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INITIAL TEMPERATURES OF ZIRCONIA PHASE CHANGES AND SOLID-SOLUTION REACTIONS

by

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Abstract

Mixtures of zirconia with yttria, magnesia, calcia, ceria and combinations of calcia and magnesia were investigated by x-ray diffraction at temperatures up to 2870°F. The initial stabilizing reactions occurred at temperatures ranging between 900°F and 2700°F. Magnesia apparently showed the lowest temperature of initial reaction; yttria the highest. Combinations of calcia and magnesia showed initial solid-solution at temperatures lower than calcia but higher than magnesia although magnesia seemed to be the first to react. Inconclusive evidense indicated that some exsolution occurred in some combinations when temperatures were lowered.

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Introduction

This study was undertaken to establish the variations in the temperature of the initial transition from monoclinic to tetragonal zirconia and

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and the temperature of the initial solid-solution, stabilizing reaction using various stabilizing compounds and combinations. Further, it was undertaken to get some data concerning the rate of the solid-solution with increased temperature after the reaction had started.

A review of the literature concerning zirconia stabilization indicated that the stabilizing, solid-solution can be completed at various temperatures. The literature further suggested that the temperatures of stabilization are dependent upon such things as 1) the stabilizing compounds, 2) purity of the system, 3) concentrations of stabilizing compounds, and 4) length of time at temperature.

Ryshkewitch[1] reported that stabilization was completed at temperatures as low as 1000°C with 15 mole percent MgO. He reported that with over 10 mole percent Y_2O_3, however, the stabilizing reaction was carried out at 1300°C. Recently it was found that titania had to be present to promote stabilization of ZrO_2 with the transition metals of Groups V and VI at 1500°C[2]. Duwez and his co-workers[3], showed that increased concentrations of stabilizers lowered the temperature of transition between the tetragonal and monoclinic zirconia phases upon cooling. They also proved the instability of the $MgO \cdot ZrO_2$ solid solution. Weber et al[4], and others have shown that the nature of the anion associated with the stabilizing cation effects the stabilizing reaction only slightly. Grain and Campbell[5] showed that in substantially a pure system, the monoclinic to tetragonal transformation occurred over a 100°C range starting at about 1100°C. They also showed that upon cooling the tetragonal to monoclinic transformation took place over a wider, lower range between about 980°C and 710°C. Other investigators had reported monoclinic to tetragonal transition temperatures as low as 1700°F although the impurity of the oxides used in some of those experiments probably had a good deal to do with the lower inversion temperatures reported.

Preceding this study, it had been recognized that the stabilizing reaction was in part at least dependent upon these various factors. It was not the intent of this study, however, to determine either the concentration of stabilizers needed or temperature requirements for complete stabilization. This discussion, therefore, has been restricted to 1) the initial temperatures of transition from monoclinic to tetragonal phases, 2) initial temperature of solid-solution between the stabilizers and zirconia, and 3) some indications as to the rate of solid-solution after it has once started with increased temperatures. The systems investigated included zirconia with calcia, magnesia, yttria, ceria, and combinations of calcia and magnesia. A reference sample consisting only of zirconia was also investigated.

Materials

The materials used in these studies were all of extremely high-purity so that data collected would not be dependent on impurity eutectics and migration. The zirconia as received was near nuclear grade, only hafnium being out of specifications (about 300 PPM). Other than hafnium, the impurities include Si, Al, Fe, Ti, Mg, Cr and Mn in a total concentration not exceeding 900 PPM, on a metal to metal basis.

Procedure

The studies were based on use of the high-temperature x-ray diffraction furnace recently described by Scott and Ruh.[6] Powdered samples were prepared by dry-mixing in glass jar-mills. A few plastic balls were used in the mills to increase the mixing action. The mixed samples were mounted by pressing them into a platinum-rhodium sample holder. An organic binder was also used in many of the samples.

Before heating, fast scan patterns were made from 20° to 40° 2θ to check alignment. Starting at about 900°F and about every 100°F up to or above 2700°F, fast scan patterns were made between 27° and 33° 2θ. This interval included the two most prominent monoclinic peaks (111 and 11$\bar{1}$), the most intense tetragonal peak (111) and the 111 solid-solution cubic peak. Slow scan patterns were made from about 29° to 31° 2θ usually at the top temperature of the run and, in some cases, at other selected temperatures. Heat-up rates between hold temperatures were about 3 minutes per 100°F. The cooling was controlled so that fast scan patterns could be made at about 100°F intervals.

Results and Discussions

The calcia-zirconia system was represented in this study by two samples, one with 3% CaO, the other with 4% CaO by weight. Figure 1 represents the unit cell dimension changes in both samples when they were heated to 2700°F and then cooled again to room temperature. The diffraction peak positions indicated that the sample with 3% CaO exhibited a peak representing, probably, the tetragonal phase at a temperature about 200°F lower than the temperature of the first appearance of the corresponding peak in the sample with 4% CaO. The reason for this unexpected reaction was not apparent. It was quite apparent, however, that the 4% CaO sample was expanded considerably more at top temperature and after cooling than was the 3% sample. As the Ca^{++} ion is about 20%

larger than the Zr^{4+} ion (1.06Å as compared to .87Å), this increased expansion of the unit cell dimension indicated there had been more calcium that had entered the zirconia structure in the 4% sample than had in the 3% sample.

In order to find a reference expansion rate with which to compare the expansions obtained by the mixing of the various stabilizing compounds with zirconia, the rate of unit-cell thermal expansion of both stabilized (cubic) zirconia and the tetragonal phase zirconia were measured by two different methods. Thermal expansion measurements were made on completely stabilized zirconia. From these measurements, it was concluded that volume thermal expansion of completely calcia-stabilized (cubic) zirconia is nearly a straight line function expanding at a rate of about 0.0035Å/100°F on a unit cell basis. Further, unit cell expansion of tetragonal (pure) zirconia was measured directly by x-ray diffraction at temperatures from 2000°F up to 2700°F (see Figure 2). The direct measurements of the tetragonal phase thermal expansion indicated an expansion very similar to that of the fully-stabilized material amounting to about 0.0040Å/100°F from 200°F up to 2700°F.

From these two evidences, it was assumed that the average volume expansion for the combined tetragonal stabilized (cubic) phases in the range of about 0.0035Å to 0.0040Å/100°F. Therefore, volume expansion in excess of that range was taken as evidence for expansion due to substitution of larger ions for the zirconium ions in the solid-solution structure. If expansions were less than that range, it was taken as evidence that substitution of smaller ions for the zirconium ions had taken place.

One sample of $MgO \cdot ZrO_2$ was included in this study. The sample, on an oxide basis, consisted of 6% MgO and 94% ZrO_2 by weight. Figure 3 shows the changes in the unit cell dimension that took place in the solid-solution structure of the ZrO_2 when that sample was heated to 2700°F and then cooled to room temperature. The magnesium ion is only about .78A in radius, which is smaller than the zirconium ion radius. It would be expected, therefore, that the effect of Mg^{++} substitution on the unit cell dimension would be one of contraction. The first recognizable appearance of the tetragonal phase was at about 900°F in this system. It can be seen that there was very little change in the unit cell dimension of the zirconia from 900° to 2700°F. Since there was not even evidence of thermal expansion, it was concluded that the first appearance of the 111 peak very closely coincided with the beginning of solid-solution of the Mg^{++} ions into the structure, as, otherwise, it would be expected that there would have been unit cell expansion due to thermal expansion and then contraction, or leveling off due to the contracting effect of the Mg^{++} solution. Upon cooling, it appears that there was contraction at a rate much greater than simple cooling contraction and, after reaching room temperature, the structure was considerably contracted to about 5.05Å.

The zirconia-yttria system was represented by a sample consisting of 15% Y_2O_3 and 85% ZrO_2 by weight. The mixture was heated to 2870°F, where a furnace failure occurred which prevented the gathering of data while cooling as the cooling rate was too rapid. Figure 4 shows the unit cell dimension changes that were recorded upon heating and the results after cooling to room temperature. The unit cell dimension changes indicated that the first recognizable tetragonal peak was detected at about 1950°F and that it expanded at about the rate expected from thermal expansion to about 2700°F. From 2700°F to 2870°F, there was a large increase in the rate of expansion (about 15 times thermal expansion rate). As the yttrium ionic radius is about 1.06Å, it would be expected that as solid-solution took place, the zirconia structure would be expanded. It was therefore concluded that the yttrium did not start into solid-solution below about 2700°F.

The ceria-zirconia system was represented by a sample consisting of 20% CeO_2 and 80% ZrO_2 by weight. This sample was unique in the study as it exhibited a pair of x-ray peaks at elevated temperatures corresponding to a pair of 111 reflections. One was assumed to be from the tetragonal phase and the other was assumed to be from the cubic-stabilized phase. Upon heating, a single peak was first detected at about 1000°F; at 1900°F, the peak was assymetrical enough to suggest another phase with a larger unit cell. From 1900°F to 2700°F, the assymetrical feature resolved into an easily discernable pair of peaks. The two peaks were detectable upon cooling down to about 1100°F; below that temperature, only one peak remained. Figure 5 shows selected slow-scan patterns exhibiting the double peaks in various stages of development upon heating and cooling. Figure 6 shows the unit cell dimension changes indicated by both peaks upon heating and cooling.

Figure 5 represents the tracings of the slow scan patterns of the 111 peaks at four temperatures; 2300°F, 2700°F with increasing temperatures and 1200°F and at room temperature upon cooling. The first peak to develop was the high angle peak, which appeared first at 1100°F. This peak probably was from the tetragonal phase and its rate of unit cell expansion was about that expected from thermal expansion from 1100°F to 2700°F (see Figure 6). The low angle peak which developed also expanded at about the same rate although it represented a larger structure at all subsequent temperatures. Upon cooling, the high-angle peak disappeared below about 1000°F while the low-angle peak, that represented the stabilized, solid-solution phase, remained even at room temperature. Figure 6 shows the unit cell dimension changes of both peaks as compared to the temperature changes. These evidences indicated that the 20% ceria 1) suppressed the temperature of monoclinic to tetragonal transition to about 1100°F and 2) that the initial temperature of stabilization was about at 1900°F.

Various systems containing combinations of stabilizing agents were also investigated. Two of these represented the combined system $CaO-MgO-ZrO_2$. As the calcium ions are larger than the zirconium ions and the magnesium ions smaller, it was expected that variations in the unit cell dimension changes with changes in temperature would be easily correlated with the type of solid solution that had been taking place at specific temperatures; the structure would expand with Ca^{++} substitution, contract with Mg^{++} substitution.

The two combinations discussed herein consisted of (A) 1% CaO, 2½% MgO and 96½% ZrO_2 and (B) 2% CaO, 1% MgO and 97% ZrO_2 by weight. Figure 7 shows the unit cell dimension changes that took place in both samples from room temperature to 2700°F and back to room temperature. The changes were not what had been expected. Note, for instance, that the 1% CaO, 2½% MgO sample expanded more than the other sample even though there was less calcia available. The larger proportion of MgO in that sample, however, was reflected in the low rate of expansion up to 1800°F as compared to the low MgO sample, with 1% MgO, which showed a rapid rate of expansion from almost the first appearance of the 111 peak.

From these two samples, it appeared that the magnesium ions entered the structure at lower temperatures than did the calcium ions. However, they also suggest that the more magnesia present, the greater was the proportion of the available calcium that entered the zirconia structure.

There was one feature that was common to most of the samples studied that should be pointed out. Unit cell dimensions at the highest temperatures were, generally, considerably greater than they were at room temperature after the solid-solution had taken place. In most cases, the differences between expansions at peak temperatures and contraction or cooling to room temperature were considerably greater than could be accounted for by thermal expansion data. These results indicated that there had been a greater amount of substitution of the larger, stabilizing ions in the structures at the elevated temperatures than had remained in solution upon cooling. The obvious exception to this was the sample containing the 6% MgO as the magnesium ions were smaller than the zirconium ions. In that sample (Figure 3) the final unit cell dimension was even more contracted at room temperature than at peak temperature which suggested that some additional solution had occurred upon cooling from 2700°F. In the samples containing ions of larger radius than the zirconium ion, however, the reduction in unit cell size was so striking that it suggested that some exsolution had occurred upon cooling.

Figure 8 summarized the significant changes that were indicated by x-ray diffraction patterns of the discussed systems.

SUMMARY OF DATA

Component Systems	$CaO-ZrO_2$		$MgO-ZrO_2$	$Y_2O_3-ZrO_2$	CeO_2-ZrO_2	$CaO-MgO-ZrO_2$	
Weight of Stabilizer	4% CaO	3% CaO	6% MgO	15% Y_2O_3	20% CeO_2	1% CaO, 2½% MgO	2% CaO, 1% MgO
Initial Temperature of Tetragonal-Cubic Phase Appearance, F°	1700	1500	900	1950	1000	1000	1000
_a_ of Initial Peak, Å	5.148	5.122	5.112	5.171	5.091	5.104	5.123
Initial Temperature of Divergence from Thermal Expansion, F°	1700	1500	900	2700	1900	1800	1400
Maximum Temperature of Run, F°	2700	2700	2700	2850	2700	2700	2700
_a_ of Stabilized Phase at Maximum Temperature, Å	5.252	5.183	5.117	5.270	5.212	5.276	5.223

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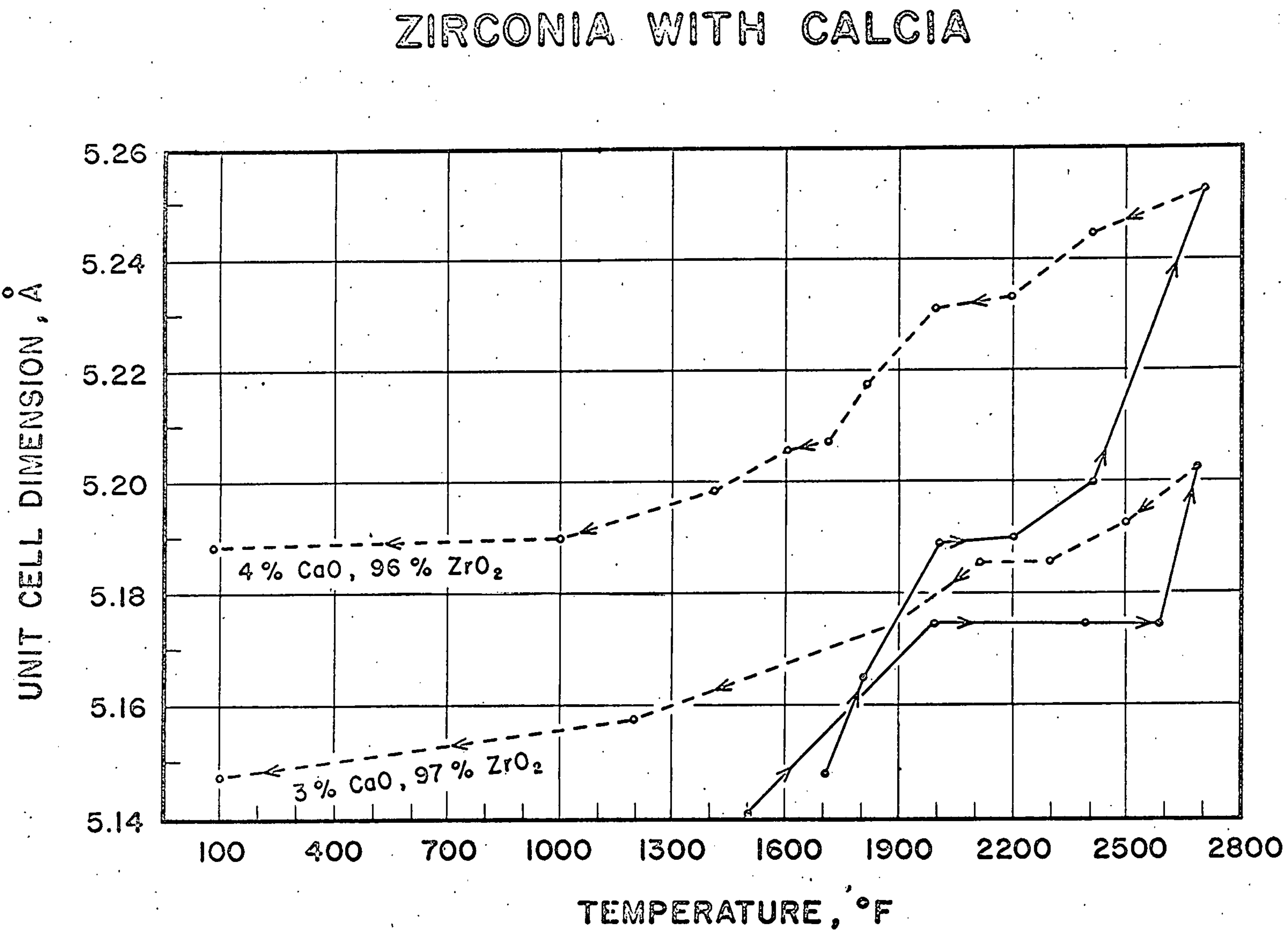

ZIRCONIA WITH CALCIA
UNIT CELL DIMENSION, Å
5.26
5.24
5.22
5.20
5.18
5.16
5.14
TEMPERATURE, °F
100
400
700
1000
1300
1600
1900
2200
2500
2800
4 % CaO, 96 % ZrO₂
3 % CaO, 97 % ZrO₂

FIGURE 1

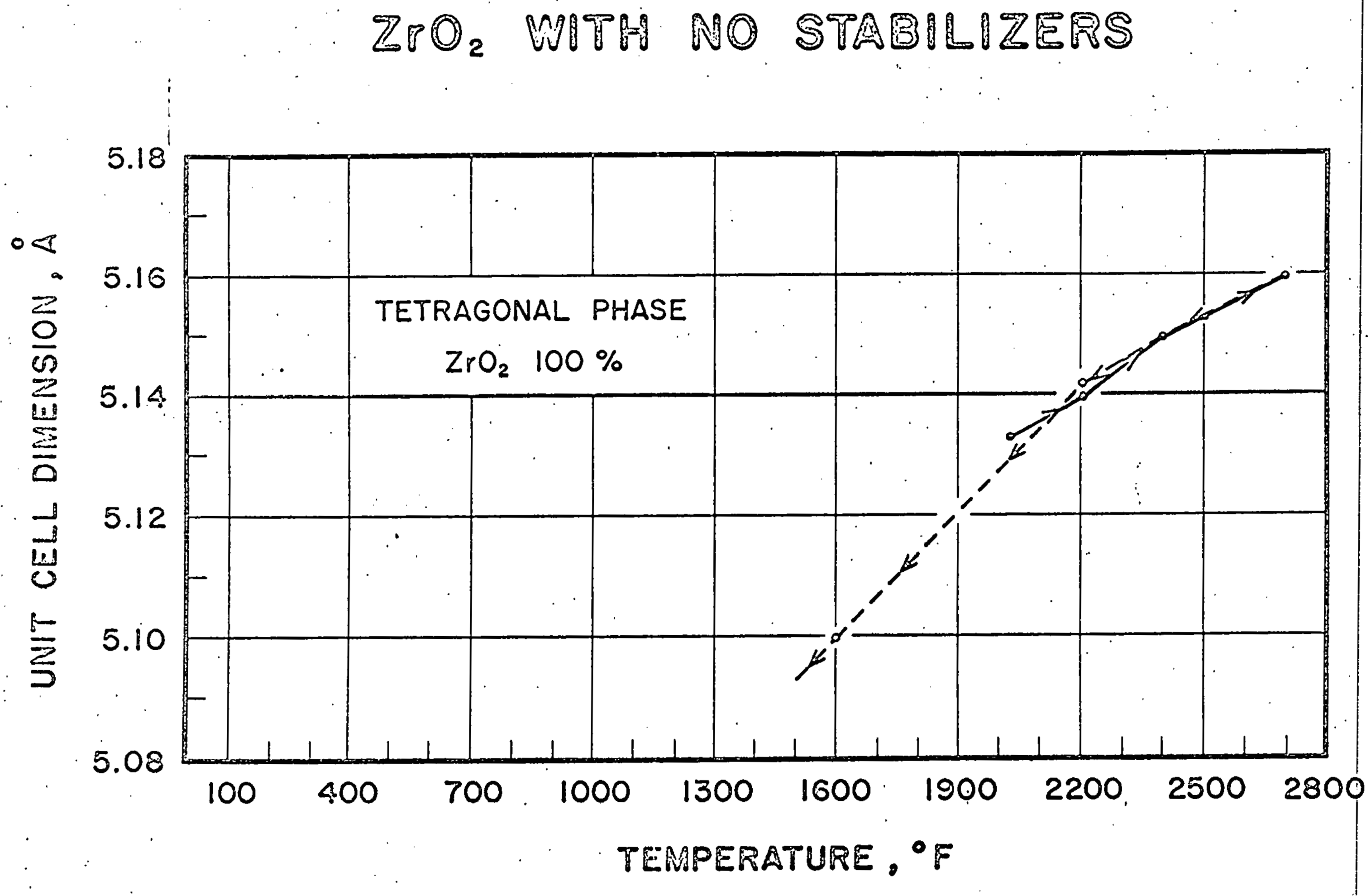

ZrO2 WITH NO STABILIZERS
TETRAGONAL PHASE
ZrO2 100 %
UNIT CELL DIMENSION, Å
5.18
5.16
5.14
5.12
5.10
5.08
100
400
700
1000
1300
1600
1900
2200
2500
2800
TEMPERATURE, °F

FIGURE 2

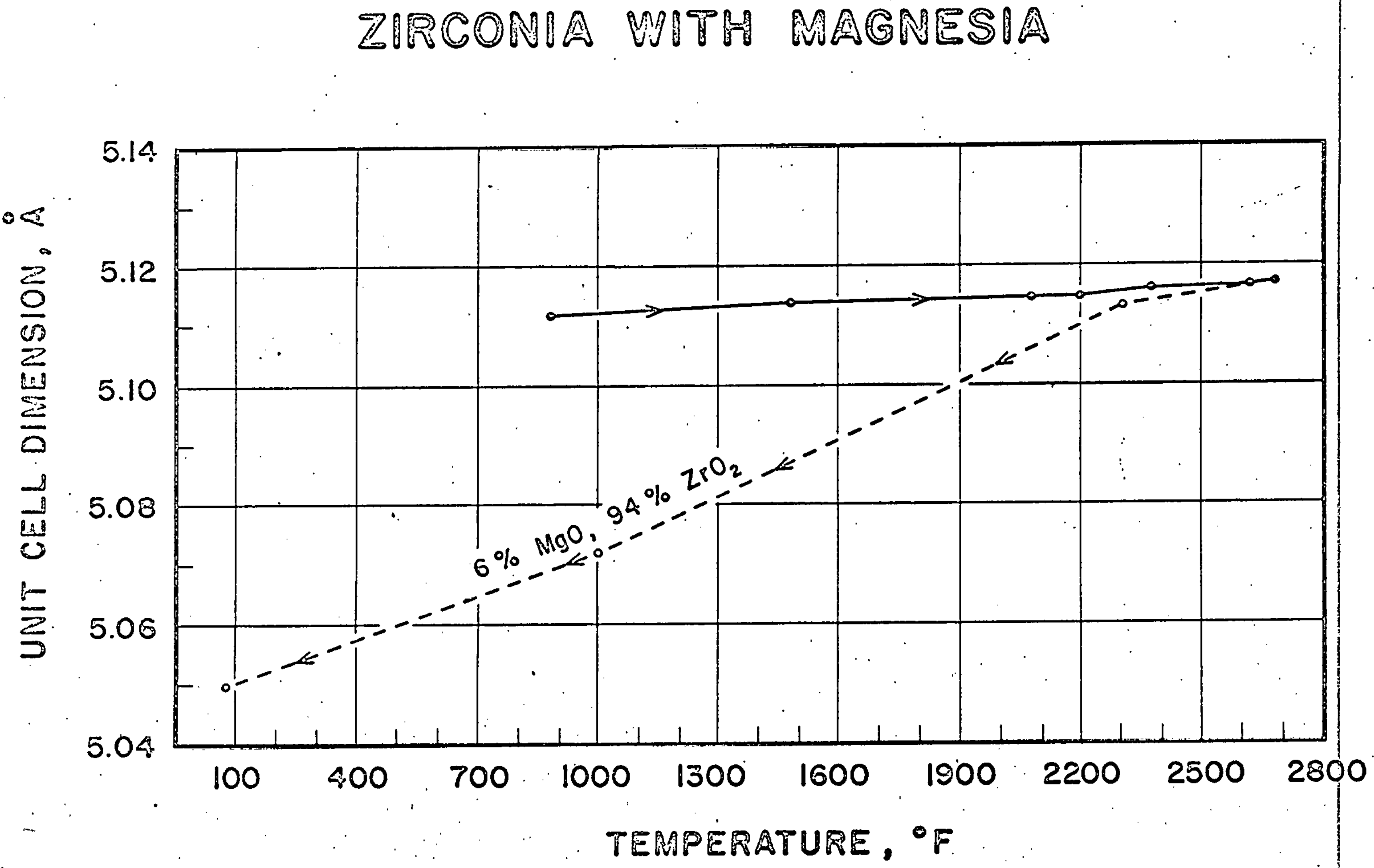
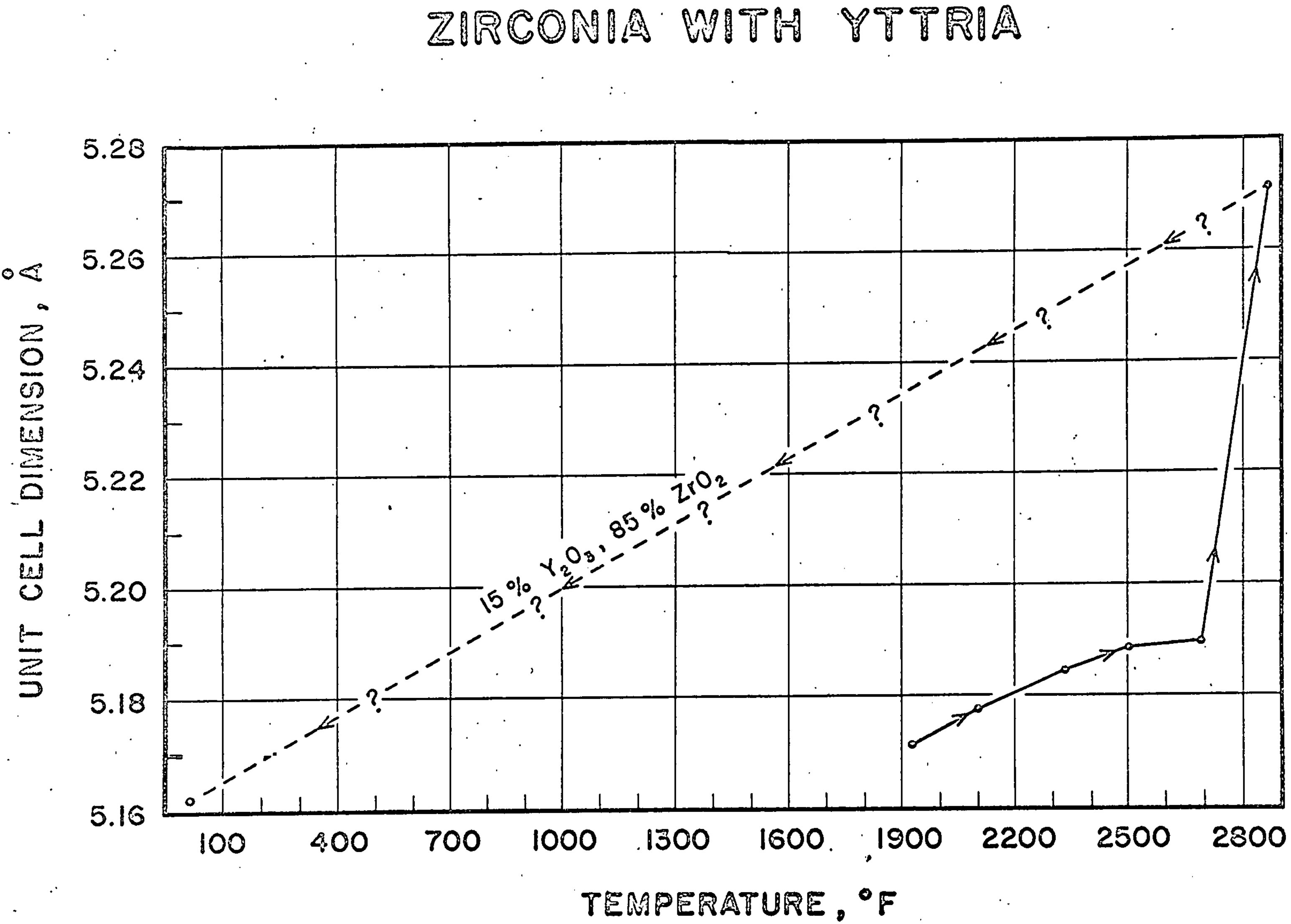

ZIRCONIA WITH MAGNESIA
UNIT CELL DIMENSION, Å
5.14
5.12
5.10
5.08
5.06
5.04
100
400
700
1000
1300
1600
1900
2200
2500
2800
TEMPERATURE, °F
6 % MgO, 94 % ZrO2

FIGURE 3



ZIRCONIA WITH YTTRIA

FIGURE 4

EFFECT OF HEATING ON X-RAY DIFFRACTION PEAKS (111) SYSTEM CeO_2, ZrO_2

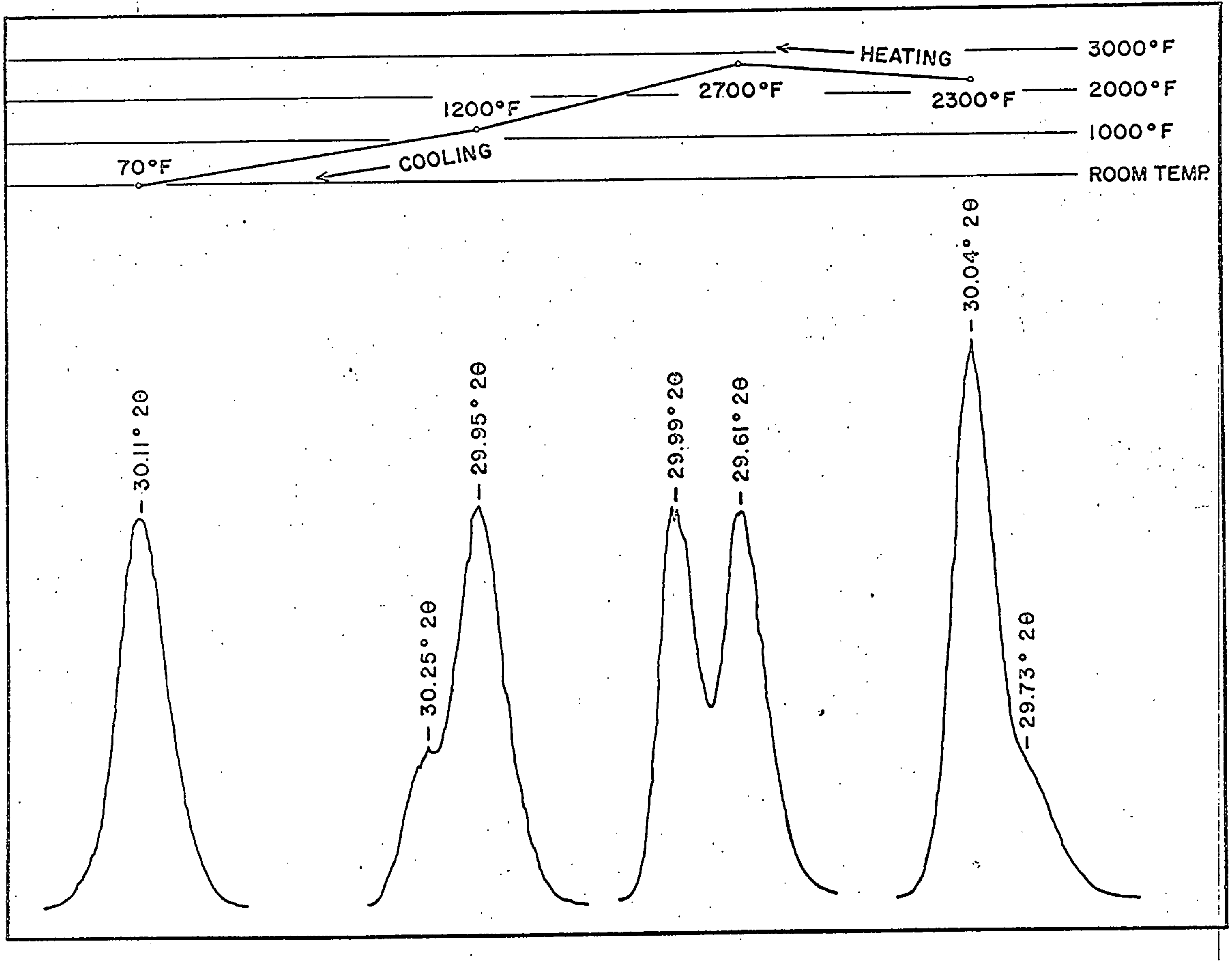


FIGURE 5

ZIRCONIA WITH CERIA

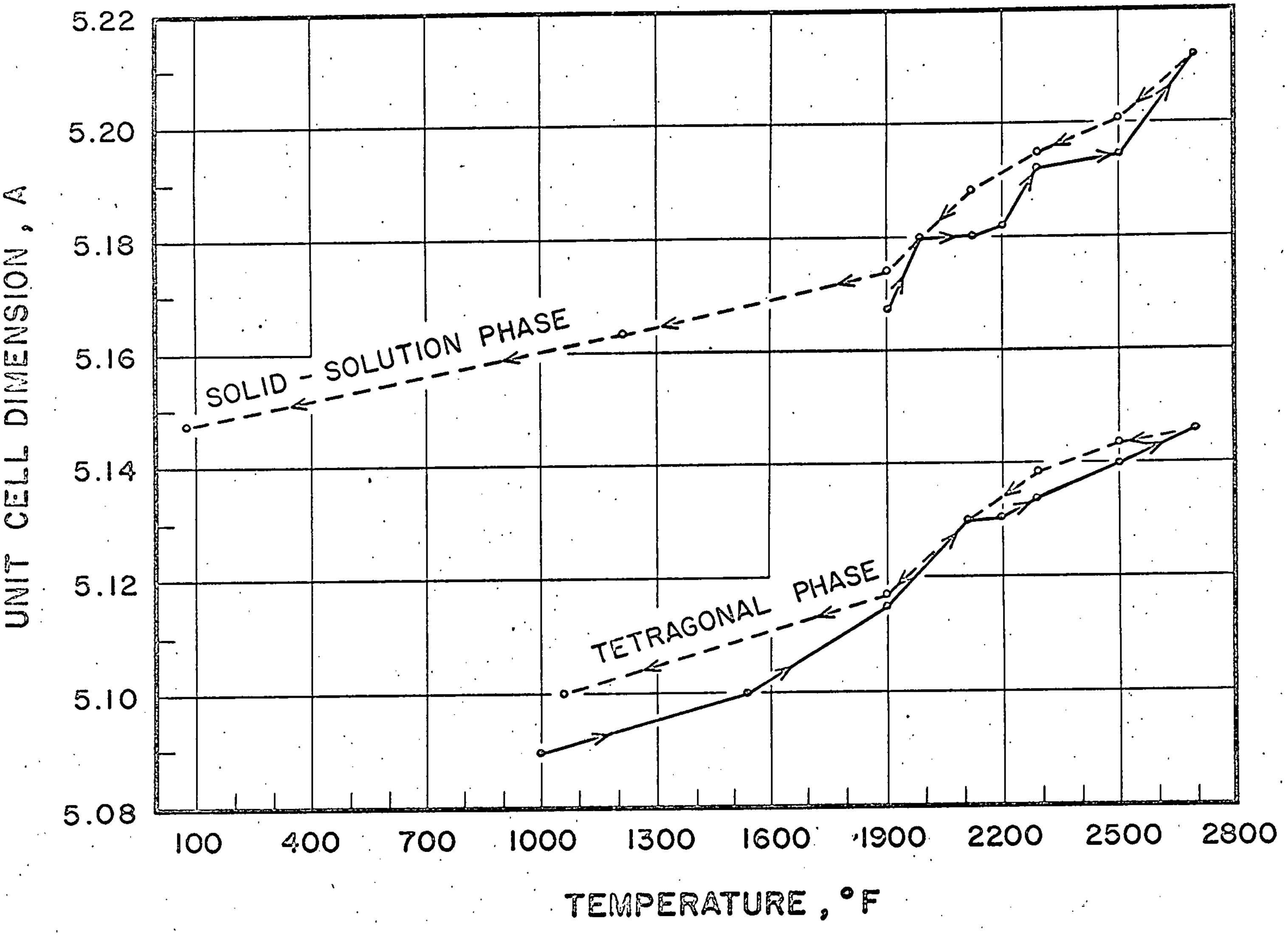


FIGURE 6

ZIRCONIA WITH CALCIA AND MAGNESIA

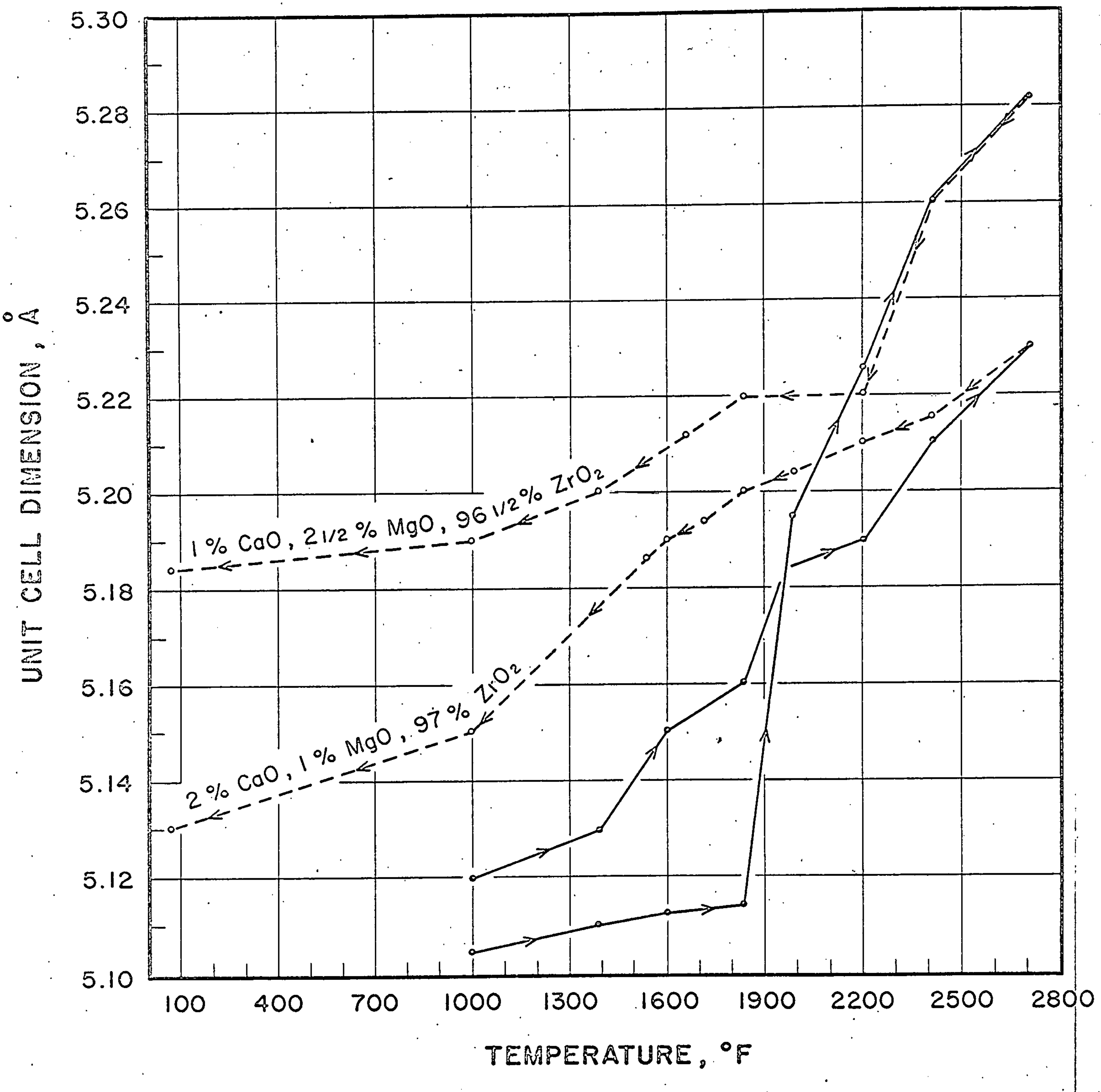


FIGURE 7