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Preparation of Ce–Pr mixed carbide by carbothermic reduction

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Abstract

Carbothermic reduction was adapted to convert mixtures of cerium oxide and praseodymium oxide into cerium–praseodymium mixed dicarbides ($Ce_xPr_{1-x}C_2$). XRD results indicate that the lattice parameters of $Ce_xPr_{1-x}C_2$ vary continuously with x and that the complete miscibility exists between CeC_2 and PrC_2. © 1998 Elsevier Science S.A.

Keywords: Ce; Pr; Mixed carbide; Mixed oxide; Carbothermic reduction

1. Introduction

Carbothermic reduction is often employed to convert some metal oxides into their carbides. This method was adopted to form Ce–Pr mixed dicarbides ($Ce_xPr_{1-x}C_2$) in the present work. As far as the authors are concerned, little is known about the solid solubility between CeC_2 and PrC_2 [1]. CeC_2 and PrC_2 have a body centered tetragonal structure (CaC_2 type). The lattice parameters reported previously are $a=0.388$ nm and $c=0.649$ nm for CeC_2 and $a=0.3855$ nm and $c=0.6434$ nm for PrC_2 [2,3]. The lattice parameters of the respective dicarbides obtained by carbothermic reduction in our laboratory are in good agreement with these reported values. For preparation of Ce–Pr mixed dicarbides, two kinds of starting materials were used, one being heat-treated products which were obtained by sintering mixtures of CeO_2 and $PrO_{1.83}$ with the desired mixing ratio in air for 12 h at 1400°C and the other mixtures of CeO_2 and $PrO_{1.83}$. The phase relationships deduced from the X-ray diffraction (XRD) analysis of these sintered oxides are largely consistent with Nauer et al. [4]. However, the results reported by Takasu et al. [5] are different from the present work and that of Nauer et al.

2. Experimental procedure

CeO_2 powder (99.999%) and Pr_6O_{11} powder (99.999%) supplied from the Nilaco Corporation were mixed in a predetermined atomic ratio in an agate mortar. This mixture of CeO_2 and Pr_6O_{11} was pressed into pellets of 10.2 mm diameter and 1.6 mm height under a pressure of 250 MPa for 10 min. The pellets were loaded on an alumina boat and put into an alumina reaction tube. The temperature was raised up to 1400°C at a rate of $12°C\ min^{-1}$. Then the temperature of the pellets was kept at 1400°C for 12 h in air atmosphere and cooled down at a rate of $-2°C\ min^{-1}$. The pellets were ground in an agate mortar and powdered again. Part of thus heat-treated product was subject to X-ray diffraction analysis and the rest was blended with amorphous carbon in the atomic ratio $C/M=4.8$ (M=Ce or Pr). This powder was compacted to several pellets, whose sizes were identical with the mixed oxide pellets above mentioned, under 250 MPa after polyvinylalcohol was added to it as a binder. These pellets were put on an alumina boat and sintered in vacuum for 12 h at 1400°C. During this reaction, the pressure in the reaction tube gained momentarily up to the order of 10^{-3} Pa presumably due to the generation of CO according to the reaction equation; $MO_{2-x}+(4-x)C=MC_2+(2-x)CO$, and a gradual decrease followed. The previous level (10^{-5} Pa order) was reestablished within 12 h. After sintering the furnace was removed from the reaction tube. The product was rapidly cooled down to avoid its decomposition because rare earth dicarbides, especially CeC_2, have a tendency to decompose to sesquicarbide and carbon at low temperatures. The product was brought in a glove box filled with argon and ground to fabricate the sample for XRD. For comparison the reactions of oxide mixtures without the heat treatment and carbon were also performed. The kind and number of phases in all reaction products were determined at room temperature by XRD with a diffractometer (Rigaku Denki: Geiger flex rad-rA) operated at 40 kV and 150 mA (Cu

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Table 1
The results and conditions of the sintering mixture of CeO_2 and Pr_6O_{11}

Run	Mass of starting material (g)		x =Ce/(Ce+Pr)	Products	Lattice parameter [nm]
	CeO_2	Pr_6O_{11}			
1	0.1048	0.9389	0.10	$(Ce,Pr)O_2$ $(Pr, Ce)O_{1.83}$	0.5405 0.5468
2	0.2109	0.8356	0.20	$(Ce,Pr)O_2$ $(Pr, Ce)O_{1.83}$	0.5399 0.5467
3	0.1820	0.4183	0.30	$(Ce, Pr)O_2$ $(Pr, Ce)O_{1.83}$	0.5402 0.5469
4	0.2414	0.3586	0.40	$(Ce, Pr)O_2$ $(Pr, Ce)O_{1.83}$	0.5401 0.5470
5	0.2990	0.3002	0.50	$(Ce, Pr)O_2$ $(Pr,Ce)O_{1.83}$	0.5403 0.5462
6	0.3314	0.2686	0.55	$(Ce, Pr)O_2$ $(Pr, Ce)O_{1.83}$	0.5403 0.5462
7	0.3606	0.2398	0.60	$(Ce, Pr)O_2$	0.5406
8	0.4200	0.1794	0.70	$(Ce, Pr)O_2$	0.5406
9	0.4808	0.1190	0.80	$(Ce, Pr)O_2$	0.5 407
10	0.5407	0.0598	0.90	$(Ce, Pr)O_2$	0.5409

Kα) using silicon as external calibration. The lattice parameters were calculated by using Cohen's method [6].

3. Results and discussion

3.1. Sintering oxide mixture

X-ray diffraction patterns of sintered oxides indicate the presence of a single phase of cerium–praseodymium mixed dioxide $(Ce, Pr)O_2$ (CeO_2 type) up to a Pr_6O_{11} content of 40 mol%, and two phases of $(Ce, Pr)O_2$ and $(Pr, Ce)O_{1.83}$ (Pr_6O_{11} type) within the range of $0.1 \leq x \leq 0.55$ (x denotes the ratio of cerium to metal). In Table 1 the results and conditions of sintering the oxide mixtures are summarized. These results are similar to those reported by Nauer et al. [4], but they are inconsistent with those reported by Takasu et al. [5]. However, the obtained data agree with the latter in that two fluorite phases coexist even at low CeO_2 contents. In Fig. 1 the relationship between the lattice parameters of the sintered oxide mixtures and the mixing ratio are shown. The lattice parameter of $(Ce, Pr)O_2$ changes linearly over the domain of the single phase region. In the two-phase domain the lattice parameters of both $(Ce, Pr)O_2$ and $(Pr, Ce)O_{1.83}$ are constant and the respective values are 0.5403 and 0.5466 nm. The lattice parameter of $(Ce, Pr)O_2$, 0.5403 nm, corresponds to $x=0.58$, which is the terminal composition of the single phase domain.

3.2. Carbothermic reduction of oxide mixture

A single phase of cerium-praseodymium mixed dicarbide, $CexPr_{1-x}C_2$ (bct structure), was obtained by carbothermic reduction of the sintered oxide mixture above mentioned for several selected values of x (x=0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1). Similar results were obtained from carbothermic reduction of as-blended oxide mixtures. The results of XRD suggest that if compared at the same x value, the heat treatment of the oxide mixture has no effect in the final results. The results and conditions of carbothermic reduction of non-sintered oxide mixtures are shown in Table 2. It is also found from these results that cerium dicarbide and praseodymium dicarbide are completely miscible, as suggested by Adachi et al. [1]. They pointed out that lattice parameters of cerium–praseodymium mixed dicarbide followed Vegard's law over the whole range. However, the results of this work show clearly a negative deviation from Vergard's law. The relationship between lattice parameters and cerium to metal ratio are given in

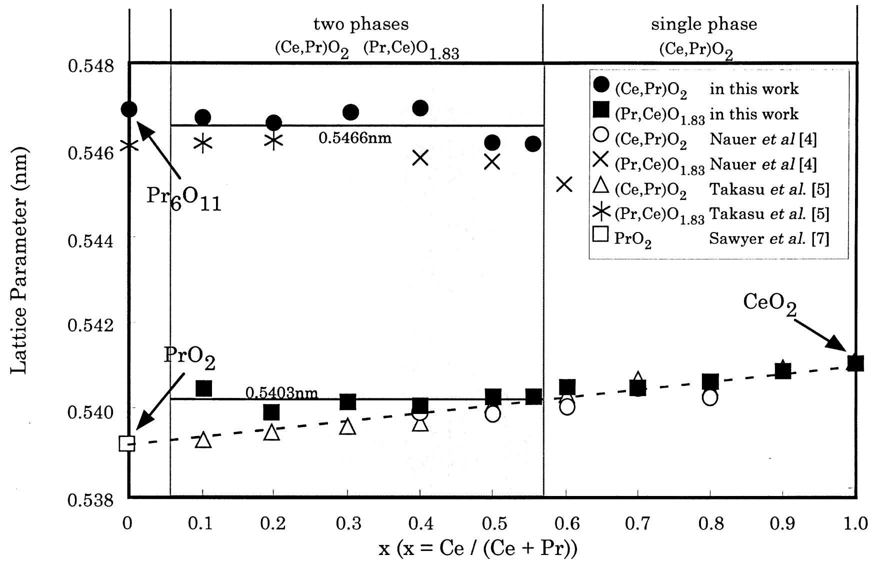

Fig. 1. Relationship between lattice parameters of obtained products and mixing ratio of CeO_2 and $PrO_{1.83}$.

Table 2
The results of carbothermic reduction of mixtures of CeO_2 and Pr_6O_{11}

Run	Mass of starting materials (g)		C^b	Product^b	Lattice parameters [nm]	
	CeO_2	Pr_6O_{11}			*a*	*c*
11	0.1946	0	0.0675	CeC_2	0.3883	0.6495
12	0.9451	0.1030	0.3585	$Ce_{0.90}Pr_{0.10}C_2$	0.3877	0.6480
13	0.7361	0.3121	0.3638	$Ce_{0.70}Pr_{0.30}C_2$	0.3870	0.6468
14	0.5208	0.5144	0.3687	$Ce_{0.50}Pr_{0.50}C_2$	0.3863	0.6456
15	0.3171	0.7317	0.3549	$Ce_{0.30}Pr_{0.70}C_2$	0.3859	0.6444
16	0.1056	0.9407	0.3534	$Ce_{0.10}Pr_{0.90}C_2$	0.3855	0.6438
17	0	0.1998	0.0731	PrC_2	0.3854	0.6434

[a] Including a few weight percents of excess carbon.
[b] Amorphous carbon.

Fig. 2. The lattice parameters of CeC_2 and PrC_2 prepared by carbothermic reduction in this work are $a=0.3883$ nm and $c=0.6495$ nm, and $a=0.3854$ nm and $c=0.6434$ nm, respectively, and these are in good agreement with those reported previously ($a=0.388$ nm and $c=0.649$ nm for CeC_2 and $a=0.3855$ nm and $c=0.6434$ nm for PrC_2). [2,3] The smooth variation of the lattice parameters *a* and *c* values and of the c/a value may suggest that cerium and praseodymium atoms are distributed at random. It is observed that the dicarbides are easily formed irrespective of whether the mixtures of CeO_2 and $PrO_{1.83}$ has been heat-treated or not. This fact may suggest that CeC_2–PrC_2 mixed carbides are thermodynamically considerably stable compared with their simple mixtures. However, it is not

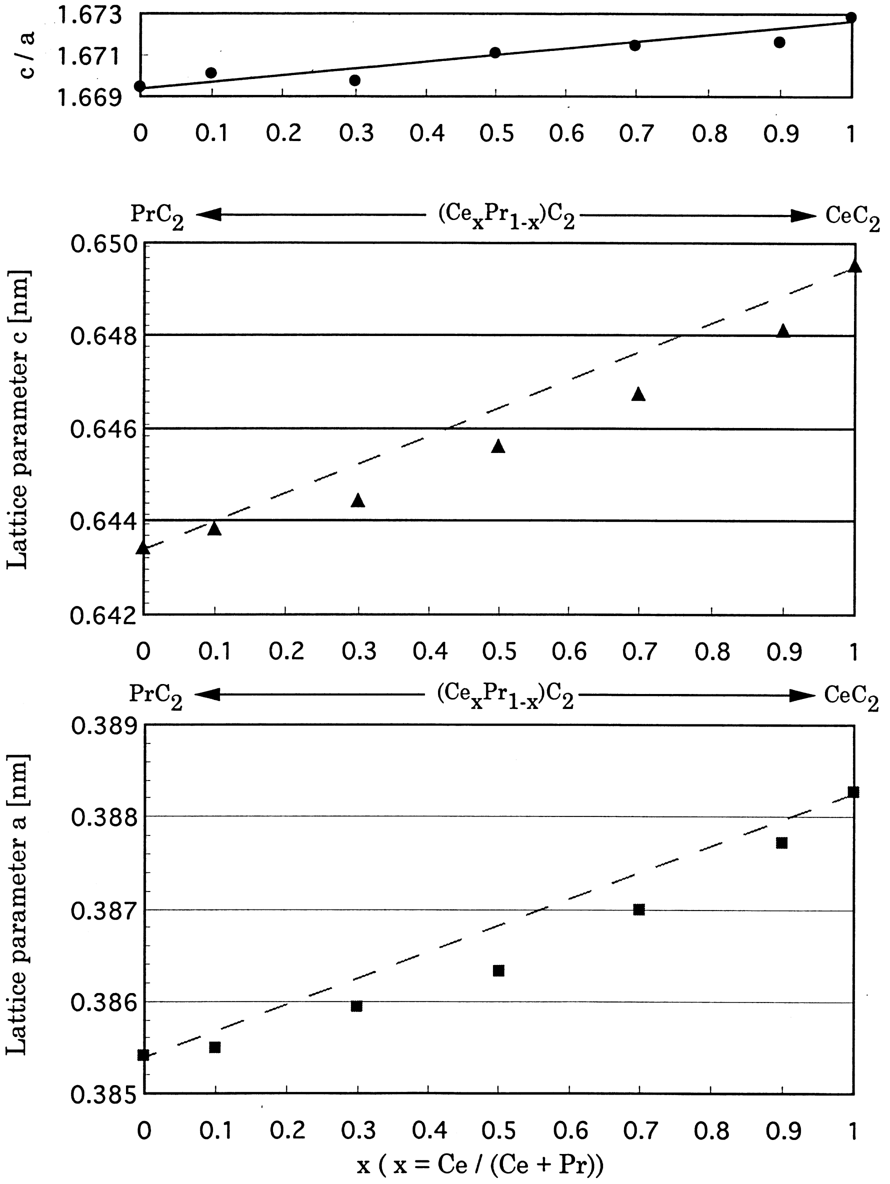

Fig. 2. Relation between lattice parameters of Ce–Pr mixed dicarbide and *x*.

clear in what stage of the carbothermic reduction the mixing of Ce and Pr atoms occur. Further work is now in progress to clarify this point.

4. Conclusions

Single (Ce, Pr)O_2 phase was obtained by sintering the mixture of CeO_2 and Pr_6O_{11} up to Pr_6O_{11} contents 40 mol% and two fluorite phases, (Ce, Pr)O_2 and (Pr, Ce)$O_{1.83}$, were obtained within $0.1 \leq x \leq 0.55$ (x is a cerium ratio to metal). The lattice parameters of (Ce, Pr)O_2 change linearly with composition in the domain of the cerium-rich single phase. In a two-phase region, the values of lattice parameters of (Ce, Pr)O_2 and (Pr, Ce)$O_{1.83}$ are constant and they are 0.5403 nm and 0.5466 nm, respectively. The former corresponds to that of $(Ce_{0.58}Pr_{0.42})O_2$.

Cerium–praseodymium mixed dicarbides $Ce_xPr_{1-x}C_2$ were obtained by carbothermic reduction of sintered oxide mixtures as well as non-sintered ones. The results of XRD of obtained $Ce_xPr_{1-x}C_2$ indicate a negative deviation from Vegard's law. It is confirmed that CeC_2 and PrC_2 are completely miscible.

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