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EFFECTS OF SOME OXIDE ADDITIONS ON THE THERMAL LENGTH CHANGES OF ZIRCONIA

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ABSTRACT

The oxides of cerium, yttrium, silicon, magnesium, and calcium were added in various proportions to zirconia of 99-percent purity, and the effects of these additions, combined with preheating at various temperatures ranging from 1,450° to 1,950° C, on thermal length changes of the zirconia during heating and cooling between room temperature and a maximum of 1,700° C were observed. The results are compared with similar observations on zirconia of 96-, of 98-, and of 99-percent purity without oxide additions.

The results show that the irregular thermal length changes accompanying phase transformations in zirconia may be prevented by changing the crystal to the stable cubic form. This was accomplished by (a) 11.5- and 15-percent additions of Y_2O_3 and heating at 1,700° C or higher; (b) 8- and 15-percent additions of MgO and heating at 1,550° C or higher, but only for the range from room temperature to 1,200° C; and (c) 5-, 6-, 8-, and 15-percent additions of CaO and heating at 1,550° C or higher, but additions of more than 6 percent caused the specimens to be very porous and proportionately weak. In all cases, however, the expansion during heating and contraction during cooling was relatively high. The coefficients of linear thermal expansion of the specimens that were all, or nearly all, cubic ranged from 8.8 to 11.8×10^{-6}. Also, zirconia has a low thermal conductivity relative to such materials of high thermal expansion as alumina, magnesia, and beryllia (unpublished data). Consequently, a high resistance to thermal shock cannot be expected of the stabilized product, even though it is not subject to the structural disintegration characteristic of the commercially pure material.

CONTENTS

I. INTRODUCTION

The large number of articles in the literature on the general subject of zirconia and its possibilities and limitations, as shown by

Kreidl's excellent bibliography,[1] evidence the interest in this material. As early as 1916, articles appeared in England[2] and in Germany[3] describing ZrO_2 and its uses in refractory ware. Zirconia has a number of excellent qualities as a ceramic body ingredient. Principally, these are its hardness, chemical stability at both ordinary and elevated temperatures, and the wide temperature range over which it may be used.[4]

Most of the earlier investigations were concerned with studies of oxide additions that would promote reduction in porosity and increase the mechanical strength of ZrO_2 shapes. It was found that ware made of zirconia would undergo rapid weakening and structural disintegration in service, even though the initial strength was quite satisfactory. It had been made evident during the course of another investigation[5] that refractory shapes of ZrO_2 have a discouragingly short life in service. Some thermal-expansion curves for ZrO_2 had been published,[6] but these did not contain information upon which an explanation for the structural weakening could be based. It is known from the literature[7] that zirconia has several crystalline forms, of which the monoclinic is stable at ordinary temperatures and occurs as the mineral baddeleyite. Optical data for the various forms are incomplete, as shown by the following summary:

Form	Birefringence	Mean index	Interference figure	Unit cell size, in angstroms
Monoclinic (baddeleyite).	High	2. 15	Biaxial (−)	$a=5.21$, $c=5.37'$ $b=5.26$, $\beta=80°32'$
Tetragonal	Low	>2. 15	Uniaxial (−)	$a=5.07$, $c=5.16$
Trigonal	Medium (?)	?	Uniaxial (+)	$a=3.598$, $c=5.875$

That changes from one form to another, specifically the monoclinic ⇄ tetragonal inversion, might be accompanied by destructive volume changes was indicated by Ruff and Ebert,[8] who published considerable data on ZrO_2 with oxide additions. They reported a fourth, or cubic, crystalline modification, which is actually a solid solution of some oxide in zirconia. The effect of this solid solution is a distortion of the tetragonal lattice to a "stabilized" cubic crystal, which is not subject to further inversions. Ruff and Ebert[8] demonstrated, by examinations with a heated X-ray camera, that the monoclinic-tetragonal inversion takes place somewhere between 800° and 1,200° C in relatively pure zirconia, and that CaO, MgO, Sc_2O_3, Y_2O_3, and CeO_2 additions brought about the formation of the stable cubic form. They did not, however, present thermal-expansion curves to prove that this stabilized zirconia was free from undesirable volume changes, but ample evidence[9] has been published that unstabilized

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[1] Norbert J. Kreidl, J. Am. Ceram. Soc. **25**, 129 (1942).

[2] J. A. Audley, Trans. Ceram. Soc. (England) **16**, 121 (1916).

[3] O. Ruff and G. Lauschke, Z. anorg. Chem. **97**, 73 (1916).

[4] D. Kirby, Metallurgia **30**, 65 (1944), states that ZrO_2 can be used up to 2, 400° C.

[5] R. F. Geller, J. Research NBS **27**, 555 (1941) RP1443.

[6] G. E. Merritt, Trans. Am. Electrochem. Soc. **50**, 165 (1926). F. H. Norton; J. Am. Ceram. Soc. **8**, 799 (1925).

[7] Willi M. Cohn and S. Tolksdorf, Z. physik. Chem. [B] 8, 331 (1930); Willi M. Cohn, Trans. Electrochem. Soc. **68**_ 65 (1935).

[8] Otto Ruff and Fritz Ebert, Z. anorg. Chem. **180**, 19 (1929); see also U. S. Patent 1,969,099.

[9] Willi M. Cohn, Keram. Rundschau **38**, 721, 753, 777, 781, (1930); R. F. Mather, J. Am. Ceram. Soc. **25**, 93 (1942).

ZrO_2 is subject to erratic length changes between room temperature and 1,400° C.

Because of the incomplete evidence on the thermal length changes of zirconia and the favorable properties of the oxide, a study was undertaken to determine the oxide additions and heat treatments that would most efficiently form the cubic zirconia, and thereby presumably overcome the erratic thermal length changes. The results of the study, covering the effect of CeO_2, Y_2O_3, SiO_2, MgO, and CaO additions, and preheating at various temperatures ranging from 1,450° to 1,950° C., on the thermal length changes of ZrO_2 from room temperature to 1,700° C. are reported in this paper. During the course of the investigation there were several developments which it would have been interesting to study in detail, but the scope of the work was restricted to determining if the several oxides, as minor additions, would produce ceramic bodies with industrial possibilities.

II. MATERIALS

Zirconia of three grades was used in the tests. All of the zirconia was washed through a No. 325 U. S. Standard Sieve before being formed into specimens. The chemical compositions [10] are as follows:

Zirconia (grades)	ZrO_2	SiO_2	Al_2O3	Fe_2O_3	CaO
	%	%	%	%	%
A, fused	96.0	2.05	0.67	0.14	0.19
B, fused	98.0	1.21	.34	.08	.17
C, calcined	99.0	.27	.08	.02	.24

The materials used as additions to the zirconia are described as follows:

CeO_2 (two grades were used): (a) Purified cerous oxalate, which was calcined at 1,425° C and hand-ground to pass dry through a No. 325 sieve. The color of the ground sample was a reddish brown; (b) pure ammonium hexanitrato cerate $(NH_4)_2Ce(NO_3)_6$, which was calcined, hand-ground, and sieved the same as grade (a). The color of the ground sample was a light buff.

Y_2O_3: Commercially pure material, which was repurified by twice dissolving it in hydrochloric acid and precipitating it as the hydroxide, followed by a third solution, precipitation as the oxalate, and calcination at 1,425° C. It was then hand-ground to pass wet through a No. 325 sieve. Color of the powder was cream.

SiO_2: Pulverized quartz, which had been passed wet through a No. 325 sieve, and which, by chemical analysis, contained 99.6 percent of SiO_2.

MgO (two types were available): (a) Periclase of nominal 97-percent purity and passing the No. 200 sieve. The material used was that portion of the sample that passed dry through a No. 325 sieve; (b) commercial $MgCO_3$, which had been calcined at 816° C, and which was of very fine particle size. Described by the producer as containing 2.3 percent of CaO, 0.2 percent of soluble salts, and having a 5.0 percent ignition loss.

CaO: Reagent quality $CaCO_3$, hand-ground to pass dry through a No. 325 sieve.

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[10] The chemical compositions were supplied by Eugene Wainer, of the Titanium Alloy Mfg. Co.

For calibration and comparison, the following materials were tested also:

A water-clear single crystal of MgO, from which an expansion specimen was obtained by cutting with a diamond saw and grinding. The measured expansion was parallel with the octahedral axis.

Beryllia, claimed by the producer to contain at least 99.9 percent of BeO, and which, by spectrographic analysis, contained less than 0.01 percent each of Cu, Fe, Mg, and Si. The material was fused in an electric arc supplied with oxygen through the electrodes to prevent formation of the carbide;[11] ground in an iron mill to pass, wet, a No. 325 sieve; and acid-treated to remove iron contamination.

Thoria of nominal 99-percent purity, which was fused and ground by the same method used for the beryllia, passed dry through a No. 325 sieve, and acid-treated. A spectrogram of the unfused sample indicated over 0.01 percent each of Al, Si, and Ca, and less than 0.01 percent each of Cu and Mg.

Zirconium silicate of two types: (a) the mineral zircon, containing by chemical analysis (see footnote 10) 64.82 percent of ZrO_2 and 34.78 percent of SiO_2, (which, by calculation, equals 96.5 percent of $ZrSiO_4$); and (b) zirconium silicate prepared by intimately mixing zirconia C and silica in the proper proportions, pressing into specimens, and heating at 1,500° and at 1,700° C.

III. APPARATUS AND TEST METHODS

Specimens consisting of one oxide were made by thoroughly mixing the oxide with about 10 percent of a 5-percent solution of soluble starch, and pressing the mixture in a hardened steel mold under a pressure of 9,300 lb/in.^{2} to form rods 1.6 cm in diameter by about 5 cm long. After drying, these rods were ground to equilateral triangular prisms approximately 0.5 cm^2 in cross-sectional area.

The specimens consisting of ZrO_2 and an admixture were made by first mechanically blunging a 40-g batch of the body with 40 percent of water, drying, pulverizing, and then following the same procedure used for the single-oxide specimens.

A few of the specimens were matured in a gas-heated kiln at 1,550° or 1,600° C. The others were matured either in an electrically heated platinum-wound furnace, when the temperatures did not exceed 1,450° C, or in the resistor furnace shown in figure 1. This furnace is the same in principle as the one previously described [12] but is larger, having a heating chamber 3¼-in. inside diameter by 4 in. high and requiring eight resistors.

For the thermal-expansion tests, this furnace was modified slightly to accommodate the dilatometer shown in figure 1. This dilatometer is practically the same in design as the one used in an investigation of clays,[13] except for one important detail. The three members supporting the gage, and the center member extending from the specimen to the gage stem, were single-crystal artificial-corundum rods, approximately ⅛ in. in diameter by 18 in. long. The three rods supporting the gage were cemented into a base made of beryllia.[14] The

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[11] U. S. Patent 1,545,951.

[12] R. F. Geller, J. Research NBS **27**, 555 (1941) RP1443.

[13] R. F. Geller and E. N. Bunting, J. Research NBS **25**, 15 (1940) RP1311.

[14] Reaction between the rods and the beryllia, particularly at temperatures above about 1,700° C, warrants the recommendation that the base be made of Al_2O_3 instead of BeO.

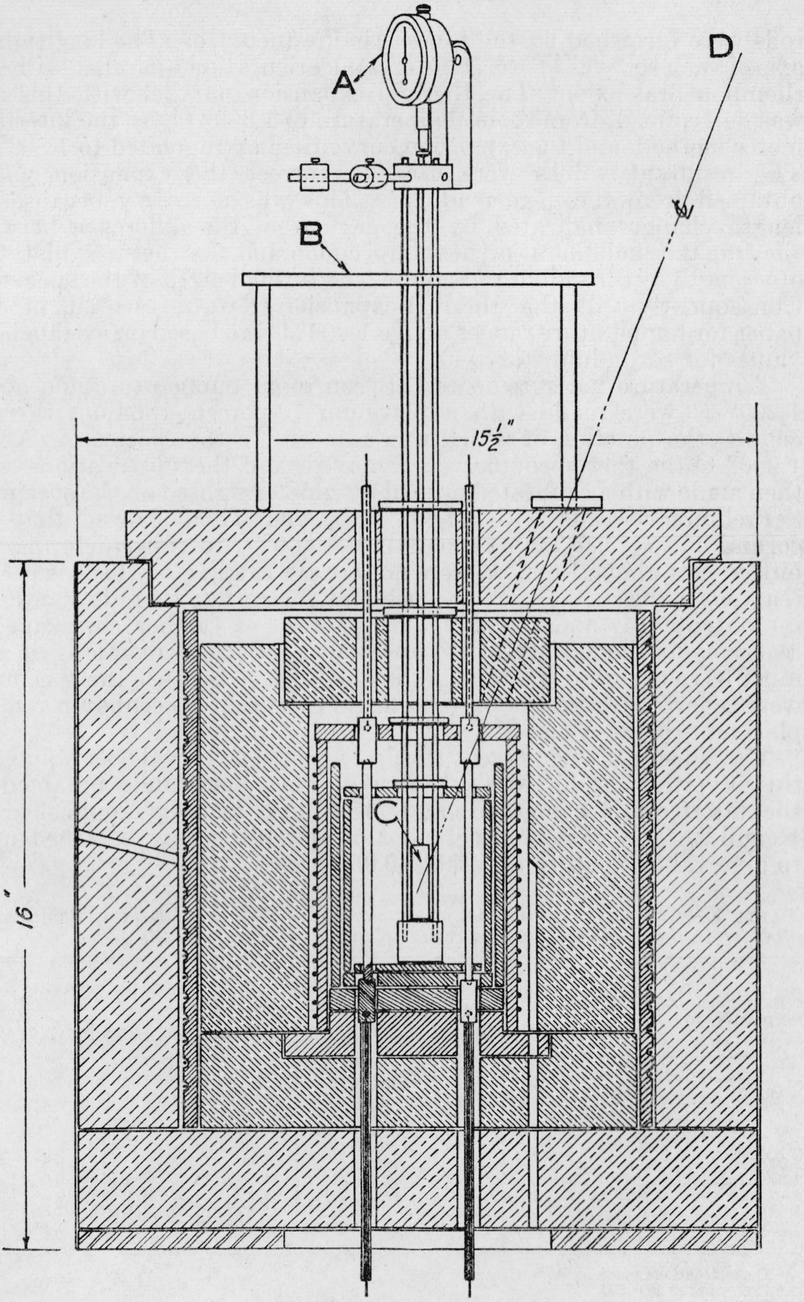

FIGURE 1.—*Dilatometer installed in furnace.*

A, Gage, 0.01-mm divisions; *B*, Bakelite shield; *C*, specimen; the center line *D*, is the axis of the openings in the furnace parts, through which the Pt–10-percent Rh thermocouple was inserted for temperature measurements up to 1,200° C. At about this temperature, the thermocouple was removed and higher temperature measurements were made with an optical pyrometer sighted on the specimen through the same openings. Only two of the eight ThO_2–Y_2O_3 resistors used for heating the furnace are shown in place. The ⅛- by 18-in. rods supporting the gage and the rod extending from the specimen to the gage stem are artificial corundum.

rods were furnished by the Linde Air Products Co. The longitudinal axis of each rod was at the same crystal orientation (parallel with the rhombohedral axis). The thermal expansion parallel with this axis was determined, from room temperature to 1,000° C, by the interferometer method, and the expansion curve then extrapolated to 1,800° C. The resultant values were used to correct the expansion values obtained from the gage readings. This was necessary because the length changes indicated by the gage were the difference between the true thermal dilatation of the specimen and the thermal dilatation of a length of corundum rod equivalent to the length of the specimen. Consequently, all the thermal-expansion data presented in this paper for temperature ranges above 1,000° C are based on extrapolated values for corundum (table 1).

Temperature measurements between room temperature and about 1,200° C were made with a platinum–10-percent-rhodium thermocouple, the junction of which was adjacent to the specimen. Above 1,200° C the thermocouple was removed, and the observations were then made with a calibrated optical pyrometer sighted on the specimen.

Preliminary tests with MgO, BeO, and ThO_2 showed that the corundum rods had ample strength at 1,800° C to resist deformation, but results above 1,600° C were not always satisfactory because of the reaction between the beryllia base and the corundum rods mentioned in footnote 14, and possibly also because of further shrinkage, or reactions at the surface of the specimens. Surface reactions, if any, must have occurred with vapors in the furnace because the specimens were separated from the base, and from the center corundum rod, by platinum-rhodium plates.

The substantial agreement (table 1) between the values obtained in this investigation for MgO, BeO, and ThO_2 and values obtained by the interferometer method, and also those for MgO published by Heindl[15], show that the method and apparatus may be relied upon to give values good to at least ±0.05 percent.

TABLE 1.—*Comparison of thermal-expansion values obtained with the dilatometer used in this investigation and results obtained by other methods*

From room temperature to—	Interferometer method [a]						Dilatometer method			Heindl
	ThO_2 [b]	BeO [b]	MgO [c]	Al_2O_3 [d]	Al_2O_3 [e]	Al_2O_3 [f]	ThO_2 [g]	BeO [h]	MgO [i]	MgO [j]
°C	%	%	%	%	%	%	%	%	%	%
200	0.14	0.10	0.19	0.10	0.12	0.11	0.14	0.12	0.16	0.19
400	.31	.26	.45	.26	.29	.26	.32	.28	.43	.45
600	.51	.45	.73	.43	.47	.43	.52	.48	.71	.70
800	.70	.65	1.04	.60	--------	.61	.73	.69	1.01	1.02
1,000	--------	--------	--------	--------	--------	.81	.94	.92	1.32	1.32
1,200	--------	--------	--------	--------	--------	(1.01)	1.15	1.16	1.64	1.65
1,400	--------	--------	--------	--------	--------	(1.22)	1.37	1.40	1.98	1.96
1,600	--------	--------	--------	--------	--------	(1.45)	1.59	1.66	2.34	2.27
1,700	--------	--------	--------	--------	--------	(1.57)	1.71	1.78	2.46	2.43

[a] Determinations made by A. S. Creamer.

[b] Preheated at 2,000° C.

[c] Preheated at 1,900° C.

[d] Corundum crystal, perpendicular to "C" axis.

[e] Corundum crystal, parallel to "C" axis.

[f] Expansion was measured parallel with the rhombohedral axis, or 57° 34′ from the "C" axis. These values were used to correct the gauge readings. The values in parentheses are extrapolated.

[g] Preheated at 1,850° C.

[h] Several preheatings with a total of 15 above 1,800° C.

[i] Cut from a single crystal of periclase.

[j] R. A. Heindl, BS J. Research **10**, 715 (1933) RP562.

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[15] R. A. Heindl, BS J. Research **10**, 715 (1933) RP562.

The heating and the cooling rates in all of the tests did not exceed 3½ degrees centigrade per minute.

The absorptions were determined by boiling the test prisms in CCl_4 for 5 hours and dividing the increase in weight by the density of the CCl_4. The resultant values are comparable with data for absorption obtained conventionally by boiling in water.

IV. RESULTS

Because of the very irregular thermal length changes of most of the compositions tested, the results are usually presented as graphs rather than as coefficients.

1. ZIRCONIA

The first series of graphs is shown in figures 2 and 3 and illustrates the thermal length change behavior of the three zirconias (A, B, and C) without oxide additions. One specimen of each zirconia had been preheated within the range of temperatures to which refractories are subjected in present-day commercial practice, and another specimen had been preheated at a relatively much higher temperature:

Zirconia A.—The specimen preheated at 1,450° C (fig. 2) was heated in the expansion test to 1,200°, 1,300°, 1,400°, and 1,100° C consecutively, with intermediate cooling to about 800° C. The following points of interest are illustrated by the graph: (a) The contraction during heating and the expansion during cooling will apparently take place an indefinite number of times during repeated heating and cooling cycles; (b) the beginning of contraction during heating is not clearly defined but the beginning of expansion during cooling occurs sharply (and actually was duplicated within 2 degrees); (c) the length changes will have no irregularities if the maximum temperature to which the zirconia is subjected remains below 1,100° C, as shown by the curve for the first heating and for the last heating and cooling cycle; and (d) an appreciable permanent shrinkage (0.65 percent) occurred while holding the specimen for 2½ hours at 1,400° C, even though it had been preheated at 1,450° C.

The zirconia preheated at 1,850° C (fig. 2) had acquired several cracks during the preheating, and it is conceivable that the minor irregularities in the curve between 1,200° and 1,700° C reflect further cracking and deforming of the specimen. This cracking was characteristic of all the zirconia pieces heated at or above 1,850° C. In fact, it was only after repeated trials that specimens were obtained sufficiently intact to be placed in the dilatometer. One specimen of zirconia A, preheated at 1,950° C, failed completely in the expansion test while the rapid expansion (during cooling) was taking place. For this specimen, as well as for the one preheated at 1,850° C, this "cooling-expansion" started at 1,004° C.

Zirconia B.—The two tests for which curves are presented in figure 2 represent specimens preheated at 1,415° and at 1,950° C. The latter was cracked, similar to the specimen of zirconia A heated at 1,850° C, and again the expansion during cooling started sharply at 1,004° C. The most noticeable difference between the two specimens of zirconia B is the very large permanent shrinkage of the one preheated at

1,415° C as compared to the other, which showed a net expansion or "growth." Similar growth had been noted also by Mather.[16]

Zirconia C.—The difficulties encountered in making usable test prisms, mentioned in connection with zirconia A, were seemingly insurmountable with the C material. It was found necessary to admix some of the fused zirconia, and the curves shown in figure 3 were obtained with pieces made of 90 parts of zirconia C and 10 parts of zirconia B.

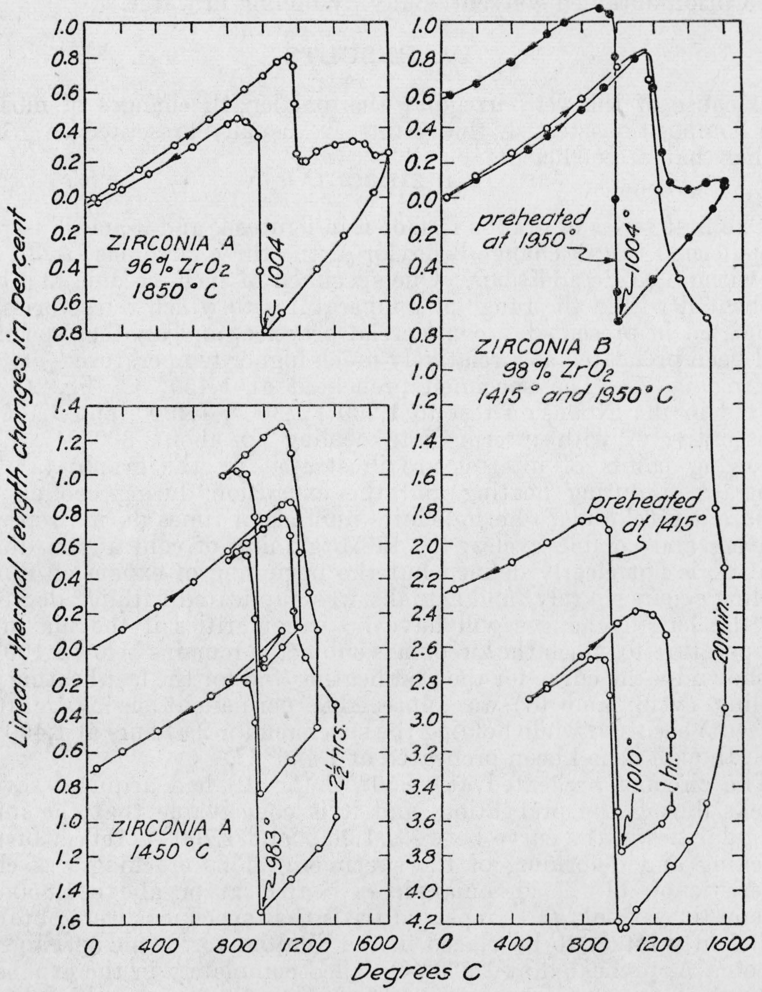

FIGURE 2.—*Thermal dilatation curves for fused zirconias of 96- and of 98-percent purity.*

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing. The time notations on the curves indicate the interval of holding at the maximum temperature.

The expansion during cooling started at temperatures significantly higher than for either of the less pure zirconias, A and B, and the

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[16] R. F. Mather, J. Am. Ceram. Soc. 25, 93 (1942).

resultant length change was at least as great. In the case of zirconia C heated at 1,950° C, the length changes during both the "heating-contraction" and the "cooling-expansion" were greater than for any other specimen tested. Consequently, this material was selected for

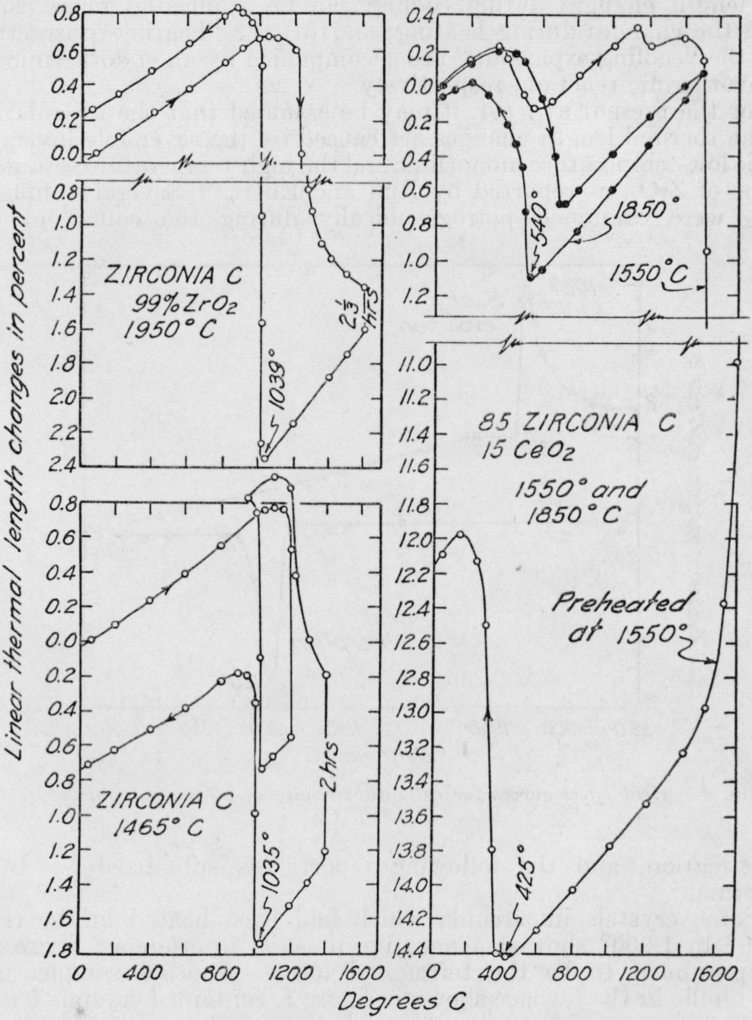

FIGURE 3.—*Thermal-dilatation curves for calcined zirconia of 99-percent purity and calcined zirconia with* CeO_2 *additions.*

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing. The time notations on the curves indicate the interval of holding at the maximum temperature.

differential thermal analysis,[17] the result of which is shown in figure 4.

In general, it may be concluded, with respect to zirconia, that (a) preheating to temperatures in the range from 1,450° to 1,950° C will not change, significantly, the amount of length change accompany-

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[17] This analysis was made by E. N. Bunting, using a platinum-to-platinum-10-percent-rhodium differential thermocouple, a K-type potentiometer, and corundum as the reference material.

ing the rapid contraction during heating, or the expansion during cooling; (b) the trend is for these length changes to be greater, and for the "cooling-expansion" to begin at a relatively higher temperature, with increase in purity of the zirconia; (c) for any one material, the length changes during cooling can be duplicated more closely than the changes during heating; and (d) the "heating-contraction" and the "cooling-expansion" are accompanied by an endothermic and an exothermic reaction, respectively.

For the present at least, it may be assumed that the irregularities in the thermal length changes are caused by the reversible inversions of the low-temperature monoclinic and the high-temperature tetragonal forms of ZrO_2, as reported by Ruff and Ebert.[18] Several samples of ZrO_2 were examined petrographically during the course of this investigation, and the following report was submitted by B. L. Steierman:

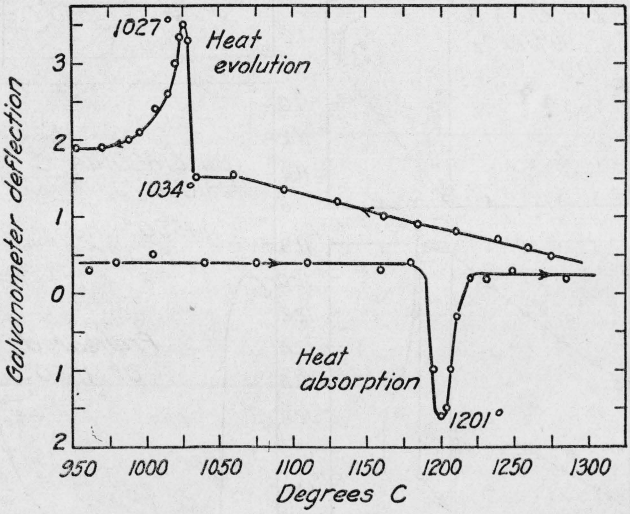

FIGURE 4.—*Heat effect curves for calcined zirconia of 99-percent purity preheated at 1,950° C.*

"Some crystals in zirconia which had been heated in the range 1,000° to 1,900° showed a negative uniaxial interference figure and are presumed to be the tetragonal form. Another sample, used as a muffle in the furnace shown in figure 1, contained crystals 5 to 10 microns in size, with medium birefringence and apparently uniaxial positive in character, indicating the trigonal form. A third sample, which had been used as a pedestal for supporting test pieces in the furnace described in NBS Research Paper RP 1443 [see footnote 12] and which had been heated to a maximum temperature of 2,025°, was extremely weak, crushed easily to a fine powder, and was composed solely of ZrO_2 crystals ranging from 2 to 8 microns in size. These crystals were mostly monoclinic. Occasional grains were tetragonal and also present, but not common, were grains with internal bladed crystals indicative of the tetragonal-monoclinic inversion."

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[18] Otto Ruff and Fritz Ebert, Z. anorg. allgem. Chem. **180**, 19 (1929).

The conclusion to be drawn from the petrographic data is, that the reversion from a high temperature to the low-temperature form is not necessarily complete, even with relatively slow cooling.

2. ZIRCONIA WITH ADDITIONS

(a) EFFECT OF CeO_2

Only one composition, containing 85 weight percent of zirconia C and 15 percent of CeO_2, was investigated. It is evident from the graphs in figure 3 that this addition of ceria would not prevent the irregular and rapid thermal length changes noted for zirconia alone. Similar results were obtained with ceria from both sources (section II, page 89).

The very large permanent shrinkage, beginning at about 1,400° C, of the specimen preheated at 1,550° C is of secondary interest only. Of primary interest is the low-temperature range in which the inversions take place as compared with the corresponding ranges for the three zirconias. That oxide additions may depress the inversion temperatures was shown by Mather's work with zirconia and spinel, see footnote 16, in which case the expansion during cooling started as low as about 600° C for a mixture containing 90 mole percent of spinel. As the data show, only 15 weight percent (11.2 mole percent) of CeO_2 was sufficient to lower the beginning of the expansion during cooling to 425° C. The small contraction between 1,150° and 1,200° C, for the specimen preheated at 1,550° C, may be caused by ZrO_2 unaffected by CeO_2, during the preheating. Petrographic examination of specimens containing CeO_2 obtained from the oxalate, and which had been heated at 1,550°, at 1,800°, and at 2,000° C also showed that all the zirconia was in the monoclinic form.

(b) EFFECT OF Y_2O_3

Typical results are shown by the graphs in figure 5. The addition of 8 percent of yttria to zirconia C and preheating at 1,850° C, produced length changes resembling in general those obtained with the 15-percent addition of CeO_2. In contrast to this, adding 11.5 percent of Y_2O_3, and preheating to only 1,700° C, had almost completely eliminated the irregularities indicative of the monoclinic-tetragonal transformation, but there was an appreciable permanent shrinkage at temperatures above about 1,400° C. The three other curves in figure 5 illustrate the effect of the preheating temperature on the composition containing 15 percent of Y_2O_3 and 85 percent of zirconia C. A correlation of the information furnished by the curves in figure 5 with the results of petrographic examinations, summarized in table 2, shows that the decrease in the irregularities of the thermal length changes during both heating and cooling is directly related to the presence of the "stabilized" cubic zirconia.

Increasing additions of Y_2O_3 to ZrO_2 tend to produce mechanically weaker and more porous bodies, as shown by the following values for absorption:

ZrO_2+ 8.0 percent of Y_2O_3 preheated at 1,850 C	3.6 percent.
ZrO_2+11.5 percent of Y_2O_3 preheated at 1,700 C	5.6 percent.
ZrO_2+15.0 percent of Y_2O_3 preheated at 1,700 C	12.5 percent.
ZrO_2+15.0 percent of Y_2O_3 preheated at 1,850 C	7.7 percent.

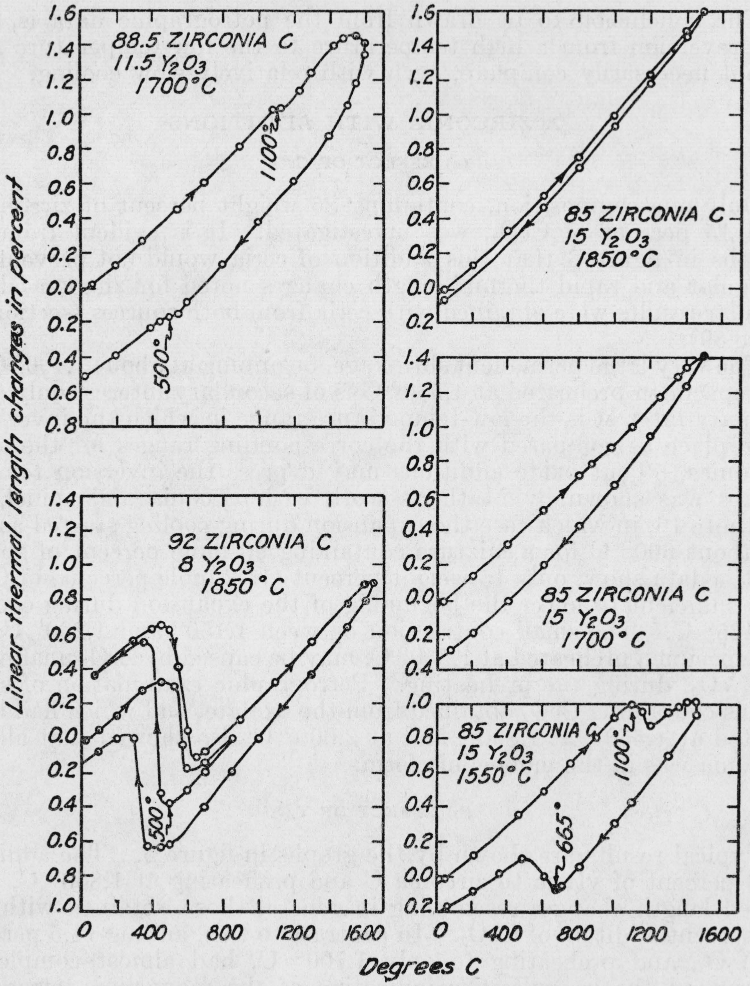

FIGURE 5.—*Thermal dilatation curves for calcined zirconia of 99-percent purity with Y_2O_3 additions.*

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing.

TABLE 2.—*Petrographic data on heated specimens of zirconia with yttria additions*

Test number	Composition		Maximum preheating temperature	Form of ZrO_2 determined microscopically
	ZrO_2	Y_2O_3		
	%	%	°C	
307-L	85	15	1,550	85 to 90 percent cubic.
304-L	85	15	1,650	At least 95 percent cubic.
305-L	85	15	1,700	95 percent cubic, 5 percent monoclinic.
301-L	85	15	1,750	About 99 percent cubic.
335-L	92	8	1,850	Monoclinic with possibly some tetragonal, but definitely no cubic.
295-L	85	15	1,850	All cubic.
299-L	85	15	1,850	Do.
441 [a]	92	8	1,900	15 percent cubic, and 85 percent monoclinic, of which about one-third appears to have inverted from the tetragonal.
441 [a]	85	15	1,900	All cubic.

[a] The X-ray patterns of the samples from this test contained the lines for cubic zirconia having a face-centered cubic cell with a_0=5.108 A. The pattern for the sample with 8 percent of yttria contained also lines for monoclinic zirconia.

(c) EFFECT OF SiO_2

It was thought of potential interest to investigate some ZrO_2-SiO_2 combinations because of the ready availability of silica and because of the well-established use in industry of zircon ($ZrSiO_4$).

Samples of the mineral zircon were heated for 1 hour at 1,700°, at 1,750°, and at 1,800° C, and samples of the zirconia-silica mixture in 1:1 mole ratio were heated for 1 hour at 1,700° and at 1,800° C. The macroscopic and petrographic appearance of the mineral before and after heating at 1,700° and at 1,750° C was identical, but after the 1,800° C treatment the orignially granular sample had sintered into a hard mass, and the X-ray pattern contained only lines for monoclinic zirconia. The X-ray pattern for the ZrO_2:SiO_2 mixture heated at 1,700° C contained strong lines for zircon and weak lines for monoclinic zirconia, and the pattern for the mixture heated at 1,800° C was identical with that for the mineral zircon heated at 1,800° C. This is good evidence that zircon breaks down between 1,750° and 1,800° C to form zirconia and liquid (as there were lines for only one crystalline phase). It is in agreement with the petrographic report in Heindl's paper[19] that zircon heated at 1,800° C was composed wholly of zirconium oxide and glass. Matignon[20] and Wartenburg and Gurr[21] also noted the decomposition of zircon above 1,800° C. In reference 21 a curve is published showing the amount of SiO_2 lost by volatilization. The data are based on chemical analyses of zircon samples after having been heated for 30 minutes at each of a series of temperatures. At 1,800° C, for example, the loss of silica was practically negligible, at 2,000° C it was about 18 percent, at 2,200° C it was about 65 percent, and at 2,300° C it was indicated to be complete. The observed decomposition of ZrO_2 is not in agreement with published diagrams for the system ZrO_2-SiO_2,[22] showing congruent melting of $ZrSiO_4$ above 2,400° C.

Thermal-expansion tests were made on the following specimens: (a) 85 percent of zirconia C and 15 percent of silica (by weight) preheated at 1,700° C; (b) zirconia and silica in equimolar proportions preheated at 1,500° and at 1,700° C; and (c) the mineral zircon preheated at 1,700° C. The results are plotted in figure 6.

Although the results of the two tests made on each of the two test pieces containing 15 percent of silica do not duplicate in detail, they are sufficiently alike to justify the conclusion that the expansion following the break during heating in the first test and the contraction following the break during heating in the second test are caused by an actual change in the structure of the body. The nature of the change was not discernible by either petrographic or X-ray examination, and the subject was not investigated further because, for the present at least, it was of academic interest only.

The relatively small length changes accompanying the inversions of the zirconia in the two specimens made of equimolar proportions of ZrO_2 and SiO_2 indicate that the ZrO_2 is present mostly as $ZrSiO_4$. This is in the accord with the X-ray pattern and, although only indicative, is the best information that could be obtained because the structure was so finely crystalline that quantitative estimates of the

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[19] R. A. Heindl, BS. J. Research **10**, 715 (1933) RP562.
[20] M. Camille Matignon, Compt. rend. **177**, 1290 (1923).
[21] H. von Wartenburg and W. Gurr, Z. anorg. allgem. Chem. **196**, 374 (1931).
[22] E. W. Washburn and E. E. Libman, J. Am. Ceram. Soc. **3**, 634 (1920); N. Zirnowa, Z. anorg. allgem. Chem. **218**, 198 (1934).

crystalline phases present were not possible by optical examination.

The zircon specimen preheated at 1,700° C showed a slight decrease in expansion per degree above 1,500° C, but this was probably caused by permanent shrinkage. The length changes during heating and during cooling between room temperature and 1,500° C were nearly uniform throughout this range. The average coefficient during heating is 5.1×10^{-6}, and during cooling it is 5.2×10^{-6}.

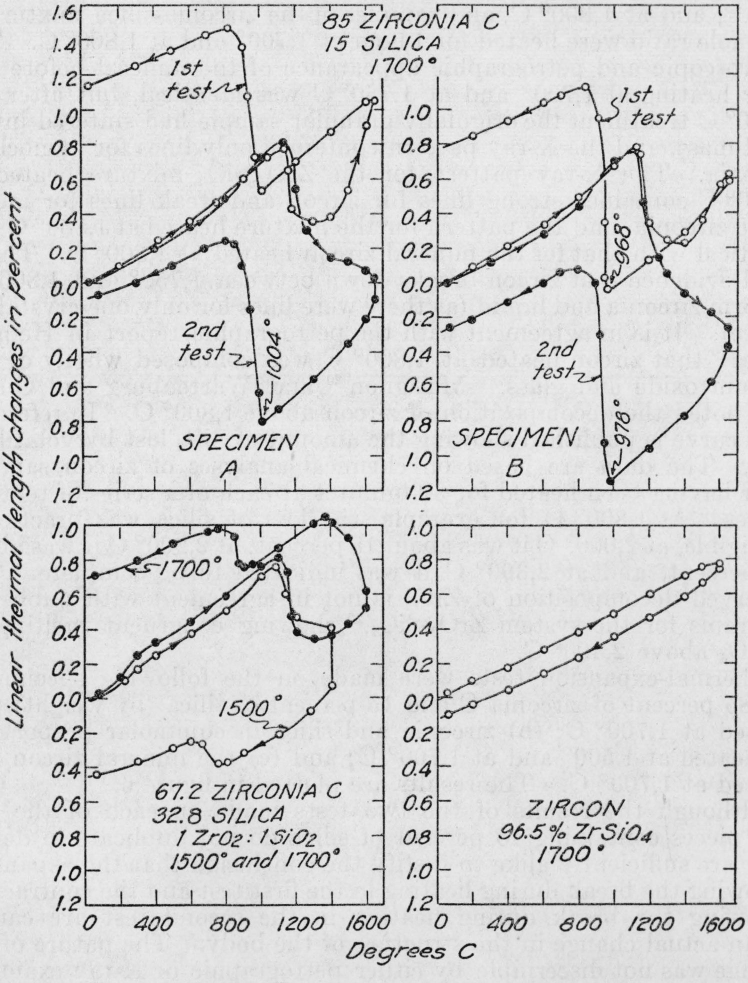

FIGURE 6.—*Thermal dilatation curves for calcined zirconia of 99-percent purity with* SiO_2 *additions, and for mineral zircon.*

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing.

The two prisms containing 15 percent of SiO_2 had absorptions of 5.7 and 8.7 percent, respectively, and were relatively strong, as judged by observation. The $ZrO:SiO_2$ mixture preheated at 1,500° C was very porous and mechanically weak, but the specimen preheated at 1,700° C was firm and had an absorption of 3.5 percent. The zircon test piece also was very firm and its absorption was 7.7 percent.

(d) EFFECT OF MgO

X-ray and petrographic evidence shows that additions of either 8 percent or 15 percent of MgO, and preheating at temperatures as low as 1,550° C, converted most of the zirconia to the stable cubic form. Attempts to determine the amounts of cubic zirconia quantitatively produced conflicting results between duplicate observations on the same specimens by different observers as well as between supposedly duplicate specimens by the same observer. The cubic crystal was face-centered with the unit cell size $a_0=5.063$ A in a sample heated at 1,600° C, and $a_0=5.07$ A in a sample heated at 1,800° C. The X-ray patterns contained also weak lines for monoclinic zirconia and very weak lines for MgO. Petrographic estimates (based on relative birefringence of the nonisotropic phases) indicated a small amount of tetragonal ZrO_2 in some samples.

The thermal length changes of the specimens containing magnesia (figs. 7 and 8), during both heating and cooling between room temperature and about 1,100°C, are very likely determined primarily by cubic zirconia. Comparison of coefficients for specimens containing 15 percent of MgO with the coefficients for the 85-percent-zirconia 15-percent-yttria test piece preheated at 1,850° C (fig. 5), which was reported to be 100-percent cubic ZrO_2 (table 2), shows good agreement (table 3). Above 1,100° C, however, the magnesia additions produced length changes that are unique among those observed in this investigation. They are characterized by (a) two small but well-defined irregularities or "breaks" during heating, but no corresponding break during cooling, such as observed for curves in preceding figures; and (b) a relatively very high average coefficient of length change during heating above 1,400° C and during cooling above about 1,100° C.

The first of the two breaks observed during heating is probably associated with the inversion of monoclinic to tetragonal zirconia. The second break, which occurred at about 1,500° C, is shown most clearly by the two curves for the duplicate tests of the 92-percent-zirconia 8-percent-periclase composition preheated at 1,850° C (fig. 7). These and the other curves for ZrO_2-MgO bodies provide ample evidence that the break at 1,500° C is significant. It may accompany the inversion of tetragonal to trigonal zirconia, although Cohn[23] states that the trigonal is formed only after prolonged heating at, or above, 1,900° C. The assumption that there has been a change in phase at 1,500° C is supported by the differences in the coefficients of thermal expansion (table 3) for the temperature ranges above and below the range of the second break. The gradual change in slope of the cooling curves, occurring between 1,200° and 1,000° C, probably means that a change in phase is taking place, but the absence of the expansion during cooling noted in preceding curves would seem to imply that the presence of MgO in the zirconia crystal lattice prevents

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[23] Willi M. Cohn, Trans. Electrochem. Soc. 68, 65 (1935).

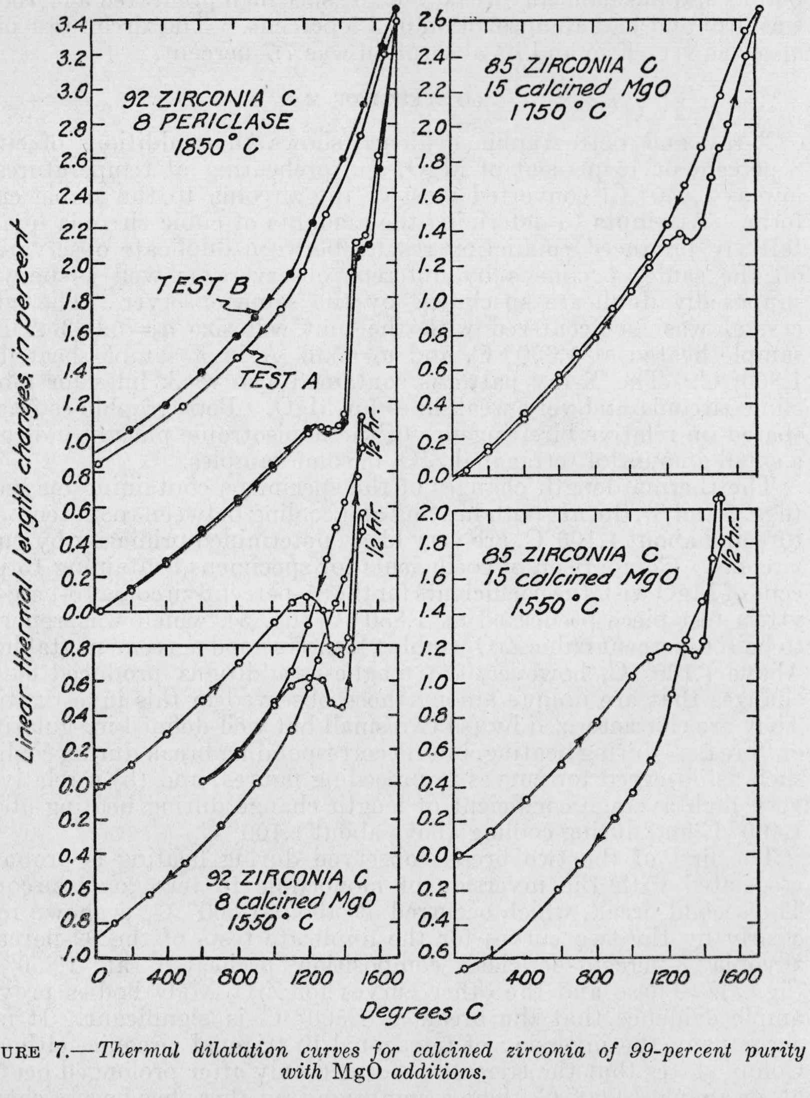

FIGURE 7.—*Thermal dilatation curves for calcined zirconia of 99-percent purity with* MgO *additions.*

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing. The time notations on the curves indicate the interval of holding at the maximum temperature.

the inversion taking place with sufficient rapidity to produce a measurable irregularity.

The thermal length changes above 1,400° C during heating, and above about 1,000° C during cooling (table 3, tests 363–E, 390–E, and 391–E), are much greater than can be explained with the average coefficients of linear thermal expansion for MgO and various crystal

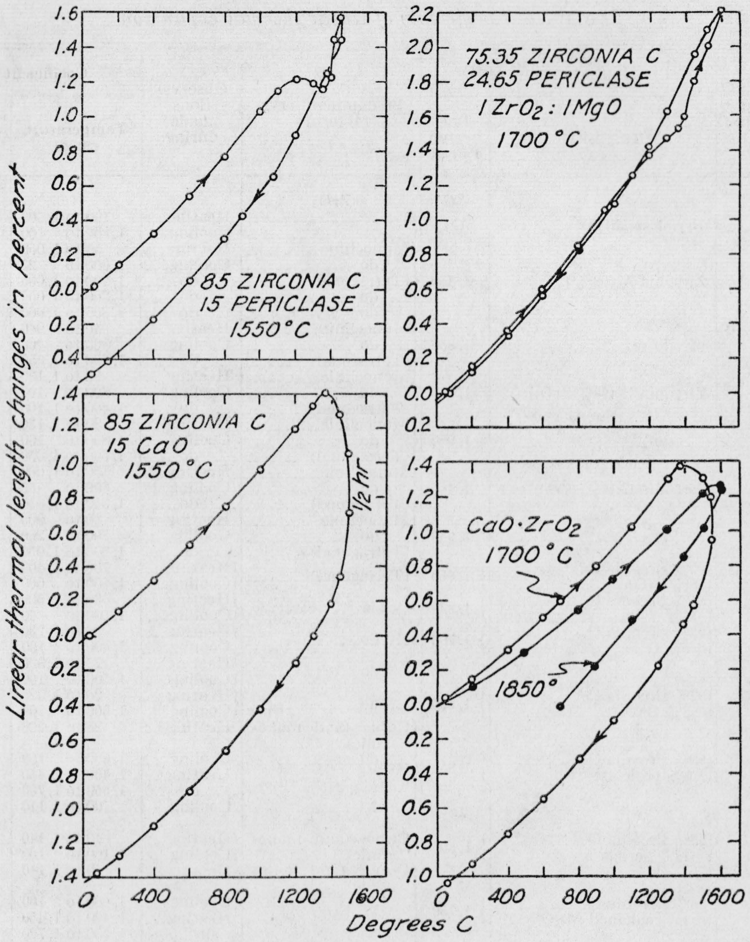

Figure 8.—*Thermal dilatation curves for calcined zirconia of 99-percent purity with* MgO *additions and with* CaO *additions, and curves for artificial* $CaO.ZrO_2$.

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing. The time notation on the curves indicates the interval of holding at the maximum temperature.

phases of ZrO_2 that may be present. These coefficients, given in table 3, are summarized as follows:

	Heating	Cooling
Periclase	$15.3x10^{-6}$	$16.0x10^{-6}$
Monoclinic zirconia	7.2 to $8.0x10^{-6}$	5.4 to $7.3x10^{-6}$
Tetragonal (?) zirconia	10.9 to $11.0x10^{-6}$	11.4 to $13.5x10^{-6}$
Cubic zirconia	10.5 to $11.1x10^{-6}$	11.4 to $11.8x10^{-6}$

TABLE 3.—*Coefficients of linear thermal expansion*

Test number	Specimen		Predominant crystal form [a]	Observations made during	Coefficient	
	Composition	Preheated 1 hr at			Temperature range	Value
		°C	ZrO_2		°C	$\times 10^{6}$
332-E	Periclase (MgO)	(b)		Heating	100 to 1,600	15.3
				Cooling	1,800 to 100	16.0
340-E	Zirconia A (96% ZrO_2)	1,450	Monoclinic	Heating	50 to 1,050	8.0
			do	Cooling	1,000 to 25	6.4
			(Tetragonal)	do	1,200 to 1,000	12.0
			do	do	1,300 to 1,000	11.7
			do	do	1,300 to 1,000	11.7
378-E	do	1,850	Monoclinic	Heating	40 to 940	7.3
			do	Cooling	800 to 60	6.1
			(Tetragonal)	do	1,600 to 1,050	13.1
338-E	Zirconia B (98% ZrO_2)	1,415	Monoclinic	Heating	30 to 1,130	7.4
			do	Cooling	800 to 100	5.4
			(Tetragonal)	do	1,400 to 1,100	13.0
384-E	do	1,950	Monoclinic	Heating	30 to 1,130	7.2
			do	Cooling	800 to 100	6.3
			(Tetragonal)	do	1,500 to 1,050	12.4
339-E	Zirconia C (99% ZrO_2)	1,465	Monoclinic	Heating	70 to 1,000	7.7
			do	Cooling	800 to 50	6.5
			(Tetragonal)	do	1,350 to 1,050	13.0
343-E	do	1,950	Monoclinic	Heating	80 to 900	7.3
			do	Cooling	800 to 200	7.3
			(Tetragonal)	do	1,600 to 1,050	13.5
337-E	92% zirconia C 8% Y_2O_3	1,850	(Tetragonal)	Heating	700 to 1,400	10.9
				Cooling	1,500 to 600	12.8
347-E	85% zirconia C 15% Y_2O_3	1,850	Cubic	Heating	30 to 1,500	11.0
				Cooling	1,500 to 50	11.4
375-E	95% zirconia C 5% CaO	1,700	do	Heating	30 to 1,230	10.7
				Cooling	1,400 to 100	11.5
377-E	do	1,850	do	Heating	25 to 1,300	11.1
				Cooling	1,500 to 100	11.7
361-E	92% zirconia C 8% CaO	1,550	do	Heating	25 to 1,325	10.5
				Cooling	1,300 to 100	11.4
391-E	92% zirconia C 8% periclase	1,850	Cubic (and monoclinic)	Heating	25 to 1,200	8.8
			do	Cooling	1,000 to 100	9.4
			?	Heating	1,400 to 1,450	132.0
			?	do	1,550 to 1,700	77.0
			?	Cooling	1,700 to 1,110	25.7
381-E	85% zirconia C 15% periclase	1,550	Cubic (and monoclinic)	Heating	40 to 1,140	10.8
				Cooling	1,100 to 100	11.6
363-E	85% zirconia C 15% calcined MgO	1,750	Cubic (and monclinic)	Heating	40 to 1,140	11.3
			do	Cooling	1,000 to 100	11.8
			?	Heating	1,400 to 1,450	54.0
			?	do	1,550 to 1,700	37.3
			?	Cooling	1,700 to 1,100	23.7
390-E	MgO:ZrO_2 (molar)	1,700	Cubic	Heating	40 to 1,140	11.8
			do	Cooling	1,100 to 100	12.2
			?	Heating	1,400 to 1,600	31.0
			?	Cooling	1,600 to 1,100	19.2
397-E	Zircon	1,700		Heating	25 to 1,500	5.1
				Cooling	1,500 to 100	5.2

[a] Phases given in parentheses are believed to be present in appreciable amounts, but this was not established.

[b] Specimen cut from a single crystal of water-clear periclase and the expansion determined is parallel with the octahedral axis. This is the same specimen for which values are given in table 1.

It can be said, in general, that (a) the thermal length changes of zirconia with magnesia additions of from 8 to 24.65 percent are high but regular between room temperature and 1,100°, and that these bodies should have a fairly good resistance to thermal shock in this temperature range; and (b) these bodies will have a poor resistance to thermal shock in temperature ranges above 1,200° C because of inversions, or crystalline formations, the identity of which have not been established.

It is of interest that all these bodies were mechanically hard and strong, and that specimens of MgO and ZrO_2 in 1:1 molar ratio, when heated at 1,700° C, were the only ones encountered in this investigation that were completely vitrified (water absorption less than 0.1 percent).

(e) EFFECT OF CaO

Curves illustrating the length changes observed for zirconia with lime additions are shown in figures 8, 9, and 10. The formation of the compound $CaO.ZrO_2$ having been reported in the literature,[24] it was thought that a determination of the thermal-expansion behavior would be of interest. A mixture containing CaO and ZrO_2 in equimolar ratio (31.3 weight percent of CaO) heated at 1,700° C was over 90 percent one phase, and heating at 1,850° C produced over 99 percent one phase. This phase was described as having medium birefringence, with index of refraction of about 2.05 maximum and 2.035 minimum. The X-ray pattern corresponds to the cubic form but, since the optical properties are not those of a cubic substance, it is probable that the symmetry is of lower degree. This is in agreement with Ruff, Ebert, and Stephan (footnote 24). There was distinct cleavage in one direction with polysynthetic twinning parallel to the cleavage.

The thermal-expansion and contraction curves for specimens of $CaO.ZrO_2$, preheated at 1,850° and at 1,700° C, are shown in figure 8. The average coefficient of linear thermal expansion for the composition preheated at 1,850° C, in the range from room temperature to 1,500° C, is 8.3×10^{-6}. (Specimens of this composition were very porous and friable, and the results obtained during cooling below 700° C are not believed to be significant.) The average coefficient of linear thermal change in the range from room temperature to 1,300° C is 10.1×10^{-6} during heating, and 10.6×10^{-6} during cooling, for the composition heated at 1,700° C. These values approximate those for the composition 85 ZrO_2—15CaO (fig. 8), which are 10.4×10^{-6} during heating and 11.2×10^{-6} during cooling. An X-ray pattern for the latter composition contained lines for only cubic zirconia and $CaZrO_3$.

Curves for zirconia with 6- and 8-percent CaO additions are shown in figure 9. The 6-percent addition and preheating at 1,450° C converted about two-thirds of the sample to cubic zirconia. The remaining one-third consisted of $CaZrO_3$ and (probably) monoclinic ZrO_2. The presence of an appreciable amount of noncubic zirconia is indicated by the breaks in the curve. Preheating the same composition at 1,565° C had converted all the uncombined ZrO_2 to the cubic form. It also had almost eliminated the permanent shrinkage, amounting to 2.0 percent for the test piece preheated at 1,450° C. Both of the specimens containing 8 percent of CaO, for which curves are shown in figure 9, contained only cubic zirconia and calcium zirconate, and, in the range from room temperature to 1,400° C, their curves are practically identical with the curve for the 6-percent-CaO composition preheated at 1,565° C. The average coefficient of linear thermal expansion for this group (fig. 9), in the range 25° to 1,400° C, is 11.0×10^{-6} during heating and 11.5×10^{-6} during cooling. All the specimens containing 6 or 8 percent of CaO were porous. The

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[24] Otto Ruff, Fritz Ebert, and Edward Stephan, Z. anorg. Chem. **180** 215 (1929), who presented identification data based on X-ray examinations.

lowest recorded water absorption was 9 percent for the 8-percent-CaO expansion piece preheated at 1,750° C.

The results for mixtures of zirconia with 4 and 5 percent of CaO are recorded in figure 10. The curves show what is the most striking development of the entire investigation—namely, that a 4-percent addition of CaO has little effect on the thermal expansion of zirconia, whereas a 5-percent addition eliminates the irregularities in the thermal length changes and causes an apparently complete conversion of the uncombined ZrO_2 to the stabilized cubic form. The average coefficients of linear thermal expansion for the 5-percent-CaO speci-

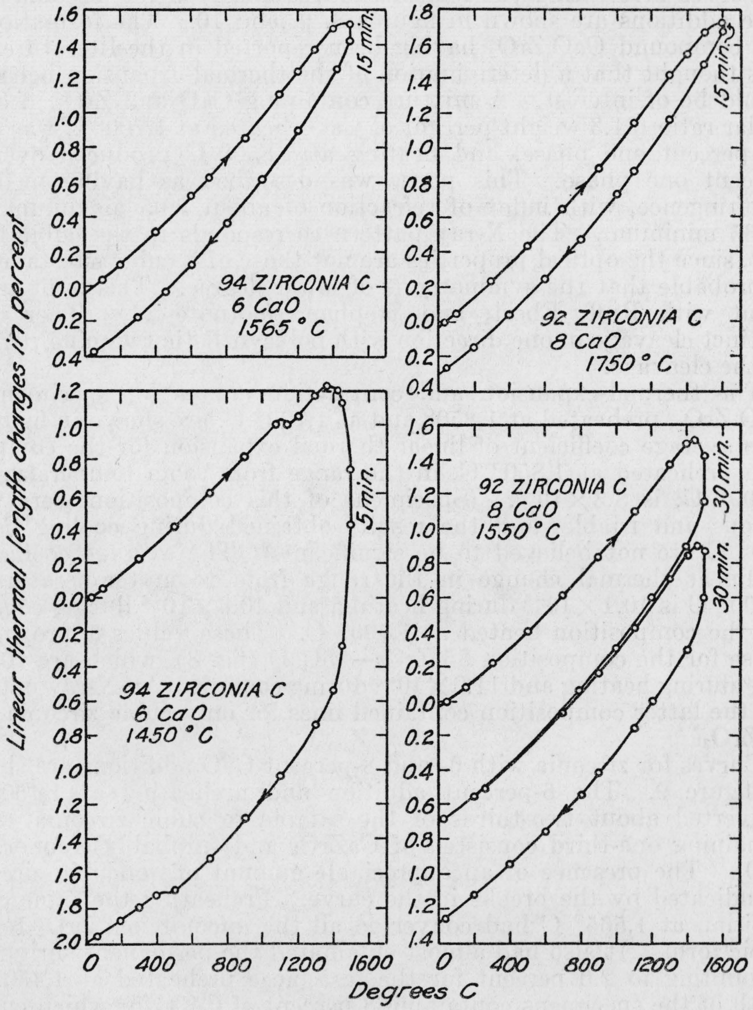

FIGURE 9.—*Thermal dilatation curves for calcined zirconia of 99-percent purity with* CaO *additions.*

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing. The time notation on the curves indicates the interval of holding at the maximum temperature.

mens preheated at 1,700° and at 1,850° C are 10.8×10^{-6} during heating and 11.3×10^{-6} during cooling, in the range 25° to 1,400° C. All the specimens in this group (fig. 10) heated at 1,600° C or higher were fairly hard and dense, the absorption ranging from 3.08 to 6.15 percent.

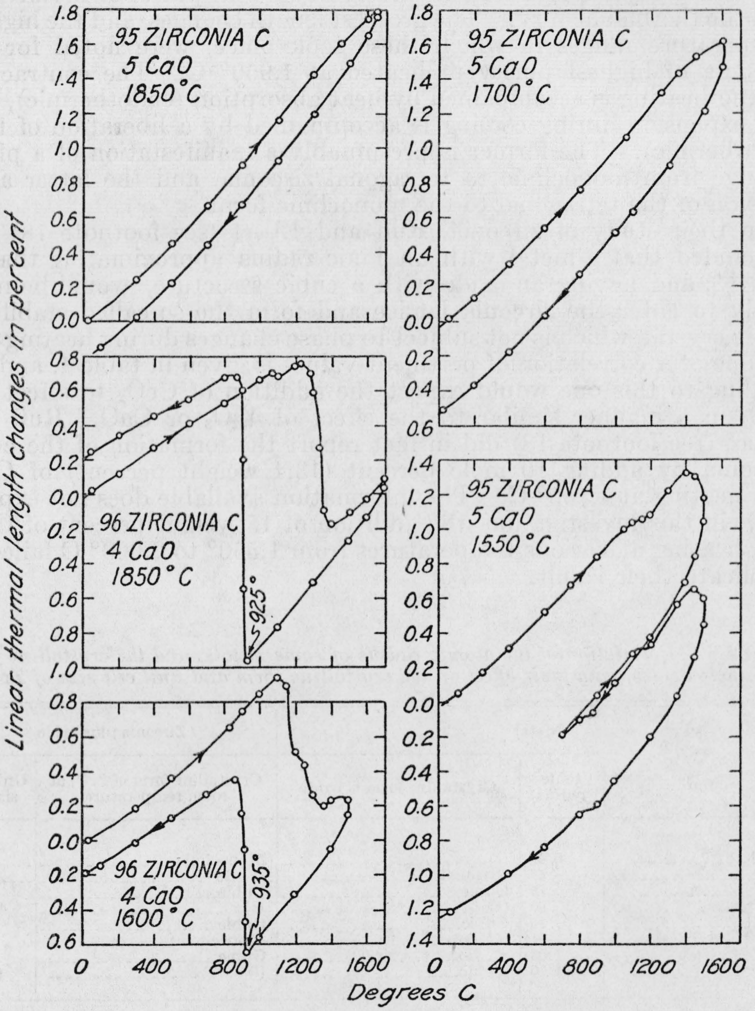

FIGURE 10.—*Thermal-dilatation curves for calcined zirconia of 99-percent purity with* CaO *additions.*

The temperatures in the legends indicate the heat treatment the specimens had received prior to the testing.

V. DISCUSSION AND CONCLUSIONS

It seems evident from the data presented in figures 2 and 3 that zirconia (96 to 99 percent pure), whether calcined or fused, and whether preheated in a test piece at a relatively low temperature (1,450° C) or as high as 1,950° C, will undergo large and rapid length changes during both heating and cooling in the temperature ranges to which it would normally be subjected as a refractory in service. The temperature ranges through which these length changes occur, the sharply defined temperatures at which expansion begins during cooling, and the amounts of length change, will duplicate very closely in repeated tests for any one specimen, but are affected by the purity of the zirconia and the thermal history. The greatest length changes, and the highest temperature ranges in which these took place, were noted for the zirconia of highest purity preheated at 1,950° C. The contraction during heating is accompanied by heat absorption (endothermic), and the expansion during cooling is accompanied by a liberation of heat (exothermic). The former is presumably a manifestation of a phase change from monoclinic to tetragonal zirconia, and the latter a reversion of the tetragonal to the monoclinic form.

In their study of zirconia, Ruff and Ebert (see footnote 18) had concluded that a metal with an ionic radius approximating that of Zr^{++++}, and having an oxide with a cubic structure, would be most likely to enter the zirconia lattice and form the so-called stabilized cubic crystal, which is not subject to phase changes during heating and cooling. A correlation of pertinent values is given in table 4, and according to this one would expect the addition of CeO_2 to affect the ZrO_2 in a manner similar to the effect of Y_2O_3 or CaO. Ruff and Ebert (see footnote 18) did in fact report the formation of the cubic zirconia by adding 10 mole percent (13.4 weight percent) of CeO_2 and heating at 1,750° C. The information available does not explain why, in this investigation, the addition of 15 weight percent of CeO_2 and heating at various temperatures from 1,550° to 2,000° C failed to duplicate their result.

TABLE 4.—*Correlation of the atomic radius of some metals, and the crystalline form of their oxides, with their effect on the crystalline form and unit cell size of* ZrO_2

Metal			Zirconia plus oxide	
Ion	Ionic radius	Crystalline form of oxide	Crystalline form of ZrO_2 at room temperature	Unit cell size a_0
	A			*A*
Si^{++++}	0.40	(a)	Monoclinic	
Al^{+++}	.55	Trigonal	do [b]	
Mg^{++}	.75	Cubic	Cubic	5.063
Zr^{++++}	.80	(c)	(c)	[d] 5.062
Y^{+++}	.95	Cubic	Cubic	5.108
Ce^{++++}	1.01	do	Monoclinic [e]	
Ca^{++}	1.05	do	Cubic	5.138
Th^{++++}	1.10	do	(f)	(f)

[a] Quartz is trigonal, cristobalite is pseudoisometric, and tridymite is orthorhombic.

[b] Data from R. F. Geller, J. Research NBS **27**, 555 (1941) RP1443.

[c] Zirconia of high purity is normally monoclinic at room temperature.

[d] L. Passerini, Value for cubic zirconia, extrapolated to pure ZrO_2, Gazz. chim. ital. **60**, 762 (1930); in Phys. Rev. [2] **27**, 798 (1926), Wheeler P. Davey proposes a face-centered cubic structure with $a=5.098$ A.

[e] Otto Ruff and Fritz Ebert (Z. anorg. allgem. Chem. **180**, 19 (1929) obtained cubic ZrO_2 by adding 10 mole percent of CeO_2 and heating at 1,750° C.

[f] By heating a 1:1 (mole) composition of ThO_2 and ZrO_2 at 2,600° C, Otto Ruff, Fritz Ebert, and Hans Woitinek (Z. anorg. allgem. Chem. **180**, 252, 1929) prevented the reversion to monoclinic ZrO_2 and obtained two mixed crystals with fluorite (cubic) type lattice and unit cell sizes of 5.32 A and 5.51 A, respectively. After heating at 2,400° C, the zirconia retained its monoclinic structure.

The addition of at least 11.5 percent of Y_2O_3 and heating at 1,700° C was required to transform most of the zirconia to the stabilized condition, and complete conversion was obtained by adding 15 percent and heating at 1,850° C. However, because of the comparative rarity and high cost of yttria, this would be at present a commercially impracticable method for producing usable zirconia ware except in special applications.

Silica (added as quartz) reacted partially with zirconia at 1,500° and at 1,700° C to form zircon ($ZrSiO_4$), but zirconia which had not combined retained the monoclinic structure. As a result, the length changes of these compositions retained the irregularities of the unstabilized ZrO_2. The amount of length change at the monoclinic⇄tetragonal inversions was, however, much smaller for the ZrO_2-SiO_2 mixture in 1:1 mole proportions than for the zirconias without additions. The thermal length changes of mineral zircon preheated at 1,700° C were very uniform throughout the range from room temperature to 1,500° C during both heating and cooling, and the coefficient averaged 5.15×10^{-6}. This mineral would be an excellent refractory material for high temperature work if it did not break down between 1,750° and 1,800° C to form zirconia and liquid. Assuming complete breakdown, about one-third by weight, or one-half by volume, of the resultant body would be silica-rich glass. In view of the evidence presented for incongruent melting of ZrO_2, one must conclude that the published diagrams for the SiO_2-ZrO_2 system (see footnote 22) are incorrect and a modification is suggested in figure 11.

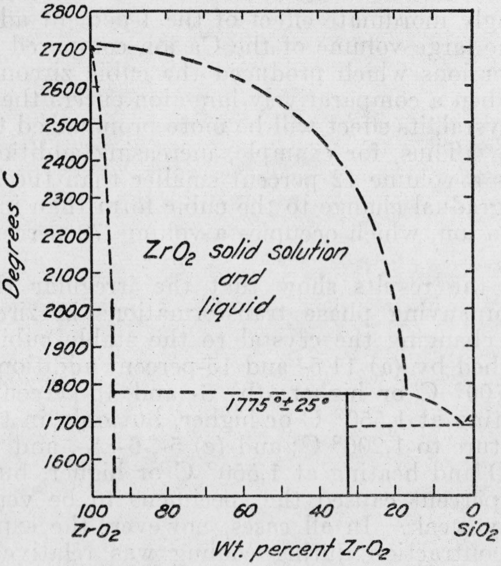

Figure 11.—*Proposed equilibrium diagram for the system ZrO_2-SiO_2, based on the observed incongruent melting of zircon at about 1,775° C.*

Magnesia was more effective than yttria for eliminating irregularities in the thermal length changes below 1,100° C. Above this temperature, however, the additions of MgO caused very high expansions and contractions during heating and cooling, respectively, the average linear coefficients ranging from 19.2×10^{-6} to 132×10^{-6}. The zirconia-magnesia compositions were dense and appeared very strong. The only nonabsorbent specimens obtained in this investigation contained equimolar proportions of zirconia C and periclase and were heated at 1,700° C.

The CaO additions were not only the most effective means noted in this work for producing the cubic zirconia, but they also provided an interesting demonstration of the radical changes in properties which may be caused by small changes in composition. As was observed, a 4-percent addition of CaO and preheating as high as 1,850° C had little effect on the inversions of the zirconia, whereas an addition of 5 percent and heating at 1,550° C brought about an almost complete transformation to the cubic form. A suggested explanation for the seemingly inordinate effect of the 1-percent addition of CaO is based on the large volume of the Ca ion compared to the Zr ion, or to the other ions which produced the cubic zirconia. One may assume that when a comparatively large ion enters the framework of the zirconia crystal, its effect will be more pronounced than the effect of a small ion. Thus, for example, increasing additions of the Mg ion, which has a volume 12 percent smaller than the Zr ion, should effect a more gradual change to the cubic form than increasing additions of the Ca ion, which occupies a volume 72 percent larger than the Zr ion.

In general, the results show that the irregular thermal length changes accompanying phase transformations in zirconia may be prevented by changing the crystal to the stable cubic form. This was accomplished by (a) 11.5- and 15-percent additions of Y_2O_3 and heating at 1,700° C or higher; (b) 8- and 15-percent additions of MgO and heating at 1,550° C or higher, but only in the range from room temperature to 1,200° C; and (c) 5-, 6-, 8-, and 15-percent additions of CaO and heating at 1,550° C or higher, but additions of more than 6 percent caused the specimens to be very porous and proportionately weak. In all cases, however, the expansion during heating and contraction during cooling was relatively high. The coefficients of linear thermal expansion ranged from 8.8 to 11.8×10^{-6} for specimens that were all, or nearly all, cubic. Also, zirconia has a low thermal conductivity relative to such materials of high thermal expansion as alumina, magnesia, and beryllia (unpublished data). Consequently, a high resistance to thermal shock cannot be expected of the stabilized product, even though it is not subject to the structural disintegration characteristic of the commercially pure material.

In order to apply the findings of this study, some shapes were cast of 94 percent zirconia and 6 percent lime, and installed in the furnace shown in figure 1. Only 29 tests have been made with the furnace since that time, but so far no tendency of the shapes to disintegrate has been noted.

The authors are indebted to B. L. Steierman and to H. F. McMurdie for the petrographic examinations and for the X-ray patterns and their interpretations.

WASHINGTON, April 13, 1945.