AN INVESTIGATION
OF
LOW EXPANSION CORDIERITE-ZIRCONIA BODIES

by
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I. INTRODUCTION

Missiles, space probing satellites, and atomic power are spectacular developments of the present which, nevertheless, have presented many new and exciting problems. Less spectacular but no less important advances have come in supersonic aircraft, microwave transmission, thermoelectric power, high temperature chemical reactions, and a host of other developments little known to the average man, but of great importance to his progress. And again such advances have presented just as many new problems as they have solved.

Never before in the history of mankind have so many remarkable scientific and engineering advances been made in such a short period of time. And each required solutions to the problems it presented, or as is the case in many areas, is still awaiting solutions to problems before further advances can be made.

With so many changes in so many different fields, it is natural to expect a great many different problems to arise, and such has been the case. But a common denominator can be found within the many fields covered by these spectacular advances. This common denominator is the need for new and better engineering materials.

Economical use of atomic energy, wider use of electromagnetic phenomena, and more efficient missiles are dependent on new and better materials. In addition, our knowledge of the properties of the materials we are already using must be extended. This quest for materials and their fundamental properties has become so important that future historians might well call this the "Age of Materials."

No class of materials has felt the impact of investigation, discovery, and development more than those designated as ceramics. Areas formerly served by metals and plastics have been taken over by ceramics at an ever increasing rate since World War II. Though they were initially sought because of their ability to withstand the temperatures at which other materials failed, it soon became apparent that ceramics possessed additional characteristics which made them more desirable than certain materials being used.

However, characteristics also were found that revealed serious deficiencies in ceramics. Because they are brittle materials they have poor resistance to tensile stresses. Their low thermal conductivity and relatively high thermal expansion joined with their poor resistance to tensile loading to give them poor thermal shock properties. The outcome of this revelation of their poor qualities has lead to the intensified study of the fundamental properties of ceramic materials, singly and in combination, and at least two new ceramic compounds have been found which overcome many of the shortcomings already mentioned.

These compounds have very low coefficients of thermal expansion and hence have excellent resistance to thermal shock. Coupled with the ability to be used at temperatures of approximately 12-1300°C, which allows them to be employed in certain kiln ware and electrical ware applications, it would appear that the objections to the use of certain ceramics have been overcome. Such has not been the case however, since additional problems have arisen, now that some of the old ones have been solved.

A case in point is the material cordierite, $2\ MgO.2Al_2O_3.5SiO_2$, a ceramic material with a melting point of 1470°C, a

very low coefficient of thermal expansion, and excellent thermal shock resistance. Its undesirable properties, however, include a very short firing range, an incongruent melting point with the subsequent formation of a high expansion material, and a low maximum use temperature of 1200° C.[1]

Early investigators found these poor properties of cordierite and succeeded in improving them by the addition of zirconia (ZrO_2) which lengthened the firing range of this material. However, their investigations were incomplete in that there is no systematic record of the thermal expansion coefficients obtained from these bodies, no thermal shock data, and no record of the maximum temperature at which these bodies may be used.

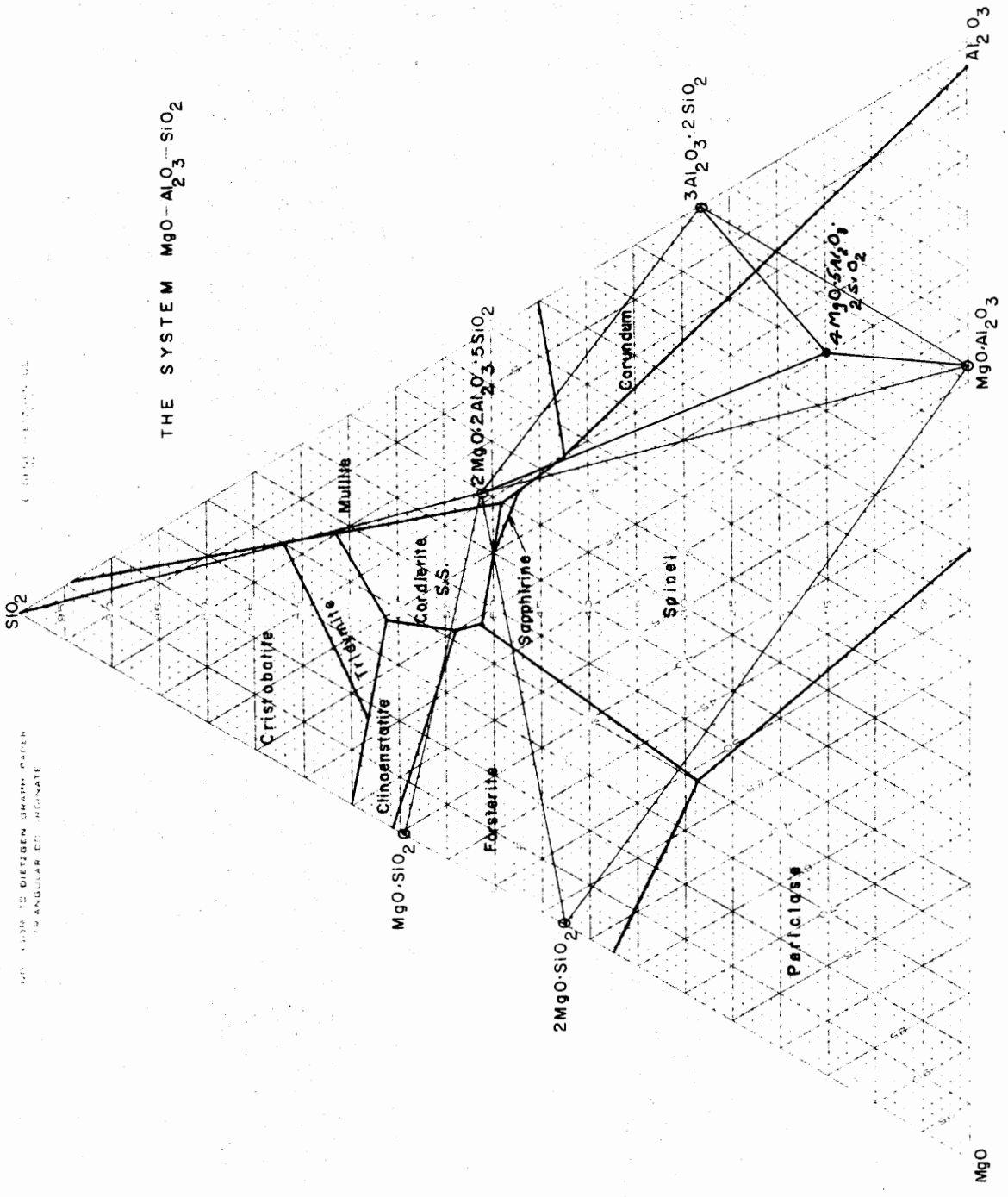
Therefore, the purpose of this investigation is to undertake a systematic study of cordierite - zirconia compositions to determine to what extent the ultimate refractoriness and use temperature can be increased without increasing the thermal expansion above 4-4.5 x 10^{-6} cm./cm./° C.

II. Literature Review

Cordierite is one of two three component compounds in the $MgO-Al_2O_3-SiO_2$ system. See Figure 1. It contains 13.7% MgO, 34.9% Al_2O_3, and 51.4% SiO_2. Therefore, cordierite falls in the field in which mullite is the primary phase. Karkhanavala and Hummel[2] have reported that cordierite may exist in two stable (α,β) and one metastable modification. Cordierite occurs most commonly in the high temperature (α) form. The low temperature form (β) can be formed under hydrothermal conditions from the glass, or from the crystals of (α) or the metastable form (μ). The metastable form can be developed by devitrifying the glass at around 850 to 950°C. However, it can not be formed by heating the high temperature form under the same conditions. Heating the β and μ forms in air develops the α form in the range of 830 to 1050°C.

All studies done on the compound cordierite have been performed with synthetic cordierite. Very few natural deposits of the material are known, and its presence is difficult to determine. The existence of deposits have been reported in Horns Nek Transvaal, by Shand[3]. In addition, Newhouse and Hagner[4] have reported a deposit in Albany County, Wyoming. However, Hausner[1] has stated that to the best of his knowledge, natural cordierite has never been used in ceramic bodies.

Present commercial compositions for the manufacture of cordierite consist of from 30 to 50% talc and from 50 to 70% clay, plus additions of Al_2O_3 and pyrophyllite. Although this type of body falls within the cordierite field, small amounts of mullite, spinel, forsterite and corundum are present which tend to increase thermal expansion and decrease resistance to thermal shock.


THE SYSTEM MgO–Al2O3–SiO2
SiO2
Al2O3
MgO
3Al2O3·2SiO2
2MgO·2Al2O3·5SiO2
4MgO·5Al2O3·2SiO2
MgO·Al2O3
MgO·SiO2
2MgO·SiO2
Mullite
Cristobalite
Tridymite
Cordierite S.S.
Clinoenstatite
Forsterite
Sapphirine
Corundum
Spinel
Periclase

The compound cordierite was first reported by Rankin and Merwin[5] in their work on the system $MgO-Al_2O_3-SiO_2$. The compound had the composition $2MgO.2Al_2O_3.5SiO_2$. In this work the cordierite crystals were described as "six-sided prisms with basal termination and negative elongation." They were uniaxial negative and had refractive indices n_α = 1.524 and n_r = 1.528. The compound melted inconqruently at 1470°C into mullite and a liquid.

For several years no more work was done on the compound, cordierite until W. M Cohn[6] developed a body containing 43% Goepfersqruener talc, 35% Zingendorfer plastic clay, and 22% Al_2O_3. This body, when fired to cone 14, had a thermal expansion of 0.53×10^{-6} between 0° and 200°C.

Such a low thermal expansion caused great interest, since it promised a body with good thermal shock resistance. Therefore, the work continued in 1931 when R. F. Geller and H. Insley[7] attempted to duplicate Cohn's work. Using 43% talc, 35% Florida kaolin, and 22% electric furnace corundum, they were able to fabricate a body with a linear thermal expansion coefficient of 10×10^{-7} in the range of 20°to 200°C. They also found that the thermal expansion coefficient depends considerably on the length of firing time and that, although cordierite could be prepared by sintering at 1350°C, the sintering time could be reduced by heating in the range of 1400° to 1425°C. Heating at temperatures much above 1425°C caused a decomposition of cordierite, which melts incongruently at 1470°C, with the formation of small amounts of spinel and mullite. Geller and Insley surmised that the low expansion of the body they had developed was the rasult of 90 to 95% cordierite contained in the body.

In more recent years R. S. Lamar[8] has developed cordierite bodies using mixtures of siernalite and kaolin. The bodies possessed very low coefficients of thermal expansion and had good thermal shock resistance. They had the typical short firing range characteristic of cordierite, but the range was lengthened by the addition of from 5 to 20% zircon. The thermal expansion and shock resistance were not materially affected by this addition.

Two interesting results of Lamar's investigation were evident. He found that bodies made with mixtures of sierralite and clay did not abrade the dies when extruded or pressed. Such abrasion is usually evident in normal cordierite bodies due to the alumina used in their manufacture.

In addition, Lamar prefired his preparations to various temperatures and found considerable variations in results, just as Geller and Insley had discovered. A thin section of specimen fired to 2350° F showed large amounts of cordierite and relatively small amounts of mullite and forsterite. However, a specimen fired to 2300° F showed poor reaction of the constitutent materials, only 50% cordierite, and evidence of mullite and enstatite. The short firing range of cordierite was thus easily observed.

Improving the firing range of cordierite bodies has also received some attention. As was stated, Lamar improved the firing range of his compositions by the use of 5 to 20% zircon. However, he was following the lead of Parmelee and Thurnauer[9] who investigated the effects of several compounds on the firing range of talc bodies.

They found that the use of zirconia in amounts of 20 to 30% was very helpful in increasing the firing range and that the bodies could be fired to cones 14 and 15, which would give better cordierite formation.

R. J. Beals and R. L. Cook[10] have more recently investigated the crystalline nature and expansion characteristics of cordierite. Using X-ray methods and an internal standard, they determined the percentage of cordierite present in their samples and found a close correlation between the cordierite present and the thermal expansion. They succeeded in formulating a body composed of 47.91% Sierramic talc, 29.27% Florida kaolin, and 12.82% A-10 alumina, which had a coefficient of linear thermal expansion of 9.8×10^{-7} for the range 20° to 300° C when prefired to 1400° C. The internal standard indicated that the body was 96% cordierite. Again, as was found in previous papers, the amount of cordierite formed depended on the thermal treatment of the body.

Work with dense cordierite bodies has been initiated by Gebler and Wisely.[11] Using clay and calcined $MgCO_3$ and talc, they developed a vitrified cordierite body with virtually zero porosity, low thermal expansion, good mechanical strength, and excellent thermal shock resistance.

Other studies of interest have included work by Hummel and Reid,[12] and Lamar and Warner.[13] The former, in their work on the expansion of glasses in the MgO-Al_2O_3 - SiO_2 system, have stated that the glasses which probably develop in cordierite bodies have a thermal expansion which is greater than twice that of the cordierite crystal

in the range up to 600° C. In combination with the impurities which are already present in the raw materials, development and retention of these high expansion glasses probably accounts for the poor heat-shcok resistance of vitrified cordierite bodies. Such poor resistance is often evident in commercial type cordierite ware.

Lamar and Warner have also commented on the increase in thermal expansion caused by various components or impurities. They found that less than 5% mullite in an otherwise pure cordierite body would affect the thermal expansion by as much as 100% in the range up to 500° C. The authors felt that the values for the thermal expansion of cordierite, as given in the literature for the range 20° to 500° C, were more than twice the correct value for pure cordierite. They attributed this to small amounts of mullite or spinel or unreacted alumina present in the body. They gave values of 1.64×10^{-6} and 1.28×10^{-6} from 25° to 1000° C and stated that these were probably more nearly correct. These values were obtained from samples which showed no evidence of the presence of mullite when examined by X-ray diffraction methods.

It can be seen from the preceding that there are various problems associated with the study or manufacture of cordierite and cordierite bodies. For convenience, several of these, as mentioned in the literature, will be listed below:

(1) Cordierite melts inconqruently at 1470° C with the formation of mullite and a liquid.

(2) At temperatures much above 1425° C, cordierite begins to decompose with the formation of small amounts of mullite and spinel.

(3) Cordierite has a very short firing range which can be lengthened by the addition of from 5 to 20% zircon.

(4) The development and retention of glass and alumina or mullite in cordierite bodies will greatly increase the thermal expansion in the range up to 600° C. These impurities probably account for the variation in values for cordierite thermal expansion reported throughout the literature.

(5) Impurities in the batch constituents account for the poor thermal shock resistance of commercial cordierite bodies.

(6) A maximum operating temperature of 1200° C, as given by Hausner,[1] limits the usefulness of cordierite even though its melting point is some 250° C above this temperature.

III. Method of Procedure

1. Selection of Cordierite Batch Compositions

Cordierite does not occur naturally in sufficient quantities to be of commercial importance. Therefore, bodies composed of cordierite are made by introducing the synthetic material or, more commonly, by so compounding the body that cordierite in substantial quantities is developed during the firing process.

The first step in this investigation was the synthesis of a quantity of cordierite to be used in the subsequent work.

There are many combinations of relatively pure raw materials which can be used to synthesize the cordierite composition, $2MgO.2Al_2O_3.5SiO_2$. Six mixtures were finally selected. The oxide compositions including impurities are shown in Table 1. The batch composition and raw material analysis are given in Tables 1a and 1b respectively.

Four specimens approximately one inch in diameter and one quarter inch thick were mixed by hand from each batch. The pills were pressed in an hydraulically operated laboratory press of three ton capacity. One pill from each batch was fired in an electrically heated furnace using silicon-carbide resistors and controlled by a Minneapolis Honeywell Controller. Plate 1 is a photograph of the furnace used. The pills were fired to a temperature of 2550° F, following the heating schedule shown in Figure 2.

A small quantity of material was taken from the center of each fired pill for an X-ray diffraction study. Each small sample was well pulverized and mounted, one sample at a time, in a plastic sample holder. The samples were

TABLE 1

Batch Oxide Compositions on a Percentage Basis

	BATCH						
	I	II	III	IV	V	VI	$M_2A_2S_5$
MgO	13.5	13.8	13.8	13.6	13.9	13.7	13.8
Al_2O_3	33.7	34.8	34.8	33.8	34.1	34.2	34.8
SiO_2	50.6	51.4	51.4	50.0	50.4	50.2	51.4
CaO	2.0	---	---	0.3	0.4	0.4	---
Fe_2O_3	---	---	---	0.5	0.2	0.7	---
TiO_2	---	---	---	1.5	0.4	0.4	---
Alkalies	---	---	---	0.4	0.3	0.4	---

Table 1a

Batch Compositions on a Percentage Basis

Compound	BATCH I	II	III	IV	V	VI
MgO	---	---	13.8	11.7	12.2	---
Al_2O_3	32.7	30.3	34.8	---	---	10.9
SiO_2	24.8	44.6	51.4	7.8	---	---
$MgCO_3$	---	25.1	---	---	---	---
1-R Loomis Talc	42.6	---	---	---	---	---
Pioneer Georgia Kaolin	---	---	---	80.4	---	---
Pyrophyllite	---	---	---	---	26.6	---
Klondike Washed Kaolin	---	---	---	---	60.8	48.4
Yellowstone Talc	---	---	---	---	---	40.7

Table 1b

Chemical Analysis of the Batch Ingredients

	A-2 Alumina*	Potters Flint**	1-R Loomis Talc[1]	Pioneer Georgia Kaolin[2]	Pyrophy-llite[3]	Klondike Washed Kaolin[4]	Yellow-stone Talc[5]
SiO_2	0.02%	99.82%	56.7%	45.3%	75.0%	42.01%	62.52%
Al_2O_3	99.02	0.12	1.0	37.3	20.9	41.48	0.31
MgO		0.01	30.8	0.2		0.47	30.23
CaO		0.01	4.8	0.3	0.1	0.60	0.27
Fe_2O_3	0.04	0.01		0.6	0.1	0.30	1.51
TiO_2	0.002			1.5		0.72	
Alkalies	0.55	0.04		0.4	0.02	0.47	0.20
Loss on Ignition			6.7	14.4	3.9	13.95	4.95

*-Supplied by Aluminum Co. of America
**- " " Penn. Pulverizing Co.
1- " " W.H. Loomis Talc Corp.
2- " " Georgia Kaolin Co.
3-Supplied by Tenn. Mineral Products Corp.
4- " " EPK Co.
5- " " Sierra Talc Co.

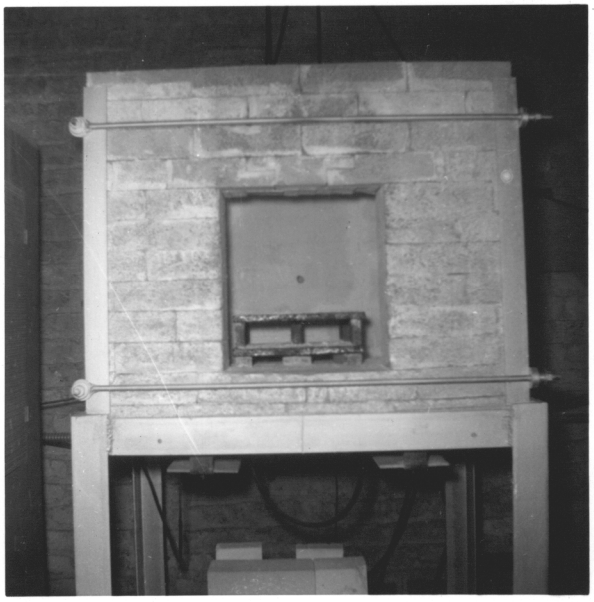


Plate 1. Electrically Heated Furnace

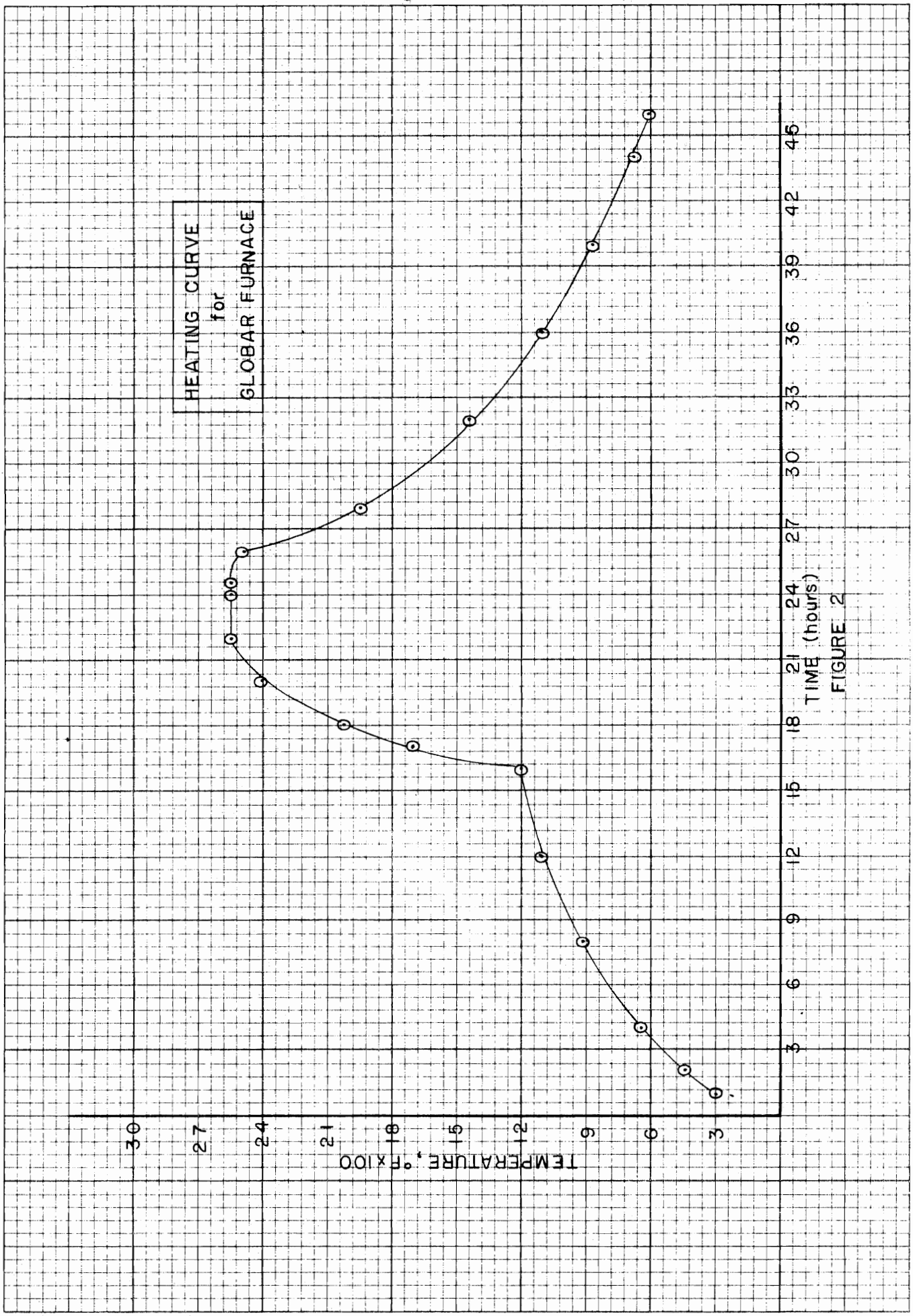

HEATING CURVE
for
GLOBAR FURNACE
TEMPERATURE, °F x 100
30
27
24
21
18
15
12
9
6
3
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
TIME (hours)

FIGURE 2

subjected to X-ray analysis in a General Electric XRD-5 diffractometer, using nickel-filtered copper K_α radiation. The reported interplanar spacings and intensities for cordierite are tabulated in Table 2.

On the basis of the X-ray patterns Batches II and III were immediately eliminated. The remaining four batches were subjected to a more precise X-ray examination. Using an internal standard to increase the reliability of quantitative estimates of cordierite development, Batches I, IV, V, and VI were reassessed and Batch VI was selected as the one giving the best yield.

Using high-alumina jar mills of one gallon capacity, 4750 grams of Batch VI were milled. Three charges of 1250 grams and one charge of 1000 grams were prepared and ground wet using 13 pounds of alumina grinding cylinders in each mill. One hundred and twenty grams of water was added for each 100 grams of dry batch. Milling time in each case was 16.5 hours.

The material was removed from the ball mills and dried. The dried material was pressed into pills 2.26 inches in diameter and varying from 1.0 to 1.5 inches in thickness. These pills were fired to 2550° F (Figure 2).

An X-ray pattern of a small specimen taken from the fired batch indicated excellent reaction with a general sharpening of peaks as compared to the pattern taken on the earlier sample of Batch VI.

The fired pills were reduced to powder in a hammer mill. The iron introduced into the material by this operation was removed by dispersing the powder in water and passing it through a Franz Ferro-Filter. The material, after drying, was screened and all particles passing a 200 mesh screen were used to make thermal expansion specimens.

TABLE 2

Reported Interplanar Spacings and Intensities for Cordierite

dA	I/I_1
8.29	70
4.83	10
4.60	5
4.03	50
3.34	80
3.11	60
3.00	100
2.63	40
2.44	5
2.42	5
2.32	20

2. Thermal Expansion Determinations of Cordierite-Zirconia Bodies

To determine the effect of zirconia additions on the thermal expansion of cordierite, a series of compositions ranging from 100% cordierite to 100% zirconia and varying by 10% increments by weight were made up. Specimens numbers and compositions are given below:

Specimen	Cordierite	Zirconia
ZrO_2-1	0%	100%
CZ-1	10	90
CZ-2	20	80
CZ-3	30	70
CZ-4	40	60
CZ-5	50	50
CZ-6	60	40
CZ-7	70	30
CZ-8	80	20
CZ-9	90	10
$M_2A_2S_5$-1	100	0

Fifty grams of each composition were weighed out and mixed in a mortar with a pestle. The specimens were formed in a 4 inch x 0.5 inch steel die. See Figure 3. To keep the thickness as near 0.5 inch as possible each charge was weighed. The actual weight of the specimens varied with the ratio of cordierite to zirconia, the weights increasing as the amount of zirconia increased.

All specimens were pressed at approximately 4000 pounds per square inch on an eight ton hydraulic press. See Plate 2.

To facilitate pressing and improve the green strength of the specimens, 5% by weight of a paraffin emulsion (Socony-Vacuum Oil Company's 'Ceremul C') was mixed with each batch before forming.

All the thermal expansion test pieces were fired to

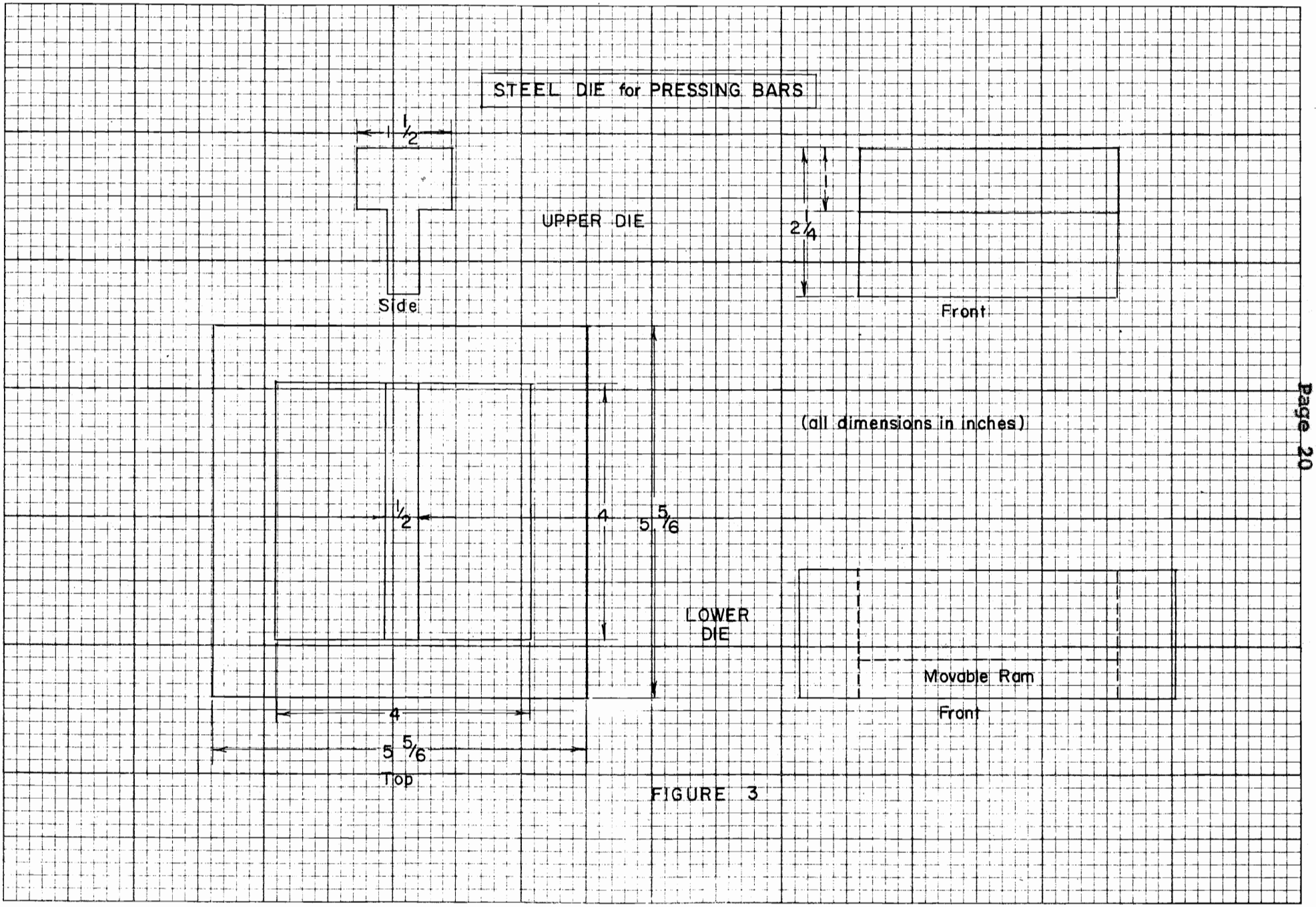

STEEL DIE for PRESSING BARS
1/2
UPPER DIE
Side
2 1/4
Front
(all dimensions in inches)
1/2
4
5 5/6
LOWER DIE
Movable Ram
Front
4
5 5/6
Top

FIGURE 3

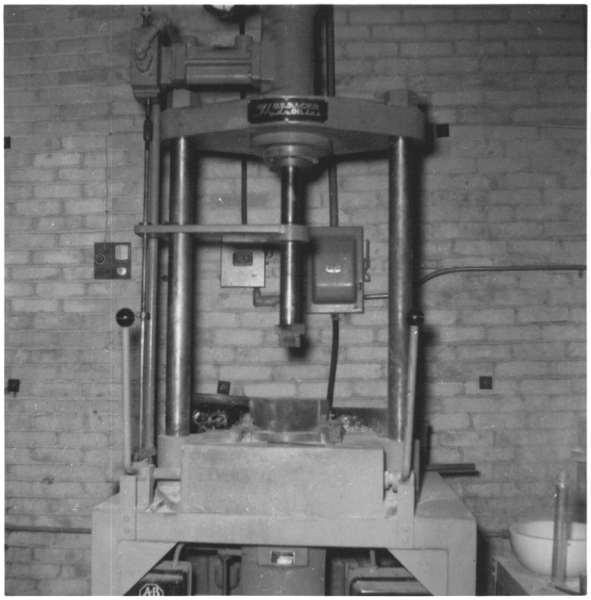


Plate 2. Eight Ton Hydraulic Press

2550° F in an electric furnace heated by silicon-carbide resistance elements. The heating schedule is shown in Figure 2.

After firing, the bars were visually inspected. Bars CZ-1 through CZ-7 had bloated, the bloating becoming more and more evident as the zirconia content increased. The bloating was attended by visibly rounded surfaces and edges. This indicated that some melting had taken place. The interior structure of the bloated specimens was cellular in appearance. Bar CZ-3 had distorted and bloated to the greatest extent, and it appeared to have formed the greatest amount of liquid. Bars CZ-8, CZ-9, and $M_2A_2S_5$-1 possessed sharp edges and level surfaces, but had warped very slightly. This was probably caused by unequal temperatures within the furnace caused by temperature gradients through the furnace length.

The bloated bars were ground to the desired 0.5 x 0.5 inch cross section.

Thermal expansion determinations were made in a fused silica dilatometer manufactured by the Industrial Engineering Instrument Co. A photograph of this appratus is shown in Plate 3. A cross-section of the furnace with the dilatometer and sample in place is shown in Figure 4. As can be seen from the drawing, the dilatometer consists of a fused silica tube, closed at one end, in which the sample is placed. On top of the sample a fused silica rod is placed which extends beyond the top of the outer tube and transmits any movement of the sample to a dial indicator. The latter is graduated in 0.01 mm divisions. Temperatures are determined by means of a chromel-alumel thermocouple placed inside of the enclosing tube with its hot junction located as close as possible to the mid-point

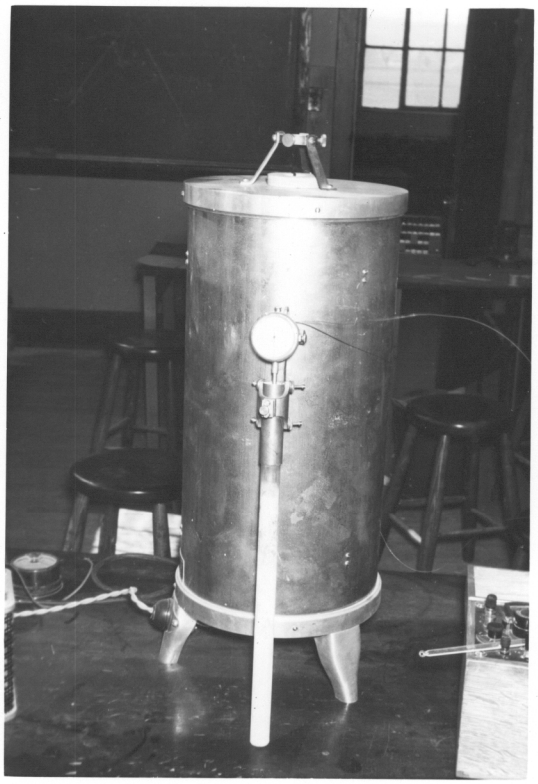
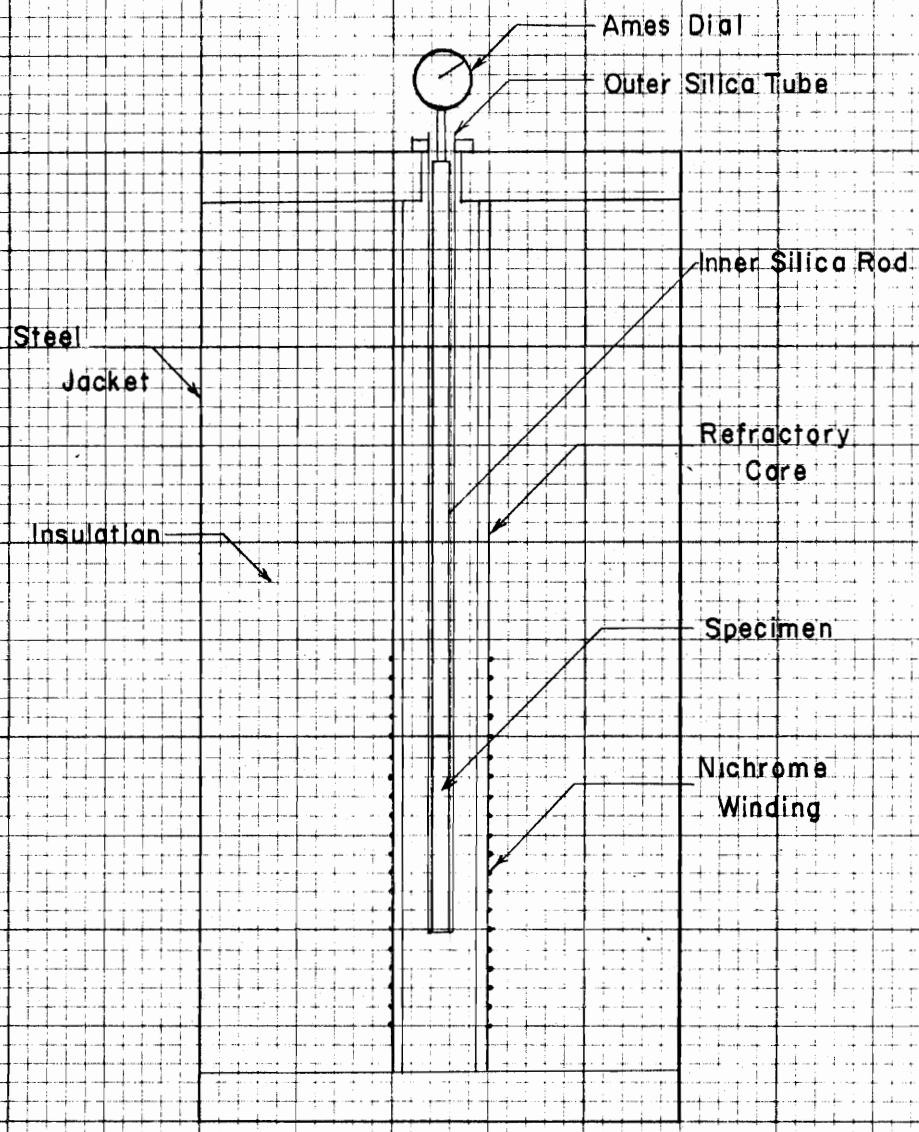


Plate 3. Fused Silica Dilatometer



SKETCH of THERMAL EXPANSION FURNACE

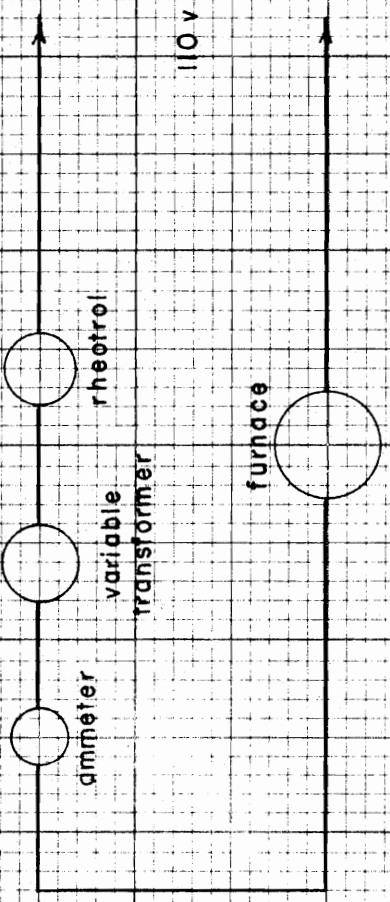
FIGURE 4

of the specimen. A detailed description of the operation of this type of dilatometer may be found in Reference 14 of the Bibliography.

The furnace used with this apparatus is a wire wound, vertical tube furnace controlled by a variable transformer. A diagram of the control circuit used is given in Figure 5. To give a more uniform rate of temperature increase a proportioning relay manufactured by Wheelco Instruments Co. and called a Rheotrol was incorporated in the circuit. The Rheotrol is simply a relay which is opened and closed by a cam driven by a small electric clock motor. It can be adjusted to give different proportions of on-off time.

Each specimen was heated at a uniform rate of 5.5° C per minute as shown in Figure 6.

The transformer and rheotrol values used to attain this rate of heating are shown on the figure. At increments of 100 degrees centigrade the temperature was held constant for five minutes to allow the sample to come to equilibrium at the furnace temperature. At the end of the five minutes any change on the dial indicator was noted. Following the heating schedule the temperature was then raised 100 degrees and again held until equlibrium was attained. This plan was followed for each specimen up to 1000° C.



ELECTRICAL DIAGRAM of THERMAL EXPANSION APPARATUS and CONTROLS

FIGURE 5

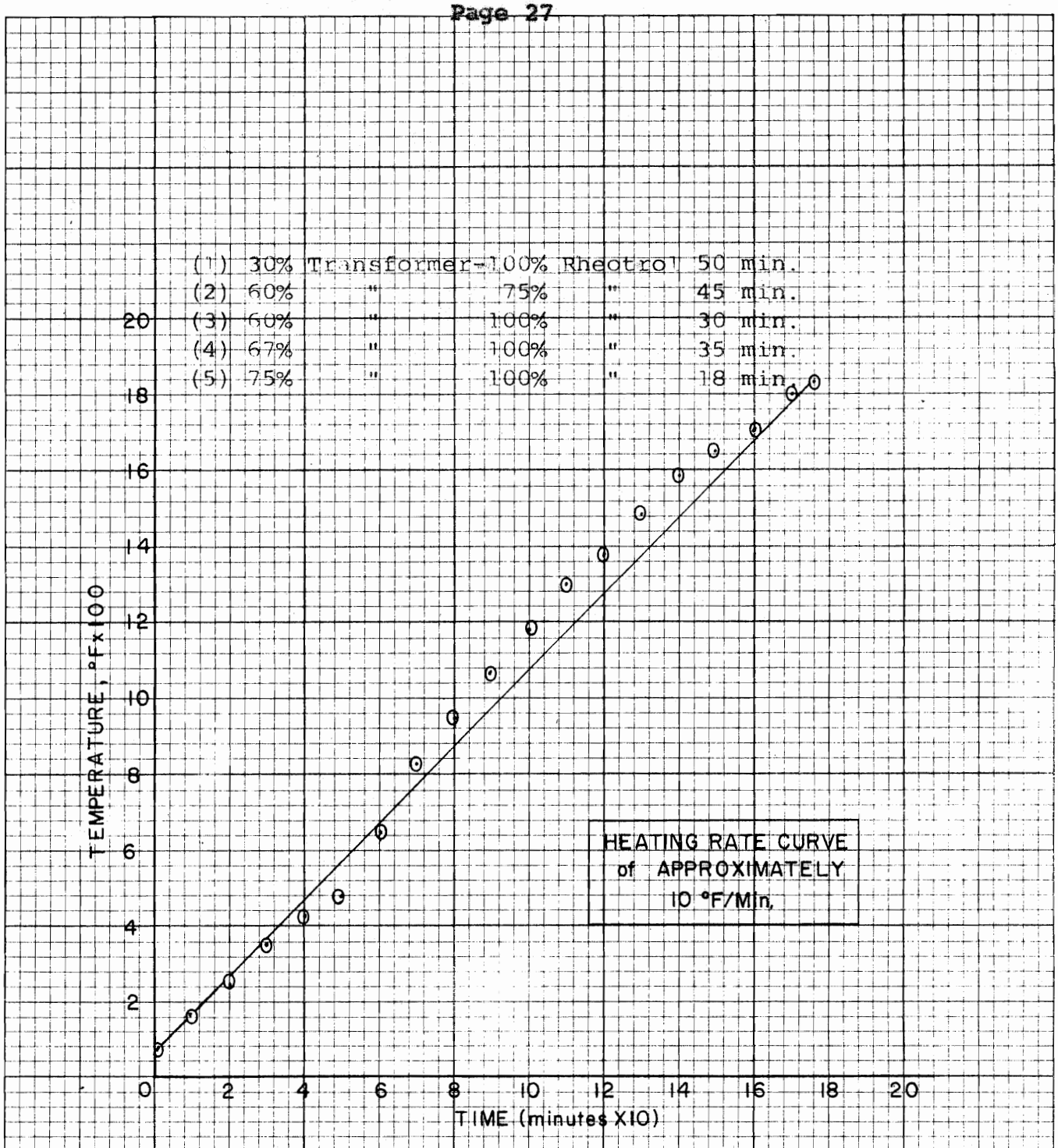

(1) 30% Transformer-100% Rheotrol 50 min.
(2) 60% " 75% " 45 min.
(3) 60% " 100% " 30 min.
(4) 67% " 100% " 35 min.
(5) 75% " 100% " 18 min.
TEMPERATURE, °F x 100
0
2
4
6
8
10
12
14
16
18
20
TIME (minutes X10)
HEATING RATE CURVE
of APPROXIMATELY
10 °F/Min.

FIGURE 6

3. Determinations of Resistance to Thermal Shock

Specimens which possessed a thermal expansion coefficient less than approximately 4 x 10^{-6} cm/cm/^{o} C were tested for their resistance to thermal shock.

The specimens used were the same 4 x 0.5 x 0.5 inch bars which had been used for the thermal expansion determinations. The specimens were heated in a wire wound laboratory furnace at an initial temperature of 100^{o} C. The temperature was raised by 100 degree increments to a maximum temperature of 1000^{o} C and the test was repeated at each 100 degree level.

At each level the temperature was held constant for approximately ten minutes to allow the specimens to come to equilibrium at the furnace temperature. The specimens were then removed from the furnace one at a time and plunged into water at room temperature. This was repeated five times at each temperature.

1000^{o} C was selected as the maximum test temperature since thermal expansion data had been determined up to this temperature.

4. Determination of Pyrometric Cone Equivalent

For this test, the specimens with acceptable thermal expansion coefficients were again used. Test cones were prepared from each composition in accordance with the method given at ASTM Standard Method of Test C 25-46 for refractory materials. A dextrin solution was used as a binder.

The test cones were arranged on a plaque with standard cones ranging from Cone 14-17. The test was run in an electrically heated furnace, and the heating rate was approximately 2.5^{o} F per minute in the range of deformation

of the test cones. Plate 4 is a drawing of the plaque after deformation was complete.

5. Determination of Temperature Effects on the Characteristics of CZ-7 Bodies

It was found that 30% ZrO_2 could be added to a cordierite body without impairing its thermal expansion properties to any great extent. In order to determine the maximum temperature at which this body would be used, a series of tests were performed.

A group of discs 2.25 inches in diameter and 0.25 inches thick were formed at varying pressures and fired to 1300°C. After firing, the discs were submerged in water for 24 hours to determine the effect of forming pressure on the absorption.

This test indicated that high pressures were desirable for low absorption and subsequent samples were pressed at 10,075 pounds per square inch which was the maximum pressure obtainable with the available equipment.

Samples were fired at increasing temperature increments until melting occurred. The degree of absorption obtained at each temperature was determined by a 24 hour submersion test. The degree of warping and percentage absorption of a body initially fired at 1300 °C, then pulverized, repressed, and refired to 1375 °C was determined. A similiar determination was made on a body fabricated from the original raw batch ingredients.

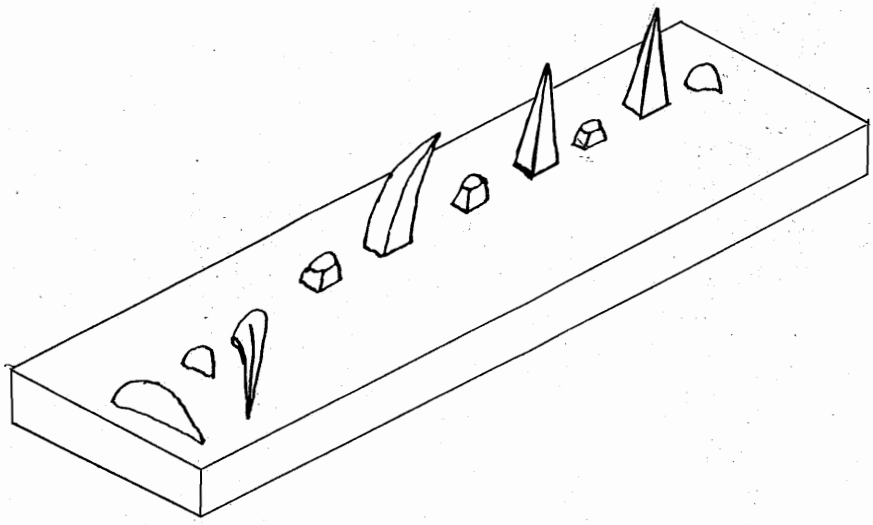


Plate 4. P.C.E. Plaque After Test

6. Sample Calculations

A. Calculation of the Percentage Composition of Batch V

1. See Table 1b for the chemical analyses of Pyrophyllite and Klondike Washed Kaolin

2. Solve a simultaneous equation where
x = pyrophyllite and y = kaolin

$$.209x + .415y = 34.8 = Al_2O_3 \text{ needed}$$
$$.750x + .420y = 51.4 = SiO_2 \text{ needed}$$

$$x = 30.08$$
$$y = 68.67$$

13.8 g of MgO also needed

3. Recalculate on a 100 g basis
4. Thus, Batch V contains:

26.6 g Pyrophyllite
60.8 Klondike Washed Kaolin
12.2 MgO

5. All other batches calculated in a similiar manner.

B. Calculation of the Coefficient of Thermal Expansion

The coefficient of thermal expansion is calculated using the formula below:

$$a = \frac{L - l}{l\,(t' - t)}$$

In this expression, a is the coefficient of thermal expansion (over the interval $t' - t$), t is room temperature and t' the final furnace temperature (both in $^{\circ}C$), l is the length of the specimen at room temperature and L its length at the final temperature (both in centimeters).

Example

For a given sample the values in the above formula are as follows:

$$L = 9.591 \text{ cm.} \quad t' = 1000^{\circ} C$$
$$l = 9.571 \text{ cm.} \quad t = 22.2^{\circ} C$$

Substituting in the above equation, a becomes

$$a = \frac{9.591 - 9.575}{9.575\,(1000-22.2)} \text{ cm./cm. } ^{\circ} C$$

$$a = 1.71 \times 10^{-6} \text{ cm/cm}^{\circ} C$$

All other values of the coefficient of thermal expansion were calculated in this manner.

C. Calculation of the Percentage Absorption

To determine the percentage absorption of the 30% ZrO_2 - 70% cordierite bodies, the bodies were submerged in water for 24 hours. The absorption was calculated using the following formula:

$$\% \text{ Absorption} = \frac{(\text{Wet Wt. of Sample}) - (\text{Dry Wt. of Sample})}{(\text{Dry Wt. of Sample})} \times 100$$

IV. Tabulated Results

TABLE 3

Thermal Expansion Coefficients of Several Cordierite-Zirconia Bodies

Coeff. of Expansion (x 10^{-6})

Room Temp. to	ZrO_2	CZ-2	CZ-4	CZ-6	CZ-7	CZ-8	CZ-9	$M_2A_2S_5$-1
100°C	6.70	4.67	4.31	1.47	1.22	0.00	0.00	0.00
200	7.09	5.09	4.70	1.95	1.53	0.75	0.06	0.00
300	7.40	5.05	4.92	2.15	1.97	1.32	0.46	0.38
400	7.54	5.44	5.25	2.66	2.21	1.62	0.85	0.66
500	7.71	5.50	5.34	2.88	2.33	1.84	1.10	0.87
600	7.86	5.62	5.48	3.20	2.54	1.98	1.37	1.08
700	7.95	5.75	5.74	3.57	2.69	2.21	1.53	1.28
800	8.20	5.96	6.00	3.86	2.99	2.36	1.70	1.46
900	8.37	6.16	6.41	4.87	2.99	2.46	1.85	1.58
1000	8.46	6.34	6.63	5.00	3.06	2.52	1.98	1.71

TABLE 4

Thermal Shock Results For Several Cordierite-Zirconia Bodies

(Quenched From Indicated Temperature to Room Temperature)

Temperature	CZ-7	CZ-8	CZ-9	Cordierite-1	Comments
200°C	/////	/////	/////	/////	
300	/////	/////	/////	/////	
400	/////	/////	/////	/////	
500	/////	/////	/////	/////*	*section separated from pressure crack
600	/////	/////	/////	/////	
700	/////	/////	/////	/////	
800	*/////*	/////	/////	/////	*same as above
900	/////	/////	/////	/////	
1000	/////	/////	/////	/////	
	(test continued for ten more cycles)				

/ - passed test ----- x - failed test

TABLE 5

Pyrometric Cone Equivalent For Several Cordierite-Zirconia Bodies

	Specimen			
	CZ-7	CZ-8	CZ-9	Cordierite-1
Deformed at Cone	15^1	15^2	15^3	16^1

TABLE 6

Effect of Firing Temperature on Several Physical Characteristics of Cordierite-Zirconia Bodies

Temp. to Which Body Fired	% Absorption	Change in Diameter	Comments
1300°C	14.4	0.00 in.	No shrinkage or apparent warping
1350	8.1	0.20	Very slight warping
1375	1.9	0.30	Very slight warping
1400	----	-----	Melted
1300 & 1375	1.9	0.30	This body originally fired to 1300, subsequently reground, repressed, and fired to 1375-No warping evident after second fire.
1375	5.8	0.03	This body made from original batch ingredients and zirconia-Slight warping

V. Discussion

As stated in the Method of Procedure, cordierite must first be synthesized if it is to be used as a constituent in a ceramic body. The production of the compound therefore became an important consideration because subsequent studies in this investigation depended on an easily fabricated supply. It was also felt that others interested in producing the compound might benefit by the data obtained from this phase of the investigation.

Several different compositions were used to produce cordierite. This was done to take advantage of differing crystal structure changes and dissociations occurring within the raw materials when firing took place which might aid in the formation of the desired product. For instance, Batches II and III were the same except for the raw material from which MgO was obtained. In one case $MgCO_3$ was used and in the other case MgO itself was used. It was anticipated that with heating the decomposition of $MgCO_3$ and the attendant crystal structure change would produce a more favorable reaction than that occurring with the use of the compound MgO alone. The pure oxide was used in a second batch to see if such would be the case.

Similiar considerations prevailed when using the various other compositions in one combination or another. The pyrophyllite, as opposed to the kaolins, possessed a lower alumina to silica ratio. One talc as opposed to the other had a higher silica content. Therefore, various combinations of these materials provided all the

silica, alumina, and/or magnesia necessary for a given batch. Again, crystal changes and various decompositions occurring as the batch was heated were expected to produce favorable reactions.

It was thought that Batches I, IV, V, and VI, when fired would more closely approach equilibrium than Batches II and III. Such a result was expected since the pure oxide SiO_2, which was present in large quantities in Batches II and III, reacts very slowly and is often present in substantial quantities after firing in those bodies in which it is used. The X-ray patterns of these two batches displayed the expected results. See Charts 1 and 2. Firing the batches for 25 hours left an unusually strong peak at the d value of approximately 4.07, which is also a strong cristobalite (cr.) peak. Firing the batches for 15 additional hours served only to shorten the peak slightly. Refiring also strengthened the cordierite (co.) peaks. Both of these observations indicated the advisability of longer firing periods to allow the SiO_2 to proceed further toward complete reaction.

The anticipated result of using $MgCO_3$ in a batch in preference to MgO was not realized. In fact, there appeared to be an effect opposite to that anticipated. From Table 7 it is evident that the cordierite peak intensities are stronger for the batch using MgO than the batch using $MgCO_3$. Further investigation in this direction is suggested to determine the reason for this phenomenon. The use of an internal standard in the X-ray analysis would probably be helpful in determining the relative peak intensities to be certain the conclusions drawn from the X-ray pattern were correct.

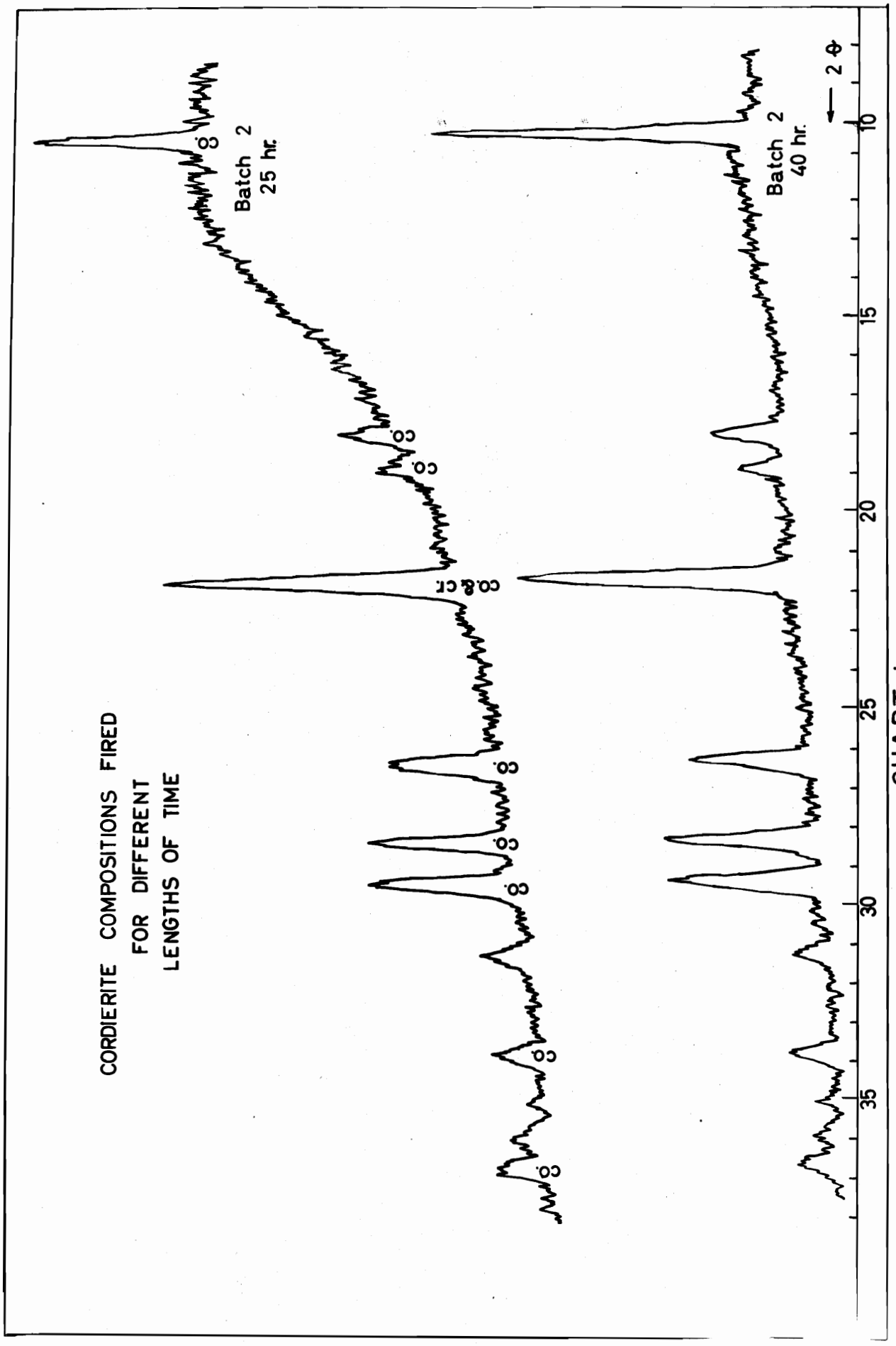

CORDIERITE COMPOSITIONS FIRED
FOR DIFFERENT
LENGTHS OF TIME
Batch 2
25 hr.
Batch 2
40 hr.
2 Θ
10
15
20
25
30
35

CHART I

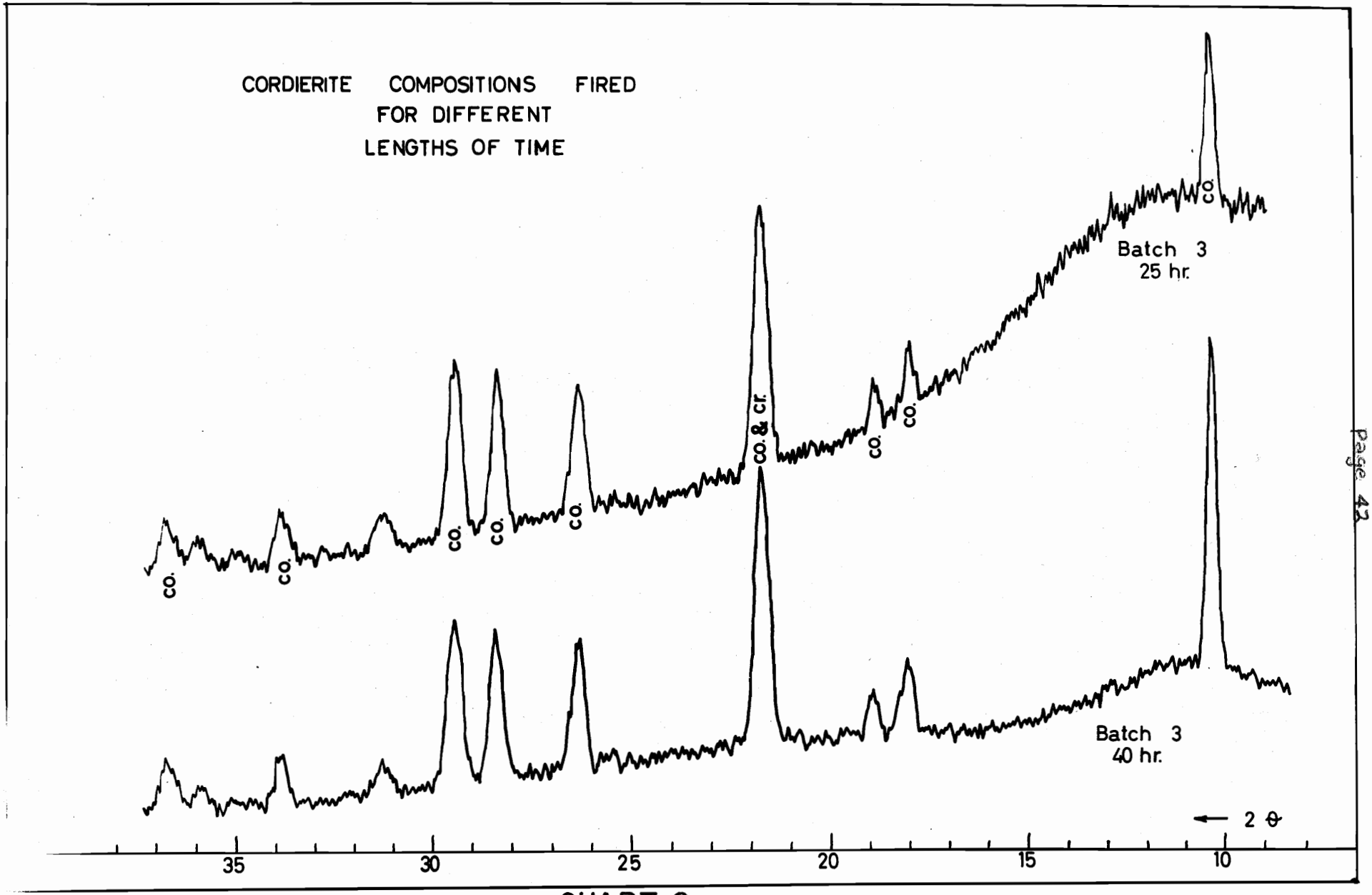

CORDIERITE COMPOSITIONS FIRED
FOR DIFFERENT
LENGTHS OF TIME
Batch 3
25 hr.
Batch 3
40 hr.
co.
co. & cr.
2 θ
35
30
25
20
15
10

CHART 2

TABLE 7

Interplanar Spacings and Intensities for Batches I-VI

Batch I		Batch II		Batch III		Batch IV		Batch V		Batch VI	
d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1
8.59	100	8.51	59	8.51	66	8.59	100	8.51	100	8.51	100
4.93	26	4.90	21	4.90	22	4.93	24	4.90	30	4.90	27
4.70	33	4.67	12	4.69	21	4.70	11	4.67	19	4.70	12
4.11	42	4.06	100	4.08	100	4.11	57	4.08	65	4.10	56
3.39	43	3.38	40	3.38	49	3.39	59	3.39	71	3.39	52
3.14	46	3.13	47	3.14	60	3.14	72	3.14	77	3.14	62
3.04	55	3.03	51	3.03	66	3.04	78	3.04	82	3.03	67
2.65	17	2.85	15	2.86	16	2.65	26	2.64	26	2.64	20
2.44	8	2.64	15	2.64	20	2.44	7	2.44	6	2.44	7
--	-	2.49	7	2.49	10	--	-	2.34	13	2.34	9
--	-	2.44	13	2.44	19	--	-	--	-	--	-

Several additional peaks found on the Batch II and III patterns indicated the presence of small amounts of forsterite and/or clino-enstatite. Though not anticipated, these peaks do suggest non-equilibrium and intermediate reaction on the part of the batch while moving toward equilibrium.

The above considerations and results eliminated Batches II and III as sources of readily available cordierite. As stated, closer approach to equilibrium was expected for Batches I, IV, V, and VI because much of the required MgO, Al_2O_3, and SiO_2 was already chemically combined in the various batch ingredients. The addition of no more pure oxide than required to any one batch was felt to increase the chances for the batch ingredients to form cordierite more quickly and to approach equilibrium more closely. Also, various transformations occurring within the batch ingredients when firing took place would again hopefully produce the desired reactions.

The study of the X-ray patterns of the fired batches indicate the validity of the assumptions made. See Chart 3 and 4. The interplanar spacings and intensities of these batches may be compared with those of Batches II and III by again referring to Table 7. All reported peaks for cordierite are evident and they are strong and sharp. This indicates the presence of a large amount of essentially pure cordierite. No peaks are in evidence that would indicate the presence of some other compound.

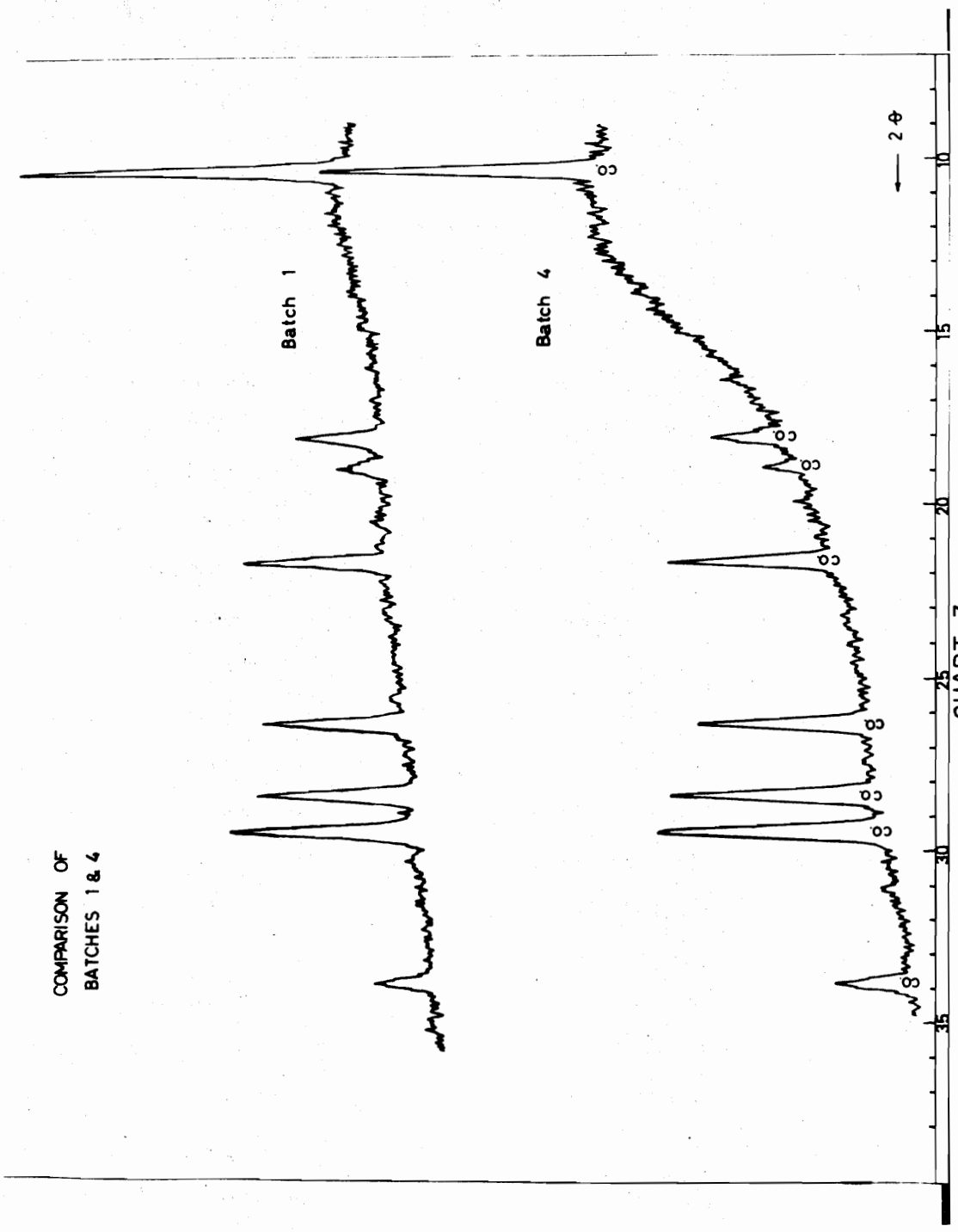


CHART 3

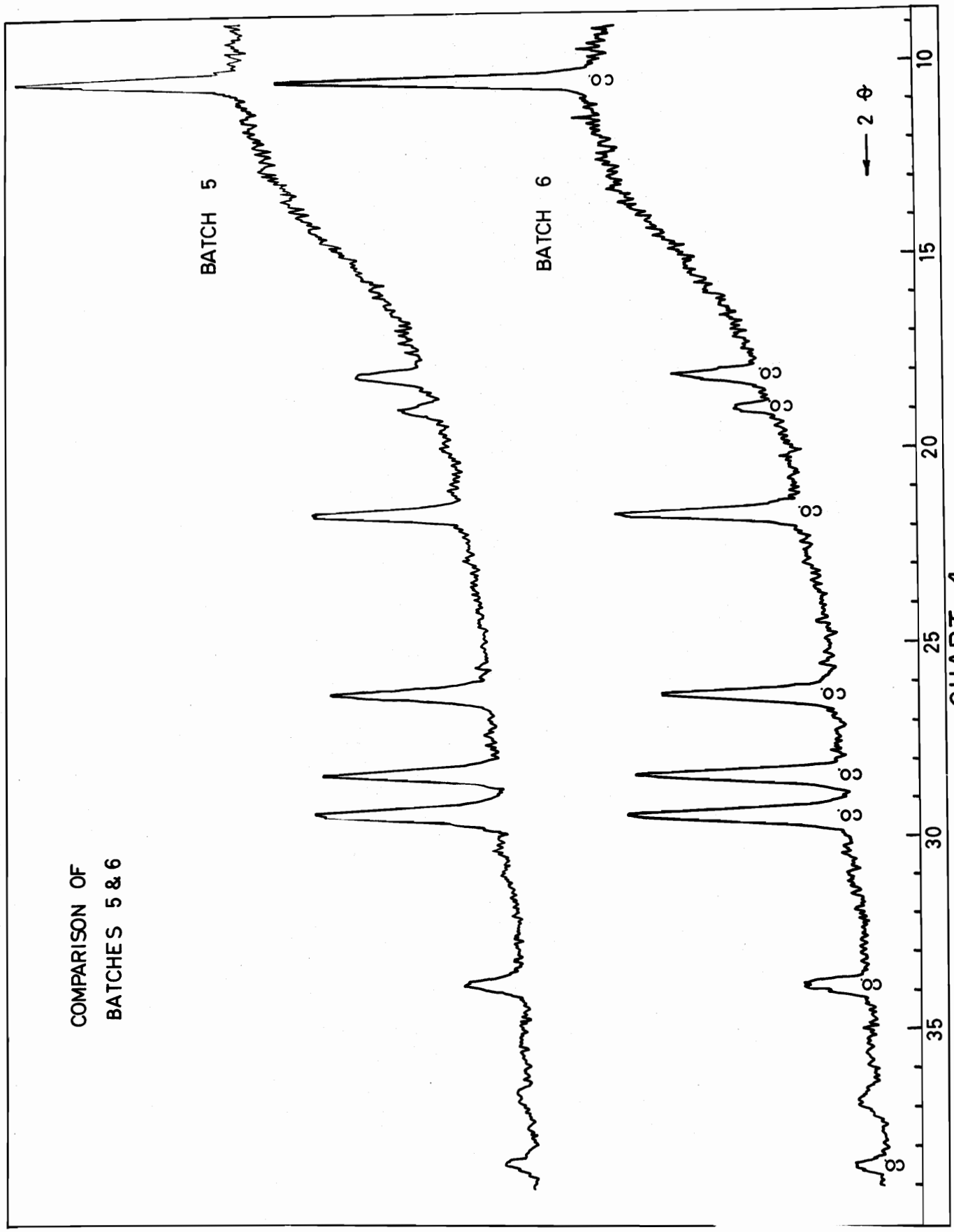
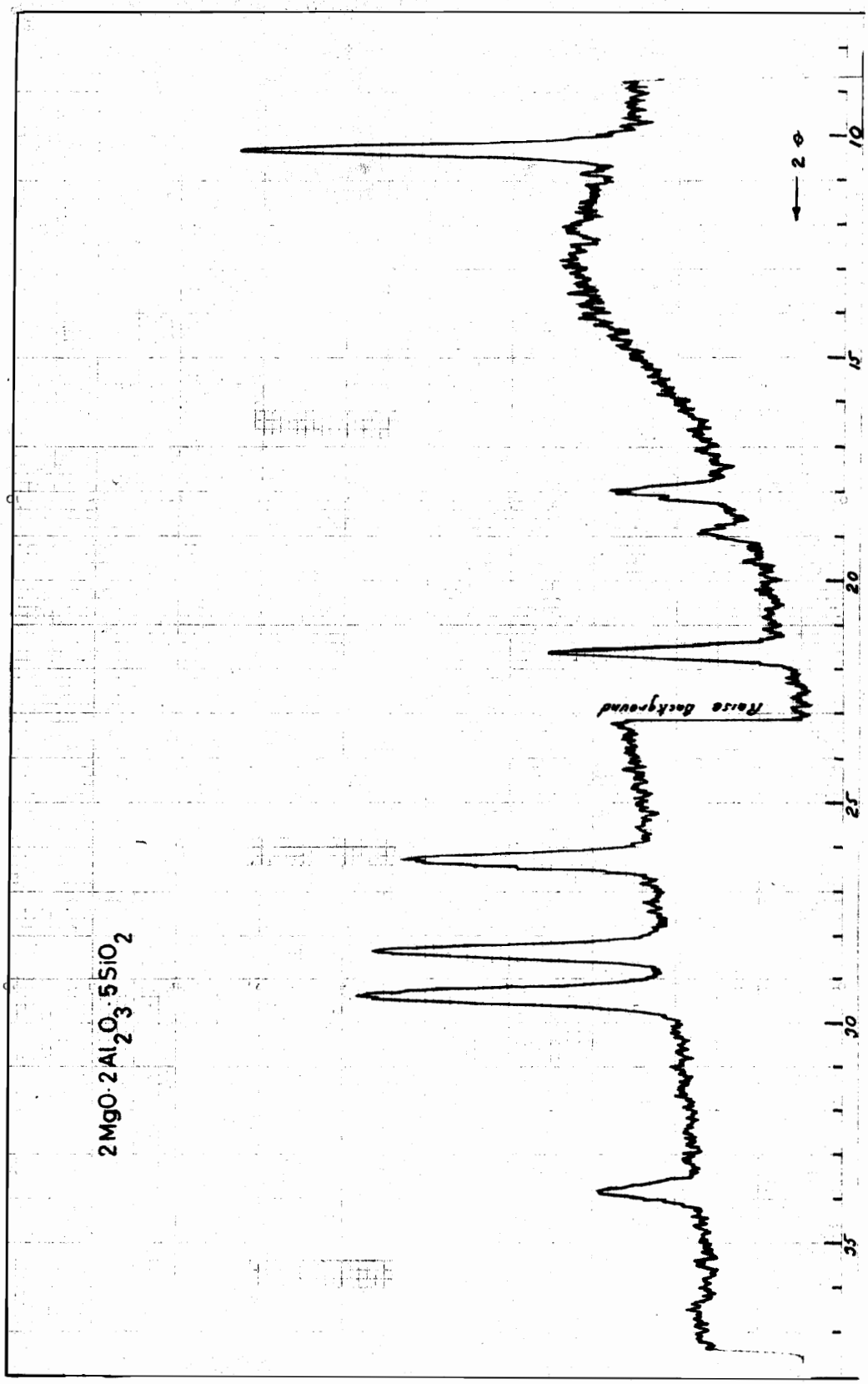


CHART 4

The displacement of interplanar spacing values from reported values at low angles of incidence (comparing values in Table 2 and Table 7) is attributed to differences in the source of the cordierite used to make the standard determination. Reported values were obtained from A.S.T.M.[16] information. It is not known whether this cordierite was artificial or natural. Nevertheless, values obtained in this investigation are the same as those obtained by Lamar and Warner from their batch designated B-B (50% E.P.K. Kaolin, 50% Sierralite). They indicated that this batch contained a high percentage of cordierite. This similarity is most pronounced for Batches I, IV, V, and VI. Thus the values indicated for Batches I, IV, V, and VI are considered to be correct.

Because the intensity of the peaks of the four remaining batches were very similiar, an internal standard was placed in each batch to help estimate the relative peak intensities. Although this quantitative estimate showed the four batches contained comparable amounts of cordierite, it did indicate that Batch VI contained somewhat more than the others.

Cordierite subsequently produced from Batch VI showed evidence of excellent reaction. See Chart 5. This is attributed to the ball milling operation which undoubtedly gave excellent mixing and produced some reduction in particle size. The intimate contact and homogeneous mixing would aid greatly in causing the reaction to go to completion when the mixture was fired.


2MgO·2Al2O3·5SiO2
Raise background
2θ
10
15
20
25
30
35

Commercial refractories containing zirconia are available with thermal expansions of approximately 4.5 x 10^{-6} cm./cm.^{o}C. The development of a refractory body with a low thermal expansion would thus require the selection of some expansion value less than 4.5 x 10^{-6}. Therefore, thermal expansion data were obtained from the various cordierite-zirconia specimens to determine the maximum amount of zirconia which could be added before the coefficient of thermal expansion exceeded 4.0 x 10^{-6} cm./cm.^{o} C. No purpose would be served by selecting a value higher than this.

The thermal expansion specimens containing large amounts of zirconia possessed expansions much greater than 4.0 x 10^{-6}. This established a trend and only the even numbered high-zirconia content specimens were tested. This is evident from the tabulated thermal expansion results. Once the specimen possessing the selected thermal expansion value had been located, both even and odd numbered remaining specimens were tested.

An increase in the thermal expansion of a cordierite-zirconia body was expected as the zirconia content increased because zirconia has a higher thermal expansion than cordierite. The total thermal expansion of any such body can be thought of as an additive property. Because chemical reaction was expected to occur between the zirconia and cordierite, the final thermal expansion would also be dependent on the resultant compounds formed.

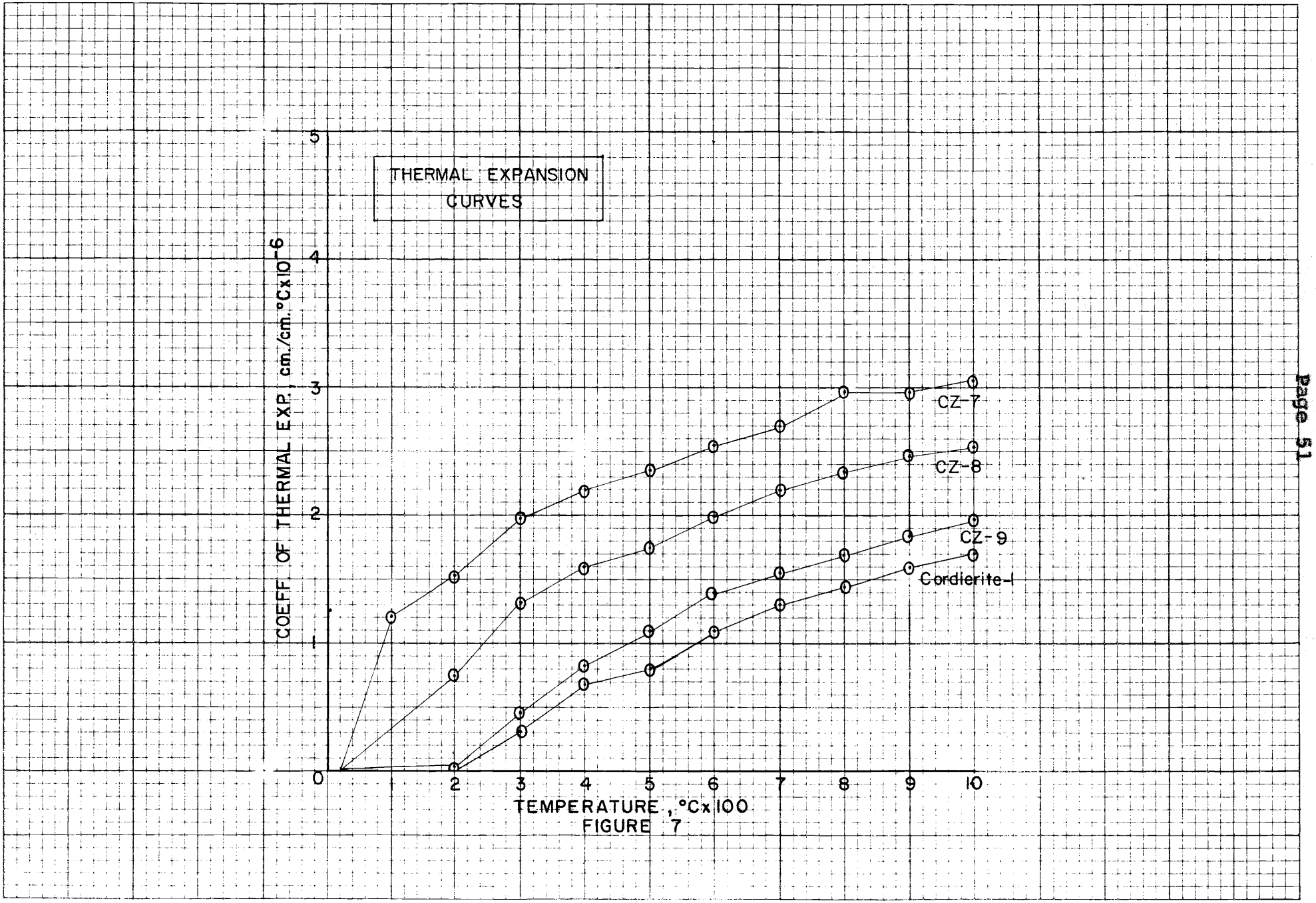
The results of the thermal expansion tests indicated that several earlier investigators were correct in stating that the addition of up to 30% zirconia to a cordierite body

would not prove detrimental to the thermal expansion of the body. Figure 7 is a plot of the thermal expansion values versus temperature for those specimens which met the low expansion requirements.

The low thermal expansion values found for the pure cordierite sample were very close to those given in the literature. This indicated that the compound used in this investigation was relatively free from impurities.

As stated earlier, some type of reaction was expected to take place when a cordierite-zirconia body was fired. It was only possible to postulate that the compounds formed by such a reaction would be cordierite, zirconia in the form of an oxide or silicate, and spinel. To determine more precisely the compounds which would be present, an X-ray diffraction pattern of Specimen CZ-7 was made. It was felt that this particular specimen was representative of all the specimens since it possessed the maximum thermal expansion desired in this investigation.

Chart 6 is an X-ray diffraction pattern of a mechanical mixture of Specimen CZ-7 and fired sample of the same specimen. The compounds present in the fired specimen are cordierite and zirconium-silicate with a small amount of spinel apparent. The specimen was maintained at 1340° C for a four hour period, but equilibrium has not necessarily been attained. The significance here is that zirconia is no longer present and $ZrO_2.SiO_2$ has begun to form.


THERMAL EXPANSION CURVES
COEFF. OF THERMAL EXP., cm./cm.°C x 10⁻⁶
0
1
2
3
4
5
2
3
4
5
6
7
8
9
10
TEMPERATURE, °C x 100
CZ-7
CZ-8
CZ-9
Cordierite-I
FIGURE 7

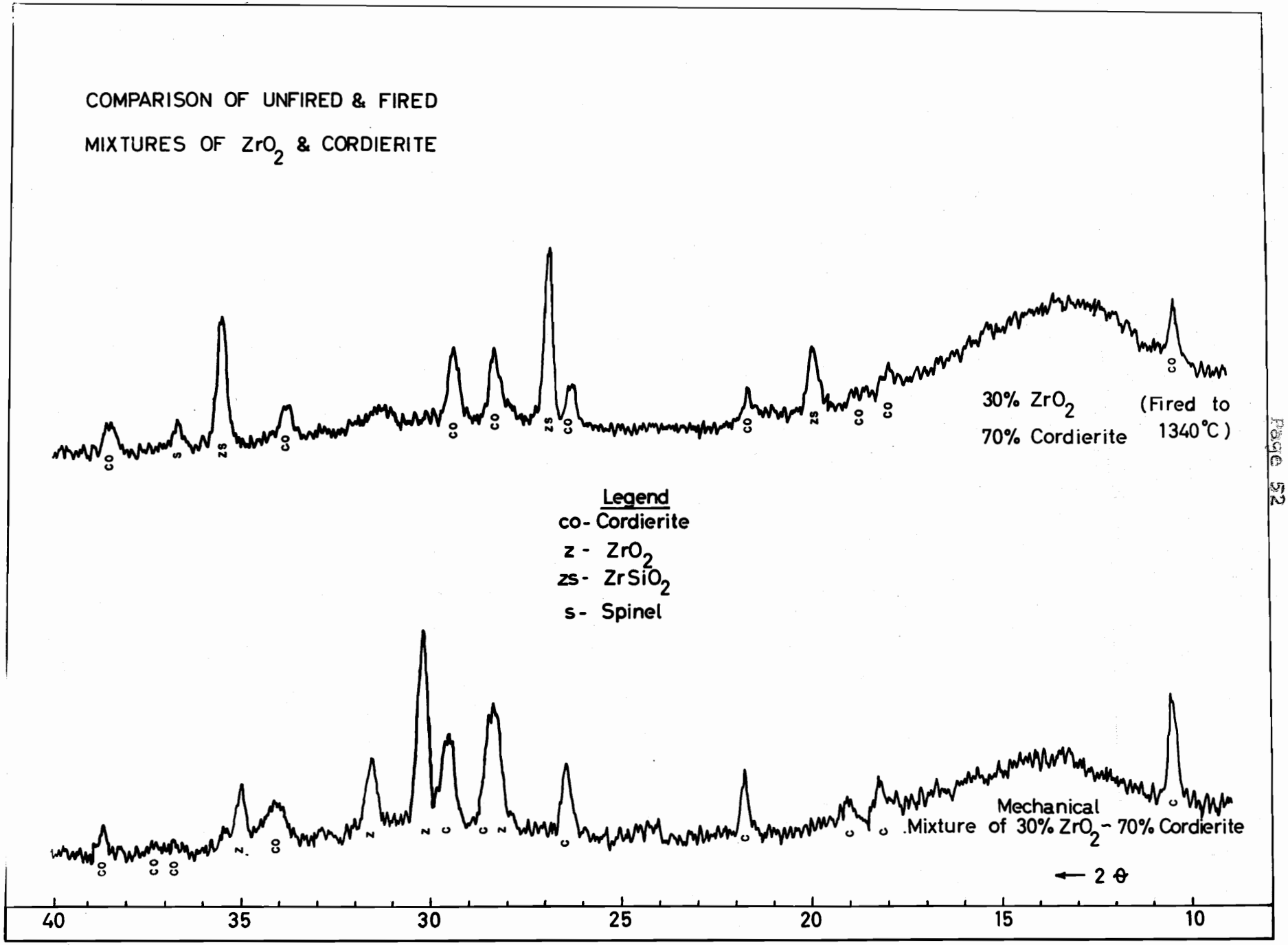

COMPARISON OF UNFIRED & FIRED
MIXTURES OF ZrO_2 & CORDIERITE
30% ZrO_2
70% Cordierite
(Fired to 1340°C)
Legend
co- Cordierite
z - ZrO_2
zs- $ZrSiO_2$
s - Spinel
Mechanical Mixture of 30% ZrO_2 - 70% Cordierite
← 2θ
40
35
30
25
20
15
10

CHART 6

These findings are in accord with the data given by Herold and Smothers[17] in their work on the $MgO-Al_2O_3-SiO_2-ZrO_2$ system. Because cordierite and zirconia are incompatible, one or the other will not be present after reaction depending upon the percentages of cordierite and zirconia originally used. The authors indicate that additions of zirconia in low percentages will produce the compounds cordierite, zirconium-silicate, and spinel when the bodies are fired. Chart 6 indicates that bodies in this investigation conatining up to 30% zirconia fall within this general area.

It can be shown by calculation that if equilibrium was reached the body would contain approximately 60% cordierite, 20% zirconium-silicate, and 20% spinel assuming that all the silica given up goes to form $ZrO_2.SiO_2$. Multiplying these percentages by their respective expansions and adding gives a value of approximately 3.76 while the actual thermal expansion for this body was 3.06 cm./cm.$^{\circ}$ C. It can thus be said that the thermal expansion of this body was roughly additive and depended upon the expansion of the materials of which it was composed.

The thermal shock resistance of all the cordierite-zirconia bodies was expected to be excellent. The shock itself would be most severe in the rapid cooling of the specimen. A shock of lesser magnitude would be experienced when the quenched specimen was placed directly into the hot furnace.

Results of the test indicate that the thermal shock resistance was excellent as expected. At 1000° C the rapid

cooling and heating cycle was performed several times beyond the usual five cycles in anticipation of eventual failure of the specimen. The test was discontinued after fifteen cycles, however, because the specimens had still not ruptured. In the two instances where small chips did separate from the specimens it was noted that these failures occurred at surface pressure cracks. Such cracks were often unavoidable because of the high pressures used in the forming operation.

The results of the Pyrometric Cone Equivalent Test may be seen in Plate 4, a drawing of the P.C.E. plaque after the final cone of interest had deformed. The test was performed on all expansion samples which had fallen below the maximum 4.0 cm./cm. ^{o}C limit selected for this investigation. Specimen CZ-6 was also included in the test for comparison purposes.

The cones from left to right are Cone 14, CZ-6, Cone 15, CZ-7, Cone 16, CZ-8, Cone 17, CZ-9, Cone 18, Cordierite-1. The results of the test indicate at which cone the specimens deformed. For instance, if the designation for CZ-8 was 15^{3}, this would mean that the tip of specimen CZ-8 had touched the plaque base at a time when Cone 15 had deformed to the 3 o'clock position. The results indicate that specimens with increased amounts of zirconia had lower pyrometric cone equivalents. Thus the liquidus curve of the cordierite-zirconia system slowly drops away from cordierite as the percentage of zirconia is increased, at least up to 40% zirconia.

The specimens formed a large amount of liquid at their melting points. This is the reason for the severely melted appearance of the specimen cones on the fired plaque.

The effects of firing temperatures and body compositions on several characteristics of cordierite-zirconia bodies are apparent from the tabulated data. The material tested was that representing Specimen CZ-7. Data concerning Specimens CZ-8, CZ-9, and Cordierite -1 would be comparable.

Assuming that variations in forming pressure would vary the absorption of the fired body, it was found that increased forming pressures decreased the percentage absorption. This, however, would probably reach a limiting case. The decrease in absorption with pressure is logical because the closer the particles of the mass are, the fewer are the number of voids in the body. Fewer voids naturally mean lower absorption.

An indication of the degree of warping of the fired discs was given by placing the edge of a steel ruler along the diameter of the disc. If the disc had not warped, no curvature could be seen between the ruler and the surface of the disc.

It will be noted that a body fired twice with intermediate regrinding and repressing did not warp, whereas bodies fired only once to comparable temperatures did warp slightly. This was probably caused by the more homogeneous mixture attained by the second regrinding and repressing operation. Shrinkage for both firing techniques were comparable.

Another interesting fact is evident in the batch made from the original raw batch ingredients and zirconia. The absorption of the body when fired to 1375°C was about three times the absorption of a body produced from cordierite and zirconia which had been fired to the same temperature. The shrinkage of the body was only one-tenth the shrinkage of the cordierite-zirconia body.

Both of these observations are logical. The raw material particles have not had time to completely react, thereby leaving more voids between particles. Incomplete reaction has therefore forestalled shrinkage. Firing the specimen for a longer length of time would have allowed the reaction to approach equilibrium, thereby reducing the absorption and causing greater shrinkage.

All indications suggest that a cordierite body containing a maximum of 30% zirconia can be used at a temperature of 1300°C with no dimensional change occurring in the body. The percentage absorption of this body could be reduced by increased forming pressure, selected grain size distribution, and initial firing temperatures of 1350°C. It would be advisable to test these bodies under load at 1300°C to be certain that their load carrying characteristics are not impaired at this temperature.

Data obtained from this phase of the investigation indicate that zirconia has not materially increased the firing range of cordierite bodies. To obtain absorptions lower than approximately 2% the temperature can only be raised over a range of 25°C before melting occurs.

IV. CONCLUSIONS

Based on the results of the present investigation the following conclusions seem justified:

(1) The production of cordierite on a one-fire basis is most easily attained with end members containing a high percentage of the cordierite constituents already in chemical combination.

(2) Up to 30% zirconia may be added to a cordierite body without materially impairing the thermal expansion of the body.

(3) The addition of zirconia to cordierite does not materially extend the firing range of cordierite bodies.

(4) Cordierite bodies containing 30% zirconia possess thermal shock resistance comparable to pure cordierite.

(5) The addition of up to 30% zirconia to a cordierite body does not improve the refractoriness of the body.

(6) A cordierite body containing up to 30% zirconia may be used at a temperature of 1300°C.

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VII. VITA

Robert Michael McMarlin was born in Indiana, Pennsylvania on February 12, 1938. In June, 1956 he graduated from Annandale High School in Annandale, Virginia, and in September of the same year he enrolled at Virginia Polytechnic Institute. He obtained the B. S. degree in Ceramic Engineering in June, 1960. In September of 1960 he began work at Virginia Polytechnic Institute as a candidate for the M. S. degree in Ceramic Engineering.

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ABSTRACT

The purpose of the present investigation was to undertake a systematic study of cordierite compositions to determine to what extent the ultimate refractoriness and use temperature could be increased by the addition of zirconia without increasing the thermal expansion above 4.0×10^{-6} cm./cm./°C.

A procedure has been presented for making the compound cordierite. Several raw batch compositions which can be expected to produce a high percentage of relatively pure cordierite on a one-fire basis are given.

Data are presented tabulating the coefficients of thermal expansion of cordierite specimens containing increasing percentages of zirconia, the thermal shock resistance of these same specimens, the pyrometric cone equivalents of those specimens which possessed expansions lower than 4.0×10^{-6}, and the effect of firing temperature on the absorption and distortion of a specimen possessing the maximum allowable thermal expansion.

The results of the investigation indicate that zirconia does not materially extend the short firing range of cordierite compositions and the refractoriness of cordierite is not increased by the addition of zirconia at least in amounts up to 40%. It was found that a 70% cordierite-30% zirconia body could be used at a temperature of 1300°C without warping or undergoing shrinkage.