Thermodynamics and phase equilibria of the system Ru–Te–O

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Abstract

The ternary phase diagram for the system Ru–Te–O is established at 900 K. The phase diagram was calculated using a free energy minimization method and was confirmed by establishing the isothermal section of the ternary system Ru–Te–O at 900 K using DTA and XRD techniques. © 1997 Elsevier Science B.V.

1. Introduction

Thermochemical properties and phase diagrams for systems containing fission products are required for the prediction of the chemical state of the nuclear fuel and the speciation of fission products under postulated accident conditions. Ruthenium, which is a major fission product owes its importance to the high volatility of RuO_4 causing major problem in fuel reprocessing, while Te though produced in moderate yield is important in nuclear safety analysis because it is a precursor to the hazardous iodine isotopes. A search into the literature revealed that the phase relations for the Ru–Te–O system, indicating the interaction of Ru and Te in the presence of oxygen, is not available. In this work, a Ru–Te–O phase diagram was constructed at 900 K using computational methods and was confirmed experimentally by DTA and XRD.

2. Experimental

The experimental work involved differential thermal analysis (DTA) and powder X-ray diffraction (XRD) techniques. DTA was carried out in a home made apparatus described elsewhere [1] with samples sealed in specially designed evacuated quartz ampoules. As temperature sensing element, a chromel–alumel thermocouple was used at

temperatures below 1273 K and a platinel couple was used above this temperature. The systems that were studied in the DTA are (i) an equimolar mixture of $Te + TeO_2$ to confirm their complete immiscibility and (ii) mixtures of $RuO_2 + TeO_2$ to establish the phase diagram of this quasi-binary section of the Ru–Te–O system and (iii) $Ru + TeO_2$ (1:1) and $RuO_2 + Te$ (1:1) mixtures. Powder XRD was employed to establish the isothermal section of the Ru–Te–O system at 900 K by analyzing the phases in mixtures of $RuO_2 + Te$, $Ru + TeO_2$ and $RuO_2 + TeO_2$ before and after appropriate heat treatments. Chemicals used were Te ingot (purity > 99.99%, Chemistry Division, BARC), Ru powder (purity > 99.95%, Heraeus, Hannau, Germany) and TeO_2 powder (purity 99.999%, Koch–Light, U.K). RuO_2 was prepared by heating Ru powder in air at 1273 K for 24 h in a platinum boat.

3. Thermodynamics and phase diagram

3.1. Ru–O, Te–O, Ru–Te systems

The condensed state phase relations for the Ru–O system was reviewed by Shunk [2] and Rard [3]. The only stable solid oxide is RuO_2. The Te–O system was reviewed by Elliott [4] and also by Shunk [2]. The various solid oxides known in the Te–O system are: TeO_2, Te_4O_9, Te_2O_5 and TeO_3 [5]. The irreversible decompositions of Te_4O_9, Te_2O_5 and TeO_3 into TeO_2 and O_2 by 875 K indicate that TeO_2, paratellurite, is the only condensed phase which can exist at 900 K [6]. Buketov et al. [7], showed Te and TeO_2 to be immiscible both in the solid

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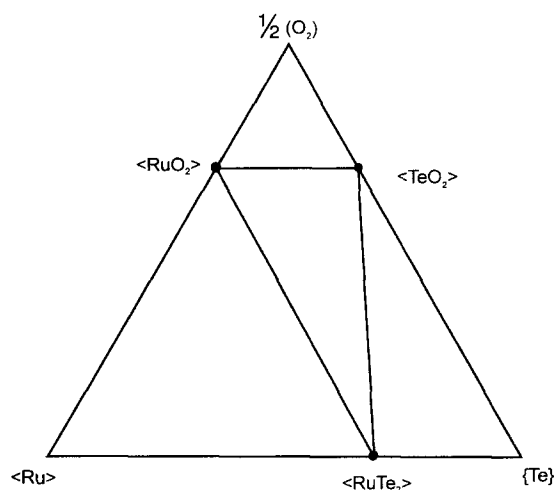
Fig. 1. Ru–Te–O phase diagram at 900 K.

and liquid states. The condensed state phase relation in the Ru–Te system has been investigated earlier [8] and was reviewed recently [9]. $RuTe_2$ is the only compound present in the condensed phase, which exists in two modifications, the metastable marcasite (m) and the stable pyrite (p).

3.2. Ru–Te–O system

A search through the JPCDS data base [5] showed that no ternary compound is known in this system. Moreover, the mutual solid solubility of RuO_2 and TeO_2 are also not known. No phase diagram was reported for the Ru–Te–O system so far in the literature.

4. Results and discussion

The phase diagram was calculated employing a computer code based on the free energy minimization principle [10]. This code is based on SOLGASMIX-PV [11], rewritten to PC environment with graphic interface. All possible condensed phases were represented in the input of the

program. At a given temperature and pressure, the program arrives at a set of possible condensed phases for a over all composition specified. The thermodynamic data for this purpose was chosen essentially from the works of Cordfunke et al. [7,12]. The data for (Te_3), (Te_4), (Te_5), (Te_6) and (Te_7) were derived using the equilibrium constants suggested by Krachler [13]. The calculated phase diagram at 900 K is shown in Fig. 1.

The calculated phase diagram was experimentally confirmed by DTA and XRD techniques. The results are given in Table 1. DTA results can be summarized as follows: (1) The DTA of an equimolar mixture of $Te + TeO_2$ confirmed their complete immiscibility (2) DTA $RuO_2 + TeO_2$ mixtures along this binary section of Ru–Te–O system show only one peak which is due to melting of TeO_2. Powder XRD was employed to establish the isothermal section of the Ru–Te–O system at 900 K. A mixture of $RuO_2 + Te$ (1:1) and (1:4) and $Ru + TeO_2$ was annealed in sealed silica ampoules at 900 K for 10 days. The XRD patterns of these annealed samples indicated the coexistence of $RuO_2 + TeO_2 + RuTe_2$ (p). Mixtures of $RuO_2 + TeO_2$ kept at 900 K for 10 days did not produce any other phase.

5. Conclusion

The ternary phase diagram for the system Ru–Te–O was calculated. The calculated diagram was confirmed by establishing the isothermal section of the ternary system Ru–Te–O at 900 K using DTA and XRD techniques.

Acknowledgements

Table 1
DTA and XRD results on samples in the Ru–Te–O system

Composition	Temperature range (K)	Effects observed in DTA[a]	Annealing conditions	Phases identified by powder XRD
$Te + TeO_2$ (1:1)	298–1100	endothermic peaks at 723 K and 1003 K	–	–
$RuO_2 + TeO_2$ (1:1)	298–1100	endothermic peak at 1003 K	900 K, 10 days	$RuO_2 + TeO_2$
$RuO_2 + TeO_2$ (1:4)	298–1100	endothermic peak at 1003 K	900 K, 10 days	$RuO_2 + TeO_2$
$Ru + TeO_2$ (1:1)	–	–	900 K, 10 days	$RuO_2 + TeO_2 + RuTe_2$ (p)
$RuO_2 + Te$ (1:1)	–	–	900 K, 10 days	$RuO_2 + TeO_2 + RuTe_2$ (p)
$RuO_2 + Te$ (1:4)	–	–	900 K, 10 days	$RuO_2 + TeO_2 + RuTe_2$ (p)

[a] Peak at 723 K is due to Te melting and the peak at 1003 K is due to TeO_2 melting. On cooling the corresponding freezing exothermic peaks were observed. But there was considerable undercooling in these samples.

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