reduction (isotherm CD) are more closely related to the stable-equilibrium condition than those obtained by oxidation (isotherm EF).

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