—Communication—

Phase Diagram Calculation of the ZrO_2-CeO_2-$YO_{1.5}$ System

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We have recently investigated the technological feasibility of a new composite electrolyte consisting of a yttria doped ceria(YDC)/yttria stabilized zirconia(YSZ)/ YDC triple layer which should be fabricated by tape cast and subsequent cofiring process and will be used as electrolyte of solid oxide fuel cell at low (800°C) temperatures.[1] During cofiring process, interdiffusion between YDC and YSZ may occur. It is therefore of great technological importance to investigate the phase relations and diffusion properties of the ZrO_2-CeO_2-$YO_{1.5}$ system. In our preliminary experiments on phase relations and diffusion couple, a tendency towards immiscibility was observed at 1473 K. Furthermore, Hinatsu and Muromura[2] observed immiscibility gap in the ZrO_2-CeO_2-$YO_{1.5}$ system at 1873 K which has not been confirmed yet by other researchers.[3] Phase diagram calculations have been thus made to confirm this tendency on the basis of our previous phase diagram calculations on ZrO_2 based ceramics[4] and other available data.

In the present communication, results of phase diagram calculations are partly reported.

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Calculation was made by using the Redlich-Kister-Maggianu formula[4] for the ternary solid solution. This is a ternary subregular solution with the two interaction parameters, $\Omega = x_i x_j \{A^0 + A^1(x_i - x_j)\}$, for the respective binary systems. As the lattice stability, a two-term equation, $G - G$(ref. state) $= a + bT$, is used.

Phase diagram calculations have been already done on the ZrO_2-$YO_{1.5}$ and the ZrO_2-CeO_2 systems.[4] In the present study, the following interaction parameters are newly determined;

1) The interaction parameters between ZrO_2 and CeO_2 are modified so as to obtain better agreement with experimental values.

2) At present, there is no experimental information about the magnitude of the interaction parameter in the CeO_2-$YO_{1.5}$ system. Since the interaction parameter in the CeO_2-SrO system is about a half of that in the ZrO_2-SrO system, a similar trend is assumed for the yttria doped system.

The immiscibility gap is the main concern in the present communication. Figure 1 shows the calculated immiscibility gap in the fluorite solid solution at 1273 K. Phase relations with other phases (ZrO_2-rich monoclinic, tetragonal phases, C-type cubic phase, $Y_4Zr_3O_{12}$) are not shown here.

Calculation results show that the immiscibility gap appearing in the ZrO_2-CeO_2 subsystem becomes wider on adding the yttria component. This can be ascribed to the fact that the interaction parameter in the ZrO_2-$YO_{1.5}$ system is strongly asymmetric in its composition dependence so that the tendency towards the

Table 1. The lattice stabilities and the interaction parameters of the fluorite phase in the ZrO_2-CeO_2-$YO_{1.5}$ system.

(a) lattice stability

substance	a/J mol^{-1}	b/J mol^{-1}K^{-1}	reference state
ZrO_2	21400	10.69	monoclinic phase
CeO_2	0	0	fluorite
$YO_{1.5}$	10000	0	C-type

(b) Interaction parameters

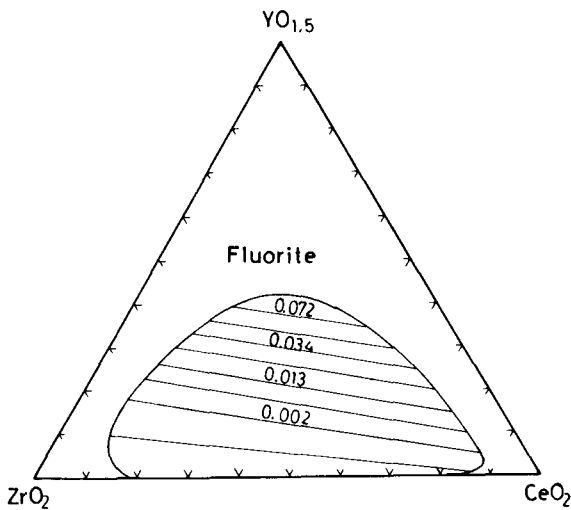| subsystem	A^0/J mol^{-1}	A^1/J mol^{-1}
ZrO_2- $YO_{1.5}$	-65000	-25000
$YO_{1.5}$-CeO_2	-30000	0
CeO_2- ZrO_2	25000	0

Fig. 1 The calculated immiscibility gap in the fluorite ternary solution in the ZrO_2-CeO_2-$YO_{1.5}$ system and activities of yttria at 1273 K.

immiscibility is widely extended from the ZrO_2-CeO_2 subsystem to the $YO_{1.5}$ rich side of the ZrO_2-$YO_{1.5}$ subsystem.

Tie lines inside the immiscibility gap shown in Fig. 1 indicate that the activity of the yttria component along the composition line with a constant yttria content is higher in the CeO_2-rich region than in the ZrO_2-rich region. This suggests that the yttria in CeO_2 is more reactive with acidic substances such as alumina,

silica, carbon dioxide. This is consistent with our experimental observation that the yttria component in YSZ does not react with alumina, while that in YDC actually reacts with alumina to form yttrium aluminates.[5]

Furthermore, reactions with carbon dioxide should be experimentally examined because, electrolyte has to be exposed to carbon dioxide and water in the anode side.

The appearance of the immiscibility gap at 1273 K suggests that this may affect the behavior of the ionic conductivity. Note that the ionic conductivity of the fluorite phase largely depends on the vacancy concentration and that inside the immiscibility gap, two solid solutions with different yttria content, that is, different concentration of oxide ion vacancies are in equilibrium. This implies the importance of the examination of microstructure associated with the phase separation behavior at low temperatures.

References

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