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TECHNICAL REVIEW

Fundamentals of Ceramic (Glass)-Metal Bonding (II)†
– Characteristics of zirconia –

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Abstract

Environment upon materials has become severer with the development of verious energy sources such as nuclear fusion reactor, MHD energy conversion and so on. Zirconia is an important compound as coating material on metal. In this review, characteristics of zirconia for obtaining stabilized form and good mechanical properties have been summed up.

KEY WORDS: (Ceramic) (Interface) (Bonding) (Metal)

1. Introduction

From the olden time an oxide having the following properties such as higher stability in the oxidizing and reducing atmosphere, lower vapor pressure at the higher temperature, lower thermal conductivity, lower specific heat, and higher resistivity against chemical corrosiveness, has been desired more and more. From the standpoint of utilization of nuclear power it has become the necessary conditions to have lower neutron cross section for the choice of oxide material. Furthermore severer environment such as MHD generator and coal liquification process has demanded higher resistance to corrosiveness of coal ash.

Zirconia was used for refractory material from 1900 and as crucible material from 1906 and as lining material for open hearth furnace in steelmaking in 1916. Now it is widely used as coating material by plasma spraying in the various fields.

It was very important matter to do fundamental study to hinder the disintegration phenomenon due to crystal transformation at about 1100°C.

In this review the author summarized the characteristics of zirconia in the past and the application of analyzing means to know thermal behavior of stabilized zirconia.

2. Phase relationship in the binary systems

2.1 Dietzel's cation field strength theory

Although many literatures have been presented as for phase relationship between zirconia and other component, there exist many disagreements because of the following causes such as impurities effect, specimen preparation and testing, thermal history, and non-equilibrium condition.

Dietzel derived the rules for the formation of compound between zirconia and other component by using relative field strength, that is to say, the difference of cation field strength between them.[1] In **Table 1**, the possibility as regards the formation of stable compound is given.

Dietzel said that the formation of compound between two oxides was likely only when the difference between the field strengths of both cations exceeded 0.3, but the

Table 1. Relative field strengths and compound formation

Foreign Oxide	z/a^2*	Compound formation
Na_2O	0.17	+
Li_2O	0.23	+
BaO	0.24	+
SrO	0.27	+
CaO	0.33	+
PbO	0.34	+
CdO	0.44	+
MgO	0.45	–
MnO	0.48	–
FeO	0.52	–
CoO	0.53	–
NiO	0.55	–
ZnO	0.59	–
ThO_2	0.64	–
Sc_2O_3	0.65	–
ZrO_2	0.78/0.95	–
Al_2O_3	0.84	–
BeO	0.87	–
CrO_{23}	0.95	–
TiO_2	1.25	–
B_2O_3	1.45	?
SiO_2	1.57	+
V_2O_5	1.85	+
P_2O_5	2.08	+

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compound melted incongruently because of poor lattice stability when the difference was only slightly greater.

2.2 ZrO_2-CaO system

It was well known that the addition of calcia to zirconia transformed the zirconia into a cubic form. The reason why the addition of calcia occurs such a stabilization and the information how many content is necessary to hold cubic structure must be obtained. Many investigatore have challenged to solve this problem. The first group concluded that cubic zirconia solid solution could be formed though the stabilizing content of calcia differed depending on the experimental conditions[2−4] **Figure 1** shows the results. Other investigators showed signs of stable compound.[5, 6] **Figure 2** gives the stabilized region.

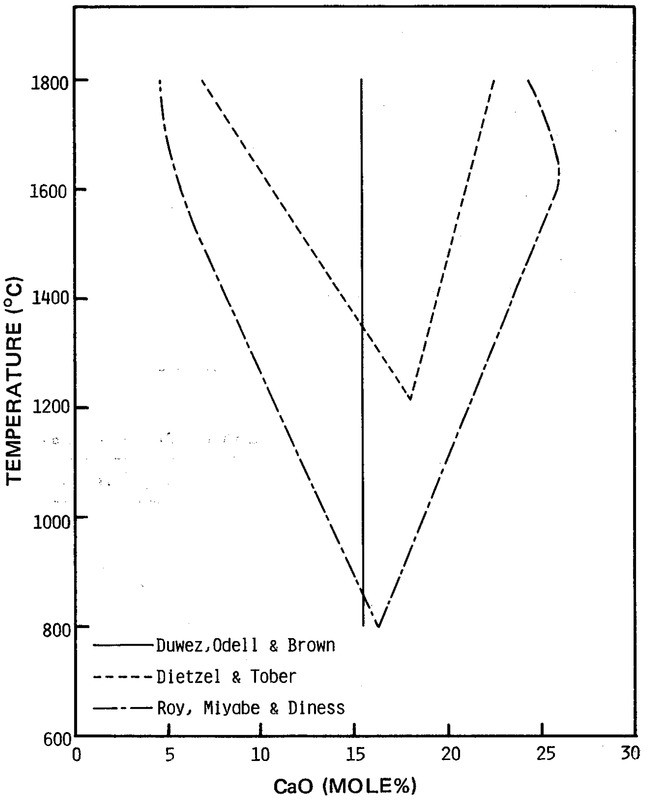

Fig. 1 Cubic fields in the system CaO-ZrO_2 which show no compound formation[8]

Garvie[7] concluded that the cubic field may then be described as originating from a solid solution series between cubic zirconia and $CaZr_4O_9$ from using lattice parameter measurement and the crystallographical consideration by russian investigator[8]. Phase diagram is given in **Figure 3**.

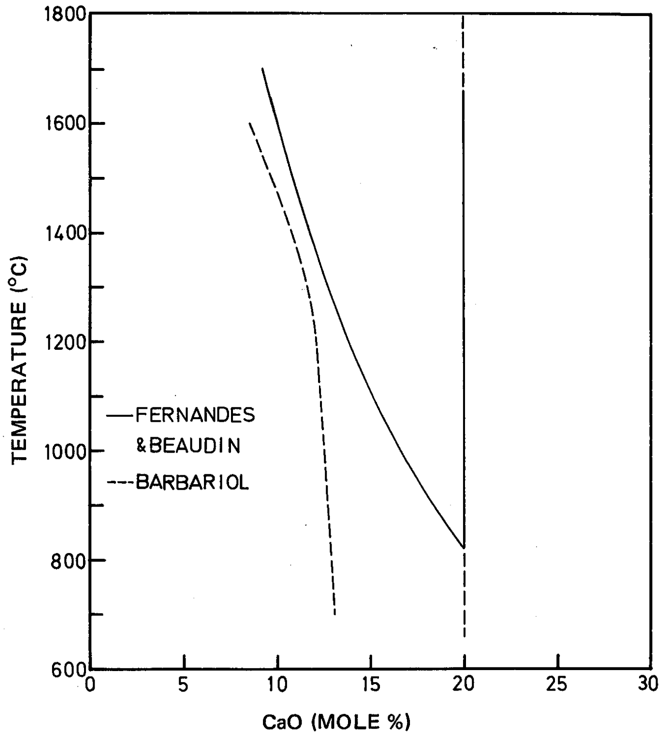

Fig. 2 Cubic field in the system CaO-ZrO_2 which show compound formation[8]

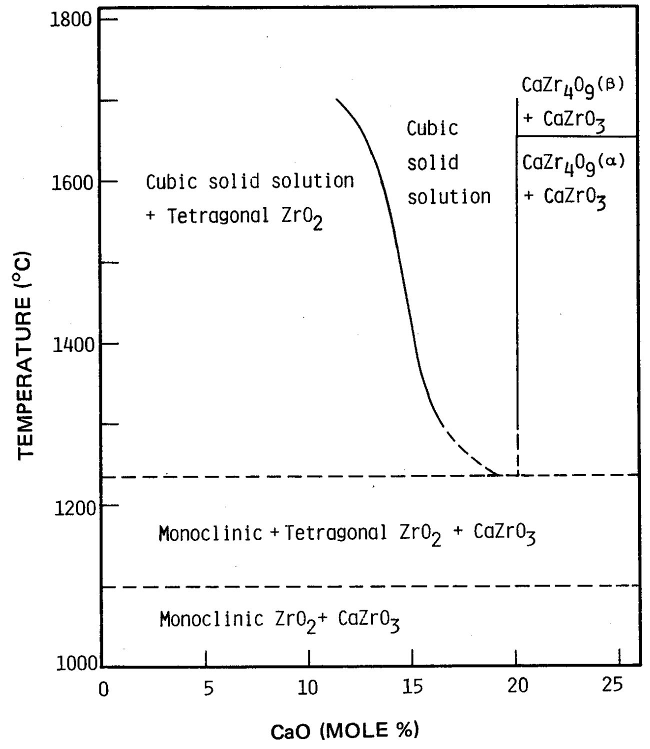

Fig. 3 Partial phase diagram (with heating) of the system CaO-ZrO_2[8]

2.3 ZrO_2-MgO system

Many investigators have reported the magnesia was effective to stabilize the zirconia in partially cubic modification for commercial usage.[9-11] From the subsequent heat-treatment on the stabilized zirconia with magnesia, it was found to be unstable.[2, 12]

Phase diagrams for the system zirconia-magnesia were presented by several researchers.[13-18] Grain[19] revised the phase diagram and the result is given in **Figure 4**. He applied the detailed measurement of lattice parameter.

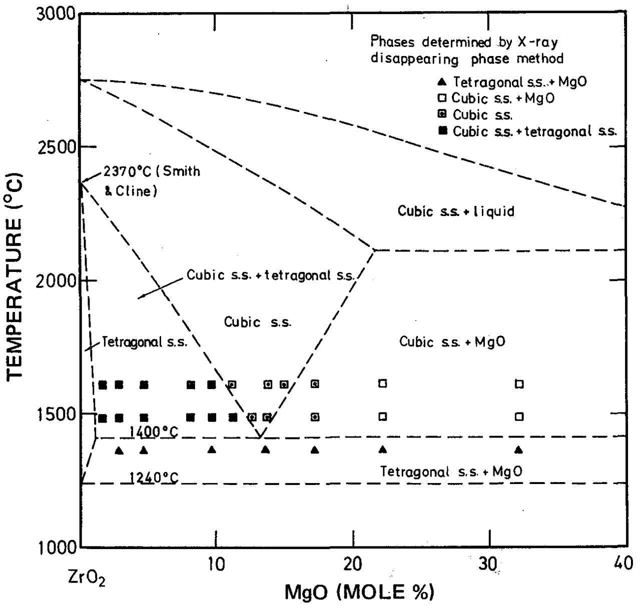

Fig. 4 Phas relations in a portion of the system ZrO_2-MgO [9)]

2.4 ZrO_2-UO_2 system

Evans[20] applied solar furnace to study the phase diagram of this system. A tentative phase diagram based on a composition of some of Lambertson and Muller's findings[21] and on his result is given in **Figure 5**. the solid solutions are, respectively, face-centered cubic and face-centered tetragonal on the UO_2 and ZrO_2 sides of the equilibrium diagram. However Wolten[22] emphasized the effect of cooling velocity of specimens held at higher termperature on phase separation based on the investigatigation by Moronov et al.[23] Further Mumpton and Roy[24] indicated the effect of atmosphere to know phase relation and the importance of phase rule point of view.

2.5 ZrO_2-TiO_2 system

Because of inconsistencies in results of this system by previous investigators,[25, 26] Brown Jr. and Duwez[27] performed study of phase relation of this system. The result is given in **Figure 6** and the compound of $ZrTiO_4$

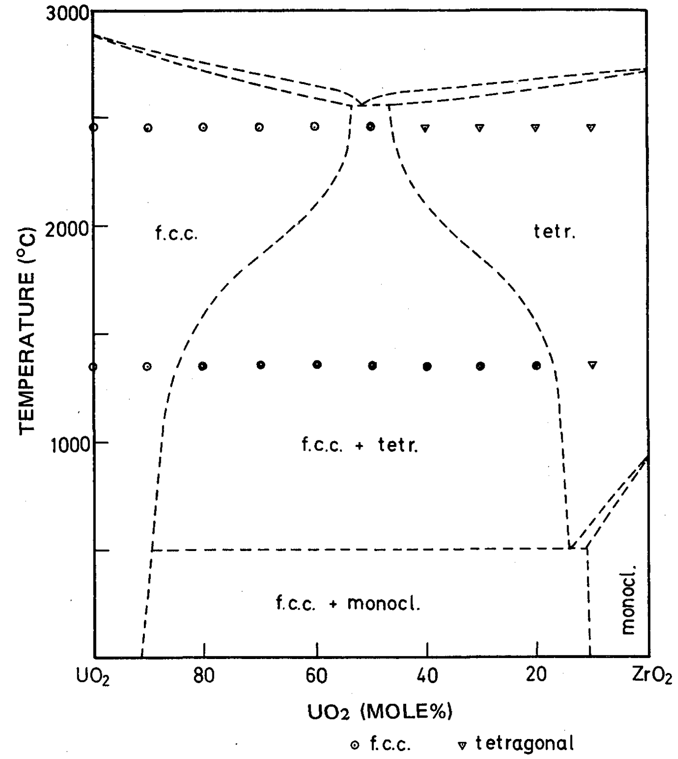

Fig. 5 Proposed phase diagram for the system ZrO_2-UO_2 [20)]

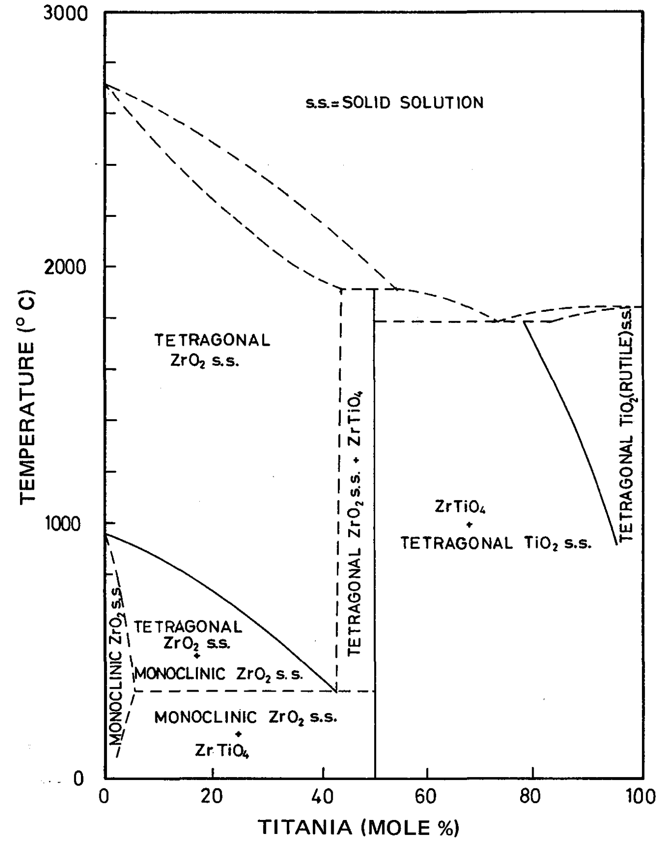

Fig. 6 Proposed phase diagram for the system ZrO_2-TiO_2 [27)]

was confirmed. Noguchi[28] determined liquidus curve by using solar furnace and revised the phase diagram as shown in **Figure** 7.

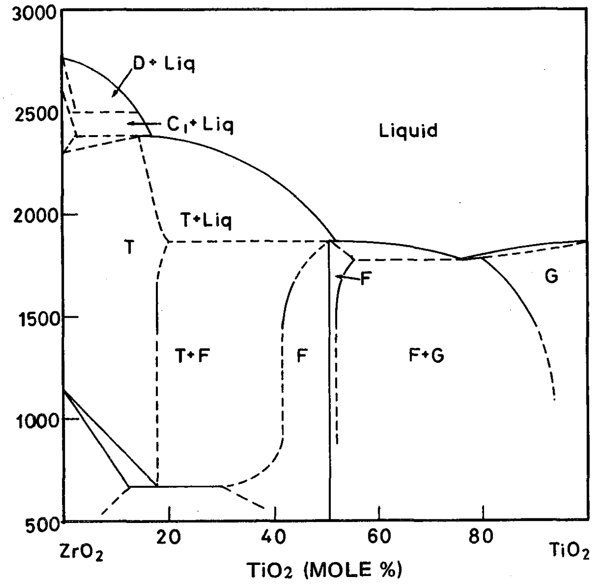

Fig. 7 Phase diagram of the ZrO_2-TiO_2 system[28)]

C_1 : cubic ZrO_2 solid solution
D : ZrO_2 solid solution
F : $ZrTiO_4$ solid solution
G : TiO_2 solid solution
T : tetragonal ZrO_2 solid solution

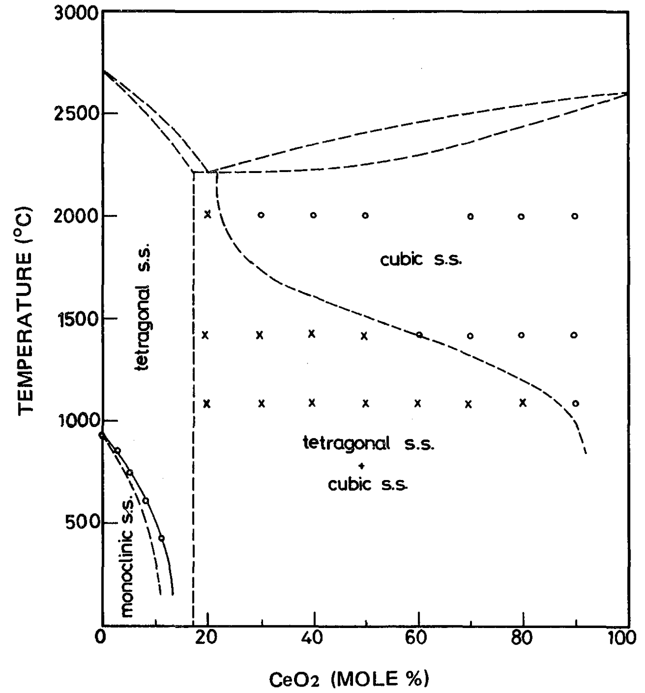

Fig. 8 Tentative phase diagram of the system ZrO_2-CeO_2 [29)]

2.6 ZrO_2-CeO_2 system

Duwez and Odell[29)] carried out phase diagram study by firing at 2000°C. As shown in **Figure 9**, zirconia and ceria are completely soluble in each other (cubic CaF_2 type of solid solution) from about 24 to 100 mole % ceria. It was determined that this solid solution was retained at room temperature by moderately fast cooling and two phase region (tetragonal and cubic solid solution) extended with the temperature decrease.

2.7 ZrO_2-ThO_2 system

Duwez and Loh[30)] studied phase relationship of this system by using solar furnace. Tentative phase diagram was given as **Figure 9**. Significant point is that the monoclinic-tetragonal transformation in zirconia rich region becomes lower as 810°C with a maximum amount of 5% solid solution of toria.

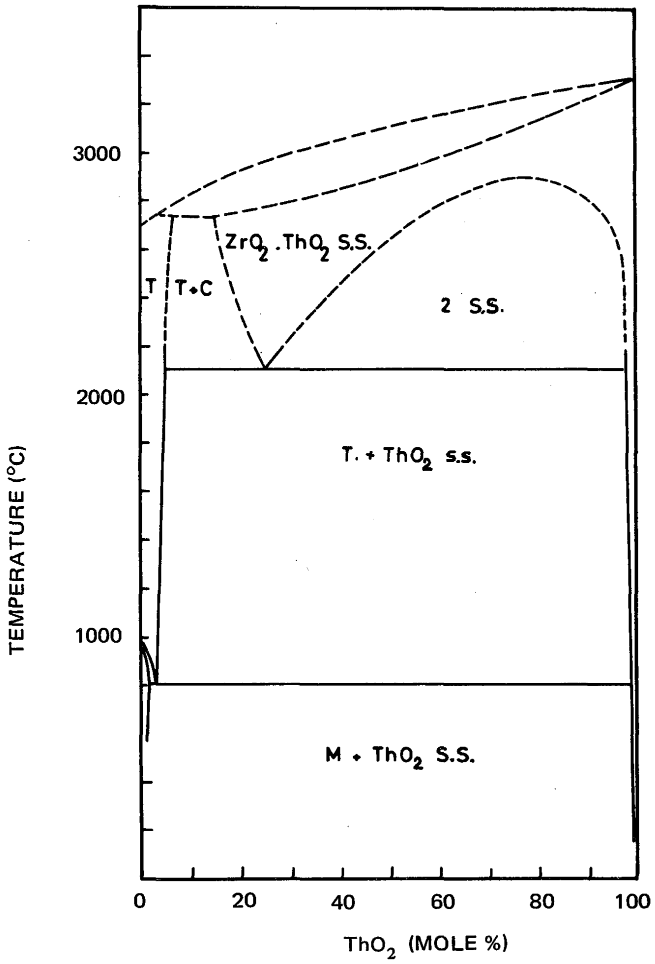

Fig. 9 Suggested phase diagram for the system ZrO_2-ThO_2 [30)]

2.8 ZrO_2-SrO system

Tentative phase diagram of this system was proposed by using solar furnace.28), 31) The result is shown in **Figure 10**. The formation of compunds such as $SrZO_3$, $Sr_4Zr_3O_{10}$, $Sr_3Zr_2O_7$ and Sr_2ZrO_4 were reported.

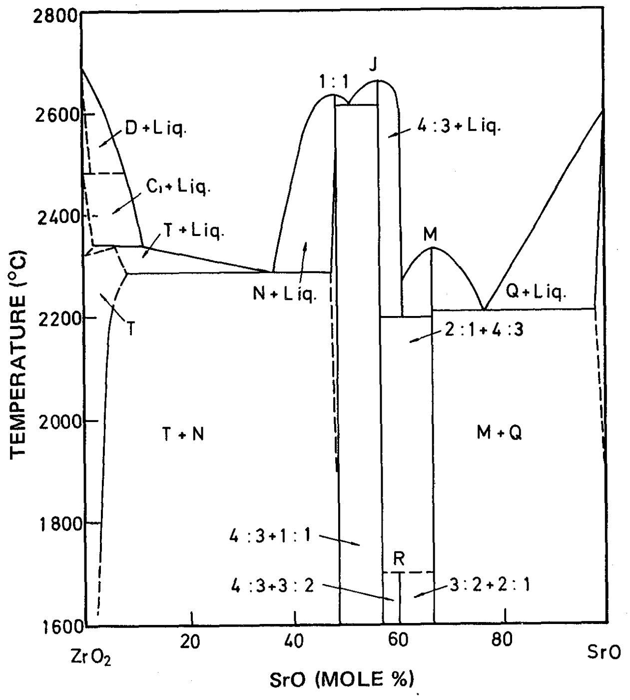

Fig. 10 Phase diagram of the ZrO_2-SrO system28, 31)

C_1 : cubic ZrO_2 solid solution
D : ZrO_2 solid solution
J : $Sr_4Zr_3O_{10}$
M : Sr_2ZrO_4
N : $SrZrO_3$ solid solution
Q : SrO solid solution
R : $Sr_3Zr_2O_7$
T : tetragonal ZrO_2 solid solution

2.9 ZrO_2-Y_2O_3 system

Recently the stabilized zirconia with yttria is noticed from the remarkable stability under thermal cycling.32) Duwez, Brown Jr. and Odell33) have given tentative phase diagram as shown in **Figure 11** and the following considerations as for the stabilization mechanism of yttria on zirconia from crystallographic viewpoint:

1) Although the crystal structure of yttria looks very complex, it shows some resemblance to that of cubic zirconia (CaF_2 structure).
2) In the case of solid solutions between MO_2 type and M_2O_3 type oxides, the formation of solid solutions are possible only if the crystal structure of MO_2 type oxide is stable with vacant oxygen sites and if M_2O_3

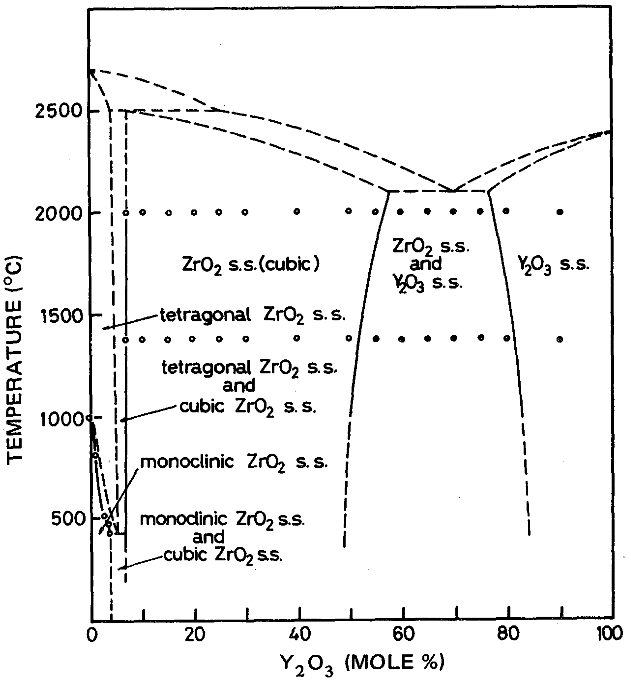

Fig. 11 Tentative phase diagram of the ZrO_2-Y_2O_3 system33)

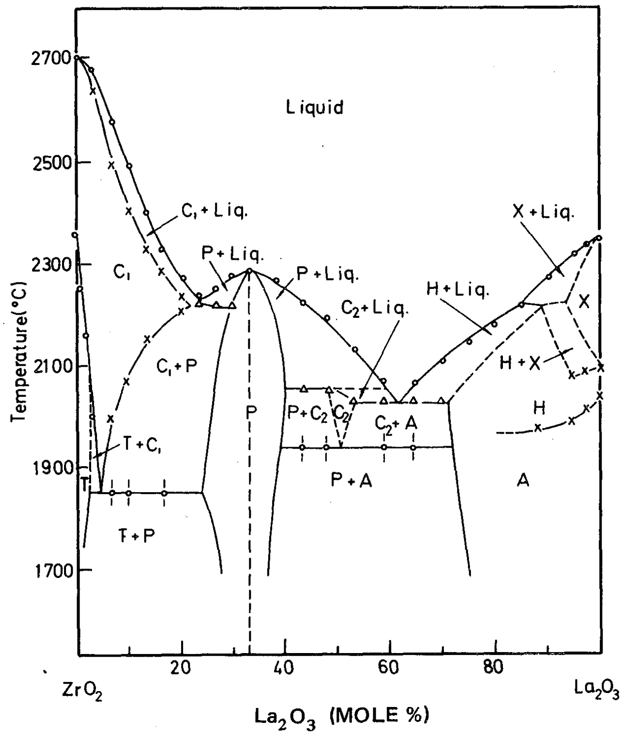

Fig. 12 Phase diagram of the ZrO_2-La_2O_3 system36,37)

A : hexagonal La_2O_3
C_1 : cubic ZrO_2 solid solution
C_2 : cubic $ZrO_2 \cdot La_2O_3$
H : hexagonal La_2O_3
P : pyrochlore type $La_2Zr_2O_7$
T : tetragonal ZrO_2 solid solution
X : cubic La_2O_3

type oxide has "holes" which is capable to accept the excess oxygens.

2.10 ZrO_2-Sc_2O_3 system

Ruf, Garret, Domagala and Patel[34] studied phase relationship using high temperature- Xray diffraction and DTA methods. In the contrary to Duwez et al'prediction, only stable cubic region was obtained beyond 77.5% scandia.[34] Sekiya et al have given another phase diagram[35].

2.11 ZrO_2-La_2O_3 system

Rouanet[36] reported phase diagram of this system using thermal analysis with a solar furnace and X-ray diffractometry as shown in **Figure 12.** which involved new phase detected by Foex and Traverse[37].

2. 12 ZrO_2-Nd_2O_3 system

Brown Jr. and Duwez[38] have given the phase diagram of this binary system as shown in **Figure 13**. As suggested by Ref. 33), there exists wider region of cubic structure.

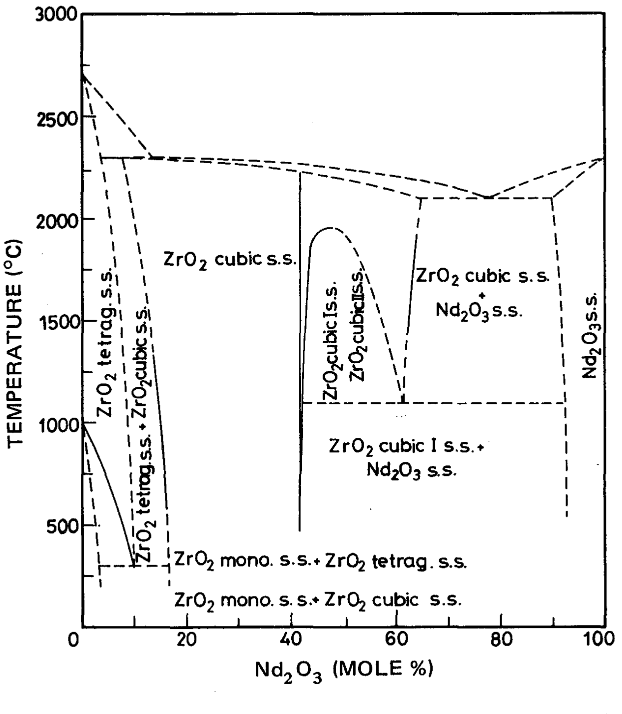

Fig. 13 Proposed phase diagram for the system ZrO_2-Nd_2O_3 [38]

2. 13 ZrO_2-Gd_2O_3 system

Rouanet and Fox[39] have reported phase diagram of this system using solar furnace and discovered new phase X at high temperature as shown in **Figure 14.**

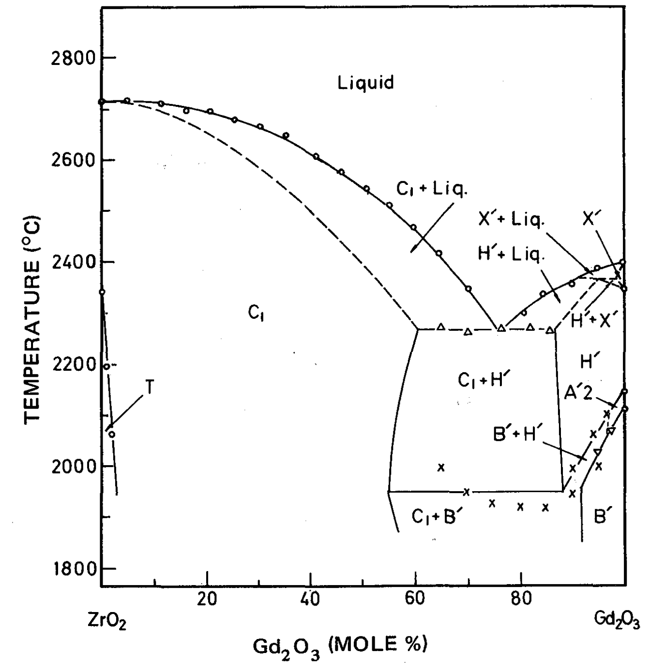

Fig. 14 Phase diagram of the ZrO_2-Gd_2O_3 system[39]

B' : monoclinic Gd_2O_3
C_1 : cubic ZrO_2 solid solution
C_2 : Cubic $ZrO_2 \cdot La_2O_3$
H' : hexagonal Gd_2O_3
T : tetragonal ZrO_2 solid solution
X' : cubic Gd_2O_3

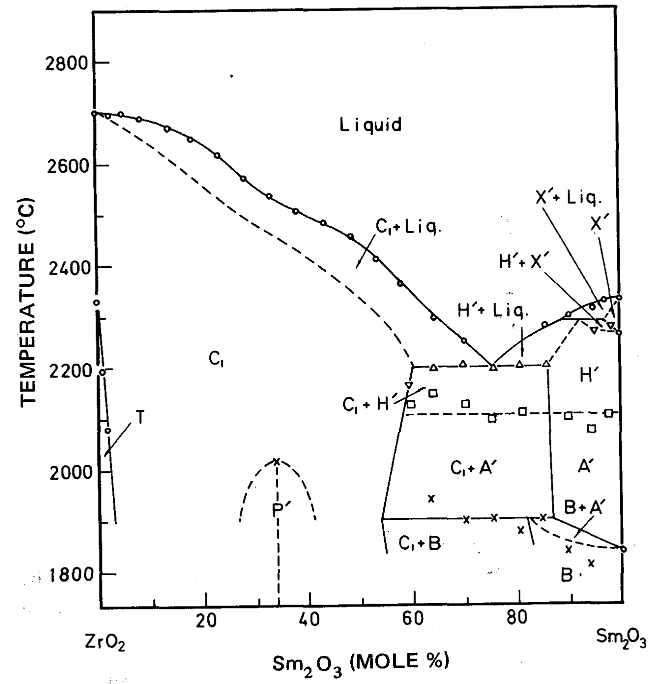

Fig. 15 Phase diagram of the ZrO_2-Sm_2O_3 system[39]

A' : hexagonal Sm_2O_3
B : monoclinic Sm_2O_3
C_1 : cubic ZrO_2 solid solution
H' : hexagonal Sm_2O_3
P' : pyrochlore type $Sm_2Zr_2O_7$
T : tetragonal ZrO_2 solid solution
X' : cubic Sm_2O_3

2. 14 ZrO_2-Sm_2O_3 system

Rouanet and Foex39) studied phase diagram using solar furnace and found the existence of a compound $Sm_2Zr_2O_7$ having cubic structure of pyrochlore type as shown in **Figure 15**.

2. 15 ZrO_2-Er_2O_3 system

Duran40) studied phase diagram of this system using high temperature X-ray diffraction and thermal expansion measurements. **Figure 16** shows that pyrochlore structure does not form.

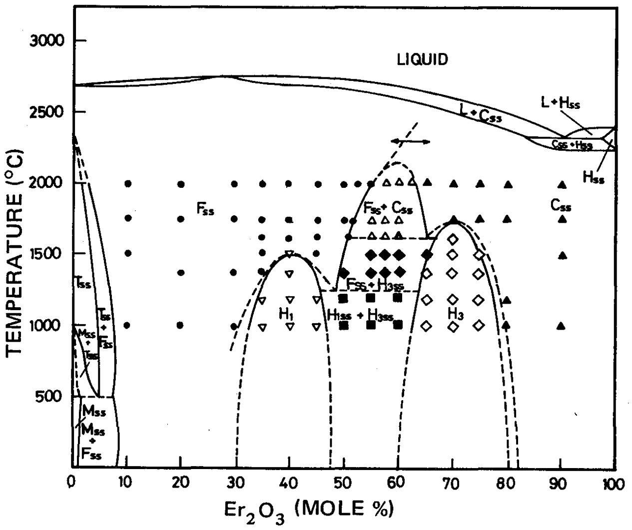

Fig. 16 Phase diagram of the ZrO_2-Er_2O_3 system40)
M (ss) : monoclinic solid solution
T (ss) : tetragonal solid solution
F (ss) : cubic solid solution
H_3 : hexagonal compound of type M_7O_{11} (70 mole% Er_2O_3)
C (ss) : cubic Er_2O_3 solid solution
H_1 : hexagonal compound (40 mole% Er_2O_3)

2. 16 ZrO_2-Dy_2O_3 or Yb_2O_3 system

Fehrenbucher, Jacobson and Lynch41) observed that a 3 mole% addition of Yb_2O_3 or Dy_2O_3 to zirconia produced a tetragonal structure and no pyrochlore structure was found with a linear thermal expansion measurement in accordance with opinion by Torba42) that the rare earth elements with the smaller ionic radii such as ytteribium or dysprosium has not yielded the pyrochlore phase with zirconia.

2. 17 Summarized view by Roth43)

Although the summarized view concerning phase stability of zirconia in binary system has been given, it seems important to check out fundamental points.

1) Divalent Ion: With oxides of smaller ion such as Mg, Ca, Mn, and Ti, stabilized zirconia solid solution can not form. On the other hand, larger divalent ions such as Zn and Be forms, perovskite-type compound though smaller ion does not form compound.
2) Trivalent ion: With oxide of smaller trivalent ion such as In can form cubic zirconia, but very smallest ion as Al does not form cubic one. Larger trivalent ions such as La^{3+} and Nd^{3+} can form $A_2B_2O_7$ pyrochlore type compounds or solid solutions.
3) Tetravalent ion: Oxides having larger tetravalent ion such Ce and U can form tetragonal zirconia solid solution which exist at room temperature. However in the case of smaller ionic radii does not form stable solid solution, but 1 : 1 compounds such as $ZrO_2 \cdot TiO_2$ and $ZrO_2 \cdot SiO_2$ are formed.
4) Pentavalent ion: Compound such as $[Zr_4(Zr_2Nb_2)O_{16}O]$ can be formed with Nb_2O_5 or Ta_2O_5.

The authors tried to make stable phase from the starting materials manufactured with coprecipitation.44) However it was impossible to form stable zirconia compound or solid solution disregard of rule above-described.

3. Phase relationship in the multicomponent systems

3.1 ZrO_2-TiO_2-VO system

As investigation of the system Zr-Ti-O12,45) showed that TiO and mixtures of TiO and TiO_2 will form cubic zirconia, Hoch and Mathur46) extended phase study in this system. (**Figure 17**) In **Table 2**, the region to form single cubic zirconia, which were surrounded with A, B, C, and D, is shown.

Table 2 Chemical composition to form cubic ZrO_2 at 1500°C

	A	B	C	D
ZrO_2	37.0	41.5	58.0	40.0
VO	28.0	12.5	12.0	31.5
TiO_2	35.0	46.0	30.0	28.5

3.2 ZrO_2-TiO_2-M (Transition metals of groups V and VI)

As investigation of the systems Nb-Ti-Zr-O47) showed the center of the single cubic zirconia phase region from 55 mole% ZrO_2, 35 mole% TiO_2 and 10 mole% Nb, Hoch and Mathur46) studied exchange effect of the elements

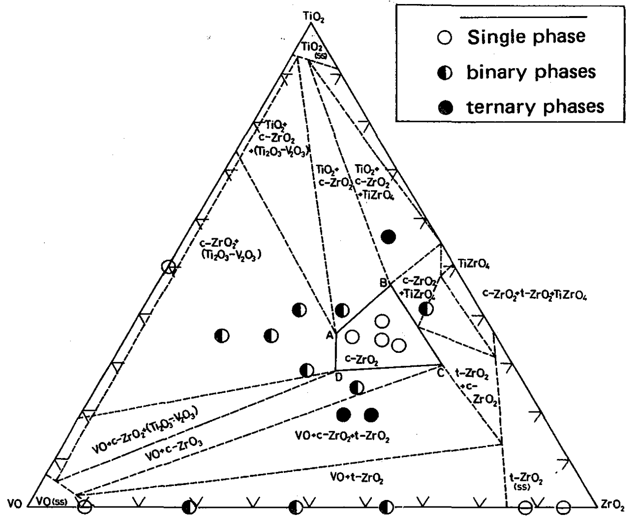

Fig. 17 Isothermal section of the system ZrO_2-TiO_2-VO at 1500°C[46]
c : cubic
t : tetragonal

such as Cr, Mo, W, V, and Ta instead of Nb and identified the formation of cubic zirconia in all cases.

3.3 ZrO_2-WO_2-WO_3 system

From the necessity to obtain an information on the oxidation behavior of tungsten-zirconium mixture at high temperature, phase relationship of this system was studied[48]. At 1200°C cubic phase as $Zr_xW_{1-x}O_{2.9-0.9x}$ where x is between 0.05 and 0.08 appeared as a homogeneity range along the ZrO_2-$W_{20}O_{58}$ join. At 1300°C the cubic phase has a larger range of solid solution than at 1200°C, but becomes more extensive along the Zr-WO_3 join toward metallic zirconium than along the ZrO_2-$W_{20}O_{58}$ join. With the increase of temperature the solid solution of the cubic phase could not be delineated.

4. ZrO_2-M (Ti, Zr, Cr, V, Si, Mo and W metals)

After the finding that the addition of Ti on zirconia inverts at lower temperature more slowly and accordingly the resistance on thermal shock is able to alter[13], several studies were performed to know solubility limit of metallic element in zirconia and to solve the cause why mechanical properties could be altered by addition of metallic element.

Ruh[49] found that the content up to 4% Ti can be retained in substitutional solid solution in zirconia and the soluble content increased with the temperature rise. Ruh and Garrett[50] determined that the content up to 1% Cr can be retained in zirconia solid solution. Ruh, Tallan and Lipsitt[51] studied the effect of metal additions on the microstructure of zirconia and certified that the increased sintering occurred only when compositions above the solubility limit were fired considerably above the melting temperature of metal added. Lipsitt and Ruh[52] studied the compressive properties of titan-modified zirconia at elevated temperatures and observed that the strain to fracture of the aged specimens becomes significantly greater than that for the virgin specimens at room temperature.

Arias[53] studied why the addition of 15 mole% Ti improves mechanical properties such as the thermal shock resistance, the modulus of rupture, and strength in comparison to calcia-stabillized zirconia. Further Arias[54] extended metal sort to be Cr, V and Zr and that other metals added in zirconia improved the themal shock resistance as well as Ti. Watson, Hill and Chapman[55] investigated the solidification behavior of stabilized zirconia and W mixture. Virkar and Johnson[56] studied the fracture behavior of zirconia-Zr composites and reported that residual stress exists (compressive in the oxide phase and tensile in the metal) due to the volume change accompanying the phase transformation in the oxide phase.

5. Impurities in raw material

Inconsistencies in reports as for the inversion temperature of tetragonal-monoclinic zirconia and physical properties can be reduced to the existence of various impurities in raw material. Heffelfinger, Blosser and Henry[57] performed chemical analysis. In **Table 3** typical impurities determined with spectrographic and chemical analysis are given.

6. Starting temperature of reaction

Smoot and Ryan[58] applied high temperature X-ray diffraction procedure to know the starting temperature for the reaction of the mixtures between zirconia with yttria, magnesia, calcia, ceria, and combination of calcia and magnesia. The results obtained are given in **Table 4**. From this table, it will be anrcipated that the combination of calcia and magnesia showed appearence of initial solid solution at temperature lower than calcia alone. From this fact, this way is applied to make stabilized zirconia in Japan.

7. Phase analysis in zirconia systems

Although Duwez and Odell[59, 60] performed quantitative study to determine correct quantities of cubic and monoclinic zirconias, there existed uncertainty as for presision. Garbie and Nicholson[61] applied matrix me-

Table 3. Typical impurities in zirconia (ppm)

Sample	Al	Ca	Fe	Hf	Mg	Na	S	Si	Ti
7TAM	400	2000	190	22000	200	200	500	2500	200
9TAM	50	300	500	<100+	100	10	6000	700	100
21Wch	<10*	20	<10*	100	<10*	10	<30+	200	<25*
25 C.M.	30	1500	800	<100+	300	30	80	500	<25+
27 C.M.	100	3000	160	<100+	500	50	10300	400	50
30ZrCA	400	2000	570	22000	400	200	570	5800	1700
32Tiz	100	300	220	24000	100	50	170	200	300
33Mons	300	300	2000	15000	200	50	N.S.#	50	1000
34Cab	3000	500	1800	20000	50	100	N.S.#	1000	200
35Deg	30	30	10	<100+	<10*	20	30	100	<25+
7Japan	60	50	200	24000	<10*	300	70	1300	300
8 S.P.E.	30	100	10	22000	20	10	<30+	20	300
41Harsh	30	500	10	22000	100	100	130	1100	1000
43Zircoa	100	500	100	<100+	100	30	70	1500	50

*Trace, +Not detected, #No sample

Table 4. Lattice parameter and initial appearance temperature of cubic ZrO_2

Compt. systems	CaO-ZrO_2		MgO-ZrO_2	Y_2O_3-ZrO_2	CeO_2-ZrO_2	CaO-MgO-ZrO_2	
Stabilizer (w/o)	4CaO	3CaO	6MgO	15Y_2O_3	20CeO_2	CaO/MgO 1 : 2½	CaO/MgO 2 : 1
Initial temp. of tetragonal-cubic phase appearance (°F)	1700	1500	900	1950	1000	1000	1000
a of initial phase (Å)	5.148	5.142	5.112	5.171	5.091	5.104	5.123

thod62) and poly morph means63). It was found that good correlation between experimental and calculated values.

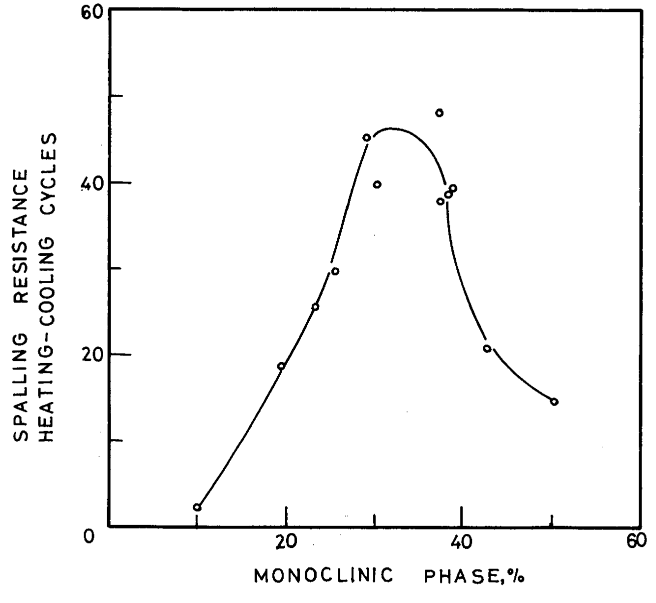

Fig. 18 Spalling resistance as a function of phase composition64)

8. Stability of thermomechanical properties

Garbie and Nicholson64) studied relationship between thermomechanical properties such as spalling resistance, stress relief, and microstructure of zirconia. In **Figure 18**, spalling resistance is given as a function of phase composition. It was recogneized that partial stabilized zirconia increases spalling resistance and there occurs quasi-static crack propagation from complex substructure of 1000 Å domains of cubic and monoclic zirconia.

9. Detection of zirconia polymorphs

McDevitt and Baun65) applied infrared absorption spectroscopy to identify monoclinic and cubic zirconias. Phillippi and Mazdiyasni66) established the infrared and Raman frequencies of monoclinic zirconia and of stabilized and metastable tetragonal and cubic zirconias. In **Figure 19** frequencies and ranges of transmission bands of each zirconia is given.

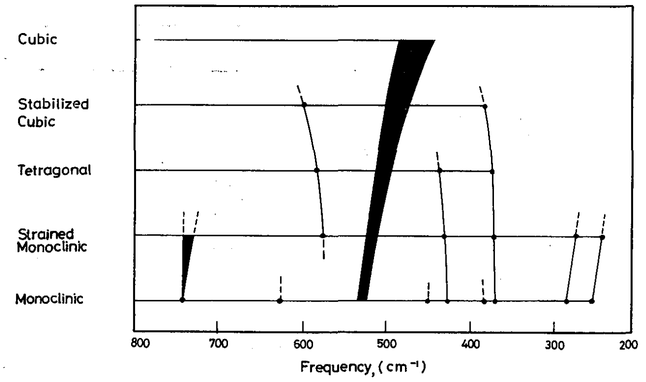

Fig. 19 Frequencies and ranges of transmission bands for phases of ZrO_2[65)]

10. Transformation mechanism of zirconia

Because of the nonquenchable transformation of zirconia from a monoclinic to a tetragonal phase with a hysterisis over a temperature interval in the neighborhood of 1000°C and no change in the relative proportions of the two phases at any constant temperature within the transformation range with time, Wolten[67)] considered that this behavior is typical of the majority of martensite transformation. Wolten performed to make clearly this behavior by applying a high-temperature X-ray diffraction procedure[68)].

11. Stability of zirconia under thermal cycling

Stabilized zirconia is often used for coating on engine in aeroplane. Stepka, Liebert and Stecura carried out failure test under thermal cycling on stabilized zirconia with yttria, calcia and magnesia.[69)] In **Table 5**, an example of their experiment is given.

As for the segregation of calcia along the grain boundary when alumina and silica were contained as impurities in raw materials, secondary electron image was given[61)]. Further the decomposition of stabilized zirconia with magnesia on heating at 1750°C for 3 hours was shown by secondary electron image.[18)] In **Figure 20**, the segregation behavior of stabilized zirconia is shown and it is understood that impurity elements in raw material will play an important role.

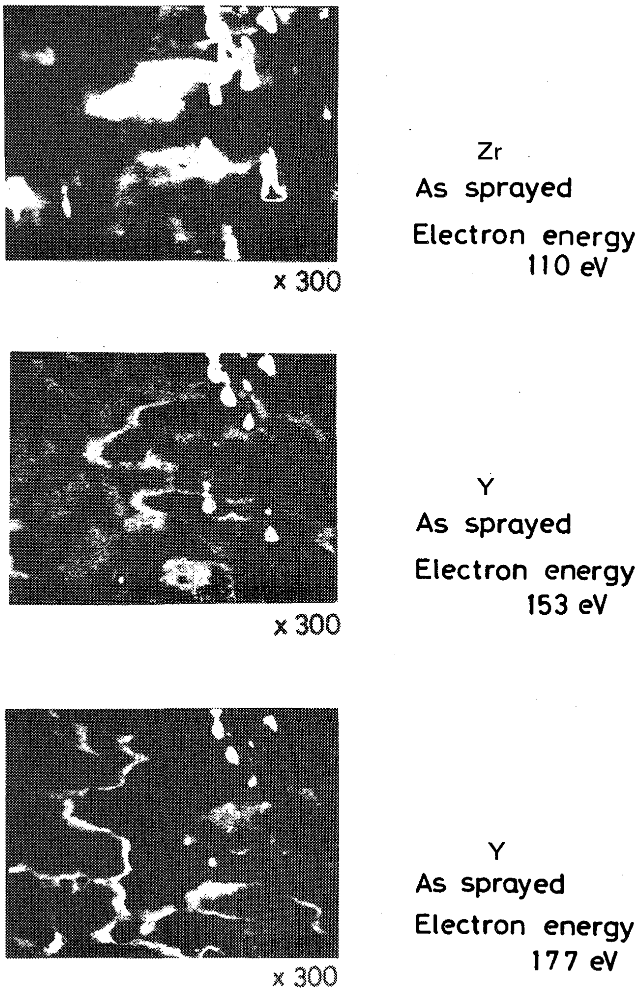

Fig. 20 Auger electron image of plasma-sprayed ZrO_2-Y_2O_3 coat[70)]

12. Summary

In this review, the author tried to sum up the characterization of zirconia. Though zirconia is an important candidate for the high-temperature systems such as MHD energy conversion, high temperature engine and so on, it has weak cystallographical point. It was emphasized that more clear explanation is necessitated for the manufacture of stabilized form.

Table 5. Cylic furnace evaluation of various zirconia

Specimen	Cycles to failure			
	ZrO_2-12Y_2O_3	ZrO_2-3.4 MgO	ZrO_2-5.4 CaO	ZrO_2-5.4 CaO
1	*673	460	255	78
2	*650	450	255	87

*Not failured, Cycle: 1 hr at 1248°K and 1 hr to cool to 553°K

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