

# STABILIZATION OF ZIRCONIA WITH COMBINED ADDITIVES AND A STUDY OF THE SOLID SOLUTION STABILITY

A. B. Andreeva, É. K. Keler,  
and A. I. Leonov

UDC 666.764.2.001.5

It is known that zirconium dioxide forms, with other refractory oxides of similar ionic radius, solid solutions that are stabilized in the cubic or tetragonal structure [1-6].

The commonest oxide-stabilizers are MgO and CaO, added in amounts of 10-15 mole %. However solid solutions on this basis are prone to decomposition upon the prolonged action of elevated (1000-1400°C) temperatures, and the zirconia is destabilized [5, 7-9].

In the search for more stable materials ZrO<sub>2</sub> has been stabilized with oxides of rare and rare-earth metals. Studies have shown that stable solid solutions are produced by yttrium oxide. However its wide industrial use has been limited because of its high cost and scarcity.

The present authors carried out a study to clarify the possibilities of obtaining more highly spalling resistant, cheaper, and more stable zirconia materials.

In the investigation a number of compositions were compiled based on zirconia, incorporating combined additives of two or more stabilizing oxides. The properties were studied in comparison with two-component solid solutions ZrO<sub>2</sub>-MgO, and ZrO<sub>2</sub>-CaO. All the oxides used in the compositions were chemically pure and had a grain size of less than 5  $\mu$ . The mixtures were carefully blended by the wet method in an agate mortar, dried, and pressed at 300 kg/cm<sup>2</sup> into specimens which were then fired in a periodic kiln heated with kerosene at 1550-1750° with a 4 h soak. To determine the bending strength prisms were pressed measuring 30 x 7 x 2.5 mm, and for the dilatometric studies specimens measuring 65 x 8 x 8 mm. The phase composition of the fired specimens was determined by x-ray, dilatometric, and microscopic methods. The compositions of the specimens and their properties after firing at 1750° are given in Table 1.

TABLE 1. Sintering and Properties of Specimens Fired at 1750° with a 4 h Soak

Specimen No.	Composition of specimen, mole %	Shrinkage, %	Water absorption, %	Apparent density, g/cm <sup>3</sup>	Apparent porosity, %	Bending strength, kg/cm <sup>2</sup>	Structure of Specimen*
1	90% ZrO <sub>2</sub> + 10% MgO	32,0	0,35	5,0	1,9	1600	K+about 10% M
2	85% ZrO <sub>2</sub> + 15% MgO	27,0	0,2	5,0	1,0	1580	K
3	90% ZrO <sub>2</sub> + 6% MgO + 4% CaO	27,0	0,2	5,25	1,0	1200	K
4	85% ZrO <sub>2</sub> + 10% MgO + 5% CaO	29,0	0,5	5,2	2,6	1000	K
5	93% ZrO <sub>2</sub> + 5% MgO + 2% Y <sub>2</sub> O <sub>3</sub>	27,0	0,4	5,3	2,1	1600	K+10% M
6	92% ZrO <sub>2</sub> + 5% MgO + 3% Y <sub>2</sub> O <sub>3</sub>	26,0	0,2	5,3	1,1	2000	K
7	90% ZrO <sub>2</sub> + 5% MgO + 5% Y <sub>2</sub> O <sub>3</sub>	26,0	0,0	5,35	0,0	1800	K
8	90% ZrO <sub>2</sub> + 5% MgO + 5% Nd <sub>2</sub> O <sub>3</sub>	25,5	0,35	5,2	1,7	1400	K
9	90% ZrO <sub>2</sub> + 5% MgO + 5% La <sub>2</sub> O <sub>3</sub>	30,0	0,5	5,1	2,5	1300	K+20% M
10	94% ZrO <sub>2</sub> + 5% MgO + 1% Nd <sub>2</sub> O <sub>3</sub>	25,1	1,3	5,1	6,5	1100	K+20% M
11	90% ZrO <sub>2</sub> + 8% MgO + 2% Y <sub>2</sub> O <sub>3</sub>	28,0	0,0	5,2	0	2000	K
12	90% ZrO <sub>2</sub> + 10% Y <sub>2</sub> O <sub>3</sub>	26,5	0,5	5,2	2,5	1100	K

\* In this and subsequent tables K indicates cubic, and M indicates monolithic

I. V. Grebenshchikov Institute of Silicate Chemistry. Translated from *Ogneupory*, No. 11, pp. 45-48, November, 1970.

© 1971 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

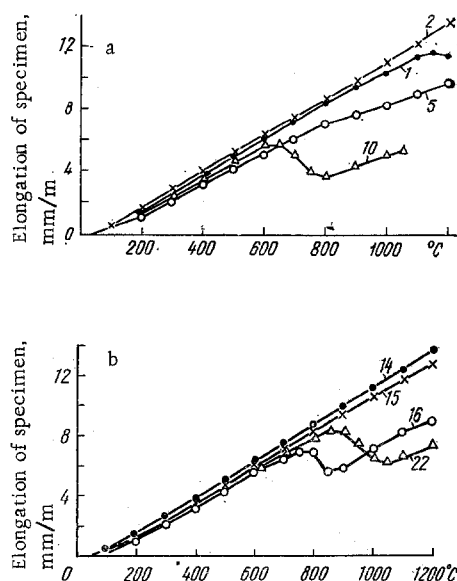


Fig. 1. Linear expansion of solid solutions of zirconia. Specimens fired at 1750°. Figures on the curves indicate specimen No. (see Tables 1 and 3).

TABLE 2. Comparison of Stability of Two- and Three-Component Solid Solutions Based on Zirconia\*

Specimen No. (see Table 1)	Original structure of solid solution	Quantity of monoclinic phase, % after heating at 1200°C			
		150 h	300 h	400 h	500 h
1	K+about 10% M	100	100	—	—
2	K	100	100	—	—
3	K	>60	>70	>85	—
4	K	>80	>90	—	—
5	K+10% M	15	20	25	30
6	K	0	0	15	15
7	K	0	0	0	0
8	K	>50	>70	—	—
9	K+20% M	100	100	—	—
11	K	0	0	10	20
12	K	0	0	0	0

\* Specimens synthesized at 1750° with a soak of 4 h, tested as powders (<5 μ)

The comparable specimens were sintered almost identically: the water absorption was from 0 to 0.4%, and the apparent porosity from 0 to 2.5%. All the specimens had the cubic structure; complete stabilization of the zirconia was achieved except for compositions Nos. 1, 5, 9, and 10 which contain 10-20% monoclinic phase. A relatively high strength is possessed by specimens stabilized with combined magnesium-yttrium additives.

Dilatometric studies showed that in the specimen densely stabilized with magnesium oxide (Fig. 1a, curve 2) there are no polymorphic inversion effects, but the coefficient of thermal expansion is rather high  $[(11.5-12.0) \cdot 10^{-6} \text{ deg}^{-1}]$ . Incomplete stabilization causes only residual development of polymorphism in the zirconia, but it is connected with low volume changes, and does not produce breakdown of the specimens (Fig. 1a). The thermal expansion coefficient of the compositions containing yttrium and neodymium is much less (about  $8 \cdot 10^{-6} \text{ deg}^{-1}$ ).

Specimens were tested for stability during isothermal heating at 1200° and with a soaking time of from 100 to 500 h. In order to accelerate the decomposition of the solid solutions we tested them in the ground state (less than 5 μ). The test results are given in Table 2.

The maximum stability was shown by zirconium-yttrium and three-component solid solutions ( $\text{ZrO}_2 - \text{MgO} - \text{Y}_2\text{O}_3$ ), which after testing for 500 h preserved completely or almost completely their original cubic structure.

In the specimens of composition  $\text{ZrO}_2 - \text{MgO} - \text{CaO}$  and  $\text{ZrO}_2 - \text{MgO} - \text{Nd}_2\text{O}_3$ , after 300 h testing more than 70% of the monoclinic phase was formed. The least resistance was shown by the solid solutions of the compositions  $\text{ZrO}_2 - \text{MgO}$ , and  $\text{ZrO}_2 - \text{MgO} - \text{La}_2\text{O}_3$ , which completely decomposed after 125 h testing.

We synthesized zirconia-CaO solid solutions with an addition of a second stabilizing oxide. The composition, sintering, and properties of the mixtures are given in Table 3.

The specimens of these compositions during firing to 1750° are sintered in the same way as zirconia-magnesia (see Table 1). In all compositions solid solutions are formed with the cubic structure; in some cases stabilization was incomplete (Nos. 13, 16, 19, and 22). The mechanical strength of the specimens critically depends on the additives and their quantities; the best factors were obtained from compositions Nos. 14, 17, 18, 20, and 21.

The results for stability testing given in Table 4 show that the most stable are ternary solid solutions ( $\text{ZrO}_2 - \text{CaO} - \text{Y}_2\text{O}_3$ ). Other compositions proved to be much less stable. After 150 h testing they develop from 35 to 60% monoclinic phase; with further heating decomposition was continued.

The dilatometric investigation of zirconia-CaO solid solutions show that during firing up to 1500 and 1650° the specimens with the combined additive, being in total less than 10 mole %, are not completely stabilized (curves 16 and 22, Fig. 1b).

The curves exhibit bends that are due to the residual inversions of the monoclinic zirconia; however, these volume changes are comparatively small and occur more smoothly than in pure zirconia. The specimens did not crack.

TABLE 3. Sintering and Properties of Specimens Fired at 1750°

Specimen No.	Composition of specimen, mole %	Shrinkage, %	Water absorption, %	Apparent density, g/cm <sup>3</sup>	Apparent porosity, %	Bending strength, kg/cm <sup>2</sup>	Structure of specimen
12	90% ZrO <sub>2</sub> + 10% Y <sub>2</sub> O <sub>3</sub>	28,0	0,6	5,3	3,0	1100	K
13	95% ZrO <sub>2</sub> + 5% CaO	24,5	5,0	4,30	21,5	500	60% K + 40% M
14	90% ZrO <sub>2</sub> + 10% CaO	26,5	0,1	5,35	0,5	2000	K
15	90% ZrO <sub>2</sub> + 6% CaO + 4% MgO	26,0	0,2	5,3	1,0	1450	K
16	93,5% ZrO <sub>2</sub> + 5% CaO + 1,5% Y <sub>2</sub> O <sub>3</sub>	26,8	0,3	5,25	1,6	1800	K + about 10% M
17	93% ZrO <sub>2</sub> + 5% CaO + 2% Y <sub>2</sub> O <sub>3</sub>	27,6	0,2	5,25	1,0	2000	K
18	92% ZrO <sub>2</sub> + 5% CaO + 3% Y <sub>2</sub> O <sub>3</sub>	28,0	0,4	5,3	2,1	2300	K
19	90% ZrO <sub>2</sub> + 5% CaO + 5% La <sub>2</sub> O <sub>3</sub>	29,0	0,5	5,2	2,5	1600	K + 20% M
20	90% ZrO <sub>2</sub> + 8% CaO + 2% Y <sub>2</sub> O <sub>3</sub>	28,0	0,1	5,2	0,5	2250	K
21	90% ZrO <sub>2</sub> + 5% CaO + 5% Nd <sub>2</sub> O <sub>3</sub>	27,0	0,2	5,3	2,0	2330	K
22	88% ZrO <sub>2</sub> + 9% CaO + 3% Nb <sub>2</sub> O <sub>5</sub>	20,0	3,0	4,4	13,2	300	K + 20% M

TABLE 4. Comparison of the Stability of Two- and Three-Component Solid Solutions Based on Zirconia\*

Specimen No.	Structure of original solid solution	Quantity of monoclinic phase, % after heating at 1200°C			
		150 h	300 h	400 h	500 h
12	K	0	0	0	0
14	K	>30	60	>80	—
15	K	60	85	>90	—
16	K+10% M	15	20	30	30
17	K	0	10	15	15
18	K	0	10	10	10
19	K+20% M	60	80	>90	—
20	K	0	0	0	5
21	K	>40	>60	90	—
22	K+20% M	45	>70	90	—

\* Specimens synthesized at 1750°C with a soak of 4 h.

The investigations showed that the solid solutions of zirconia with magnesia and CaO, containing additions of yttrium oxide, acquire an enhanced resistance against thermal decomposition. The most resistant proved to be ternary solid solutions of ZrO<sub>2</sub> - MgO - Y<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> - CaO - Y<sub>2</sub>O<sub>3</sub> with a content of 2-5% Y<sub>2</sub>O<sub>3</sub>.

The results of the work formed the basis for further detailed investigation of the mechanism and kinetics of the formation of such solid solutions, and a study of their physicoengineering properties and their stability in the high temperature region (about 2000°C).

Considering the thermal-shock resistance and the high engineering properties of double zirconia - yttria solid solutions, replacement in them of a large part of the yttrium oxide by alkaline earth oxides can be considered as a measure for reducing the proportion of the expensive and scarce yttrium oxide in the composition of zirconia products of very high refractoriness.

## CONCLUSIONS

The stability of solid solutions of ZrO<sub>2</sub> - MgO and ZrO<sub>2</sub> - CaO may be critically increased by incorporating small additions (1-2%) of yttrium oxide. Complete discontinuation of the decomposition of these solid solutions occurs with an addition of 3% Y<sub>2</sub>O<sub>3</sub>.

Stabilization of zirconium dioxide by combined additions is achieved with a lower concentration of oxide-stabilizers compared with the required concentration of each of them separately. This permits a substantial reduction in the expenditure on costly and scarce additives, for instance, oxides of rare-earth elements, and yttrium.

The synthesized ternary solid solutions possess valuable physicoengineering properties, such as high mechanical strength, and a lower average coefficient of thermal expansion than double solid solutions.

## LITERATURE CITED

1. O. Ruff and F. Ebert, *Zeitsch. Anorg. Allg. Chem.*, **180**, 19 (1929).
2. R. G. Geller and P. J. Yavorsky, *J. Research NBS*, **35**, 87 (1945).
3. C. E. Curtis, *J. Amer. Ceram. Soc.*, **30**, No. 6, 180 (1947).
4. P. Duwez et al., *J. Amer. Ceram. Soc.*, **33**, 274, (1950), **35**, No. 5, 107 (1952).
5. É. K. Keler and A. B. Andreeva, *Ogneupory*, No. 2, 65 (1957); No. 12, 552 (1958).
6. D. N. Poluboyarinov et al., *Ogneupory*, No. 4, 175 (1965).

7. A. Dietzel and H. Tober, Ber. Dtsch. Keram. Ges., 30, 47 No. 3, 47 (1953); No. 4, 71 (1953).
8. É. K. Keler and A. B. Andreeva, Ogneupory, No. 5, 224 (1963).
9. A. M. Cherepanov and S. G. Tresvyatskii, High-Temperature Materials and Products from Oxides [in Russian], Metallurgiya (1964).