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## CALCULATION OF PHASE EQUILIBRIA IN THE Y<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> SYSTEM

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### ABSTRACT

Rare earth oxide stabilized zirconias find a wide range of applications. An understanding of phase equilibria is essential to all applications. In this study, the available phase boundary data and thermodynamic data is collected and assessed. Calphad-type databases are developed to completely describe the Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, Yb<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub> systems. The oxide units are treated as components and regular and sub-regular solution models are used. The resultant calculated phase diagrams show good agreement with the experimental data. Then the binaries are combined to form the database for the Y<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> pseudo-ternary

### INTRODUCTION

Yttria-stabilized zirconia is one of the most widely used ceramics, with applications ranging from thermal barrier coatings to solid oxide fuel cells. There has been interest in using other rare earth oxides alone or in combination to stabilize zirconia. These different combinations offer improved properties, such as reduced thermal conductivity.

A survey of phase equilibria data for rare-earth oxide/zirconia systems shows a good deal of information on the Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> system, but only limited information on the other rare-earth oxide/zirconia systems (1-3). Experimental data on two or more rare earth oxides in combination with zirconia is even more limited. For this reason, a Calphad (CALculation of PHase Diagrams) assessment is valuable (4). In this method, a series of binary databases are combined to form reliable high order databases.

Due to the widespread use of the Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> binary system, there are several assessments in the literature. Kaufman (5) first approached this system by treating each oxide unit as a component. Degtyarev and Voronin (6-7) further simplified this system

by treating the two cubic phases—cubic  $ZrO_2$  and cubic  $Y_2O_3$ —as one cubic phase with a miscibility gap. Du et al.(1) have thoroughly reviewed all available literature on this system through 1990 and developed a Calphad-type database with this miscibility gap simplification. The group of Yokokawa (8-9) has also calculated the  $Y_2O_3$ - $ZrO_2$  phase diagram and extended these calculations to other rare-earth oxide/zirconia systems.

In this paper we re-assess the  $Y_2O_3$ - $ZrO_2$  system. We do not use the miscibility gap simplification, because cubic  $ZrO_2$  and cubic  $Y_2O_3$  are of different space groups. Also a miscibility gap leads to convergence problems from the corresponding multi-component systems. We also assess the  $Yb_2O_3$ - $ZrO_2$  and  $Y_2O_3$ - $Yb_2O_3$  systems and combine these to form the  $Y_2O_3$ - $Yb_2O_3$ - $ZrO_2$  ternary.

### APPROACH

The first step in the assessment process is to survey all available data in the literature. The phases in the  $Y_2O_3$ - $Yb_2O_3$ - $ZrO_2$  system are given in Table I.

Table I. Phases in the  $Y_2O_3$ - $Yb_2O_3$ - $ZrO_2$  system.

Phase	Abbreviation
Monoclinic $ZrO_2$	mz
Tetragonal $ZrO_2$	tz
Cubic $ZrO_2$	cz
Liquid $Y_2O_3$ - $Yb_2O_3$ - $ZrO_2$	liq
Cubic $Y_2O_3$	cy
Hexagonal $Y_2O_3$	hy
$Zr_3Y_4O_{12}$	delta y
Cubic $Yb_2O_3$	cyb
Hexagonal $Yb_2O_3$	hyb
$Zr_3Yb_4O_{12}$	delta yb

As noted, there is a good deal of experimental information on the  $Y_2O_3$ - $ZrO_2$  system. This has been discussed in detail in other publications (1-3) and will only be briefly summarized here. The liquidus line of Noguchi et al. (10) was used in this assessment. There are numerous measurements of the tetragonal/(cubic + tetragonal)/cubic phase boundaries (11-17). Several different techniques were used and, in general, these show remarkably good agreement. The studies of Stubican et al. (12) are the most complete examination of this system and were used in the assessment. Four invariant points have been reported for this system—these are listed in Table II. There is an intermediate compound of composition  $Zr_3Y_4O_{12}$ , which decomposes to the cubic solid solution of  $ZrO_2$ . A second, pyrochlore-type compound in the  $Y_2O_3$ -rich portion of the diagram has been reported by other investigators, but its existence is controversial (18) and it will not be considered here.

Table II. Invariant points and decomposition temperatures in the  $Y_2O_3$ - $ZrO_2$  and  $Yb_2O_3$ - $ZrO_2$  pseudo-binaries.

	Temperature (K)	Composition $x(Y_2O_3)$	Reference	Comments
Eutectic liq = cz + cy	2688	0.817	(12)	
Peritectic cy = liq + hy	2720	0.778	(12)	Introduced, not measured
Euctectoid cz = delta y + cy	1650	0.435	(13)	
Euctectoid tz = mz + cz	838	0.039	(19)	Difficult to attain equilibria at this low temperature
Euctectoid cz = delta y + mz	< 673	0.20-0.30	(12)	Difficult to attain equilibria at this low temperature Approximate euctectoid discussed in (12)
Decomposition Temperature of delta y	1655	0.4	(20)	
Eutectic liq = cz + cyb	2691	0.85	(21)	
Decomposition of delta yb	1898	0.4	(20)	

There is very little thermodynamic data for the  $Y_2O_3$ - $ZrO_2$  system. Belov and Semenov have measured activities in the system at 2773 K (22). For the intermediate compound  $Zr_3Y_4O_{12}$ , there are some recent first principles calculations of enthalpies at 0 K (23).

As noted, there is much less data for the  $Yb_2O_3$ - $ZrO_2$  system. The liquidus measurement of Rouanet (21) was used in the assessment. Limited phase boundary measurements in the  $ZrO_2$  rich side by Stubican et al. (20) were used. The single reported invariant point is given in Table II. This system also contains an intermediate compound,  $Zr_3Yb_4O_{12}$ , which decomposes at a higher temperature than the analogous  $Zr_3Y_4O_{12}$  compound (20).

The third binary needed is the  $Y_2O_3$ - $Yb_2O_3$  system. The only experimental phase diagram (24) shows a continuous cubic solid solution. Thus this system was simply modeled as an ideal solution.

One study of the  $Y_2O_3$ - $Yb_2O_3$ - $ZrO_2$  system was found (25). The major features of this are continuous tetragonal  $ZrO_2$  with  $Y_2O_3$  and  $Yb_2O_3$ ; continuous cubic  $ZrO_2$  with  $Y_2O_3$  and  $Yb_2O_3$ ; continuous cubic  $(Y,Yb)_2O_3$ ; and a continuous line compound  $Zr_3(Y,Yb)_4O_{12}$ . The presence of the line compound, of course, depends on the disordering temperatures in Table II.

## MODELING

The first step in a Calphad modeling is to determine the lattice stabilities for all phases. These were taken from the SGTE pure substance database (26), which in turn is from the IVTAN tables (27). These numbers are derived from the phase transition temperature and heats. We have modified the melting point of  $Y_2O_3$  to agree with the melting point measured by Stubican (12). The SGTE database includes a solid/solid and a solid/liquid phase transition for  $Yb_2O_3$ , but only the temperatures of transition are given—no heats are reported. Therefore we used the heats for analogous  $Y_2O_3$  transitions.

Two commercial codes were used for these calculations—ThermoCalc\* and WinPhad\*\*. Both express the solutions as:

$$G_m(x, T) = \sum_{i=1}^2 x_i {}^{\circ}G_i(T) + RT \sum_{i=1}^2 x_i \ln x_i + {}^{ex}G_m \quad (1)$$

$${}^{ex}G_m = x_1 x_2 \sum_{j=0}^n {}^jL(x_1 - x_2)^j \quad (2)$$

The first term in equation (1) is the sum of the Gibbs energies of each component, the second term is the ideal entropy of mixing, and the third term is the excess Gibbs energy. Both codes express the excess Gibbs energy as a Redlich-Kister polynomial (28). In all cases, only the first one or two terms were needed, which corresponds to the regular and sub-regular solution models, respectively.

The solution parameters, were derived from the selected experimental data using the optimizing modules of ThermoCalc and WinPhad. The most prominent features of the phase diagrams were first developed and then the fine features added. The goal is to develop a description of the entire system with a minimum number of parameters. As noted, binaries can be put together to form ternaries. In general a limited number of ternary interaction coefficients are necessary.

## RESULTS

Figure 1 is the calculated  $Y_2O_3$ - $ZrO_2$  pseudo-binary. In general agreement with experimental data is good. The four invariant points are reproduced as is the disordering temperature for  $Zr_3Y_4O_{12}$ . The (tetragonal + cubic)/cubic phase boundary is  $x(Y_2O_3) \sim 0.02$  high at the lower temperatures. A better model should help reproduce this feature. Current work focuses on the modeling of this system with the ionic model (29).

\* ThermoCalc Software, Stockholm, Sweden

\*\* CompuTherm LLC, Madison, Wisconsin

Figure 2 is the calculated  $\text{Yb}_2\text{O}_3\text{-ZrO}_2$  pseudo-binary. Agreement with the limited experimental data is good. Note the intermediate compound decomposes at a higher temperature than that in the  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  system.

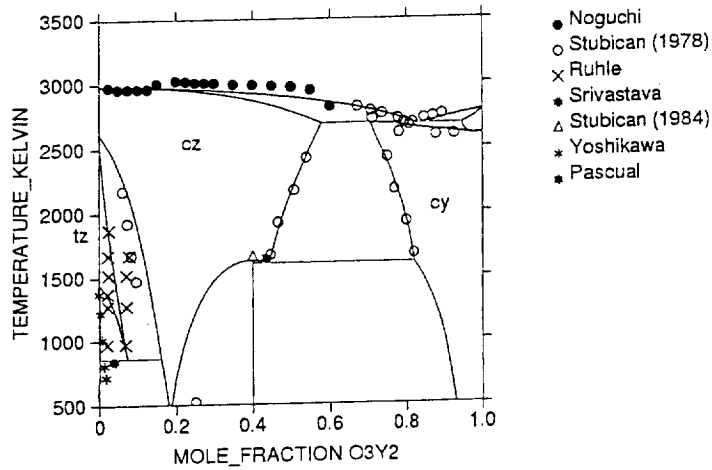


Figure 1. Calculated  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  phase diagram. The data points are the experimental points.

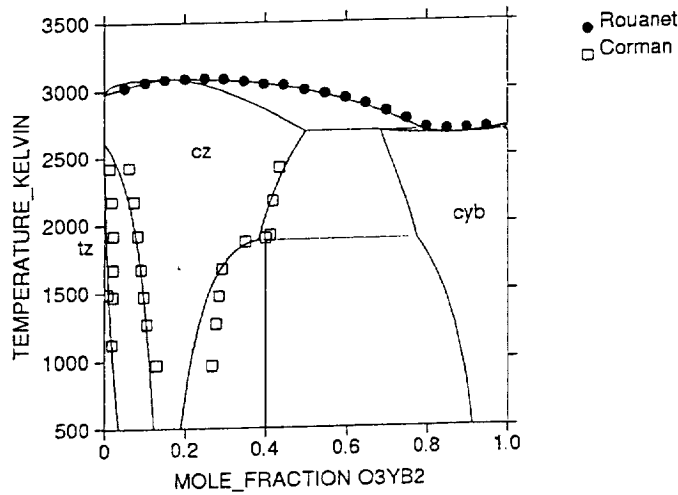


Figure 2. Calculated  $\text{Yb}_2\text{O}_3\text{-ZrO}_2$  pseudo-binary phase diagram. Data points are experimental data.

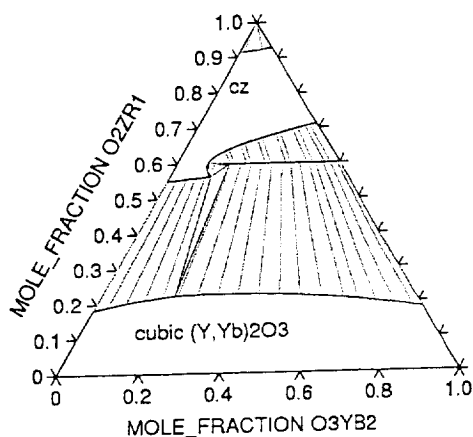


Figure 3. Calculated  $\text{Y}_2\text{O}_3\text{-Yb}_2\text{O}_3\text{-ZrO}_2$  isothermal section at 1673 K.

Figure 3 is the calculated pseudo-ternary section at 1673 K. The major experimental features of this ternary (24) have been reproduced. There are continuous tetragonal  $\text{ZrO}_2$ , cubic  $\text{ZrO}_2$ , and cubic  $(\text{Y},\text{Yb})_2\text{O}_3$  phases. Note also the intermediate line compound,  $\text{Zr}_3(\text{Yb},\text{Y})_4\text{O}_{12}$ , does not extend to the  $\text{Zr}_3\text{Y}_3\text{O}_{12}$  side as this compound has already decomposed at 1673 K (see Figure 1).

### SUMMARY AND CONCLUSIONS

The  $\text{Y}_2\text{O}_3\text{-ZrO}_2$ ,  $\text{Yb}_2\text{O}_3\text{-ZrO}_2$ , and  $\text{Y}_2\text{O}_3\text{-Yb}_2\text{O}_3$  pseudo binaries have been assessed. Available phase boundary and thermodynamic has been used to derive the solution parameters for a Calphad-type database. The oxide units are used as components. The resultant phase diagrams show good agreement with the experimental data. Then the three binaries have been combined to form a database for the  $\text{Y}_2\text{O}_3\text{-Yb}_2\text{O}_3\text{-ZrO}_2$  pseudo ternary.

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