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Journal of Nuclear Materials 350 (2006) 169–172

journal of nuclear materials

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Electron probe microanalysis (EPMA) investigations in the CeO_2–ThO_2–ZrO_2 system

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Received 23 July 2004; accepted 9 January 2006

Abstract

Several specimens of CeO_2–ThO_2–ZrO_2 of nominal compositions $Ce_{0.40}Th_{0.20}Zr_{0.40}O_2$, $Ce_{0.35}Th_{0.35}Zr_{0.30}O_2$, $Ce_{0.60}Th_{0.20}Zr_{0.20}O_2$, $Ce_{0.50}Th_{0.25}Zr_{0.25}O_2$, $Th_{0.40}Zr_{0.60}O_2$, $Ce_{0.10}Th_{0.10}Zr_{0.80}O_2$ and $Ce_{0.30}Th_{0.35}Zr_{0.35}O_2$ were annealed at 1400 ± 2 °C for 48 h and subsequently quenched to room temperature in order to retain the high-temperature phase. These specimens were subjected to detailed electron probe microanalysis (EPMA). All the compositions were found to be biphasic. Detailed compositional characterization and microstructure of these phases are also described in this manuscript. Based on the volume fraction of both the phases and microstructural evidences in these bulk compositions and phase relations at 1400 °C, an isothermal cross-section for the ternary system is being proposed.

1. Introduction

The development of uranium free inert matrix fuel is of world wide interest as by using this concept it is possible to faster annihilate the large stock of plutonium available from the dismantled weapons and the accumulated stock from the nuclear power plants. Kleykamp [1] has written a lucid review on selection of materials as diluents for burning the plutonium. As a part of the research on inert matrix fuels, recently, we had reported sub-solidus phase-equilibria in ceria (CeO_2)-thoria (ThO_2)-zirconia (ZrO_2) system [2]. ZrO_2 was included to act as the host material for holding the actinide phase because it has got high mechanical strength and a very low absorption cross-section for neutrons. CeO_2 is used as a surrogate material [3,4] in place of PuO_2. Based on the refinement of the X-ray diffraction data, several phase regions were identified in this pseudo-ternary phase-equilibria [2]. It is to be mentioned that the earlier X-ray diffraction work was essentially based on slow-cooled samples. In the present investigation, the samples are quenched from 1400 °C in order to retain the high-temperature phases and a detailed EPMA (electron probe microanalysis) studies on some of the compositions is done. Based on these studies, a suitable isotherm at 1400 °C is being proposed.

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doi:10.1016/j.jnucmat.2006.01.001

2. Experimental

2.1. Preparation

The various compositions in CeO_2–ThO_2–ZrO_2 system were prepared by a three-step heating protocol, so as to achieve better homogeneity, as reported earlier [2]. In order to construct a phase-equilibria, a few samples were heated at 1400 °C for 48 h and quenched to room temperature.

2.2. Sample preparation for EPMA

Samples for EPMA studies were polished to 1 μm diamond finish by conventional metallographic techniques. Detailed compositional analyses of the samples were done using EPMA (CAMECA SX 100). The samples were coated with thin gold layer (≈10 nm) for ensuring conductivity. In order to acquire high contrast for back-scattered electron images, the acceleration voltage was generally kept in the range of 25–30 keV and the beam current around 1–4 nA. An acceleration voltage of 20 keV and 20 nA stabilized beam current was used for quantitative analysis. For compositional analysis, electron beam size was kept at $\leqslant 1$ μm to reduce the convolution effect so as to arrive at the better estimate of the phase compositions. Pure CeO_2, ThO_2 and ZrO_2 were used as standards for calibrations. Oxygen was analyzed on the stoichiometric basis. Crystals used for diffracting different X-ray lines are given in Table 1. A PAP correction program [5] was used for necessary atomic number (Z), absorption (A) and fluorescence (F) corrections to obtain true concentrations from the corresponding raw intensity data.

3. Results and discussion

Table 1
Crystals used for diffracting X-ray lines

X-ray line	Crystal	Name	2d (nm)
Th Mα	PET	Penta erithrotol	0.87
Zr Lα	PET	Penta erithrotol	0.87
Ce Lα	LIF	Lithium fluoride	0.42
O Kα	PCI	Pseudo-crystal	6.00

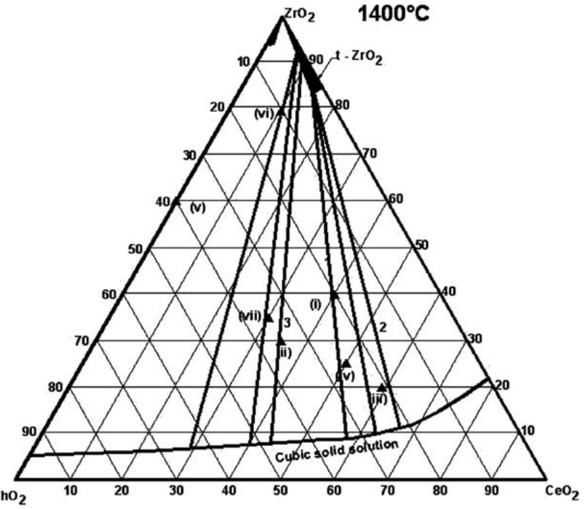

Fig. 1. Phase relations within the pseudo-ternary CeO_2–ThO_2–ZrO_2 system at 1400 °C.

Seven nominal compositions (i) $Ce_{0.40}Th_{0.20}Zr_{0.40}O_2$, (ii) $Ce_{0.35}Th_{0.35}Zr_{0.30}O_2$, (iii) $Ce_{0.60}Th_{0.20}Zr_{0.20}O_2$, (iv) $Ce_{0.50}Th_{0.25}Zr_{0.25}O_2$, (v) $Th_{0.40}Zr_{0.60}O_2$, (vi) $Ce_{0.10}Th_{0.10}Zr_{0.80}O_2$ and (vii) $Ce_{0.30}Th_{0.35}Zr_{0.35}O_2$ belonging to different phase field regions were studied by EPMA and the bulk compositions are also marked in the pseudo-ternary CeO_2–ThO_2–ZrO_2 isotherm of Fig. 1. Detailed EPMA analyses of all seven specimens indicated that they were biphasic, consisting of a bright phase and a gray phase. The bright phase in each case is essentially rich in thoria and ceria, gray phase was found to be rich in zirconia. The volume fractions of gray and bright phases for all specimens along with compositions derived by EPMA are given in Table 2. Based on this detailed EPMA data, seven tie-lines were drawn (Fig. 1) and some of the salient features of the EPMA data are given below. Typical back-scattered electron (BSE) image for the specimen of composition $Ce_{0.40}Th_{0.20}Zr_{0.40}O_2$ (i) is shown in Fig. 2 and this micrograph clearly shows the presence of two phases (bright and gray). The phases are distributed homogeneously in the matrix and exhibit sharp triple-point grain boundaries. Small dark regions observed in Fig. 2 are due to the fine pores of the matrix. The average grain size of the gray phase is about 1–3 μm and that of the bright phase is about 2–4 μm. Compositions of these phases are listed in Table 2. It is seen that the bright phase is the solid solution of ThO_2 and CeO_2 with 33.0 mol% ThO_2, 58.0 mol% CeO_2 and 9.0 mol% ZrO_2. On the other hand, the gray phase is rich in ZrO_2 with 13.0 mol% CeO_2, 0.6 mol% ThO_2 and 86.4 mol% ZrO_2. The phase is essentially a tetragonal (Zr, Ce and Th)O_2 phase and is marked as t-ZrO_2 in Fig. 1. The volume (%) estimated from the BSE images (Table 2) indicate that the bright phase is marginally more compared to the gray phase.

Table 2
Composition (mole fraction) of the bulk specimen and the phase formed along with the volume fraction of these phases estimated by EPMA analysis

No.	Bulk composition	Phases formed compositions (mol%)				Volume fraction (%)
		Nature	ZrO_2	CeO_2	ThO_2	
(i)	$Ce_{0.40}Th_{0.20}Zr_{0.40}O_2$	Bright	9.0	58.0	33.0	51
		Gray	86.4	13.0	0.6	46
		Pore	–	–	–	3
(ii)	$Ce_{0.35}Th_{0.35}Zr_{0.30}O_2$	Bright	7.1	42.5	50.4	57
		Gray	89.5	8.6	1.9	41
		Pore	–	–	–	2
(iii)	$Ce_{0.60}Th_{0.20}Zr_{0.20}O_2$	Bright	11.4	68.0	20.6	57
		Gray	85.1	13.5	1.4	41
		Pore	–	–	–	2
(iv)	$Ce_{0.50}Th_{0.25}Zr_{0.25}O_2$	Bright	10.2	64.4	25.4	55
		Gray	87.1	11.1	1.8	43
		Pore	–	–	–	2
(v)	$Th_{0.40}Zr_{0.60}O_2$	Bright	3.9	–	96.1	35
		Gray	a	–	–	60
		Pore	–	–	–	5
(vi)	$Ce_{0.10}Th_{0.10}Zr_{0.80}O_2$	Bright	a			12
		Gray	93.0	5.6	1.4	86
		Pore	–	–	–	2
(vii)	$Ce_{0.30}Th_{0.35}Zr_{0.35}O_2$	Bright	8.7	36.7	54.6	63
		Gray	83.4	8.6	8.0	36
		Pore	–	–	–	1

a: Quantitative analysis could not be done due to small (<1 μm) sized-grains of the gray phase.

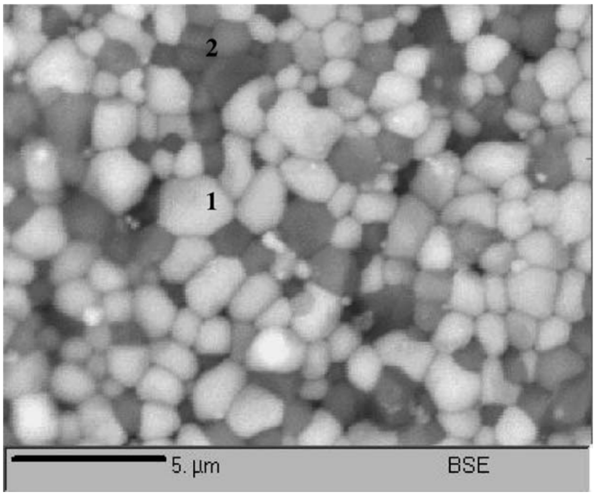

Fig. 2. BSE image of $Ce_{0.40}Th_{0.20}Zr_{0.40}O_2$ specimen showing the presence of bright (marked as 1) and gray (marked as 2) phases.

The coexistence of the bright phase and gray phase and the compositional data suggests the possibility of existence of equilibrium between t-$Ce_{0.16}Zr_{0.84}O_2$ (dark phase) and $Ce_{0.58}Th_{0.33}Zr_{0.09}O_2$ (bright phase) and there is very limited solubility of ThO_2 in the $Ce_{0.16}Zr_{0.84}O_2$ (tetragonal phase). Based on these results, a tentative tie-line (marked as 1) is drawn in Fig. 1. In order to draw these tie-lines, the solubility of ThO_2 is neglected. It can be seen from Table 2 that the maximum solubility of ThO_2 in $Ce_{0.16}Zr_{0.84}O_2$ phase is about 1.9% for the specimen $Ce_{0.35}Th_{0.35}Zr_{0.30}O_2$. Based on these data, six more tentative tie-lines (marked as 2–7) are plotted in Fig. 1. It has to be mentioned that the composition of the mixture $Ce_{0.50}Th_{0.25}Zr_{0.25}O_2$ is not exactly on tie-line-2 connecting the t-$Ce_{0.16}Zr_{0.84}O_2$ and the bright phase ($Ce_{0.63}Th_{0.27}Zr_{0.10}O_2$). However, for drawing the tie-line, the experimentally determined composition by EPMA was used. Similar criteria was used for drawing the tie-line-3. It can be seen that the solubility of ZrO_2 in the cubic phase CeO_2–ThO_2 increases with increase in CeO_2 and these results are also consistent with CeO_2–ZrO_2 binary phase diagram [6]. The increases of the ZrO_2 in $Th_{1-x}Ce_xO_2$ with corresponding increase in CeO_2 content can be attributed to a gradually lower mismatch between ionic size of Zr^{4+} and average ionic size of $(Th_{1-x}Ce_x)^{4+}$. A typical BSE image of the

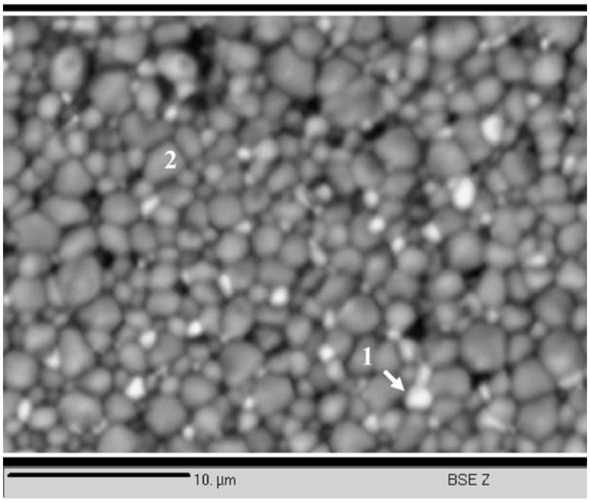

Fig. 3. BSE image of $Ce_{0.10}Th_{0.10}Zr_{0.80}O_2$ specimen showing the presence of bright (marked as 1) and gray (marked as 2) phases.

specimen $Ce_{0.10}Th_{0.10}Zr_{0.80}O_2$ (marked as vi), annealed under identical conditions, is shown in Fig. 3. This microstructure clearly shows the presence of two phases, bright and gray phase. The presence of bright phase of size <2 µm can be clearly seen at the tri-junctions of the bright and gray phases. The average grain size of the gray phase and bright phase is 2–4 µm and 0.5–1 µm, respectively. The grain sizes are marginally smaller compared to the specimen of $Ce_{0.40}Th_{0.20}Zr_{0.40}O_2$ (marked as i). The size of the bright phase was found to be too fine for any meaningful quantitative EPMA analysis. The quantitative data for these phases along with the volume fraction is listed in Table 2. Based on these data, a tentative ternary phase field is drawn in Fig. 1. It is important to mention here that the X-ray diffraction data and the EPMA data are generally complimentary. In our earlier work [2], the presence of the tetragonal ZrO_2 on the pseudo-ternary CeO_2–ThO_2–ZrO_2 phase diagram was inferred based on just one peak at $2\theta \approx 30°$ and in turn the description of the two-phase and three-phase fields was purely based on the qualitative X-ray diffraction data. The detailed EPMA data, however, rules out the possibility of a three-phase field.

4. Conclusions

The ternary system CeO_2–ThO_2–ZrO_2 is studied using electron probe microanalysis (EPMA) as a probing tool. An isothermal cross-section at 1400 °C for this ternary system is drawn based on these investigations. All the compositions, which were studied were found to contain two phases and hence the EPMA studies does not show the presence of a three-phase field as was inferred by qualitative X-ray analysis done in the slow-cooled studies. The difference in the observations by the two studies could be attributed to the fact that in the latter case, the samples were quenched from 1400 °C as against the slow-cooled conditions in the first study.

Acknowledgements

The authors are grateful to Dr S. Banerjee, Director, Bhabha Atomic Research Centre, Mr B. P. Sharma, Head, Materials Science Division and Dr S. K. Kulshreshtha, Head, Chemistry Division for their keen interest in the work.

References

[1] H. Kleykamp, J. Nucl. Mater. 275 (1999) 1.
[2] V. Grover, A.K. Tyagi, J. Nucl. Mater. 305 (2002) 83.
[3] M.D. Mathews, B.R. Ambekar, A.K. Tyagi, J. Nucl. Mater. 288 (2001) 83.
[4] A.K. Tyagi, B.R. Ambekar, M.D. Mathews, J. Alloy Compd. 337 (2002) 275.
[5] J.L. Pouchou, F. Pichoir, Microbeam Analysis, San Francisco, California, 1985, p. 104.
[6] P. Duwez, F. Odell, J. Am. Ceram. Soc. 33 (1950) 280.