SC-TM-710003

EFFECTS OF CALCINING ON THE ATMOSPHERE-FIRING OF LEAD ZIRCONATE-LEAD TITANATE CERAMICS*

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February 1971

ABSTRACT

The sinterability of a lead zirconate-lead titanate calcined powder is determined by its calcining history. The density resulting from firing was found to depend primarily on calcine temperature; the grain size is primarily determined by the final firing temperature. The soak times of calcining and firing have a lesser effect on density than do the temperatures of calcining and firing. When a calcine temperature of 900°C or 1000°C was used, high bulk densities (≥ 7.6 gm/cm^3) were achieved over a broad firing range of 1200°C to 1350°C.

*Based on a paper presented at the 23rd Pacific Coast Regional Meeting, The American Ceramic Society, San Francisco, California, October 29, 1970.

Key words: Sinterability, grain size, lead zirconate-lead titanate

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ACKNOWLEDGMENT

The authors wish to express their thanks to L. L. Pierce and J. E. Tichenor for laboratory assistance, to D. J. Gould for preparation of photomicrographs, and to G. H. Haertling for critical review of the manuscript.

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Introduction

The electrical properties of lead zirconate-lead titanate* ceramics depend on the physical quality of the specimens. This quality is a combined result of many processing parameters. A number of investigators[1-5] have reported on the ferroelectric properties of ceramics from the PZ-PT compositional field. In trying to extend work in this field, the investigator encounters a major problem in that ceramics produced by identical procedures are not always of the same quality. Even though similar raw materials and identical sintering procedures are used, the results may vary widely; this indicates that the materials and sintering procedures are not at fault. The problem lies elsewhere. Such experience has led to a close examination of the calcining operation, since the general literature often cites the preparation of the sintering powder as playing a critical role in the process.

The literature on PZ-PT preparations does not emphasize the calcining reaction. In practice, reproducibility is often approached by using identical procedures and raw materials. Calcine temperatures have been used in the range from 800 to 1000°C for from a few minutes to several hours. The belief that all such calcines are essentially complete reactions probably accounts for the lack of attention given to the particulars of calcining. Matsuo and Sasaki[6] described the reactions during calcining of the oxides to form the PZ-PT solid solution. Their data indicated an almost complete reaction if the temperature exceeded 800°C, even for a brief time. Most calcining, if reported at all, is commonly performed above 800°C. In batch calcining, the time employed is usually several hours, while in continuous calcining at 1000°C in a rotary kiln about 15 minutes is sufficient.

On the other hand, Robinson and Joyce[7] showed that about 97 percent of the reactants are converted to PZ-PT at 770°C but that appreciable unreacted raw materials persist even at higher temperatures. Seider[8] concluded that these unreacted raw materials disrupt the sintering process. He further showed that calcines from 900°C to 1100°C produce ceramics of similar densities when fired between 1240°C and 1300°C. Thus, sufficient indication exists to speculate that calcining is indeed an important process step.

In determining the effect of the calcining conditions upon the sintering properties of PZ-PT ceramics, an experimental survey study was first made. The data showed that time in calcining, but more particularly the temperature of calcining, determines the sinterability. Moreover, for certain calcines an unexpected broad firing range was experienced. A more detailed study was then designed, and this paper reports the

*Hereinafter referred to as PZ-PT

findings which relate the calcine parameters of time and temperature to the firing conditions and the ceramic quality.

Procedure

A 20-kilogram batch of the composition $Pb_{0.9897}Nb_{0.0206}(Zr_{0.95}Ti_{0.05})_{0.9794}O_3$ was prepared for this investigation. The raw material oxides used were obtained commercially and were: litharge, 99.99 percent pure; TiO_2 99.89 percent pure; ZrO_2, 99.9 percent pure, micronized; and Nb_2O_5, 99.88 percent pure. A water slurry of the weighed proportions of these oxides was blended for two hours in a ball mill and then pan dried overnight. The dried cake was granulated through a 20-mesh screen to remix any materials which might have segregated in the drying slurry. The whole batch was divided into seventeen 1125-gram portions, and each portion was subjected to a different calcining condition. The range of calcining conditions was chosen to exceed the scope of common practice. The calcining conditions were:

(1) 700°C for 0, 2, and 5-1/2 hours,
(2) 800°C for 1, 2, 4, and 8 hours,
(3) 900°C for 1/2, 1, 2, 4, 8, and 26 hours, and
(4) 1000°C for 1/2, 1, 2, and 8 hours.

In each case a covered 500 cc alumina crucible was loosely filled with one 1125-gram portion and loosely wrapped with a layer of ceramic fiber insulation. Four crucibles were placed into a silicon carbide muffle in an electric kiln. The temperature was raised at a rate of 200°C per hour to the calcine temperature. At the end of each soak period, a crucible was withdrawn from the kiln. A record of weights showed no significant differences within ±0.1 gram/kg in any of the calcines due to this procedure.

The calcines were milled for two hours in half-gallon polyethylene jars containing 800 cc of distilled water and 1900 grams of alumina grinding cylinders. Subsequent particle size analyses using the Whitby centrifuge method[9] indicated that all milled calcines had an average particle size of about 2.5 to 3.0 μm. Furthermore, there was no significant difference in the particle size distributions and none of the distributions were bi-modal.

The dried powders were mixed with a polyvinyl alcohol binder and formed into briquettes by pressing to a given die closure using a weighed amount (60 grams) of powder for each. The pressings were 0.450 x 1.250 x 1.250 inches in dimension, and the bulk densities were 65±2 percent of theoretical. The briquettes were dried and then bisque fired at 625°C for two hours. The bisque densities from all the calcines were 63±2 percent of theoretical.

The specimens were next atmosphere-fired over a range of time-temperature conditions that were broader than the scope of current practice. The firing conditions used were:

(1) 1000°C for 6 hours,
(2) 1050°C for 6 hours,
(3) 1100°C for 1 and 6 hours,
(4) 1200°C for 6 hours,
(5) 1250°C for 0, 3/4, 1 and 6 hours,
(6) 1300°C for 1, 3 and 6 hours, and
(7) 1350°C for 1, 2 and 6-1/2 hours.

The physical arrangement of the specimens and the kiln furniture was kept constant for each firing. The briquettes were dusted with zirconia sand to prevent sticking. A stack of seven briquettes was placed upon a bisqued setter of the same composition and a top setter piece was added to the stack. The stack rested on an alumina base plate. To insure a positive lead oxide atmosphere, loose lead zirconate-lead titanate powder equaling 3 percent by weight of the total ceramic weight was placed on and around the stack. A 500 cc alumina crucible was inverted over the stack and was sealed to the base by tamping a ring of fine zirconia around the closure. A second, 750 cc, alumina crucible was inverted over the assembly, and its closure also was sealed. The primary purpose of the second cover was to equalize heat distribution, but it also acted as a backup seal for the PbO vapor. Three such assemblies were needed in each firing to include at least one briquette from each calcine condition. An electric furnace was heated at 100°C per hour to the control temperature. After the soak time, the furnace was shut down and allowed to cool at its natural rate.

Measurements

Density

The fired specimens were brushed clean of all loose powder. Bulk density data were taken on the entire sintered slug. Freon-TF was used as an immersion medium to obtain slug volume via the displacement method. For specimens with closed porosity, the confidence in density accuracy is ±0.02 gm/cc. Dimensional measurements were made to determine the volume of more porous specimens. The theoretical density of this composition is 7.96 gm/cc.

Electrical Data

Slugs with densities under 7.40 gm/cm^3 were generally electrically conductive; slugs of higher density were further processed for electrical measurements. For this purpose, a 1.5 cm diameter cylindrical core was drilled from the slug's center. From this core slices 0.030 inch thick were cut with a diamond wheel. Silver electrodes were applied by silk screening on a layer of DuPont 7095 silver paste. The electrodes were fired by heating in air to 625°C for one-half hour. Only room temperature electrical data were taken.

Polarization -- An electric field hysteresis loop was run on four specimens from each slug. The slow loop data (25 seconds per cycle) were measured with the aid of a Sawyer Tower circuit[10] which applied 125 volts per mil maximum electric field. The accuracy of the reported measurements is ±2 percent.

Dielectric Constant -- The dielectric constant was derived from capacitance data taken on the poled discs at 1000 Hz using a General Radio Model 1673 capacitance bridge.

Pressure Induced Depolarization -- This composition is nearly antiferroelectric. The smaller cell volume of the antiferroelectric phase can be induced by hydrostatic pressure.[11] The pressure at which the maximum rate of depoling is observed under short circuit conditions is taken as the hydrostatic depoling pressure for a particular specimen. This pressure is generally quite sensitive to small changes in additives, stoichiometry, and maturity of the ceramic. Hydrostatic depoling pressure was measured by subjecting the specimens to pressure and plotting pressure versus charge release on an X-Y recorder. The pressure increase was governed at a rate of 4 kpsi/sec. Confidence in the measurement is to within 2000 psi.

Grain Size -- Grain size determinations were made using the line intercept method. The number of grains intersecting a straight line on a photomicrograph of known magnification was divided into the line length expressed in micrometers. No corrective factors were applied to this number, which is rounded to the nearest micrometer in Table I. Both optical microscopy and scanning electron photomicrographs were used. The data in Table I are primarily from scanning electron beam fractographs at a magnification of 300 to 1000 diameters.

TABLE I

Average Grain Size of Specimens, from Some Different Calcines, Fired at Various Sintering Conditions

Calcining		Firing		Average
Temperature (°C)	Time (Hours)	Temperature (°C)	Time (Hours)	Grain Diameter (Microns)
1000	2	1050	6	2
1000	2	1100	6	3
1000	2	1200	6	5
1000	2	1250	6	[illegible]
1000	2	1300	6	7
1000	2	1350	6-1/2	6
700	2	1200	6	5
800	2	1200	6	6
900	2	1200	6	6
800	4	1050	6	3
900	26	1200	1/3	4

Discussion of Results

Density alone is not a complete measure of the quality of a ferroelectric ceramic. Nevertheless, there is a correspondence between high density and high values of dielectric constant, remanent polarization, etc. Bulk density data are tabulated in Table II for each calcine condition. Also, remanent polarization (P_r), dielectric constant (K), and hydrostatic switching pressure (P_H) are reported. The table shows that at densities ≥ 7.60 gm/cm^3, the vast majority of the values of P_r (32 to 35 μC/cm^2), K (230 to 260), and P_H (50 to 55 kpsi) conform to a relatively narrow (±5 percent) variation in value. However, the variation in measured densities within the same groups of data is much smaller, about ±0.5 percent, therefore, density was chosen as the better parameter to graph in the figures presented to evaluate the processing parameters regarding the quality of the final ceramic.

Figure 1 depicts the general trend found throughout the data, i.e., if the calcine temperature is high enough, the length of the calcine soak does not affect the end point density. Thus, calcine time is of relative unimportance compared with the calcine temperature. With respect to calcine time, an independent observation was made in which a suitable calcination was achieved at 1000°C with material passing through a rotating tube with only 12 minutes in the hot zone of the tube. Thus, the necessary reactions were completed in a very short time. On the other hand, a 26-hour crucible calcine at 900°C was not at all deleterious, as noted in Table II. Figure 1 also illustrates the general trend that end point density very much depends upon the calcine temperature.

Figures 2 and 3 show that low temperature calcines come to a lower end point density regardless of firing time or temperature. Figure 4 depicts the relatively low end point density (7.45 gm/cm^3) achieved by an undercalcined material (800°C for 2 hours) and a marked increase in end point density (7.70 gm/cm^3) due to thorough calcination (900°C for 8 hours) To determine whether an undercalcined material could be activated, a material which had been undercalcined (700°C for 5.5 hours) was recalcined (925°C for 8 hours). The recalcined material and a material which had been originally thoroughly calcined (900°C for 8 hours) were both sintered at 1225°C for six hours. The density of the recalcined slug was 7.43 gm/cm^3. This was an improvement over the 7.16 gm/cc density achieved by the undercalcined material in a similar firing, but is notably lower than the 7.70 gm/cc density which was achieved by the material that had been calcined once at 900°C.

In sintering one sees that a well calcined material can achieve a high density ($\geq$ 95 percent of theoretical) in a very short period of time. Figure 4 shows that at zero soak time the density of a material which had been calcined at 900°C for 8 hours reached end point density during the time the furnace was heating at 100°C per hour to the control temperature. To minimize the effect of the heat-up time, a specimen of the material calcined at 900°C for 26 hours was inserted into a hot kiln for 20 minutes at 1200°C, during which time the actual soak could not have exceeded 15 minutes. The density attained was 7.69 gm/cc. Likewise, a density of 7.35 gm/cc was achieved when a similar specimen was rapidly heated to 1100°C for a similar period. Thus, the firing time is of little importance compared with the temperature. The most outstanding feature regarding the effect of firing temperature is the low sensitivity of a thoroughly calcined material to a broad range of firing conditions.

TABLE II

Data Measured on Specimens from the Various Calcining and Firing Conditions

Calcine Time (hrs)	Firing Temp (°C)	Firing Time (hrs)	Calcine Temperature												
			700°C	800°C				900°C				1000°C			
			ρ	ρ	P_r	K	P_H	ρ	P_r	K	P_H	ρ	P_r	K	P_H
0 hours	1200	6.0	6.14												
	1250	0	6.05												
	1250	6.0	6.32												
	1300	6.0	6.07												
	1350	1.0	6.41												
	1350	2.0	6.54												
	1350	6.5	6.67												
.5 hours	1000	6.0						6.02							
	1050	6.0						7.63				7.53			
	1100	6.0								254		7.52	31.3	260	52.5
	1200	6.0						7.66	32.7	244	52.0	7.72	34.5	248	55.5
	1250	0						7.68	32.0	260	51.5	7.69	34.4	260	55.3
	1250	0.75						7.63				7.70			
	1250	1.0						7.65	32.2	247	52.5	7.71	34.0	253	55.5
	1250	6.0						7.65	33.6	253	52.5	7.68	33.2	250	54.2
	1300	1.0						7.67	33.2	249	54.0	7.69	34.2	256	55.3
	1300	3.0						7.65	32.9	247	53.2	7.66	32.9	248	53.5
	1300	6.0						7.61	33.1	254	52.0	7.64	33.4	246	53.0
	1350	1.0						7.59	30.7	231	45.4	7.73	34.5	262	53.0
	1350	2.0						7.65	33.2	258	51.5	7.66	34.0	255	51.2
	1350	6.5						7.63	30.5	220	49.7	7.69	33.9	244	52.4
1 hour	1000	6.0										6.08			
	1050	6.0		6.93								7.08			
	1100	6.0		7.07				7.64	29.5		54.5				
	1200	6.0		7.15	28.0	247	51.5	7.69	33.0	247	52.6	7.69	34.4	248	54.5
	1250	0		7.07				7.70	32.7	257	53.7	7.67	33.6	260	55.0
	1250	0.75		7.04				7.66				7.69			
	1250	1.0		7.07				7.68	33.4	245	54.0	7.67	33.4	245	54.5
	1250	6.0		7.18				7.66	32.8	245	53.0	7.67	34.1	245	54.2
	1300	1.0		7.09				7.70	32.4	249	53.4	7.67	33.2	247	54.4
	1300	3.0		7.15				7.68	33.1	253	53.6	7.66	33.0	244	53.8
	1300	6.0		7.09				7.64	33.9	257	54.0	7.64	33.5	251	53.9
	1350	1.0		7.17	29.3	228	49.4	7.65	32.6	251	49.3	7.67	33.6	246	51.5
	1350	2.0		7.20				7.66	33.7	245	52.0	7.65	32.8	236	50.2
	1350	6.5		7.22				7.66	32.0	225	50.7	7.66	33.5	238	51.9
2 hours	1000	6.0													
	1050	6.0		5.96											
	1100	1.0		7.35				7.65				7.49			
	1100	6.0						7.55	30.6	292	49.0	7.59	31.5	270	53.8
	1200	6.0	6.46	7.44	31.3	242	51.0	7.69	33.7	248	54.0	7.70	34.7	252	54.5
	1250	0	6.44	7.39	31.1	243	51.0	7.70	34.0	260	54.8	7.68	34.0	263	54.7
	1250	0.75	6.35	7.42				7.66				7.69			
	1250	1.0	6.43	7.45	32.0	254	50.0	7.67	33.3	240	54.4	7.71	34.1	251	55.6
	1250	6.0	6.70	7.46	33.3	256	51.0	7.66	33.5	246	53.6	7.69	34.4	249	53.6
	1300	1.0		7.45				7.70	33.1	249	54.0	7.70	33.9	256	56.0
	1300	3.0	6.59	7.45	32.1	239	49.4	7.65	33.3	251	53.5	7.67	33.5	246	53.8
	1300	6.0	6.64	7.45	29.9	234	52.4	7.65	32.9	247	53.0	7.65	33.4	250	54.0
	1350	1.0	6.66	7.47	31.9	232	47.8	7.67	33.9	247	50.6	7.71	34.0	259	51.9
	1350	2.0	6.80	7.47	31.6	251	48.0	7.61	32.5	236	50.4	7.68	34.0	247	53.6
	1350	6.5	6.92	7.46	31.7	237	48.0	7.63	32.0	228	50.6	7.69	33.6	240	50.6

TABLE II (cont)

Data Measured on Specimens from the Various Calcining and Firing Conditions

Calcine Time (hrs)	Firing Temp (°C)	Firing Time (hrs)	Calcine Temperature												
			700°C	800°C				900°C				1000°C			
			ρ	ρ	P_r	K	P_H	ρ	P_r	K	P_H	ρ	P_r	K	P_H
4 hours	1000	6.0													
	1050	6.0		7.30				7.66							
	1100	6.0		7.27	27.5	244	52.0	7.72	33.5	267	53.2				
	1200	6.0		7.31	31.2	242	50.0	7.71	34.2	241	54.8				
	1250	0		7.50	32.0	244	51.5	7.73	34.3	255	55.0				
	1250	0.75		7.51				7.70							
	1250	1.0		7.52	31.6	233	50.0	7.69	33.5	253	54.4				
	1250	6.0		7.53	32.5	251	50.5	7.70	34.9	264	54.5				
	1300	1.0		7.54	31.4	231	54.6	7.68	32.5	243	53.6				
	1300	3.0		7.51	31.0	234	50.0	7.67	32.9	248	52.7				
	1300	6.0		7.47		246		7.59		254					
	1350	1.0		7.45	33.8	220	48.2	7.70	34.9	251	52.6				
	1350	2.0		7.52	32.0	246	50.0	7.64	32.8	249	51.0				
	1350	6.5		7.50	30.4	234	48.5	7.67	33.4	237	53.0				
5.5 hours	1200	6.0	7.17												
	1250	0	7.04												
	1250	0.75	7.02												
	1250	1.0	7.06												
	1250	6.0	7.16												
	1300	1.0	7.09												
	1300	3.0	7.12												
	1300	6.0	7.13												
	1350	6.5	7.20												
8 hours	1000	6.0		6.0				6.02				5.88			
	1050	6.0		6.65				7.72				7.17			
	1100	6.0													
	1200	6.0		7.57	32.7	250	52.5	7.74	34.4	247	52.6	7.74	35.5	249	56.2
	1250	0		7.54	31.9	253	51.5	7.74	35.3	263	56.6	7.75	34.7	256	55.8
	1250	0.75		7.52				7.68				7.71			
	1250	1.0		7.58	32.6	255	53.0	7.70	33.7	244	54.5	7.73	34.2	256	56.0
	1250	6.0		7.56	32.7	242	51.6	7.68	34.5	251	53.8	7.70	34.5	240	54.8
	1300	1.0		7.57		252		7.68	34.0	241	53.8	7.72	33.8	247	56.0
	1300	3.0		7.55	31.7	247	51.2	7.67	33.6	241	53.5	7.69	34.3	240	54.0
	1300	6.0		7.54	31.5	242	49.7	7.67	34.1	249	53.4	7.68	34.0	256	54.0
	1350	1.0		7.49	29.5	227	49.7	7.63		253		7.70	31.6	265	52.8
	1350	2.0		7.53	30.8	243	49.0	7.65	33.3	234	50.6	7.69	34.0	247	52.6
	1350	6.5		7.50	29.2	225	49.8	7.67	32.4	217	50.9	7.71	34.3	252	52.0
26 hours	1050	6.0						6.95							
	1100	0.25*						7.35	30.0						
	1100	6.0						7.71	33.4	265	53.2				
	1200	0.33*						7.69	31.5						
	1200	6.0						7.74	34.5	258	54.5				
	1250	0						7.72	33.9	268	55.2				
	1250	0.75						7.72							
	1250	1.0						7.74	34.5	251	56.2				
	1250	6.0						7.69	34.7	259	53.5				
	1300	1.0						7.69	31.9	249	54.3				
	1300	3.0						7.69	34.5	249	54.4				
	1300	6.0						7.68	34.3	252	54.0				
	1350	1.0						7.73	34.2	250	51.9				
	1350	2.0						7.69	34.2	249	52.0				
	1350	6.5						7.70	33.2	233	52.9				

* Nearly instant heating to temperature

ρ - density gm/cm^3
P_r - remanent polarization $\mu C/cm^2$

K - dielectric constant
P_H - hydrostatic depoling pressure Kpsi

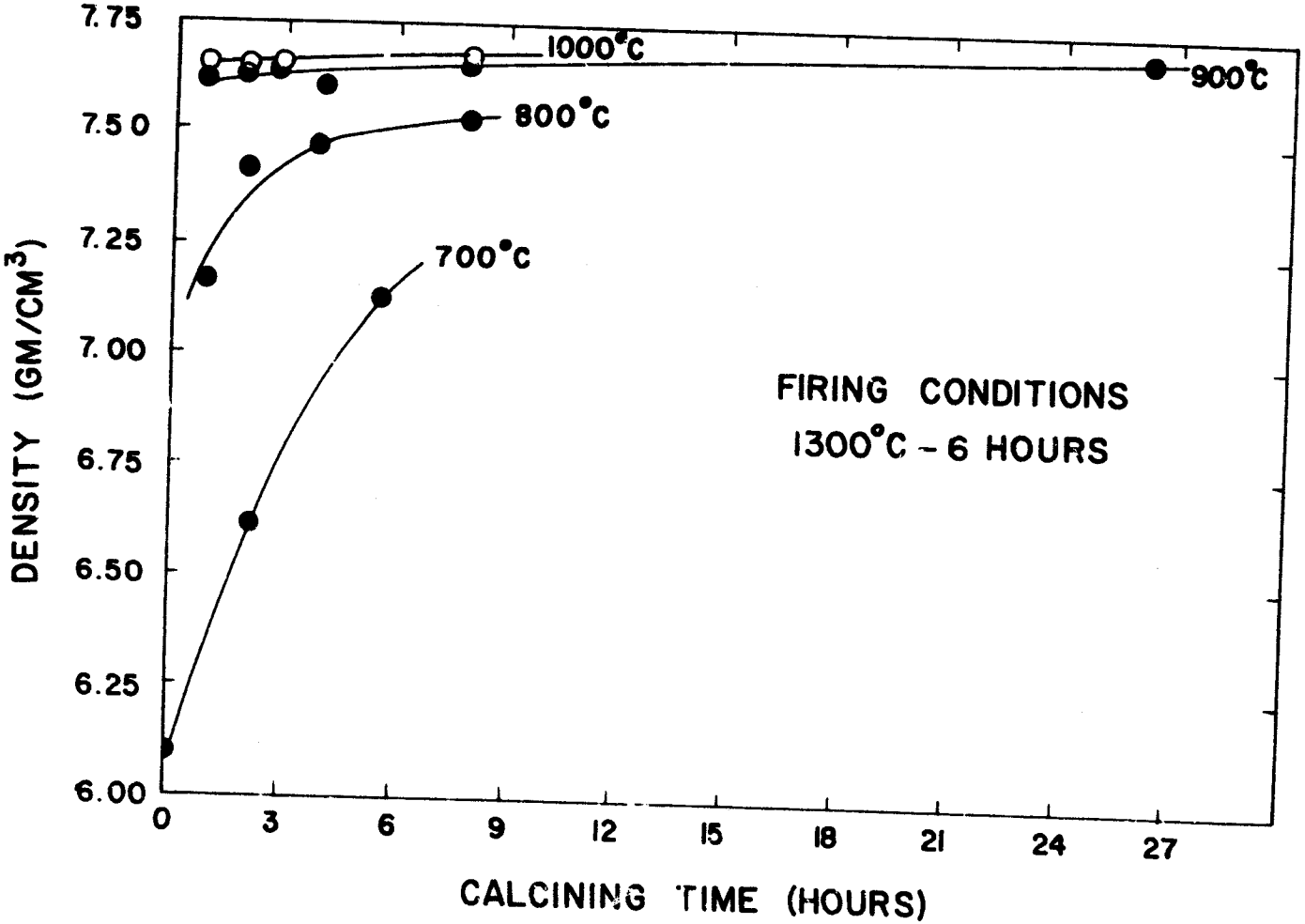

Figure 1. Density vs calcining time for various calcining temperatures

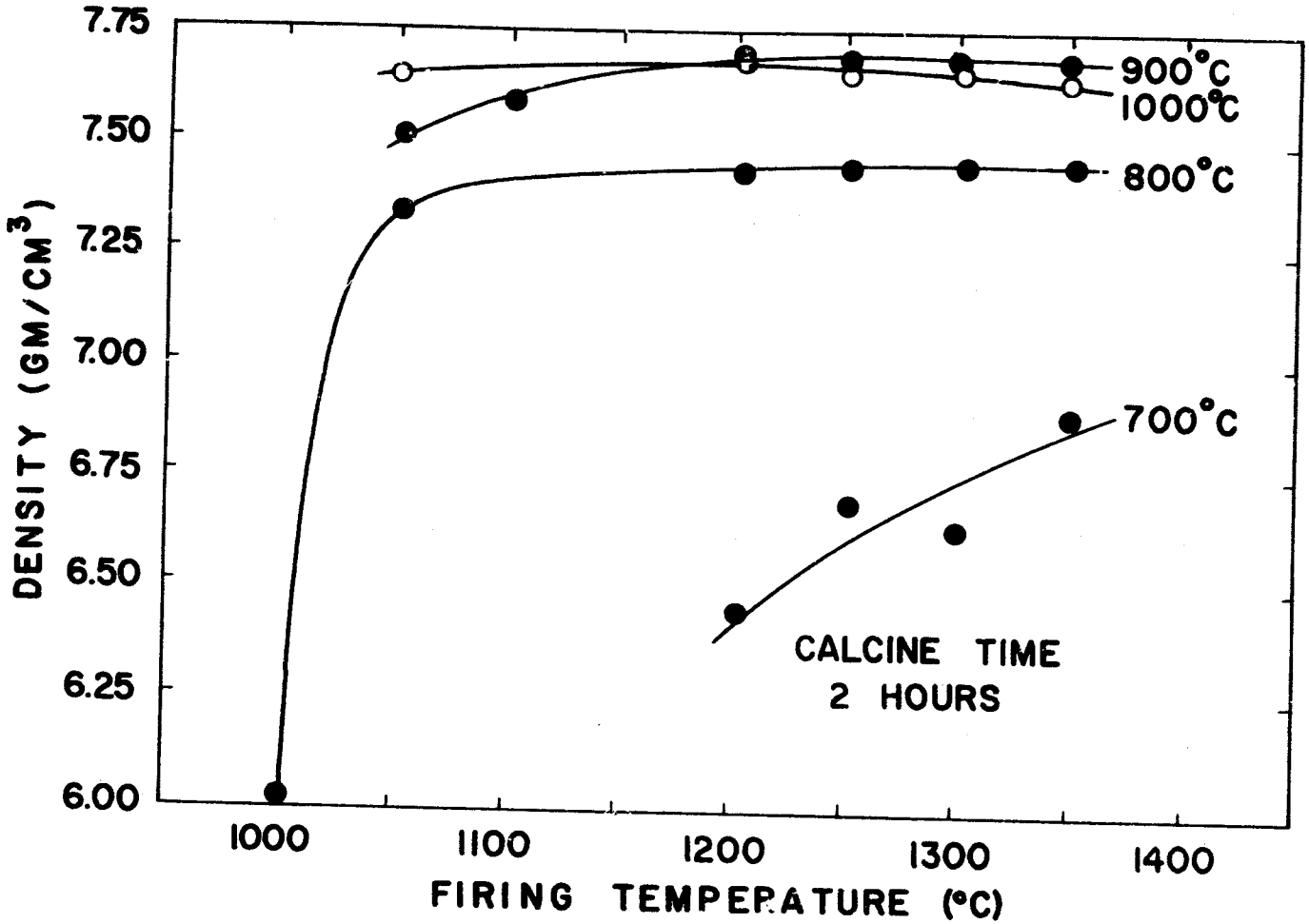

Figure 2. Density vs firing temperature for 6-hour firing soak time at various calcine temperatures

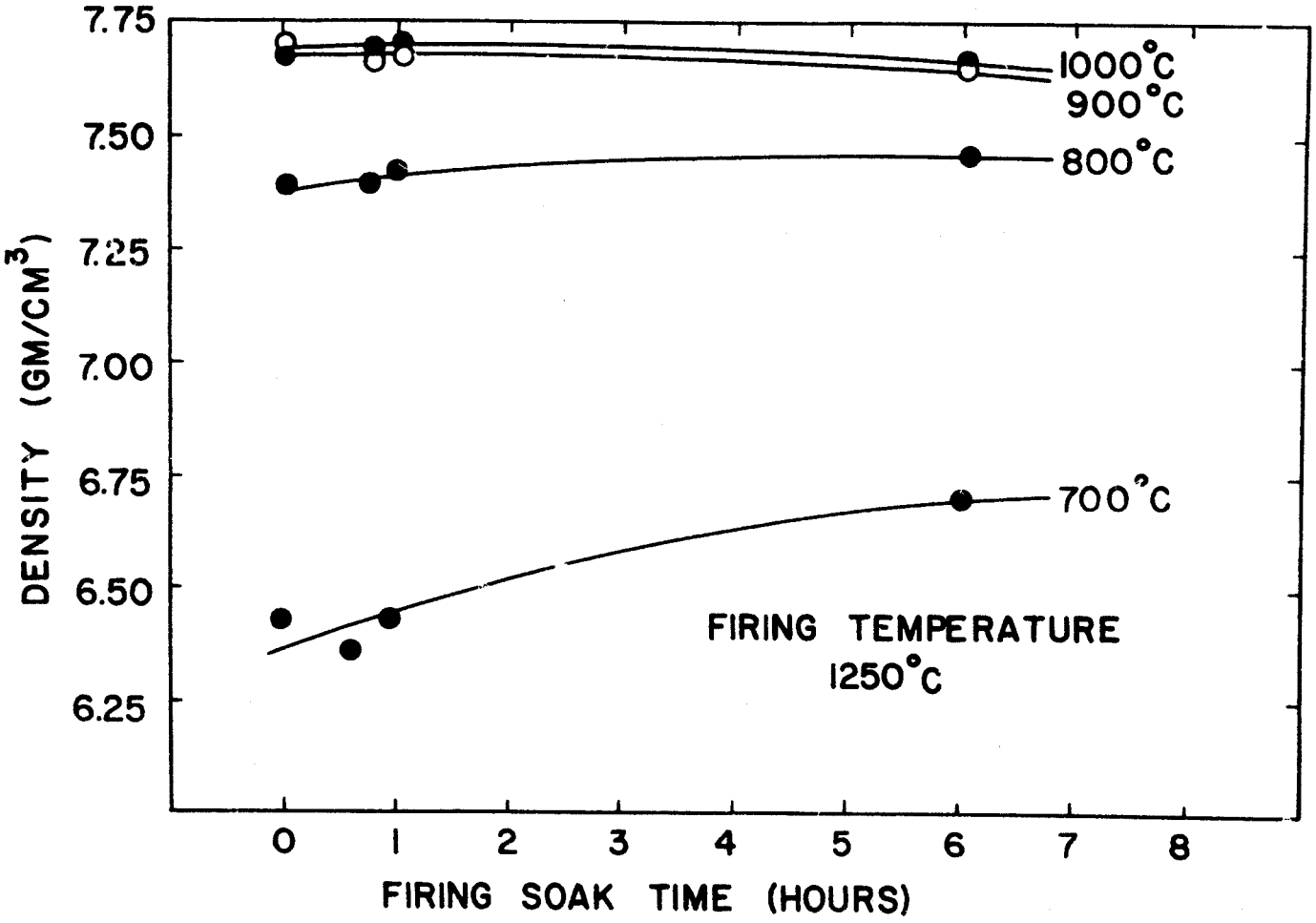

Figure 3. Density vs. firing soak time for various 2-hour calcine temperatures

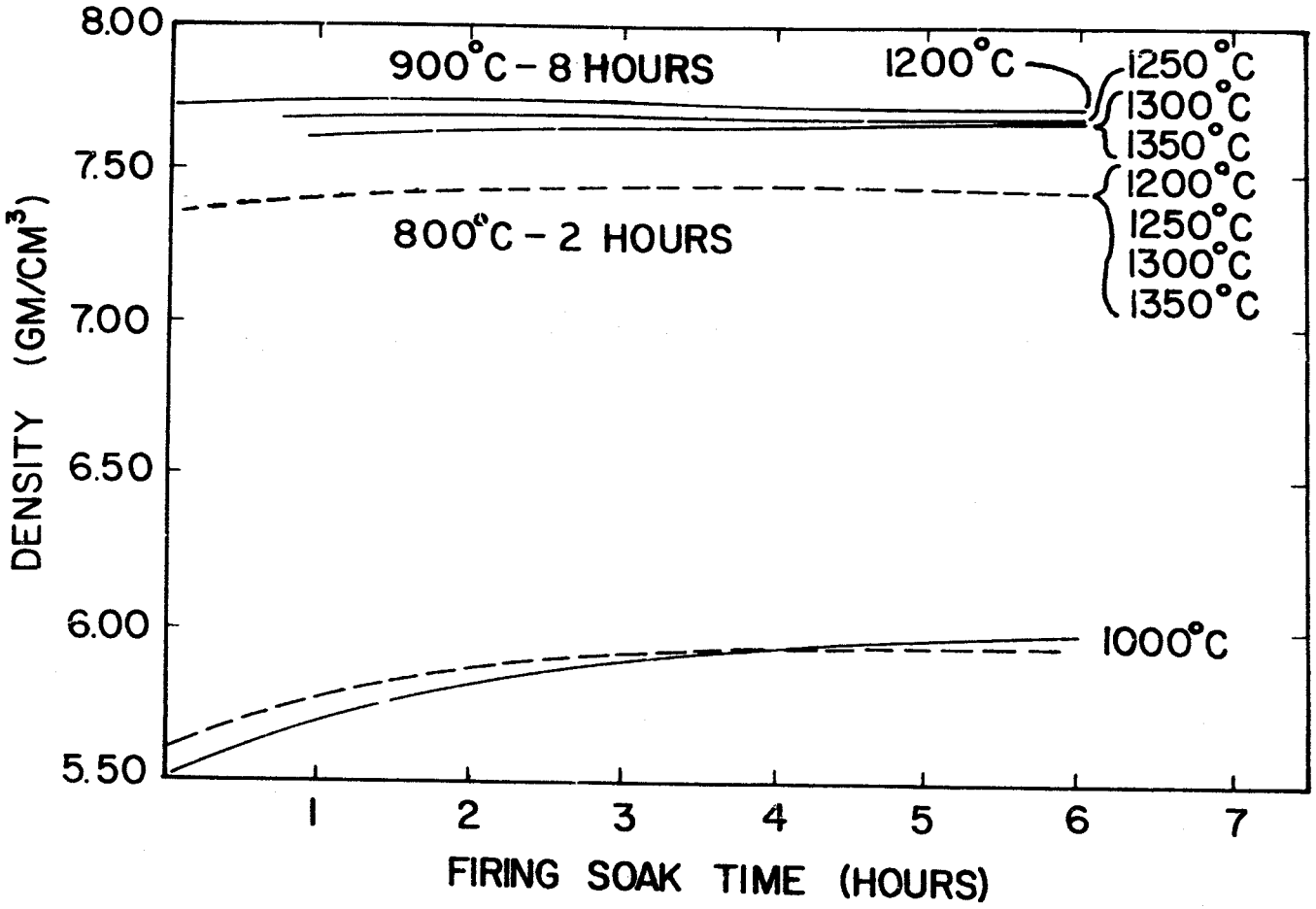

Figure 4. Density vs firing soak time at various firing temperatures for two calcines

An examination of microstructures using the scanning electron microscope indicated that the grain size was principally controlled by the firing temperature. As shown in Table I specimens fired at 1200, 1250, 1300, and 1350°C all had grains of similar size about 6 μm in diameter. Similar grain growth occurred for samples fired for long periods, viz 6 hours, as well as for the specimen which, as described above, was rapidly heated to 1200°C and held only 20 minutes in the furnace. It was also noted that those specimens which were calcined at low temperatures and therefore did not densify to a very high degree also had grains of about 6 μm. On the other hand the specimens examined which were fired at 1050 and 1100°C had smaller grains, from 2 to 3 μm in diameter. Typical photomicrographs are shown in Appendix A.

In an effort to relate the independent variables of calcine time and temperature to firing time and temperature and to determine their combined effects upon density, Figures 5, 6, and 7 were constructed on a three-coordinate grid. Figures 5 and 6 show surfaces of density versus calcine time at various firing temperatures for an 800°C and a 900°C calcine, respectively. The more thoroughly calcined material at 900°C achieves a higher end point density (about 7.70 gm/cc) than does the material calcined at 800°C (about 7.50 gm/cc). Figures 5 and 6 show that the very broad firing range from 1200°C to at least 1350°C produces essentially the same end point density nearly independent of the calcining time employed for each calcine temperature.

The foregoing discussions relegate time to a secondary role. Figure 7 shows how the density varies as a function of only the combined independent variables of calcining temperature and firing temperature. This density surface has a relatively flat plateau for the higher calcining and firing conditions, viz between 900° and 1000°C calcining temperature and between 1200°C and 1350°C firing temperature. As the combination of these thermal conditions moves away from the plateau, the density, and with it the other qualities, is shown to slope more or less steeply toward lower values. The steeper the slope of the surface the more sensitive must be the relationship of ceramic quality to the thermal processing parameters.

The density surface is shown terminated at the 1350°C firing temperature line and the 1000°C calcine temperature line. Subsequent data using a similar batch of material have shown that calcines at 1100°C were very poor, yielding fired densities ≤ 7.0 gm/cm^3, indicating the surface should be expected to slope toward lower density somewhere between 1000°C and 1100°C. Data (not presented herein) from other batches also show that the surface will slope toward a lower density at sintering temperatures above 1350°C. Since there is no known indication of improved quality at higher temperature, there is no inducement to make a practice of operating furnaces any higher than necessary.

It must be pointed out that the data apply to a particular batch. It is known that raw materials also play a role in setting the character of a PZ-PT material. Consequently, three batches were made using three different zirconias. One zirconia was coarse (average particle size about 3.5 μm), while the other two were micronized (average particle size about 1.8 μm), but were of different lots from the same manufacturer. Figures 8 and 9 show the differences in firing behavior between calcines heated at 800°C and 900°C for two and four hours, respectively. The more thoroughly calcined materials, i.e., those made from fine zirconias calcined at 900°C, produced the highest density ceramics with little change related to the duration of the calcining. In the cases of the incompletely calcined materials, i.e., those calcined at 800°C and including the product made from the coarser zirconia calcined at 900°C, it is noted that the duration of calcining produced a significant effect upon their sinterabilities.

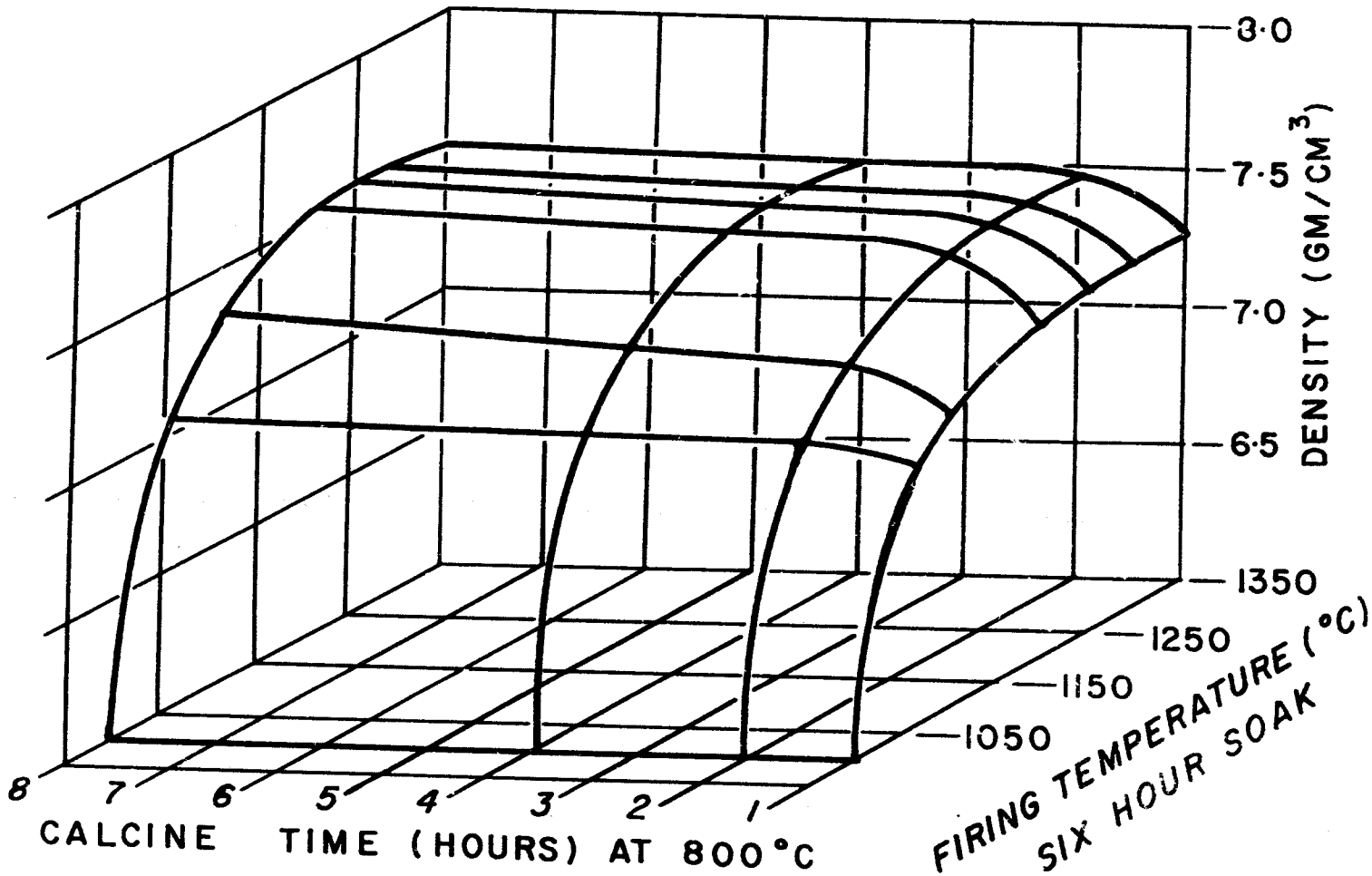

Figure 5. Density vs firing temperature and calcine time

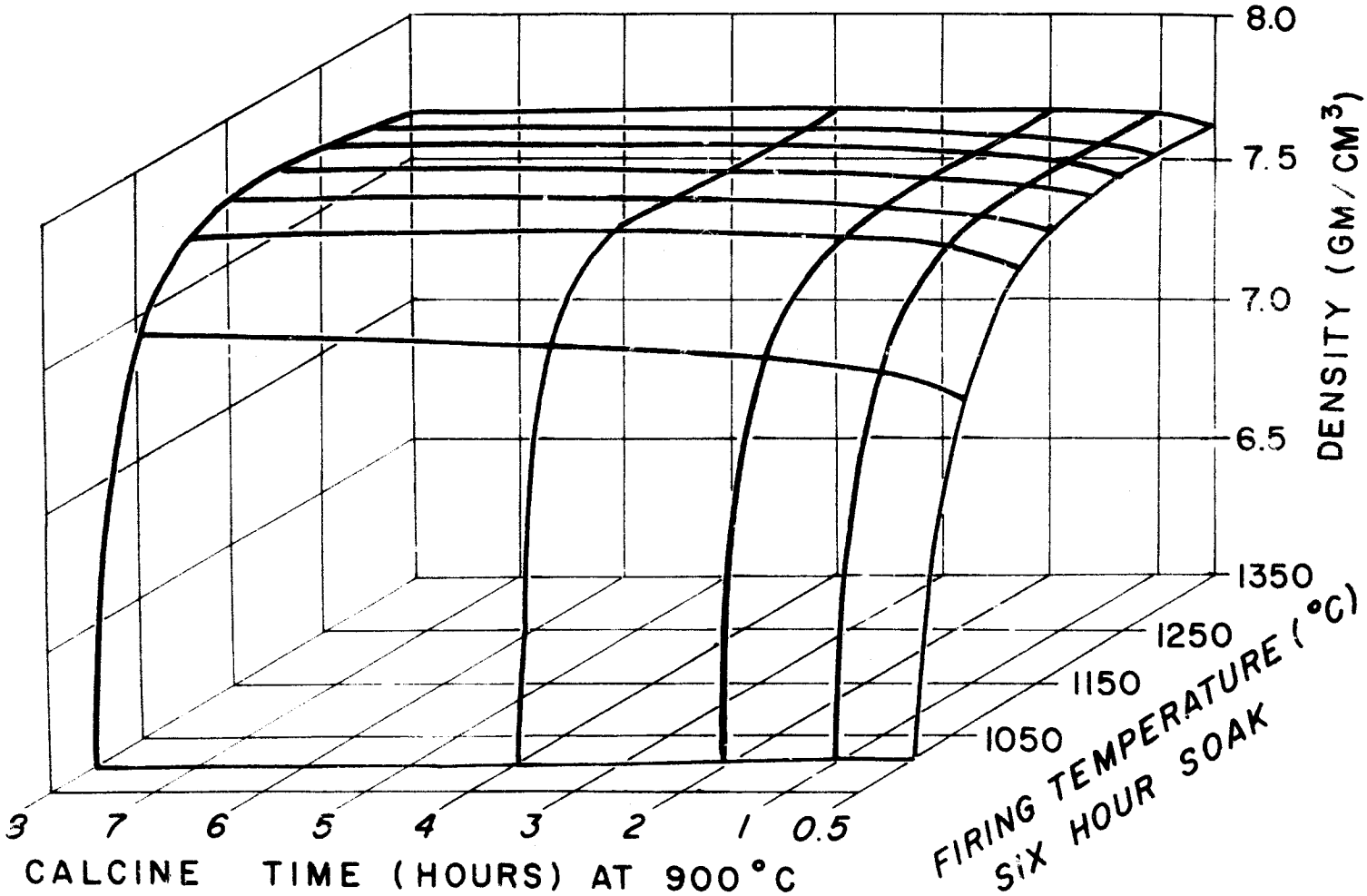

Figure 5. Density vs firing temperature and calcine time

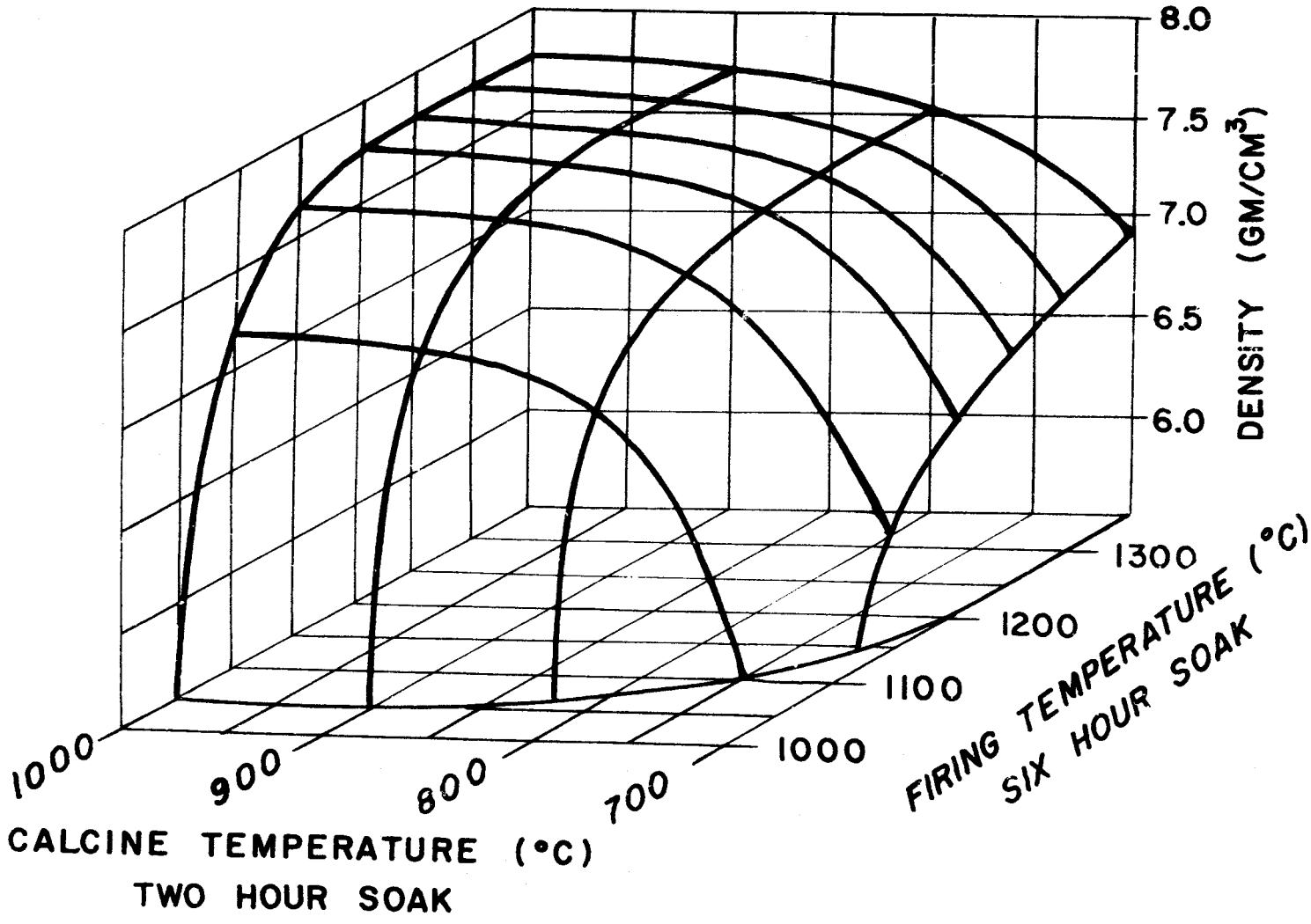

Figure 7. Density vs firing and calcining temperatures

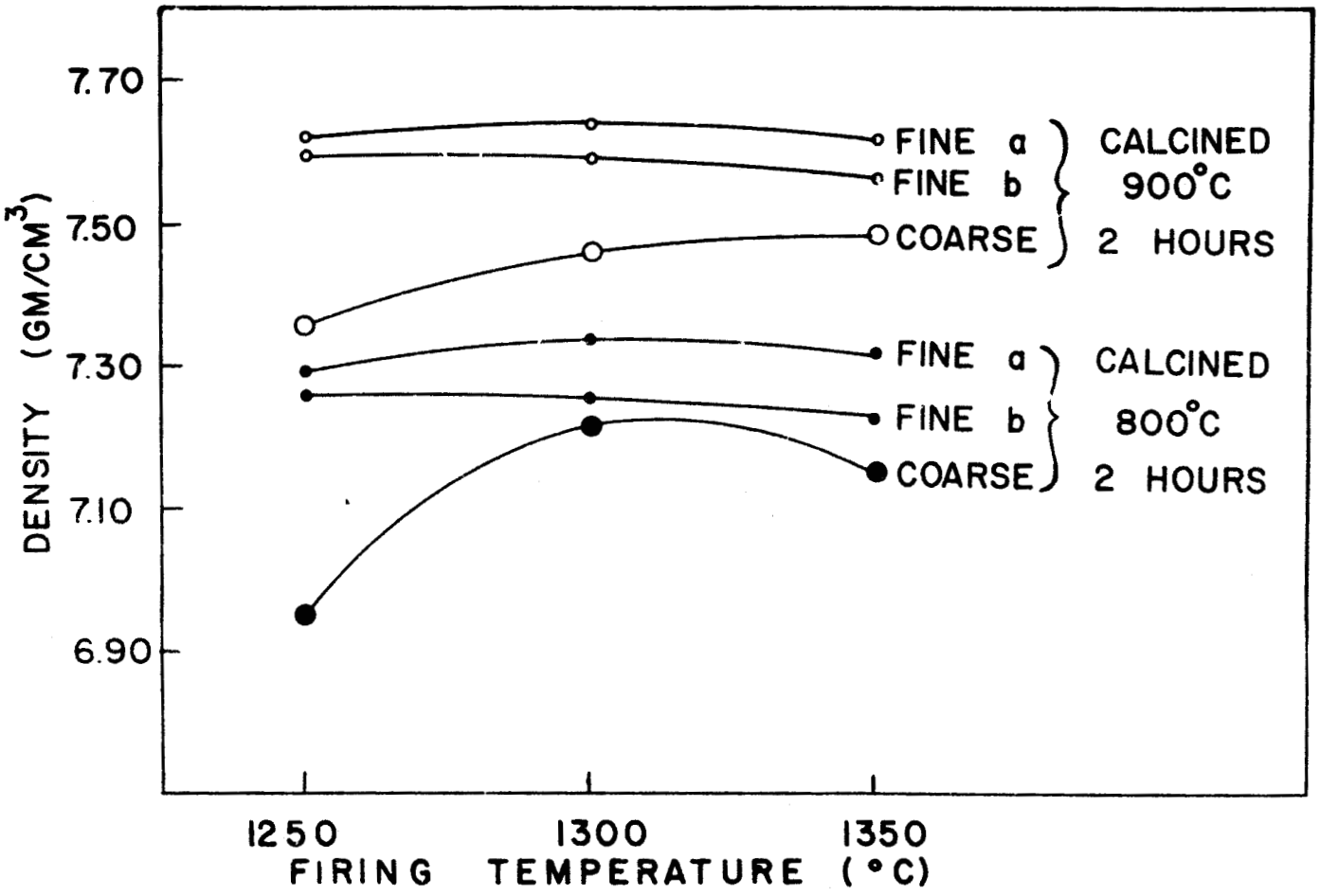

Figure 8. Density vs. firing temperature for 3 batches made from 3 different zirconias

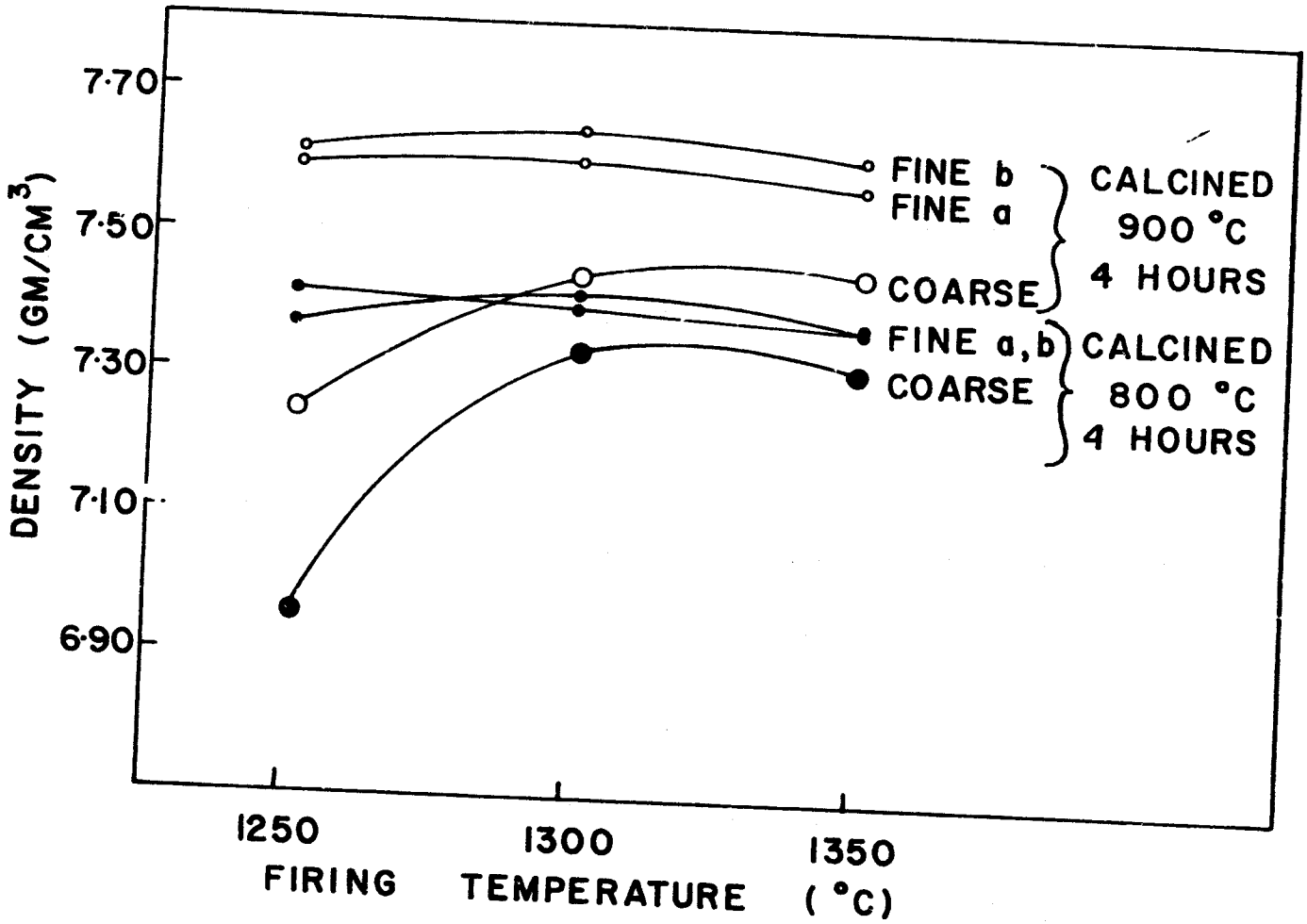

Figure 9. Density vs firing temperature for 3 batches made from 3 different zirconias

Summary and Conclusions

It is demonstrated that the choice of raw materials will in part govern the PZ-PT response to calcining treatment. Given a set of raw materials, one can readily establish a calcining condition such that an optimum final ceramic density can be attained. The final sintered density will be determined in the main by the temperature of calcining.

The optimum calcining temperature can be expected to lie within a broad temperature range near 900°C, perhaps ranging as high as 1000°C. The time required for the calcining is a secondary consideration, although the thermal mass and the particle size and/or reactivity of the constituents can be a major influence with respect to calcine soak time. Probably the time at temperature for calcining will depend in part upon the mass of material being calcined, especially if batch calcining is used. It is not known just how to translate the data presented for 1125-gram quantities to accomplish the same uniform thermal treatment in larger amounts. There is no known measurement for the calcined powder alone which will reveal whether the calcine is optimized. The method used is simply to process a sample and determine its final properties.

In final firing, the grain size of the ceramic is dependent upon the temperature. Time is again of secondary importance because events take place very rapidly. In any practical situation seeking to complete the densification of an optimum calcine, time is not a limiting consideration. The sintering temperature range is very broad, and equivalent ceramic quality has been demonstrated for sintering temperatures from as low as 1200°C to as high as 1350°C.

It is concluded that it is important to establish the correct calcining conditions. The practice of controlling final density by proper selection of the calcine conditions is a more positive method than is the method of adjusting the sintering conditions. A varying response to changing sintering conditions indicates that the calcine is incomplete and the material's sinterability corresponds to a more or less steep part of a reactivity surface, like that of Figure 7. Thus, every other factor involved in processing the final ceramic will have an accentuated effect upon the final outcome, and pronounced variations in final product quality can be expected.

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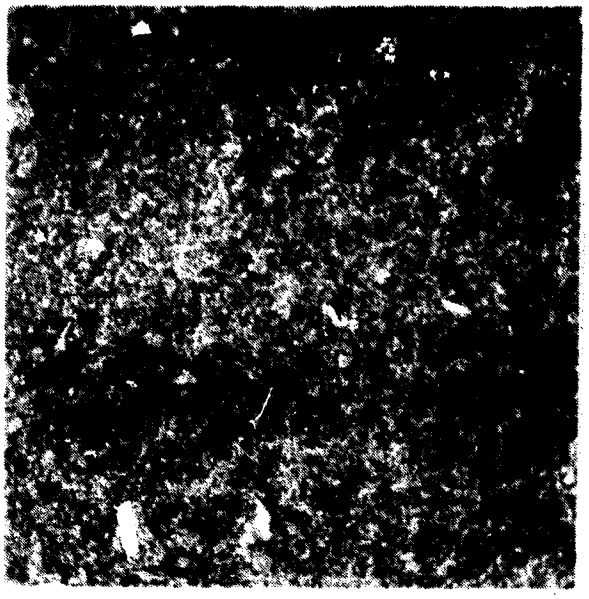
APPENDIX A

TYPICAL PHOTOMICROGRAPHS



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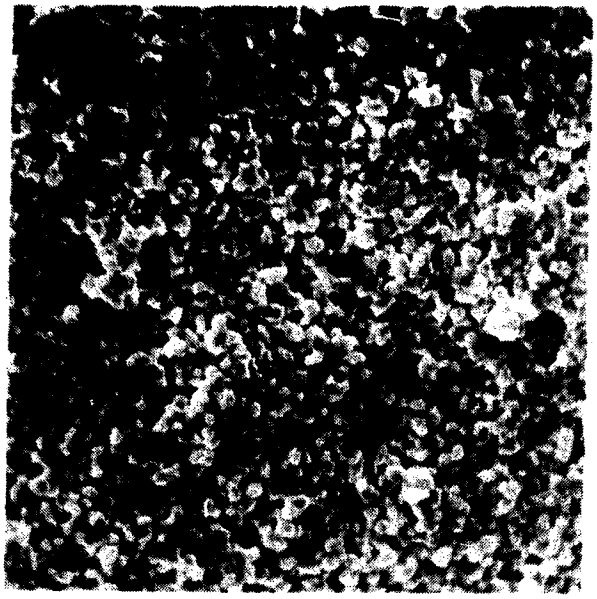

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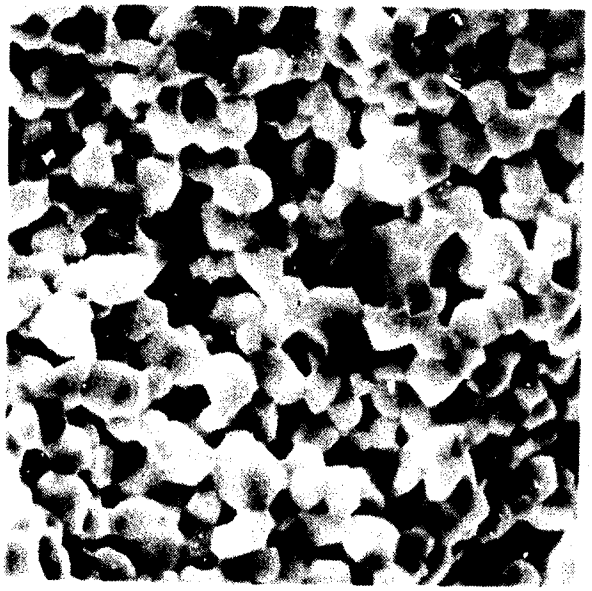

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Density : 7.49

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Firing : 1050/6
Density : 7.49

Magnification: 300
Calcine : 800/4
Firing : 1050/6
Density : 7.30

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Density : 7.30

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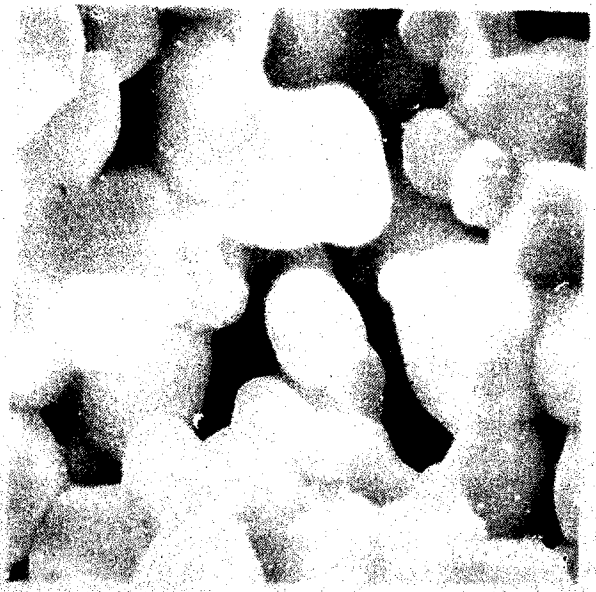
Density : 7.30



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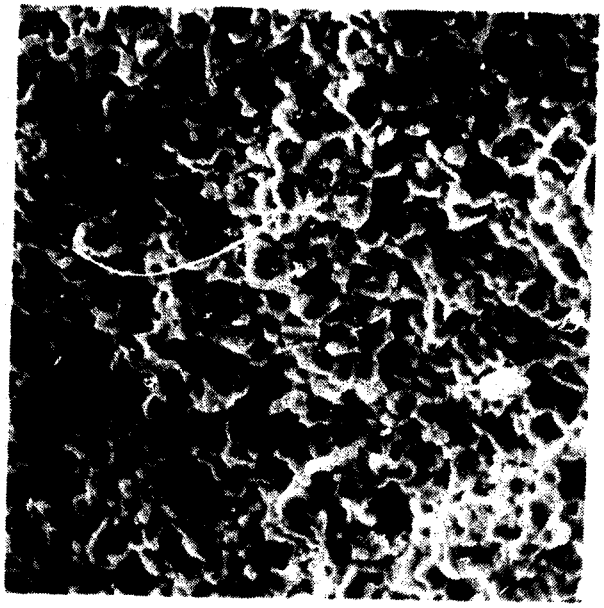

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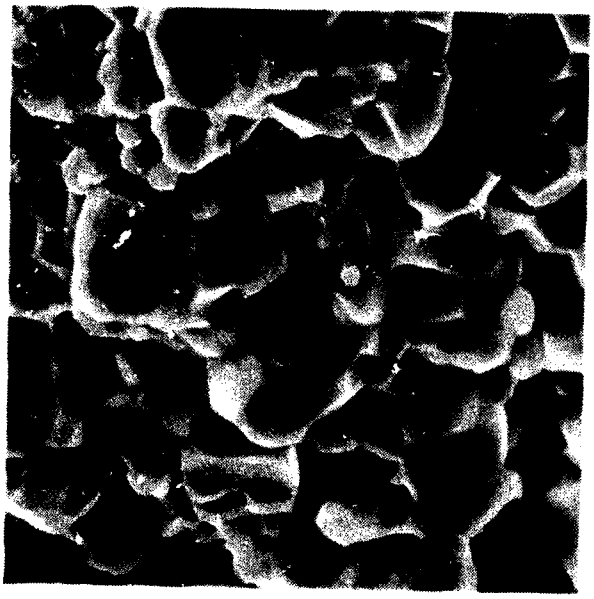

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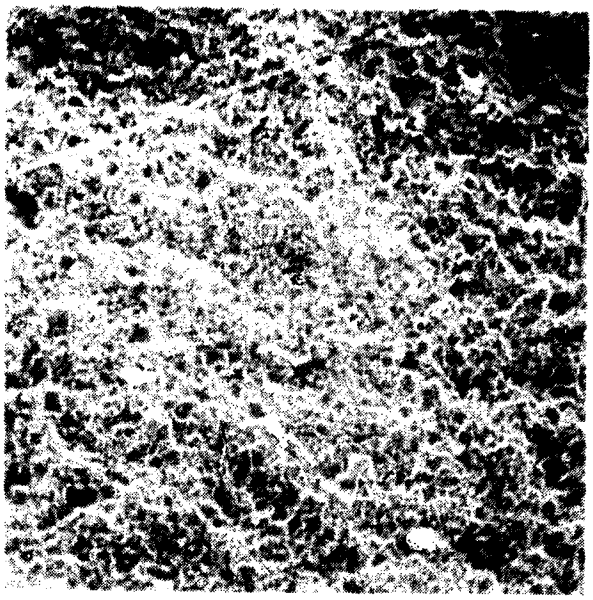

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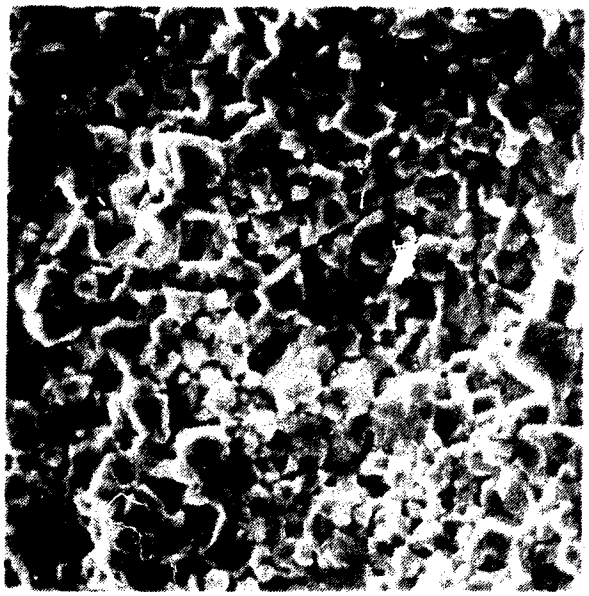

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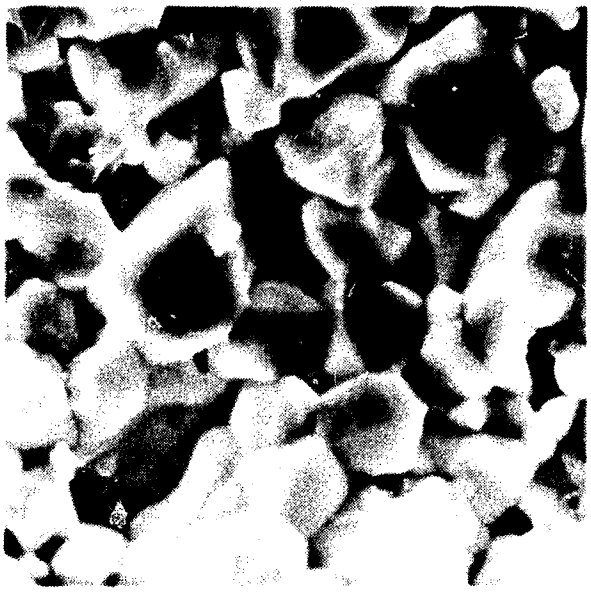

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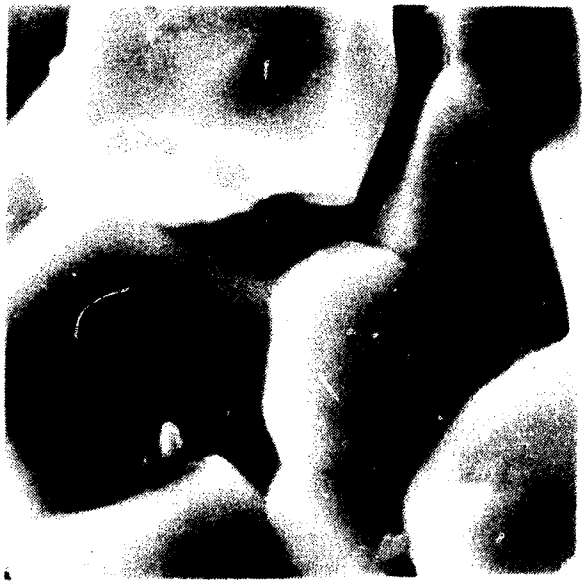

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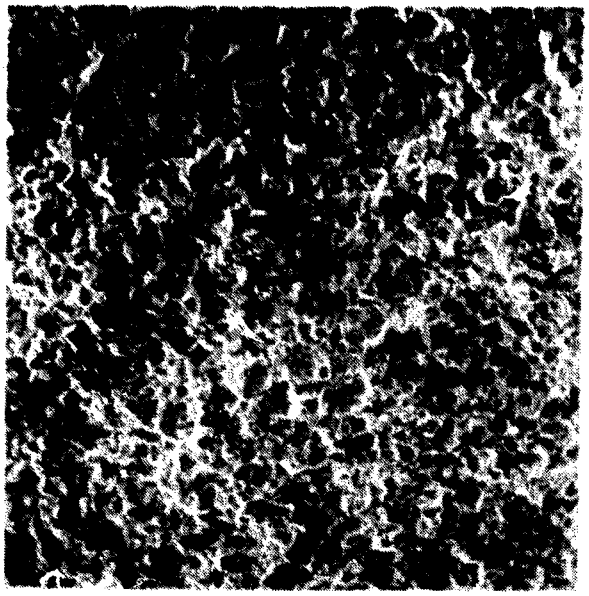

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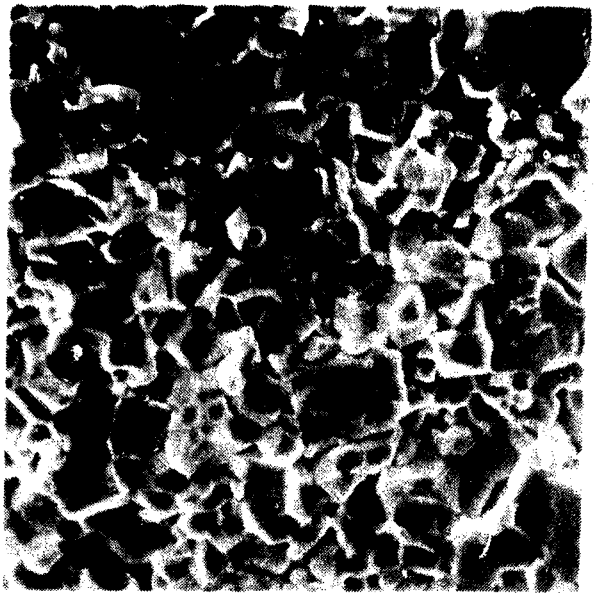

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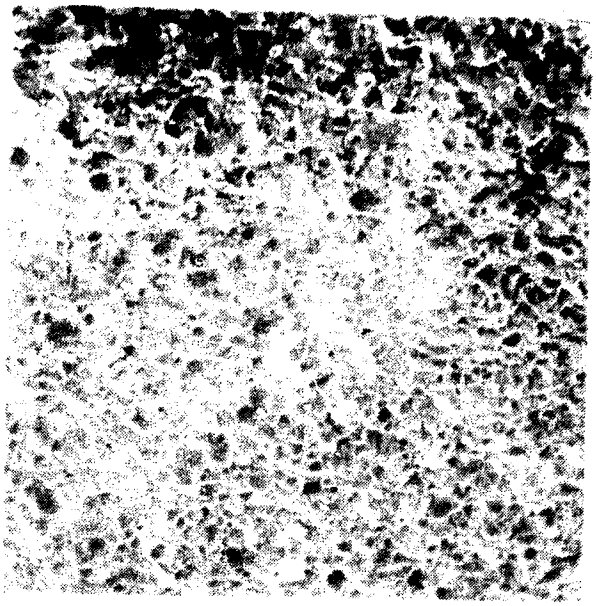

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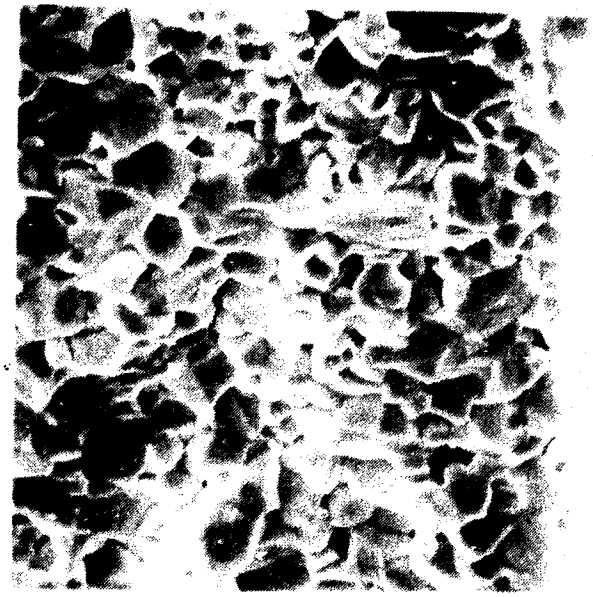

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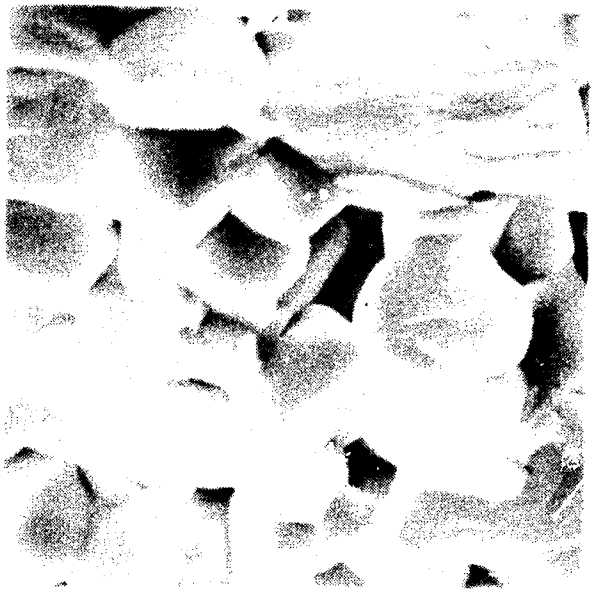

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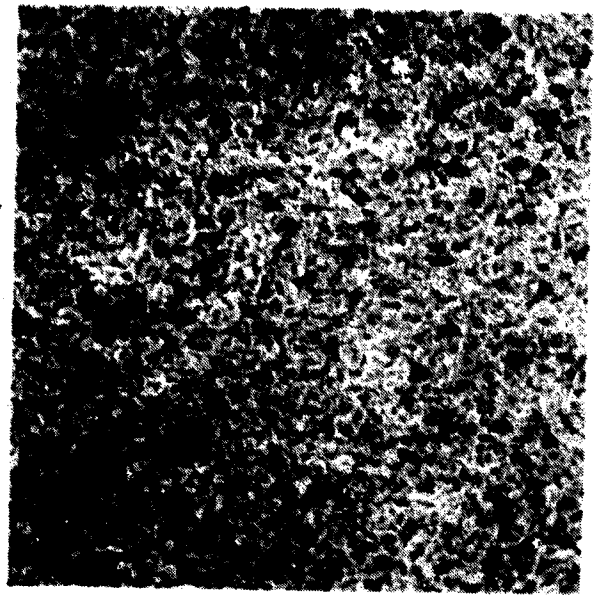

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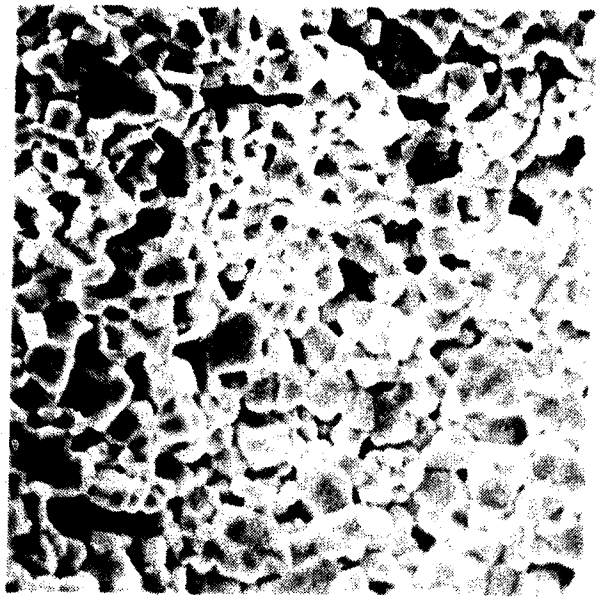

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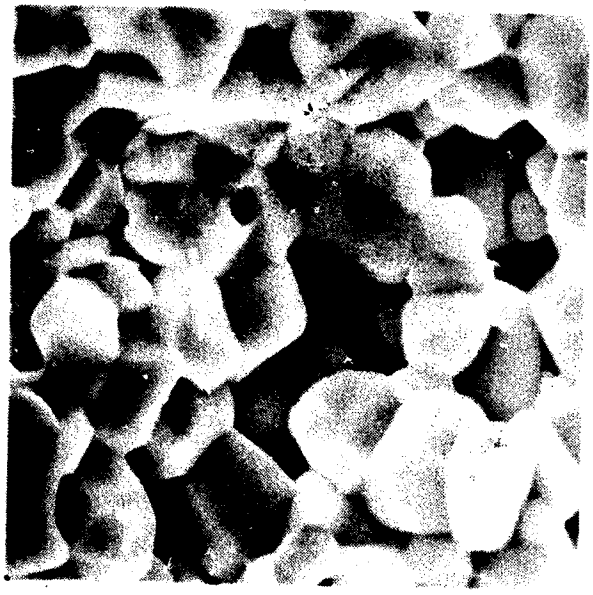

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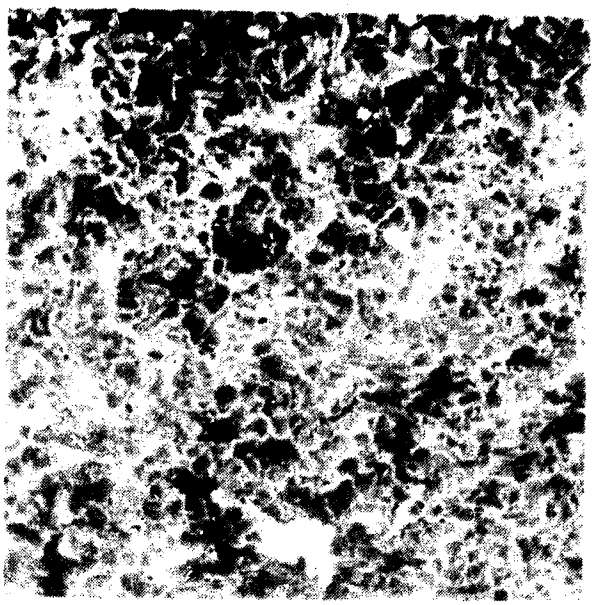

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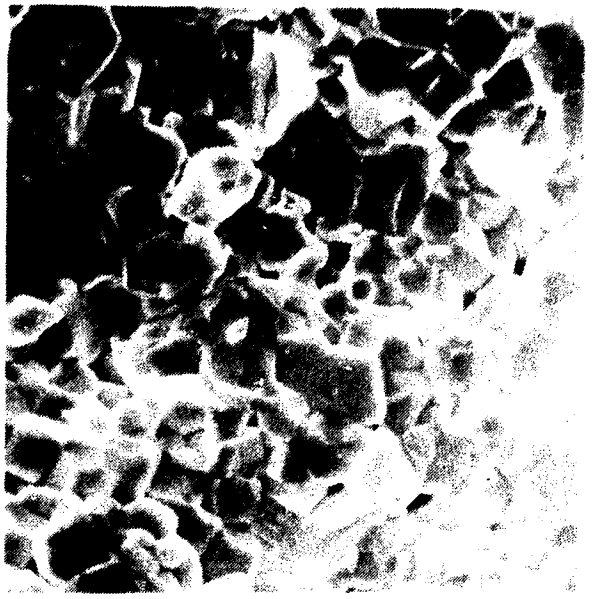

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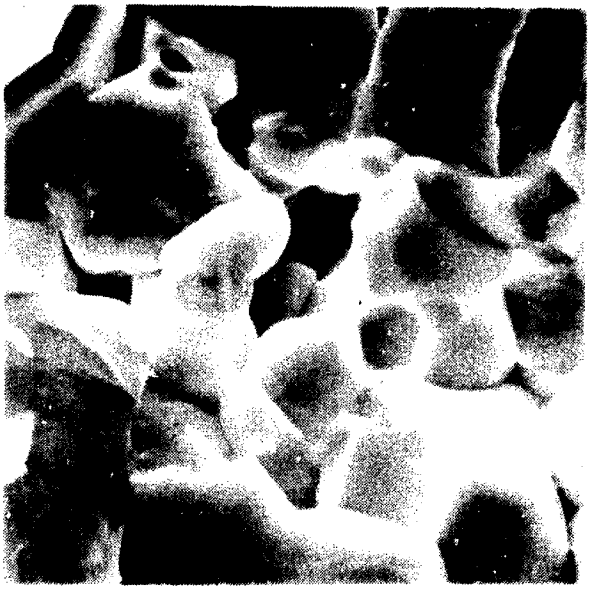

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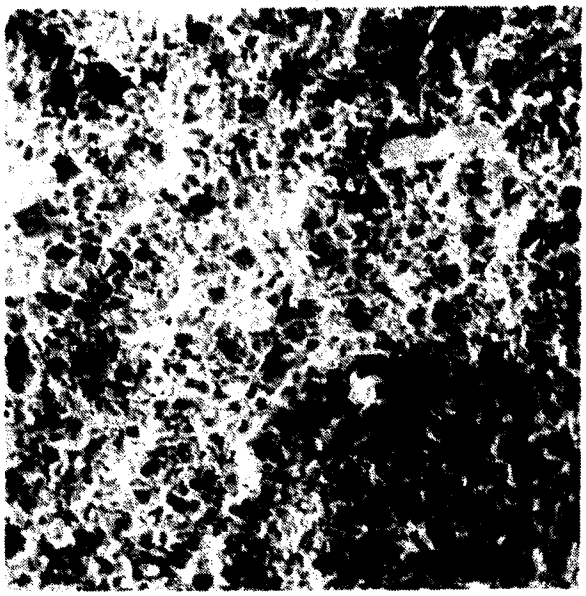

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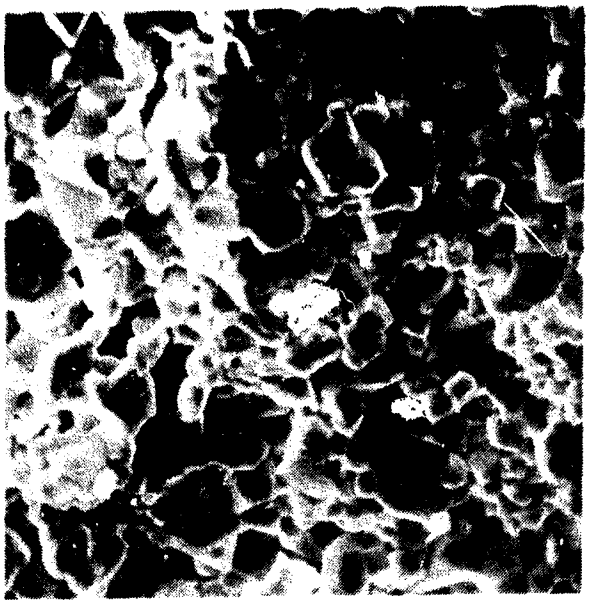

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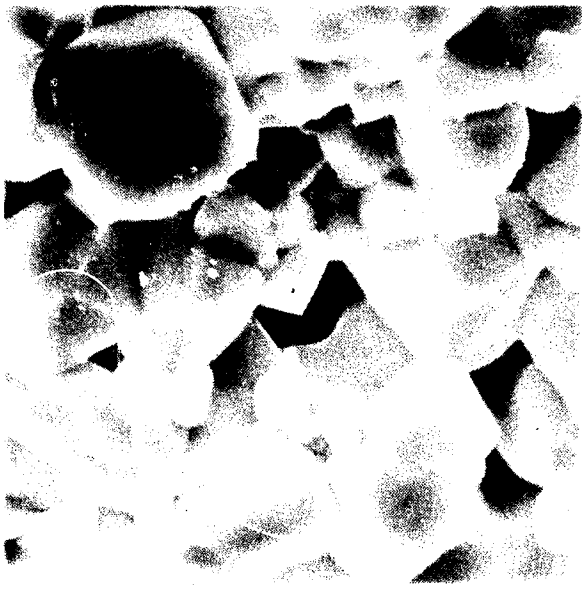

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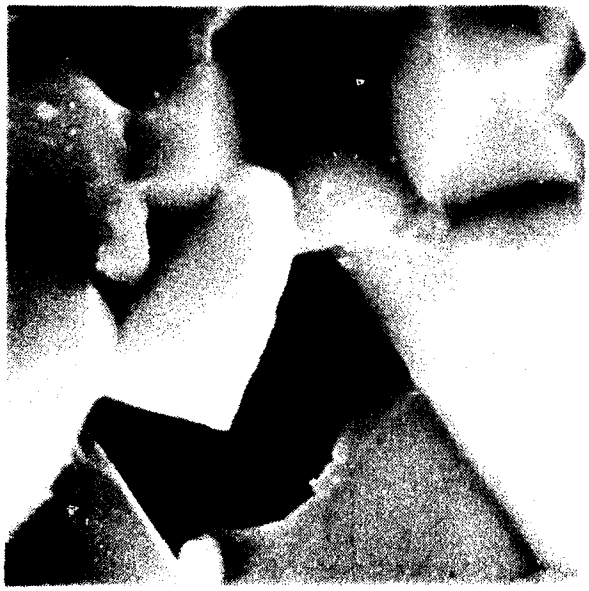

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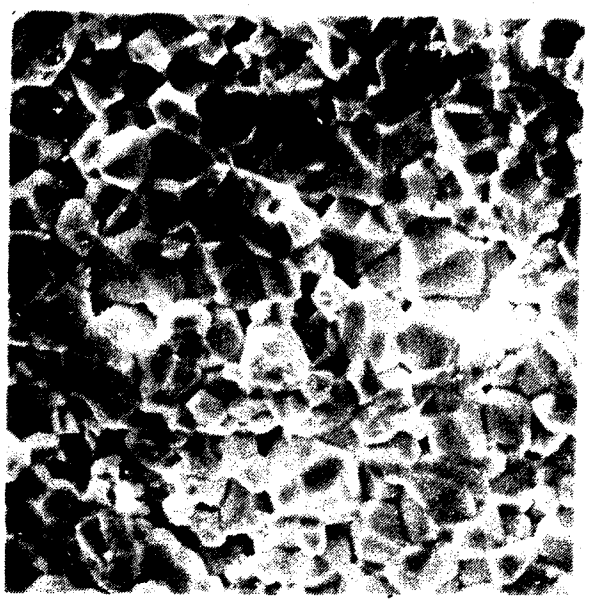

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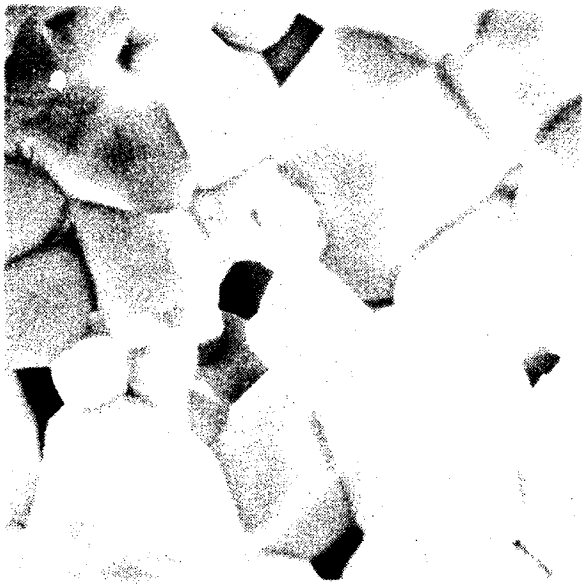

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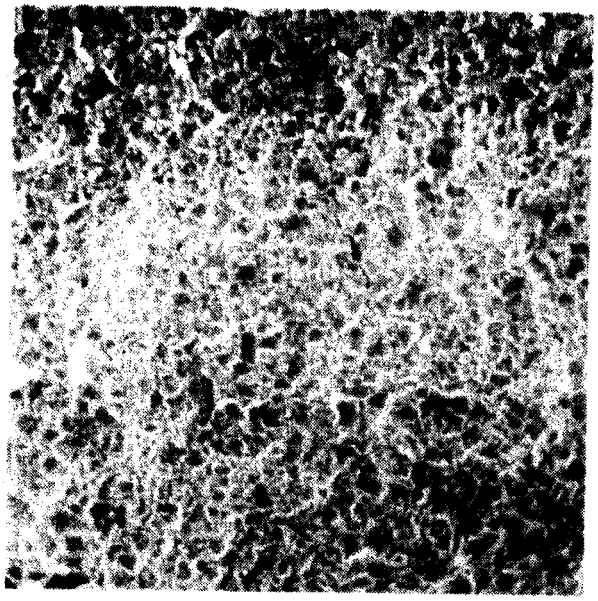

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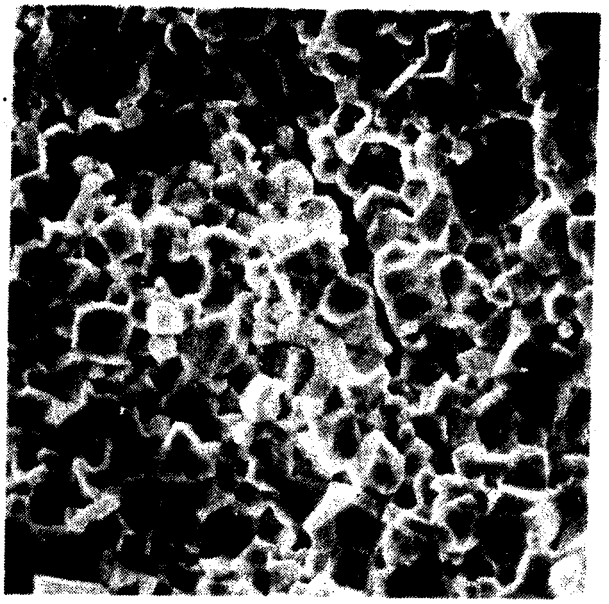

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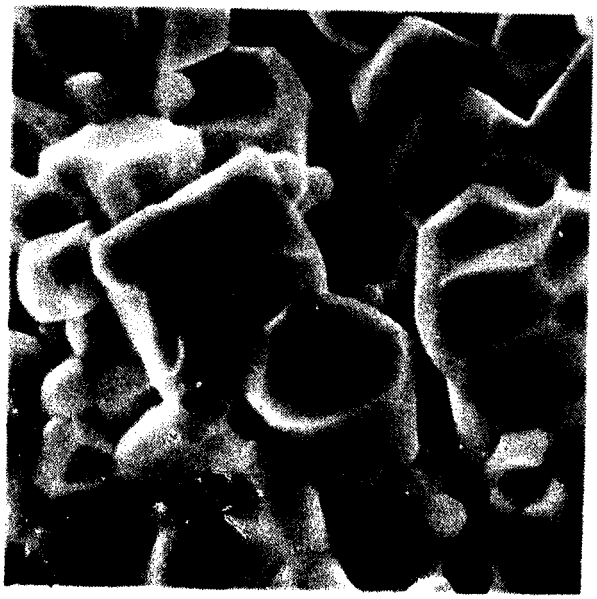

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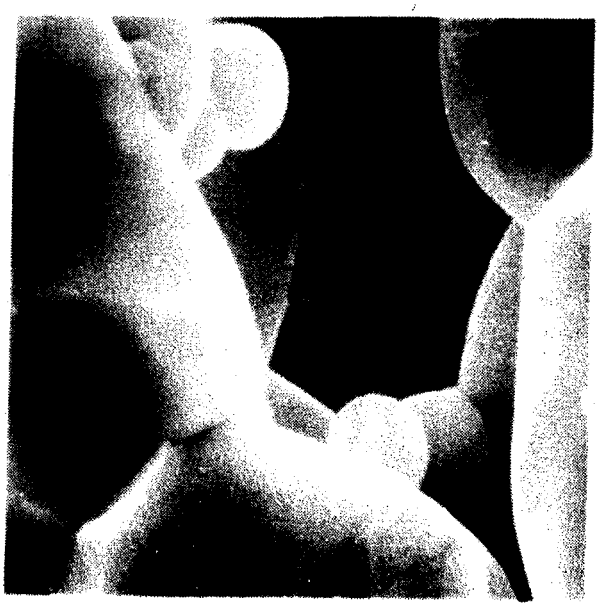

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Density : 7.69

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P. D. Wilcox - 2317 (50)
J. E. Tichenor - 2317
L. L. Pierce - 2317
J. R. Armijo - 2317
C. A. Hall - 2317
J. T. Cutchen - 2317
T. P. Conlon, Jr. - 4222
W. S. Sharp - 4222-1
R. H. Dungan - 5332
Central Files - 3422-1 (15)
L. C. Baldwin - 3412
G. C. McDonald - 3416 (3)
Attn: P. S. Wilson